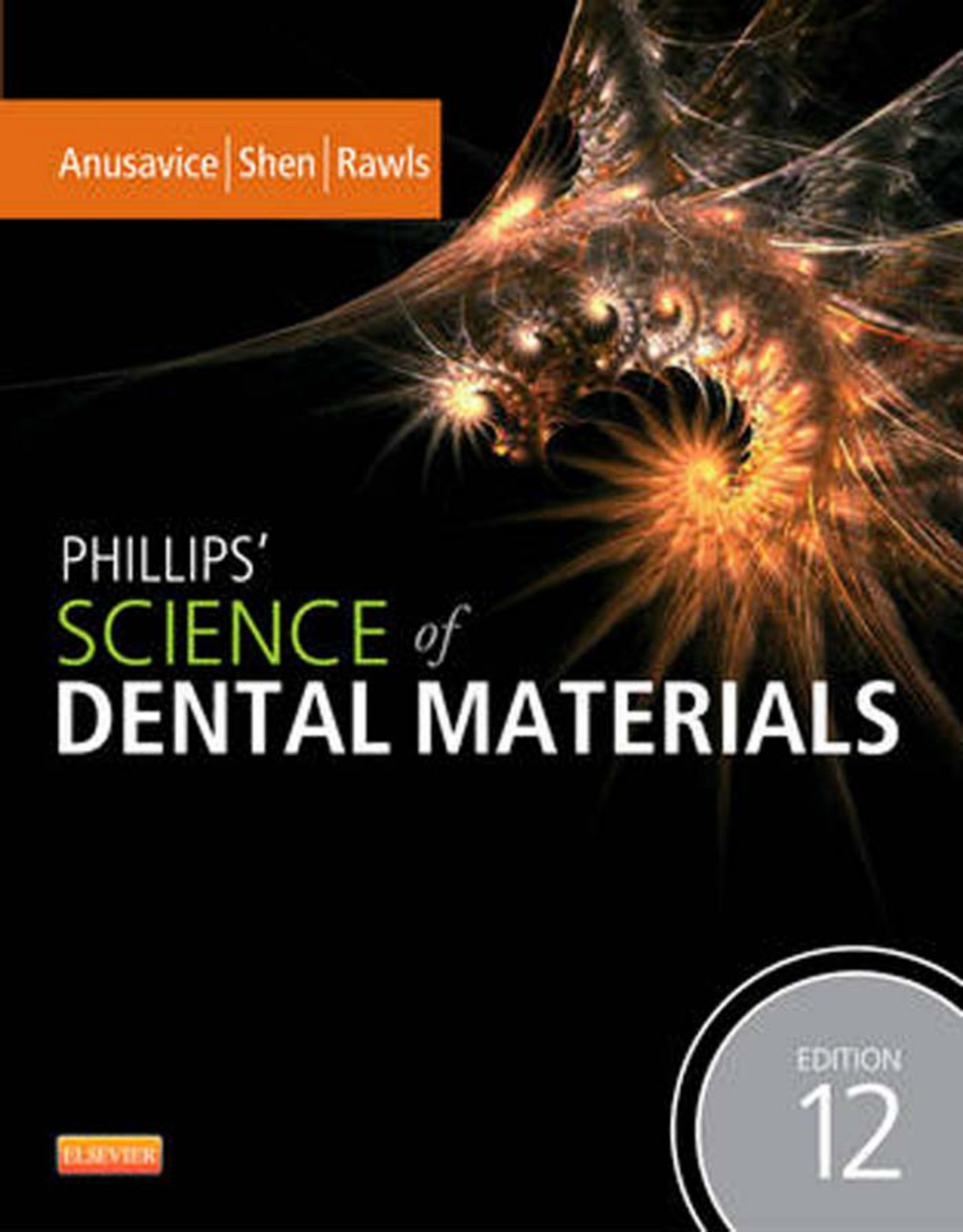

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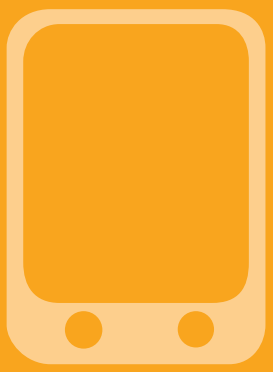
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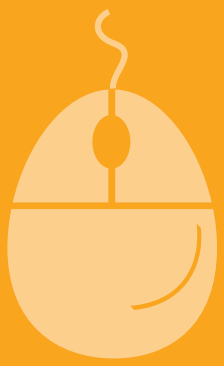
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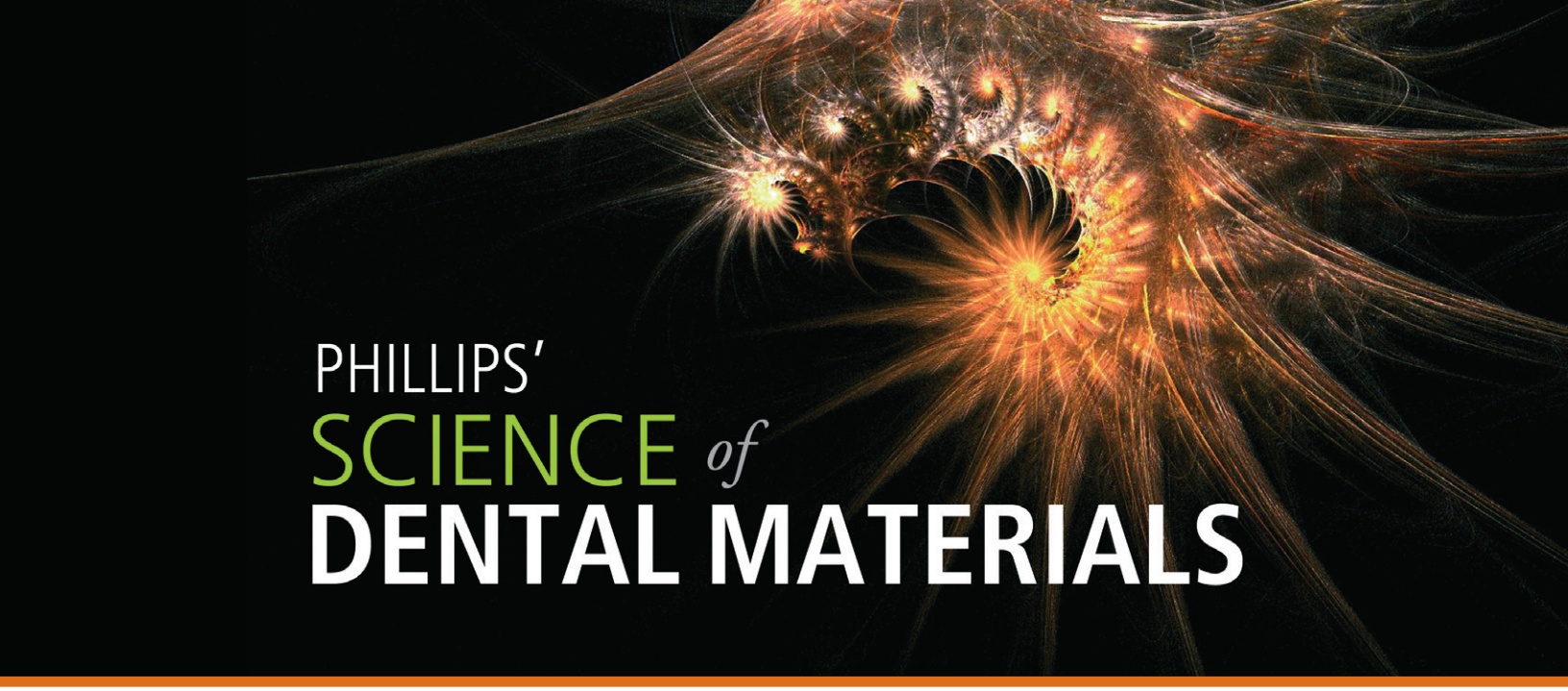
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PHILLIPS' SCIENCE *of* DENTAL MATERIALS

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Eugene W. Skinner



Ralph W. Phillips

We would like to dedicate this edition to the first two editors of this book,
***Dr. Eugene W. Skinner** (1896–1966) and **Dr. Ralph W. Phillips** (1918–1991).*

Dr. Eugene Skinner, a professor of physics at Northwestern University School of Dentistry in Chicago published the first edition of *The Science of Dental Materials* in 1936. Dr. Skinner introduced Ralph Phillips as a co-author of the 5th edition of the book in 1960. Dr. Skinner died during the proof page proof review stage of the 6th edition in 1966. Dr. Phillips renamed the book, Skinner's Science of Dental Materials in the 7th through 9th editions. After the death of Dr Phillips in 1991, the book has been subsequently renamed as *Phillips' Science of Dental Materials* for the 10th through 12th editions.

Throughout an eminent career that spanned five decades, Dr. Phillips was recognized as one of the world's foremost leaders in the field of dental materials science. He was one of the first dental scientists to investigate the relationship between laboratory tests and clinical performance. He initiated clinical investigations designed to analyze the effect of the oral environment on restorative materials and to determine the biocompatibility of restorative materials and the efficacy of newer material formulations and techniques of use. Over his many years of service he remained firmly committed to his original focus on the clinical relevance of laboratory findings, an approach that dominated both his style of teaching and his research activities. Among his main contributions to dentistry, Dr. Phillips pioneered studies of fluoride's influence on the solubility and hardness of tooth enamel and its anticariogenic potential when included in restorative materials. In the 1960s he coordinated the first workshop on adhesive dental materials, which brought together research experts in the fields of adhesion, polymer science, and tooth structure. During his career he published more than 300 scientific papers and books and organized more than 40 symposia and conferences related to biomaterials and dental research.

PREFACE

This book represents a comprehensive overview of the composition, biocompatibility, physical properties, mechanical properties, manipulative variables, and performance of direct and indirect restorative materials and auxiliary materials used in dentistry. The book is intended as a textbook for dental students, dental hygiene students, laboratory technicians, and dental materials scientists. It is also designed as an authoritative reference book for dentists, dental assistants, dental hygienists, and corporate marketing staff. Although the scientific concepts presented in some chapters are somewhat advanced, the text information in most chapters can be readily understood by individuals with a general college education.

The twelfth edition of *Phillips' Science of Dental Materials* is divided into four sections to reflect the focus of the chapters contained in each part. Part I, General Classes and Properties of Dental Materials, consists of seven chapters on the structure, physical properties, mechanical properties, casting methodology, dental polymers, and biocompatibility of restorative and auxiliary materials used in dentistry. Part II: Auxiliary Dental Materials, contains four chapters on impression materials, gypsum products, dental waxes, casting investments and casting procedures, and finishing and polishing materials. Part III: Direct Restorative Materials, is focused on four areas, bonding and bonding agents, restorative resins and cements, dental cements, and dental amalgams. Part IV: Indirect Restorative Materials, consists of six chapters including dental casting and soldering alloys, wrought metals, dental ceramics, denture base resins, dental implants, and a new chapter on emerging technologies. Direct and indirect materials are used to restore function and/or aesthetics in mouths containing damaged, decayed, or missing teeth by producing the restoration directly within the prepared tooth or by producing a prosthesis indirectly in a dental laboratory before placement in the oral cavity.

As shown in the table below, the previous 23 chapters of the 11th edition have been condensed into the 21 chapters of the 12th edition by combining Chapters 5 and 6 into the new

12th Edition	Topic	11th Edition
Chapter 1	Overview of Preventive and Restorative Materials	Chapter 1
Chapter 2	Structure of Matter and Principles of Adhesion	Chapter 2
Chapter 3	Physical and Chemical Properties of Solids	Chapter 3
Chapter 4	Mechanical Properties of Dental Materials	Chapter 4
Chapter 5	Structure and Properties of Cast Dental Alloys	Chapters 5/6
Chapter 6	Dental Polymers	Chapter 7
Chapter 7	Biocompatibility	Chapter 8
Chapter 8	Impression Materials	Chapter 9
Chapter 9	Gypsum Products	Chapter 10
Chapter 10	Dental Waxes, Casting Investments, and Casting Procedures	Chapters 11/12
Chapter 11	Materials and Processes for Cutting, Grinding, Finishing, and Polishing	Chapter 13
Chapter 12	Bonding and Bonding Agents	Chapter 15
Chapter 13	Resin-Based Composites	Chapter 14
Chapter 14	Dental Cements	Chapter 16
Chapter 15	Dental Amalgams	Chapter 17
Chapter 16	Dental Casting Alloys and Metal Joining	Chapter 19
Chapter 17	Wrought Metals	Chapters18/20
Chapter 18	Dental Ceramics	Chapter 21
Chapter 19	Prosthetic Polymers and Resins	Chapter 22
Chapter 20	Dental Implants	Chapter 23
Chapter 21	Emerging Technologies	None

Chapter 5, Cast Metal, Electrodeposited Metal, and Metallurgical Principles; replacing Chapters 11 and 12 with the new Chapter 10, Dental Waxes, Metal Casting Investments, and Casting Procedures; replacing Chapters 18 and 20 with the new Chapter 17, Wrought Metals; and adding the new Chapter 21, Emerging Technologies.

This condensed format places similar topics into one chapter, making it easier to find information on any given topic. Each of the chapters contain an introductory terminology section that is designed to familiarize the reader with key words and definitions and a number of critical thinking questions, which are intended to stimulate thinking and to emphasize important concepts. The answers to these questions are generally found in the section or sections immediately after each question. Although the terminology is associated with generally accepted scientific and dental definitions, it is not intended to be a comprehensive dictionary of all terms used in dental biomaterials science.

Several of the chapters represent totally new approaches to the specific subject. Chapter 1 has been revised to provide an introductory overview of the use of dental materials, the historical evolution of biomaterials, and the standards for safety and quality assurance. Chapters 5, 10, 16, and 17 have been restructured to reflect an updated review of casting and wrought metals. Chapter 6 reflects a new approach on the science of dental polymers. Chapter 7 is a totally new summary of the basic principles and clinical implications of biocompatibility evaluation. Chapter 9 represents an integration of the previous chapters on impression materials. Chapter 12 is a new overview of the systems and principles of bonding and dental adhesives. Chapter 13 reflects an updated review of restorative resins. Chapter 14 on dental cements describes cement compositions, manipulative characteristics, and clinical performance. Chapter 18 represents an updated summary of ceramics used for metal-ceramic and ceramic-ceramic prostheses. Chapter 20 is a new overview of dental implants with an emphasis on implant material and design considerations relative to clinical performance. Finally, Chapter 21 projects potential future technologies in dentistry and describes both recently emerged technologies and those anticipated in the coming decades.

AIMS OF THIS BOOK FOR READERS

The aims of this textbook are: (1) to introduce the science of dental biomaterials science to educators and students with little or no engineering or dental background and facilitate their study of physical and chemical properties that are related to selection and use of these products by the dentist, dental assistants (nurses), dental hygienists, and dental lab technicians, (2) to describe the basic properties of dental materials that are related either to clinical manipulation by dentists and/or dental laboratory technicians, (3) to characterize the durability and esthetics of dental restorations and prostheses made from the restorative materials, and (4) to identify characteristics of materials that affect tissue compatibility and general biological safety. It is assumed that the reader possesses an introductory knowledge of physics or mechanics, as well as inorganic and organic chemistry.

The technology and information provided are intended to bridge the gap between the knowledge of biomaterials obtained in basic courses in materials engineering, chemistry, physics, and the use of the materials in the dental lab and dental clinic. A dental technique is not necessarily an empirical process. In fact, it can be based on sound scientific principles as more information is available from biomedical and dental research. The 21 chapters in the 12th edition focus not just on what the materials are designed to accomplish but more on why the materials react as they do and how the manipulation variables affect their performance in dental laboratories or dental clinics.

What differentiates a dental professional from a tradesperson? To answer this question one should realize that viturally every experience related to preventing disease, treating damage resulting from oral disease, and restoring teeth that are broken down by disease, trauma, and/or neglect is unique. A dentist, dental hygienist, dental assistant, and lab technician must possess basic knowledge that he or she can use to determine optimal conditions for processes that are based on a foundation of science and crticial-thinking skills.

When a dentist is required to remove a fractured zirconia fixed dental prosthesis, the possible difficulties associated with cutting such a tough material without heating up the tooth appreciably requires excellent psychomotor skill, perception of the amount of heat transferred to the pulp tissue, and sound judgment of the rate of coolant application and rotational speed of the diamond bur. However, the most difficult decision is to decide which potential outcomes are likely to occur when a variety of prosthesis replacment decisions are considered. The overriding criterion for this decision as well as most clinical decisions is that the known benefits should outweigh the known risks of each treatment option.

The dentist and the engineer have much in common. Dentists must estimate the stresses that a dental prosthesis must endure and make informed decisions from personal experience and existing clinical evidence to conceptualize the optimal design of the prosthetic structure and final restoration. They should possess sufficient knowledge of the physical properties of the different types of materials that they use so that they can exercise the best judgment possible in their selection. For example, dental professionals must know whether the clinical situation such as a large restoration situation requires the use of an amalgam, a resin-based composite, a cement, a casting alloy, a ceramic, or a metal-ceramic. Through their knowledge of the physical and chemical properties of each of these materials, they are positioned to make sound clinical judgments. In addition to the mechanical requirements of the materials that are within the training experience of an engineer, the esthetic and physiologic requirements are beyond the capability of the engineer.

Once the dentist has selected the type of material to be used, an established commercial product with sufficient evidence of safety must be chosen. It is the intention of major dental manufacturers to cooperate with dentists in supplying

them with materials of the highest quality. The dentist should be able to evaluate the claims of the respective manufacturers from an informed, critical-thinking perspective. For the dentists' protection and for the protection of their patients, they must be able to recognize, and evaluate critically, the validity of such claims. Courses or lectures in dental materials attempt to provide dentists with certain criteria for selection to enable them to discriminate between fact and fiction.

Furthermore, dental school courses provide students with an overview of the scientific scope of their chosen profession. Because the daily practice of dentistry involves the selection and use of dental materials for patient treatment procedures, it is obvious that the science of dental materials is critically important.

The recent explosion of new biomaterial products suggest that further changes will continue to occur in the practice of dentistry. Based on the readers' knowledge of materials science principles, they should be prepared to analyze the benefits and limitations of these dental materials to make rational decisions on their selection and use in a clinical practice. Not all materials used in dentistry are included in this book. For example, anesthetics, medicaments, and therapeutic agents such as fluoride varnish, xylitol, and chlorhexidine are not within the scope of this book. The science of dental materials generally encompasses some of the properties of natural oral tissues (enamel, dentin, cementum, pulp tissue, periodontal ligament, and bone) and the synthetic materials that are used for prevention and arrest of dental caries, for periodontal therapy, and for reconstruction of missing, damaged, or unesthetic oral structures. These categories include materials employed in dental disciplines such as preventive dentistry, public health dentistry, operative dentistry, oral and maxillofacial surgery, maxillofacial prosthetics, implantology, orthodontics, periodontology, pediatric dentistry, removable prosthodontics, and fixed prosthodontics.

ORGANIZATION

The general engineering curriculum of most major universities includes several aspects of materials science. Topics include the microstructural features of materials and the dependence of properties on these internal structures. The sequence of instruction generally progresses from atomic or molecular to macroscopic structures, from the simple to the more complex. Knowledge in this field is developed from various disciplines, such as biology, microbiology, physical chemistry, statics, solid-state physics, polymer science, ceramics, engineering mechanics, and metallurgy. Because fundamental principles of the physical sciences and engineering and microstructure govern the properties of all materials, it is critically important to study the microstructural characteristics before proceeding to the macrostructural features and proeprties.

Following the overview of dental materials (Chapter 1), Part I focuses on the structure and properties of materials. This importance of relating properties of a material to its atomic or crystalline structure is emphasized in Chapter 2, which deals with the atomic and molecular structure of materials and certain principles of materials science that are not usually included in a college physics course. These principles are in turn related to the properties of dental materials, as discussed in Chapters 3 and 4. The requirements placed on dental microstructures and material properties are demanding and unique. To design prostheses appropriately, the dentist must be aware of the limitations of restorative materials and the demanding conditions that exist in the oral cavity. These factors are also discussed in Chapters 3 and 4. One should be increasingly aware of the difficulties involved in selecting a material that is technique insensitive, biocompatible, durable, and in many cases esthetic.

Following the chapter on the structure of matter (Chapter 2) and the physical and mechanical properties of dental materials (Chapters 3 and 4) are overview chapters dealing with metals and alloys, polymers, and ceramics, and the biocompatibility of dental materials.

The basic science of physical metallurgy is concerned with the properties of metals and alloys, whereas the study of metallography involves the microstructure of metals that result from their solidification and heat treatment (Chapter 5). The constitution of alloys in this chapter represents the equilibrium phases that result in an alloy system as a function of temperature and composition. Chapter 6 focuses on dental polymers.

It is obvious from the earlier discussion of the regulatory agencies in dentistry, such as the ADA Council on Scientific Affairs, the FDA, the FDI, and the ISO, that the precursor to the marketing or selection of a dental material is its biocompatibility with oral tissues. These biological considerations are covered in Chapter 7 and are noted throughout the book.

Chapters 8 through 11 in Part II describe auxiliary materials and techniques that are used to fabricate and finish the surfaces of dental restorations and prostheses. These materials include impression materials (Chapter 8), gypsum products (Chapter 9), dental waxes, casting investments, and casting procedures (Chapter 10), and finishing and polishing materials (Chapter 11).

As stated earlier, the chapters in Part III for direct restorative materials include bonding bonding and bonding agents (Chapter 12), restorative resins and cements (Chapter 13), dental cements (Chapter 14), and dental amalgams (Chapter 15).

Chapters in Part IV on indirect restorative materials include dental casting and soldering alloys (Chapter 16), wrought metals (Chapter 17), dental ceramics (Chapter 18), denture base resins (Chapter 19), and dental implants (Chapter 20).

The information on the properties, structure, and applications of dental biomaterials are derived from several branches of science. Practically all of the engineering applied sciences are included in these subjects. In addition, the dentists must be informed on the biological properties of dental materials, which cannot be separated from their mechanical and physical properties. Thus, knowledge of the pertinent biological characteristics must also be included in the selection, use and maintenance of dental materials for restorative applications.

ACKNOWLEDGMENTS

The twelfth edition of *Phillips' Science of Dental Materials,* previously named *Skinner's Science of Dental Materials* in the ninth and earlier editions, has undergone significant changes that are consistent with the rapidly changing trends in the field of dental materials science and the practice of dentistry. Increased emphasis has been placed on biocompatibility, adhesion, dentin bonding principles, controlled-releasing materials, resin-based composites, CAD-CAM ceramics, dental polymers, and dental implants.

Many individuals should be recognized both for their contributions to the fields of dental materials science, to contributions to earlier editions, and to the revision of this textbook. The twelfth edition is co-edited by Drs. Anusavice, Rawls, and Shen who were contributors to the eleventh edition as well. Drs. Rawls and Shen have made novel suggestions on the reorganization of the twelfth edition. Dr. William Brantley who made significant contributions to the revision of Chapters 3, 5, 6, 19, and 20 in the eleventh edition has co-authored the consolidation of previous Chapters 5 and 6 into the new Chapter 5. The new chapter 21 on emerging technologies was inspired to a great extent by Dr. Carolyn Primus. The revision of Chapter 20 on dental implants was co-authored by Dr. Jack Lemons, an internatioanlly recognized expert on implant materials and designs and Dr. Josephine Esquivel-Upshaw, a prosthodontist who has considerable experience in clinical evaluations of fixed ceramic-ceramic and metal-ceramic prosthetic restorations. Much of the new artwork was created by Jeannie Robertson. Other artwork that was reprinted from the eleventh edition was created by Dr. José dos Santos, Jr.

I express my appreciation to those who contributed to the tenth and eleventh editions of this textbook, but who were not contributors to the twelfth edition. Several of the revised chapters may contain portions of the sections they created in the previous editions. These contributors include Drs. Charles F. DeFreest, Jack Ferracane, J. Rodway Mackert, Jr., Miroslav Marek, Victoria A. Marker, Robert Neiman, Barry K. Norling, Karl-Johan Söderholm, Grayson Marshall, Sally Marshall, Atul Sarma, Harold R. Stanley, and John Wataha, and Mr. Paul Cascone. These individuals provided significant input to the tenth and/or eleventh editions in which several significant changes had been introduced to enhance readability and the clinical perspectives of dental biomaterials. In their quest to promote evidence-based dentistry, they blended basic science, clinical science, and applied or translational research findings with processing and manipulation variables to optimize production and clinical outcomes.

Finally, we would like to thank the staff at Elsevier Inc. for their assistance in organizing and expediting the activities related to publishing the twelfth edition. These individuals include John Dolan, Brian Loehr, and Sara Alsup.

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PART 1

GENERAL CLASSES AND PROPERTIES OF DENTAL MATERIALS

1 **Overview of Preventive and Restorative Materials,** *3*

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CHAPTER 1

Overview of Preventive and Restorative Materials

OUTLINE

- General Categories of Biomaterials Properties
- Applications of Dental Materials
- What Are Dental Materials?
- Historical Use of Restorative Materials
- Standards for Dental Materials
- U.S. Food and Drug Administration Regulations for Medical Devices
- International Standards
- International Organization for Standardization Standards, Subcommittees, and Working Groups
- Other Dental Standards Organizations
- How Safe Are Dental Restorative Materials?
- Why Do Dental Students, Dentists, and Dental Educators Need to Understand the Principles of Dental Materials Science?
- The Future Need for Dental Biomaterials

KEY TERMS

Auxiliary dental material—Substance that is used in the construction of a dental prosthesis but that does not become a part of the structure.

Direct restorative material—A cement, metal, or resin-based composite that is placed and formed intraorally to restore teeth and/or to enhance esthetics.

Indirect restorative material—A ceramic, metal, metal-ceramic, or resin-based composite used extraorally to produce prostheses, which replace missing teeth, enhance esthetics, and/or restore damaged teeth.

Preventive dental material—Cement, coating, or restorative material that either seals pits and fissures or releases a therapeutic agent such as fluoride and/or mineralizing ions to prevent or arrest the demineralization of tooth structure.

Restorative—Metallic, ceramic, metal-ceramic, or resin-based substance used to replace, repair, or rebuild teeth and/or to enhance esthetics.

Temporary restorative material—Cement- or resin-based composite used for a period of a few days to several months to restore or replace missing teeth or tooth structure until a more long-lasting prosthesis or restoration can be placed.

? CRITICAL QUESTION

What are the differences between preventive, restorative, preventive/restorative, and auxiliary dental materials used for the construction of a fixed dental prosthesis (FDP)?

The science of dental materials covers a broad range of terminology, composition, microstructure, and properties used to describe or predict the performance of preventive and restorative biomaterials. Previous courses in mathematics, chemistry, and physics should have prepared you to read this book and understand the terms and principles involved in describing the behavior of these materials as they are used in the testing laboratories of academia, governmental facilities, and industry. Of greatest importance is the potential of this information to predict clinical performance and to allow us to analyze the causes of structural degradation and failure of these materials when they no longer serve their intended functions.

Although many properties of biomaterials can be grouped into one of the broadest categories, i.e., physical properties, this book has been designed to separate these properties into subcategories that allow a clearer visualization of the variables that are most likely to influence the success or failure of preventive and restorative dental materials. Chemical properties generally comprise the behavior of materials in a chemical environment with or without any other external influences. Mechanical properties are related primarily to the behavior of materials in response to externally applied forces or pressures. Of course, in a clinical environment, the behavior of dental materials may be dependent on several variables simultaneously, but a general understanding of a material's performance will be controlled by our ability to differentiate primary from secondary factors or properties. Lists of the most relevant chemical, manufacturing, mechanical, optical, and thermal properties are presented below. Separate chapters are devoted to

CRITICAL QUESTION

How do mechanical properties differ from chemical properties?

more detailed descriptions: Chapter 3, "Chemical and Physical Properties of Solids," and Chapter 4, "Mechanical Properties of Solids." Because of the dramatic increase in the use of CAD-CAM technology, a category of processing or manufacturing properties has been introduced in this chapter.

GENERAL CATEGORIES OF BIOMATERIALS PROPERTIES

Chemical properties and parameters
- Corrosion
- Hygroscopy
- Solubility
- pH sensitivity
- Reactivity
- Surface energy
- Surface tension

Properties of importance in manufacturing or finishing processes
- Castability
- Brittleness
- Creep resistance
- Hardness
- Melting temperature or melting temperature range
- Flowability under hot-isostatic-pressing (HIP) temperature and pressure conditions
- Machinability
- Polishability

Mechanical properties
- Brittleness
- Compressive strength
- Ductility
- Elastic modulus
- Fatigue strength
- Fracture toughness
- Hardness
- Microtensile strength
- Poisson's ratio
- Proportional limit
- Shear strength
- Tensile strength
- Work or stain hardening
- Yield strength

Optical properties and parameters
- Absorptivity
- Color
- Fluorescence
- Luminescence
- Opacity
- Photosensitivity
- Reflectivity
- Refractive index
- Translucency
- Transmittance

Thermal properties and parameters
- Coefficient of thermal expansion or contraction
- Eutectic temperature
- Fusion temperature
- Glass transition temperature
- Heat of vaporization
- Heat of fusion
- Liquidus temperature
- Melting point
- Softening point
- Solidus temperature
- Specific heat
- Thermal conductivity
- Thermal diffusivity
- Vapor pressure
- Viscosity

PHYSICAL PROPERTIES

A physical property is any measurable parameter that describes the state of a physical system. The changes in the physical properties of a biomaterial can serve to describe the changes or transformations of the material when it has been subjected to external influences such as force, pressure, temperature, or light. Because these properties may include other properties listed above, a more detailed description of their characteristics is presented in Chapter 3, "Chemical and Physical Properties of Solids." In contrast to physical properties, chemical properties define the ways in which a material behaves during a chemical reaction or in a chemical environment.

Several properties listed above may fall into more than one category. For example, the optical properties can simply be grouped under physical properties. However, because of the importance of esthetics in dentistry, optical properties have been placed in a separate category. There are many other properties to be considered in a dental setting. However, this book focuses on those most relevant to the biomaterials and auxiliary materials designed for use in dental clinics and dental laboratories.

APPLICATIONS OF DENTAL MATERIALS

The directions taken by the dental profession will affect the future of dental materials, although the practice of dentistry will depend on current and future developments in dental materials science. Dentistry will continue to focus on the preservation and enhancement of oral health through the prevention of caries and periodontal disease and the rehabilitation of missing, damaged, and/or destroyed hard and soft tissues. A cure for dental caries will have a dramatic impact on the use of **restorative materials** to improve the form and function of teeth with cavitated lesions. The need to restore teeth will always exist because of the time-dependent failure or degradation of restorative materials and oral tissues. The

decision on which biomaterials to use for a given clinical situation will be controlled by the known benefits of each choice compared with the known risks.

WHAT ARE DENTAL MATERIALS?

Historically, a wide variety of materials have been used as tooth crown and root replacements, including animal teeth, bone, human teeth, ivory, seashells, ceramics, and metals. Restorative materials for the replacement of missing portions of tooth structure have evolved more slowly over the past several centuries.

Dental materials may fall into any of the following classes: metals, ceramics, polymers, or composites. In general, polymers, cements, and composites are used for preventive as well as restorative applications. Some of these products are capable of releasing diagnostic or therapeutic agents on a controlled-release basis to support the preventive treatments for populations at risk for dental caries.

Pure metals are rarely used for dental applications, although commercially pure titanium can be used to make dental implants, inlays, onlays, crowns, and bridges. Pure gold in a foil form can be used to make dental restorations ("fillings") directly on teeth, but this technique is used only rarely today. Metals and alloys can also be used to construct orthodontic appliances, partial denture frameworks and clasp arms, and these materials may require auxiliary products such as matrix bands, burs, cutting blades, endodontic files, brooches, and reamers to ensure proper adaptation and placement.

Ceramics can be used to produce inlays, onlays, crowns, and multiple-unit fixed dental prostheses. However, because of the need for high fracture resistance and esthetic appeal, these prostheses are often made of two or more layers, including a strong and tough core ceramic and one or two layers of a less tough but translucent, veneering ceramic. It is also possible to use yttria-stabilized zirconia for implant bodies and endodontic posts and cores.

Despite recent improvements in the physical properties of these materials, none of them is permanent. In the 21st century, dentists and materials scientists will continue to search for the ideal restorative material. Such a material would (1) be biocompatible; (2) bond permanently to tooth structure or bone; (3) match the natural appearance of tooth structure and other visible tissues; (4) exhibit properties similar to those of tooth enamel, dentin, and other tissues; and (5) be capable of initiating tissue repair or the regeneration of missing or damaged tissues.

Dental materials may be classified as preventive materials, restorative materials, or auxiliary materials. **Preventive dental materials** include pit and fissure sealants; sealing agents that prevent leakage; materials used primarily for their antibacterial effects; and liners, bases, cements, and restorative materials such as compomer, hybrid ionomer, and glass ionomer cement that are used primarily because they release fluoride or other therapeutic agents to prevent or inhibit the progression of tooth decay (dental caries). Table 1-1 summarizes the types of preventive and restorative materials, their applications, and their potential durability. In some cases a preventive material may also serve as a restorative material that may be used for a short-term application (up to several months), for moderately long time periods (1 to 4 years), or for longer periods (5 years or more). Dental restoratives that have little or no therapeutic benefit may also be used for short-term (temporary) use, or they may be indicated for applications requiring moderate or long-term durability. For example, restorative materials that do not contain fluoride can be used for patients who are at a low risk for caries.

Restorative dental materials consist of synthetic components that can be used to repair or replace tooth structure, including primers, bonding agents, liners, cement bases, amalgams, resin-based composites, compomers, hybrid ionomers, cast metals, metal-ceramics, ceramics, and denture polymers. Some of these materials can also be designed as controlled-delivery devices for release of therapeutic or diagnostic agents. Restorative materials may be used for temporary, short-term purposes (such as temporary cements and temporary crown and bridge resins) or for longer-term applications (dentin bonding, and indirect inlays, onlays, crowns, removable dentures, fixed multiple-unit, and orthodontic appliances). Restorative materials may further be classified as **direct restorative materials** or **indirect restorative materials**, depending on whether they are used intraorally to fabricate restorations or prosthetic devices directly on the teeth or tissues or extraorally, respectively, in which the materials are formed indirectly on casts or other replicas of the teeth and other tissues. **Auxiliary dental materials** are substances used in the process of fabricating dental prostheses and appliances but that do not become part of these devices. These include acid-etching solutions, impression materials, casting investments, gypsum cast and model materials, dental waxes, acrylic resins for impression and bleaching trays, acrylic resins for mouth guards and occlusion aids, and finishing and polishing abrasives.

Polymers have many uses as both preventive and restorative materials as well as auxiliary materials such as cements, impression materials, impression trays, mouth guards, orthodontic appliances, and interocclusal records. When a monomer resin contains inorganic or polymeric filler particles that are bonded to the matrix resin by means of an organosilane coupling agent, the material is classified as a dental composite or resin-based composite. The term *composite resin* is technically incorrect unless the microstructure contains only polymeric filler particles (i.e., a composite of resin components).

Temporary restorative materials are a subcategory of restorative materials and include products used for dental restorations and appliances that are not intended for moderate- or long-term applications. Examples include temporary cements used for luting, temporary cements, or other restoratives used for fillings, orthodontic wires, and acrylic resins used for temporary inlays, onlays, crowns, and fixed dental prostheses that span two or more tooth positions. Other

TABLE 1-1 Comparative Applications and Durability of Preventive and Restorative Dental Materials

Material Type	Applications of Products	Potential Preventive Benefits	Durability
Resin adhesive	A	F (certain products)	M
Resin sealant	S	S	M
Resin cement	L	F (certain products)	M
Compomer	B, L, R	F	M
Hybrid ionomer	B, L, R	F	M
Glass ionomer (GI)	A, B, L, R, S	F, S	L, M
Metal-modified GI	R	F	L, M
Zinc oxide–eugenol	B, L, T	– – –	L, M
Zinc phosphate	B, L	– – –	M
Zinc polycarboxylate	B, L	– – –	M
Zinc silicophosphate	B, L	F	M
Resin composite	R	F (certain products)	H
Dental amalgam	R	– – –	H
Ceramic	R	– – –	H
Metal-ceramic	R	– – –	H
Metal/-resin	R	– – –	M, H
Temporary acrylic resin	T	– – –	L
Denture acrylic	R	– – –	H
Cast metal	R	– – –	H
Wrought metal	R	– – –	H

Applications: A, adhesive; B, base; L, luting agent; S, pit/fissure sealant; R, restorative; T, temporary restorative.
Potential preventive benefit: F, fluoride-releasing material; S, sealing agent.
Durability: L, Low; M, moderate; H, high.

auxiliary materials include waxes, gypsum products, dental compounds, and gutta percha.

The overriding goal of dentistry is to maintain or improve the quality of life of the dental patient. This goal can be met by preventing disease, relieving pain, improving the efficiency of mastication, enhancing speech, and improving appearance. Because many of these objectives require the replacement or alteration of tooth structure, the main challenges for centuries have been the development and selection of biocompatible, long-lasting, direct-filling tooth restoratives, and indirectly processed prosthetic materials that can withstand the adverse conditions of the oral environment. Figure 1-1 is a schematic cross-section of a natural tooth and supporting bone and soft tissue. Under healthy conditions, the part of the tooth that extends out of adjacent gingival tissue is called the clinical crown; that below the gingiva is called the tooth root. The crown of a tooth is covered by enamel. The root is covered by cementum, which surrounds dentin and soft tissue within one or more root canals.

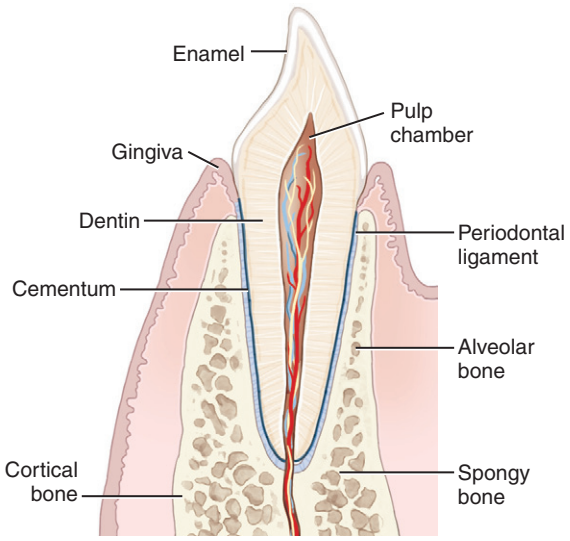


FIGURE 1-1 Schematic cross-sectional view of a natural anterior tooth and supporting tissues.

? CRITICAL QUESTION

What technological advances led to the development of a more precise fit of indirectly made prostheses?

HISTORICAL USE OF RESTORATIVE MATERIALS

Dentistry as a specialty is believed to have begun about 3000 B.C. Gold bands and wires were used by the Phoenicians (after 2500 B.C.). Around 700 B.C. the Etruscans carved ivory or bone for the construction of partial dentures that were



FIGURE 1-2 This mandible, dated 800 A.D., was found in Honduras. It shows three implanted incisors made of carved seashells. Calculus formation on these three implants indicates that they were not made solely for a burial display but served as fixed, functional, and esthetic tooth replacements. (Courtesy of the Peabody Museum of Archaeology and Ethnology, 33-19-20/254.0.)

fastened to natural teeth by means of gold wires or bands, which were used to position extracted teeth in place of missing teeth.

Although inscriptions on Egyptian tombstones indicate that tooth doctors were considered to be medical specialists, they are not known to have performed restorative dentistry. However, some teeth found in Egyptian mummies were either transplanted human teeth or tooth forms made of ivory. The earliest documented evidence of tooth implant materials is attributed to the Etruscans as early as 700 B.C. (Figure 1-2). Around 600 A.D. the Mayans used implants consisting of seashell segments that were placed in anterior tooth sockets. Hammered gold inlays and stone or mineral inlays were placed for esthetic purposes or traditional ornamentation by the Mayans and later the Aztecs (Figure 1-3). The Incas performed tooth mutilations using hammered gold, but the material was not placed for decorative purposes.

Cavities in teeth have been replaced or restored from ancient times up into the eighteenth century with a variety of materials including stone chips, ivory, human teeth, turpentine resin, cork, gums, and metal foils (lead and tin). More recently, gutta percha, cements, metal-modified cements, unfilled synthetic resin, composites, other metals (gold leaf, amalgam, and a variety of cast metals and alloys), ceramics, and metal-ceramics have been used for tooth restoration. Paré (1509–1590) (Figure 1-4), a surgeon to four kings, used lead or cork for tooth fillings. Queen Elizabeth I (1533–1603) used cloth fragments to fill the cavities in her teeth. Fauchard (1678–1761) (Figure 1-5), the father of modern dentistry, used tin foil or lead cylinders to fill tooth cavities. Wealthy patients preferred to have teeth that were made of agate, mother of pearl, silver, or gold. Modern dentistry began in 1728, when Fauchard published a treatise describing many types of dental restorations, including a method for the construction of artificial dentures made of ivory.



FIGURE 1-3 Mayan jaw with stones and metal inlay decorations still intact on the teeth.

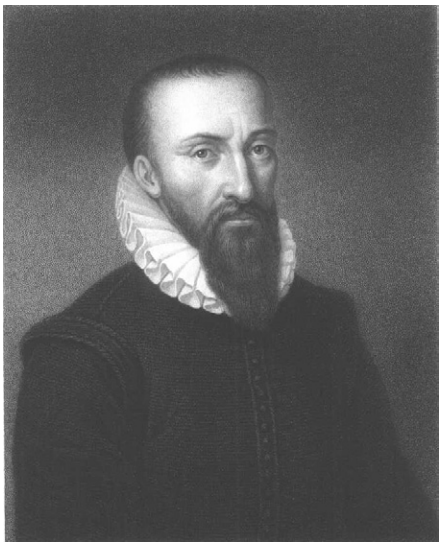


FIGURE 1-4 Ambroise Paré (1509–1590) was the royal surgeon for Kings Henry II, Francis II, Charles IX, and Henry III.



FIGURE 1-5 Pierre Fauchard (1678–1761), known as the father of modern dentistry.

Gold foil has also been employed for dental restorative purposes. Pfaff (1715–1767), the dentist of Frederick the Great of Prussia, used gold foil to cap the pulp chamber. Bull began producing beaten gold in Connecticut for dental applications in 1812. Arculanus recommended gold-leaf dental fillings in 1848. Sponge gold was introduced in 1853 in the United States and England to replace gold leaf. In 1855 Arthur promoted the use of cohesive gold in the United States. In 1897 Philbrook described the use of metal fillings made from wax patterns of the tooth cavity.

Using filings from silver coins mixed with mercury, Taveau, in France, developed what was likely the first dental amalgam in 1816. The Crawcour brothers, who emigrated from France to the United States, introduced Taveau's amalgam fillings in 1833; however, graduates of the Baltimore Dental College subsequently took an oath not to use amalgams in their practices. Many dentists criticized the poor quality of the early amalgam restorations. This controversy led to the "amalgam war" from 1840 to 1850, during which heated debates occurred over the benefits and drawbacks of dental amalgam. Research on amalgam formulations from the 1860s through the 1890s greatly improved the handling properties and the clinical performance of amalgam filling materials. In 1895, Black proposed standardized cavity preparations and manufacturing processes for dental amalgam products.

Gold shell crowns were described by Mouton in 1746, but they were not patented until 1873 by Beers. In 1885 Logan patented a porcelain fused to a platinum post, replacing the unsatisfactory wooden posts previously used to build up intraradicular (within the tooth root) areas of teeth. In 1907 the detached-post crown was introduced, which was more easily adjustable.

In 1756 Pfaff described a method for making impressions of the mouth in wax, from which he constructed a model with plaster of Paris. Pfaff's use of plaster of Paris allowed dentists to make impressions of the patient's edentulous jaws in the mouth. Duchateau, a French pharmacist, and de Chemant, a dentist, designed a process in 1774 for producing hard, decay-proof porcelain dentures. In 1789 de Chemant patented an improved version of these "mineral paste" porcelain teeth. The porcelain inlay was introduced soon thereafter, in the early 1800s. However, porcelain bonding to metals was not fully refined for metal-ceramic crowns until the mid-1900s.

The dentures of George Washington (1732–1799) fit poorly, and he suffered terribly throughout his presidency (1789–1797). Washington never wore wooden teeth, as has been reported; he wore dentures made of some of his own teeth, bovine or hippopotamus teeth, ivory, or lead. Prior to his first term as president, he had worn partial dentures that were fastened to his remaining teeth. During the inauguration for his first term as president in 1789, Washington had only one natural tooth remaining; he wore his first full set of dentures, which were made by John Greenwood. The base of these dentures was made of hippopotamus ivory carved to fit the jaw ridges. The upper denture contained ivory teeth and the lower one consisted of eight human teeth fastened by gold rivets that screwed into the denture base. The two dentures were secured in Washington's mouth by spiral springs.

In 1808, Fonzi, an Italian dentist, developed an individual porcelain tooth form that was held in place with an embedded platinum pin. Planteau, a French dentist, first introduced porcelain teeth in the United States in 1817. In 1822 Charles Peale, an artist, fired mineral teeth in Philadelphia, and Samuel Stockton began the commercial production of porcelain teeth soon thereafter, in 1825. Ash further developed an improved porcelain tooth in England around 1837.

Evans (1836) refined the method of making accurate measurements in the mouth. However, it was not until 1839 that Charles Goodyear's invention of a low-cost vulcanized rubber allowed dentures to be molded accurately to fit the mouth. Vulcanized rubber denture bases that held denture teeth accelerated the demand for accurately fitting dentures at a reasonably low cost. Since 1839 denture bases have advanced in quality through the use of acrylic resins and cast metals. In 1935 polymerized acrylic resin was introduced as a denture base material to support artificial teeth.

Up to this point, we have focused primarily on the historical evolution of direct filling materials and some rather crude indirect materials. Prior to the twentieth century, because of inadequate technology and lack of electricity, fillings were of rather poor quality and did not fit well within the teeth. However, in 1907, Taggert developed a more refined method for producing cast inlays. Cast alloys were introduced later in the twentieth century, further developing this technology. Commercially pure titanium, noble alloys, and base metal alloys of nickel-chromium, cobalt-chromium, or cobalt-nickel-chromium are now available for use in the production of cast inlays, onlays, crowns, and frameworks for fixed all-metal or metal-ceramic dentures and for removable dentures. Few major improvements in the construction of multiple-unit fixed dental prostheses (bridges) occurred until the early 1900s. Mason developed a detachable facing to a crown to hold an artificial tooth in place for an adjacent missing tooth. Thomas Steele (1904), a colleague of Mason, introduced interchangeable facings, which solved the problem of fractured facings.

Even though the practice of dentistry antedates the Christian era, comparatively few historical data exist on the science of dental materials. The use of fluoride to prevent tooth demineralization originated from observations in 1915 of low decay rates among people in areas of Colorado whose water supplies contained significant concentrations of fluoride. Controlled water fluoridation (1 ppm) to reduce tooth decay (demineralization) began in 1944, and the incidence of tooth decay in children who had access to fluoridated water has decreased by 50% since then. The use of pit and fissure sealants and fluoride-releasing varnishes and restorative materials has reduced the caries incidence even further.

Little scientific information about dental restorative materials has been available until recently. Prior to this knowledge, the use of these materials was entirely an art, and the only testing laboratory was the mouth of the patient. Today, despite the availability of sophisticated technical equipment and the

development of standardized testing methods for evaluating the biocompatibility of preventive and restorative materials, this testing still sometimes occurs in the mouths of patients. The reasons for this situation are diverse. In some instances, products are approved for human use without being tested in animal or human subjects. In other instances, dentists use materials for purposes that were not indicated by the manufacturer; for example, a ceramic product may be used for posterior fixed dental prostheses (FDPs) when the product has been recommended only for inlays, onlays, crowns, and anterior three-unit FDPs.

The first significant scientific interest arose during the middle of the nineteenth century, when research studies on amalgam began. At about the same time, some reports appeared in the literature of studies on porcelain and gold foil. These sporadic advances in knowledge finally culminated in the investigations of G. V. Black, who began his research studies in 1895. Hardly a phase of dentistry exists that was not explored and advanced by this pioneer in restorative dentistry.

STANDARDS FOR DENTAL MATERIALS

TEST STANDARDS FOR DENTAL MATERIALS

One of the major advances in the knowledge of dental materials and their manipulation began in 1919, when the U.S. Army requested the National Bureau of Standards (now known as the National Institute of Standards and Technology [NIST]) to establish specifications for the evaluation and selection of dental amalgams for use in federal service.

These test reports were received enthusiastically by the dental profession, and similar test reports were subsequently requested for other dental materials. All findings were published and became common property under this arrangement. In 1928, dental research at the National Bureau of Standards was taken over by the American Dental Association (ADA).

? CRITICAL QUESTION

What is the primary purpose of specifications and international standards for dental materials?

ADA SPECIFICATIONS PROGRAM

Research at the ADA is divided into a number of categories, including measurement of the clinically significant physical and chemical properties of dental materials and the development of new materials, instruments, and test methods. Until 1965, one of the primary objectives of the facility at the NIST was to formulate standards or specifications for dental materials. However, when the ADA Council on Dental Materials and Devices, now known as the Council on Scientific Affairs (CSA), was established in 1966, it assumed responsibility for standards development and initiated the certification of products that meet the requirements of these specifications.

Such specifications are standards by which the quality and properties of particular dental materials can be evaluated. These standards identify the requirements for the physical and chemical properties of a material that ensure satisfactory performance if the material is properly manipulated and used by the dental laboratory technician and the dentist.

The ADA, accredited by the American National Standards Institute (ANSI), is also the administrative sponsor of two standards-formulating committees operating under the direction of ANSI. The ADA Standards Committee for Dental Products (SCDP) develops specifications for all dental materials, instruments, and equipment with the exception of drugs and x-ray films.

Working groups of the ADA SCDP develop the specifications. When a specification has been approved by the ADA SCDP and the ADA CSA, it is submitted to the ANSI. On acceptance by that body, it becomes an American National Standard. Thus the CSA also has the opportunity to accept it as an ADA specification.

New specifications that apply to new program areas are continually being developed. Likewise, existing specifications are periodically revised to reflect changes in product formulations and new knowledge about the behavior of materials in the oral cavity—for example, the ANSI/ADA Specification No. 1 for dental amalgam, which was revised in January 2003.

Dental products should conform to appropriate standards or specifications. The following information is often required: (1) the serial or lot number; (2) the composition; (3) the physical properties, as obtained by standard test methods; (4) biocompatibility data (if required); and (5) data covering every provision of the official specification. Responsibility for ensuring that the product complies with a specification lies solely with the manufacturer and not the standards organization. This provision may not apply to certain biological products such as serums or vaccines. Because the uses of a product may change, the product's name should indicate the generic type of material or its composition rather than a proposed use for the product. Evidence pertaining to mechanical and physical properties, operating characteristics (when applicable), actions, dosage, safety, and efficacy must be submitted by the applicant organization. The applicant must provide objective data from properly designed clinical and laboratory studies. Extended clinical experience may be used in part as a basis for evaluation of a product.

? CRITICAL QUESTIONS

What are the differences between U.S. Food and Drug Administration (FDA) Class I, II, and III devices? Which class of regulations does a dental implant need to satisfy?

U.S. FOOD AND DRUG ADMINISTRATION REGULATIONS FOR MEDICAL DEVICES

The Medical Device Amendments of 1976 to the Federal Food, Drug, and Cosmetic Act gave the FDA the regulatory authority to protect the public from hazardous or ineffective medical (and dental) devices. According to the Federal Register, "The term *device* includes any instrument, apparatus, implement, machine, contrivance, implant, or in vitro reagent that is used in the diagnosis, cure, mitigation, treatment, or

prevention of disease in man and that does not achieve any of its principal intended purposes through chemical action within or on the body of humans or animals and that is not dependent on being metabolized for the achievement of any of its principal intended purposes."

This legislation was the culmination of a series of attempts to provide safe and effective products, beginning with the passage of the Food and Drug Act of 1906, which did not include any provision to regulate medical device safety or the claims made for devices. The 1976 amendments established three regulatory classes for medical devices, Classes I, II, and III. These classes are related to the amount of control necessary to ensure that the medical (including dental) devices are safe and effective. Class I devices are considered to be of low risk; they are subject to general controls, including the registration of the manufacturer's products, adherence to good manufacturing practices, and certain record-keeping requirements. If it is deemed that such general controls are not in themselves adequate to ensure safety and effectiveness as claimed by the manufacturer, the item is placed into the category of Class II devices. Products in this class are required to meet performance standards established by the FDA or appropriate standards from other authoritative bodies, such as those of the ADA. These performance standards may relate to components, construction, and properties of a device, and they may also indicate specific testing requirements to ensure that lots or individual products conform to the regulatory requirement.

Class I devices are subject to the least regulatory control. They have a minimal potential for harm to the user and are often simpler in design than Class II or III devices. Class I devices are subject to "General Controls," as are Class II and III devices. Most Class I devices are exempt from premarket notification and/or good manufacturing practices regulations. Examples of Class I devices include elastic bandages, examination gloves, and handheld surgical instruments.

Examples of Class II devices include powered wheelchairs, infusion pumps, surgical drapes, and dental amalgam. Class II devices are subject to special controls. The special control for dental amalgam is the FDA's "Class II Special Controls Guidance Document: Dental Amalgam, Mercury, and Amalgam Alloy" (21 CFR Part 872.1(e) for the availability of this guidance document).

The most regulated devices are in Class III. Devices are considered to fall into Class III if they support or sustain human life, are of substantial importance in preventing impairment of human health, or they present a potential, unreasonable risk of illness or injury. Test data from performance standards (Class II) or general controls (Class I) are insufficient to provide reasonable assurance that Class III devices are safe and effective for their intended uses. This 1976 legislation requires the classification and regulation of all noncustomized medical devices intended for human use. Under Section 515, all devices placed into Class III are subject to premarket approval requirements. Premarket approval by the FDA involves the required process of scientific review to ensure the safety and effectiveness of these devices.

Examples of Class III devices, which require a premarket approval, include replacement heart valves, silicone gel–filled breast implants, and implanted cerebellar stimulators. Examples of Class III devices that currently require a premarket notification include implantable pacemaker pulse generators and endosseous implants.

Some dental products, such as those containing fluoride, are considered to be drugs, but most products used in the dental clinic are considered to be devices. Thus they are subject to control by the FDA's Center for Devices and Radiological Health. Also subject to this control are over-the-counter products sold to the public, such as toothbrushes, dental floss, and denture adhesives.

The classification of all medical and dental items is developed by panels composed of nongovernmental dental experts as well as representatives from industry and consumer groups. The Dental Products Panel identifies any known hazards or problems associated with a device and then categorizes the item into one of the three classification groups based on relative risk factors.

INTERNATIONAL STANDARDS

Because of the worldwide demand for dental devices, the testing for safety and effectiveness must conform to international standards if manufacturers wish to sell their products in many countries. Two organizations, the Fédération Dentaire Internationale (FDI) and the International Organization for Standardization (ISO), are working toward the establishment of specifications for dental materials on an international level. Originally, the FDI initiated and actively supported a program for the formulation of international specifications for dental materials. As a result of that activity, several specifications for dental materials and devices have been adopted.

The ISO is an international nongovernmental organization whose objective is the development of international standards. This body is composed of national standards organizations and representatives from more than 80 countries. The American National Standards Institute is the U.S. member.

A request by the FDI to the ISO recommended adoption of FDI specifications for dental materials as ISO standards led to the formation of the ISO technical committee (TC) called TC 106—Dentistry. The responsibility of this committee is to standardize terminology and test methods and to develop standards (specifications) for dental materials, instruments, appliances, and equipment. Additional information on ISO standards is provided in the following section.

Several FDI specifications have now been adopted as ISO standards. Since 1963, more than 100 new standards have been developed or are currently under development in ISO TC 106 through cooperative programs with the FDI. Thus considerable progress has already been realized in achieving the ultimate goal of a broad range of international specifications for dental materials and devices.

The benefit of such specifications to the dental profession has been enormous, considering the worldwide supply and demand for dental materials, instruments, and devices.

Dentists are provided with criteria for selection that are impartial and reliable. If dentists use those materials that meet the appropriate specifications, they can be confident that the materials will be satisfactory. Awareness by dental laboratory technicians and dentists of the requirements of these specifications is essential in recognizing the limitations of the dental materials with which they are working. As described frequently in the chapters to follow, no dental material is perfect in its restorative requirements, just as no artificial arm, leg, or hip prosthesis can serve as well as the original member that it replaces.

Research on dental materials that is monitored by the ADA Council on Scientific Affairs or other national standard organizations is of vital concern in this textbook on dental materials. Test specifications for dental materials are referred to throughout the following chapters, although specific details regarding the test methods employed are omitted. For those products sold in other countries, the counterpart ISO standards, if applicable, should be used as a reference source.

? CRITICAL QUESTION

Of the seven subcommittees of the ISO TC 106, which subcommittees are responsible primarily for direct or indirect restorative materials?

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION STANDARDS, SUBCOMMITTEES, AND WORKING GROUPS

ISO TC 106

As of May 2011, TC 106—Dentistry of the ISO comprised 7 subcommittees and 58 working groups to develop standards for testing the safety and efficacy of dental products. TC 106 is the committee responsible for dental standards, terminology used in standards, methods of testing, and specifications applicable to materials, instruments, appliances, and equipment used in all branches of dentistry. As of May 2011 representatives from 26 member countries and 18 observer countries were involved. The following three subcommittees cover most of the dental restorative materials products included in the ISO standards program under the direction of TC 106.

TC 106/SC1: FILLING AND RESTORATIVE MATERIALS

The following 10 working groups are included:

TC 106/SC 1/WG 1	Zinc oxide/eugenol cements and noneugenol cements
TC 106/SC 1/WG 2	Endodontic materials
TC 106/SC 1/WG 5	Pit and fissure sealants
TC 106/SC 1/WG 7	Amalgam/mercury
TC 106/SC 1/WG 9	Resin-based filling materials
TC 106/SC 1/WG 10	Dental luting cements, bases, and liners
TC 106/SC 1/WG 11	Adhesion test methods
TC 106/SC 1/WG 13	Orthodontic products
TC 106/SC 1/WG 14	Orthodontic elastics
TC 106/SC 1/WG 15	Adhesive components

TC 106/SC2: PROSTHODONTIC MATERIALS

The following 16 working groups develop standards for prosthodontic materials:

TC 106/SC 2/WG 1	Dental ceramics
TC 106/SC 2/WG 2	Dental base alloys
TC 106/SC 2/WG 6	Color stability test methods
TC 106/SC 2/WG 7	Impression materials
TC 106/SC 2/WG 8	Noble metal casting alloys
TC 106/SC 2/WG 10	Resilient lining materials
TC 106/SC 2/WG 11	Denture base polymers
TC 106/SC 2/WG 12	Corrosion test methods
TC 106/SC 2/WG 13	Investments
TC 106/SC 2/WG 14	Dental brazing materials
TC 106/SC 2/WG 16	Polymer veneering and die materials
TC 106/SC 2/WG 18	Dental waxes and baseplate waxes
TC 106/SC 2/WG 19	Wear test methods
TC 106/SC 2/WG 20	Artificial teeth
TC 106/SC 2/WG 21	Metallic materials
TC 106/SC 2/WG 22	Magnetic attachments

TC 106/SC8: DENTAL IMPLANTS

The five working groups in SC 8 are as follows:

TC 106/SC 8/WG 1	Implantable materials
TC 106/SC 8/WG 2	Preclinical biological evaluation and testing
TC 106/SC 8/WG 3	Content of technical files
TC 106/SC 8/WG 4	Mechanical testing
TC 106/SC 8/WG 5	Dental implants—terminology

HOW ARE ISO STANDARDS DEVELOPED?

Manufacturers, dental suppliers, users, consumer groups, testing laboratories, governments, the dental profession, and research organizations provide input for the development of standards. International standardization is market-driven and based on the voluntary involvement of all parties in the dental marketplace.

Why do we need standards? The need for a standard is usually expressed by an industry sector, which communicates this need to a national member body. The latter proposes the new work item to the ISO. Once the need for an international standard has been established, the first phase involves definition of the technical scope of the standard. This phase is usually carried out by working groups such as those listed above, which comprise technical experts from countries interested in the subject. Once agreement has been reached on which technical aspects are to be covered in the standard, a second phase is entered, during which countries determine the detailed specifications within the standard. The final phase constitutes the formal approval of the resulting Draft International Standard (DIS), by at least 75% of all voting members, followed by publication of the agreed-upon text as an ISO International Standard.

Most standards require periodic revision because of technological evolution, new methods and materials, new quality

tests, and new safety requirements. To account for these factors, all ISO standards should be reviewed at intervals of not more than 5 years. In some cases it is necessary to revise a standard earlier.

OTHER DENTAL STANDARDS ORGANIZATIONS

The National Institute of Standards and Technology in Gaithersburg, Maryland, has stimulated comparable programs in other countries. The Australian Dental Standards Laboratory was established in 1936 and, until 1973, this facility was known as the Commonwealth Bureau of Dental Standards). Other countries that have comparable organizations for developing standards and certifying products are Canada, Japan, France, the Czech Republic, Germany, Hungary, Israel, India, Poland, and South Africa. Also, by agreement among the governments of Denmark, Finland, Iceland, Norway, and Sweden, the Scandinavian Institute of Dental Materials, better known as NIOM (Nordisk Institutt for Odontologiske Materialer), was established in 1969 for testing, certification, and research regarding dental materials and equipment to be used in the five countries. NIOM became operational in 1973.

Also in Europe, the Comité Européen de Normalisation (CEN) established Task Group 55 to develop European standards. After the establishment of the European Economic Community, the CEN was given the charge to outline recommendations of standards for medical devices, including dental materials. In fact, the proper term to describe dental materials, dental implants, dental instruments, and dental equipment in Europe is *medical devices used in dentistry*. The CE marking on product labels denotes the European mark of conformity with the Essential Requirements in the Medical Device Directive that became effective on January 1, 1995. All medical devices marketed in the European Union countries must have the CE mark of conformity. For certain products, some countries may enforce their own standards when other countries or the international community have not developed mutually acceptable requirements. For example, Sweden restricts the use of nickel in cast dental alloys because of biocompatibility concerns, whereas no such restriction applies to those alloys in the United States. Iceland, Liechtenstein, and Norway are also signatories of the European Economic Area Agreement and require the CE marking and NIOM's Notified Body registration number on medical device packaging.

Many universities have established laboratories for research on dental materials topics. This source of basic information on the subject has exceeded that of all other sources combined. Until recently, dental research activities in universities were centered solely in dental schools, with most of the investigations being conducted by the dental faculty. Now, research in dental materials is also being conducted in some universities that do not have dental schools. This dental-oriented research in areas such as metallurgy, polymer science, materials science, mechanical engineering, engineering mechanics, and ceramics science is being conducted in basic science departments. These expanding fields of research in dental materials illustrate the interdisciplinary aspects of the science. Since the final criterion for the success of any material or technique is its service in the mouths of our patient populations, countless contributions to this field have been made by dental clinicians. The observant clinician contributes invaluable information by his or her observations and analyses of failures and successes. Accurate clinical records and well-controlled practice procedures form an excellent basis for valuable clinical research.

The importance of clinical documentation for claims that are made relative to the in vivo performance of dental materials is now readily apparent. During the past two decades there has been an escalation in the number of clinical investigations designed to correlate specific properties with clinical performance criteria. These studies are designed to establish the precise behavior of a given material or system. In the chapters that follow, frequent reference is made to such investigations. In addition, an increased emphasis has been placed on evidence-based research to support clinical decision making.

Other sources of information are manufacturers' research laboratories. Most manufacturers of dental devices recognize the value of a research laboratory relative to the development and quality control of products, and unbiased information from such groups is particularly valuable.

The diversity of research activity has resulted in an accelerating growth in the body of knowledge related to dental materials and processing methods. For example, in 1978, approximately 10% of all U.S. support for dental research was focused on restorative dental materials. This percentage would no doubt be considerably higher if the money spent by industry for the development of new materials, instruments, and appliances were included. This growing investigative effort has resulted in a marked increase in the number of new materials, instruments, and techniques being introduced to the profession. For these and other reasons, it is vitally important to have an intimate knowledge of the properties and behavior of dental materials if modern dental practices are to remain abreast of changing developments and to adopt, when available, evidence-based guidelines that will ensure optimal patient care.

CRITICAL QUESTION

How is it possible that dental materials that do not meet the specifications of the American Dental Association or other organizations' standards can be sold to dentists and consumers?

HOW SAFE ARE DENTAL RESTORATIVE MATERIALS?

Standards for dental materials have been developed to aid producers, users, and consumers in the evaluation of the safety and effectiveness of dental products. Many countries have a dental standards organization that is charged with the

development of standard tests and that ensure product reliability and safety. As indicated earlier, the American Dental Association's Standards Committee on Dental Products (SCDP) develops specifications for dental materials, oral hygiene products, infection-control products, dental equipment, and dental instruments. In addition, international standards are developed by TC—106 of the International Organization for Standardization (ISO). The decision of producers to test their materials according to national and international standards is purely voluntary. However, for any manufacturer to market their products in certain European countries, a CE mark must be obtained based on the product's ability to meet one or more national or international standards for performance and quality. A CE marking (or CE mark) on a product means that the manufacturer declares that the product complies with the essential requirements of the relevant European health, safety, and environmental protection legislation, in practice by many of the so-called product directives.

The existence of materials evaluation standards does not prevent anyone from manufacturing, marketing, buying, or using dental or medical devices that do not meet these standards. However, producers or marketers of products and devices are expected to meet the safety standards established for those products in the countries in which they are sold. Thus, it is possible for a producer to be given premarket approval in the United States by the U.S. Food and Drug Administration (FDA) to sell a dental device such as a dental restorative material without the device being tested by the American Dental Association or other agency in accordance with the requirements for a material specification. Nevertheless, these agencies are becoming increasingly dependent on one another to ensure that all products marketed worldwide are safe and effective.

No dental device (including restorative materials) is absolutely safe. Safety is relative, and the selection and use of dental devices or materials are based on the assumption that the benefits of such use far outweigh the known biological risks. However, there is always uncertainty over the probability that a patient will experience adverse effects from dental treatment. The two main biological effects are allergic and toxic reactions. Paracelsus (1493–1541), a Swiss physician and alchemist, formulated revolutionary principles that have remained an integral part of the current field of toxicology. He stated that "All substances are poisons; there is none which is not a poison. The right dose differentiates a poison from a remedy" (Gallo and Doull, 1991).

Toxic agents may enter the body through the gastrointestinal tract (ingestion), lungs (inhalation), skin (topical, percutaneous, or dermal), and parenteral routes (Klaassen and Eaton, 1991). Exposure to toxic agents can be subdivided into acute (less than 24 hours), subacute (repeated, 1 month or less), subchronic (1 to 3 months), and chronic (longer than 3 months). For many toxic agents, the effects of a single exposure are different from those associated with repeated exposures. Like toxicity, chemical allergy may also be dose-dependent, but it often results from low doses of chemical agents once sensitization has occurred. For a dental restorative material to produce an allergic reaction, most chemical agents or their metabolic products function immunologically as haptens and combine with endogenous proteins to form an antigen. The synthesis of sufficient numbers of antibodies takes 1 to 2 weeks. A later exposure to the chemical agent can induce an antigen-antibody reaction and clinical signs and symptoms of an allergy. Munksgaard (1992) concluded that occupational risks in dentistry are low and that patient risk for side effects of dental treatment is extremely low. Adverse reactions to dental materials have been reported to occur in only 0.14% of a general patient population (Kallus and Mjör, 1991) and in 0.33% of a prosthetic patient population (Hensten-Pettersen and Jacobsen, 1991).

WHY DO DENTAL STUDENTS, DENTISTS, AND DENTAL EDUCATORS NEED TO UNDERSTAND THE PRINCIPLES OF DENTAL MATERIALS SCIENCE?

Dentists and engineers have similar long-range objectives in their professions—that is, to design, construct, and evaluate devices or structures that can be subjected to a wide range of environmental conditions. In 1936 E. W. Skinner described the need for the principles of physics and chemistry to be applied in restorative dentistry in a similar manner as they were applied to structural engineering. He expressed significant concerns regarding the need for knowledge of dental materials science. As he stated in 1936:

> *Unfortunately there are too many unscrupulous dental manufacturers who make impossible claims for inferior products, thus deceiving the dentist. There have been actual cases of highly advertised dental materials, which have been made extremely popular among dentists simply by clever advertising methods, whereas careful laboratory tests have shown products to be distinctly inferior. The well-informed dentist will be able to discriminate between fact and propaganda, and will refuse to be duped in this manner.*

Although many technological advances have been proposed since 1936, to improve the quality of dental materials used in dentistry, a challenge remains for end users to critically evaluate the claims made on the reported performance of dental materials and to relate these claims carefully to well-established physical principles for the specific classes of materials. The current era of evidence-based dentistry is consistent with this need to understand cause-and-effect relationships that allow us to predict with reasonable certainty the time-dependent behavior of preventive, restorative, and auxiliary materials.

? CRITICAL QUESTION

Which factors determine when dental material products become obsolete?

THE FUTURE NEED FOR DENTAL BIOMATERIALS

Future developments in dentistry and the requirement for delivering optimal oral health care will control the future of dental materials science. Dentistry will continue to focus on the preservation and enhancement of oral health through the prevention of caries and periodontal disease and their sequelae and the rehabilitation of missing, damaged, or destroyed hard and soft tissues. A cure for dental caries will have a dramatic impact on the use of restorative materials to restore form and function to teeth with cavitated lesions. However, there will be a continuing need for rerestoring teeth because of the time-dependent failure or degradation of restorations. Decisions on which biomaterials to use for a given clinical condition or situation will be controlled by the known benefits of each treatment choice compared with the known risks.

Since implementation of a cure for caries or processes for root or tooth regeneration are likely to take at least 20 years, as have most major developments of the past, most of the restorative materials employed today will likely remain in use for another decade or more. The use of dental amalgam will continue to decline until it is eliminated because of environmental restrictions on mercury release. The development of more durable and technique-insensitive restorative materials will further accelerate the decline of dental amalgam. The world has moved into an era of a high esthetic demand at the expense of durability and cost. Since many of these situations are not related to the effects of caries, the demand for esthetic enhancement will continue well into the future.

The benefits of caries prevention have led to a reduction in the need for complete and removable dentures and for materials that release fluoride. Minimally invasive concepts have led to the sealing of defective or leaking restorations with preventive resins rather than continuing the use of more destructive replacement procedures Thus, remineralizing agents, smart materials, replacement restorations, and repaired restorations will continue to be in high demand into the foreseeable future. The need for replacement restorations should decrease over the next several decades. However, this reduction will be balanced by the increased demand for esthetic procedures.

Technology has advanced tremendously over the past 30 years and its benefits have been realized in laser applications, imaging procedures, low-shrinkage composites, smart ceramics, and minimally invasive dental procedures. CAD-CAM technology has reduced the demand for impression materials and some indirect auxiliary materials that have been used by laboratory technicians to fabricate indirect prostheses.

One age-old question will have to be answered by dentists and the dental profession in the future—that is, when does a restorative material become obsolete? To answer this question, we should look back into the past. Up to the early 1970s, silicate cement restorations were used for anterior esthetic restorations. This material was used because of its tooth-colored properties in addition to its ability to release significant amounts of fluoride. However, the latter benefit led to the demise of the material since severe surface degradation, marginal breakdown, and discoloration of the surface occurred over time, resulting in defective and stained margins (Figure 1-6) and loss of anatomic contour. Furthermore, more durable resin-based composites and improved micromechanical bonding procedures made silicate cements virtually obsolete by the mid-1970s. At about the same time, direct-filling gold restorations were becoming less desirable treatment choices, even though some clinicians demonstrated exceptional skill in placing and finishing these restorations with superb marginal adaptation (Figure 1-7), comparable or superior to that of cast gold restorations. However, this type of material was extremely technique-sensitive and many restorations failed because of inadequate mechanical retention or pulp sensitivity.



FIGURE 1-6 Anterior class III silicate cement restorations exhibiting severe surface degradation, marginal staining, and general discoloration.

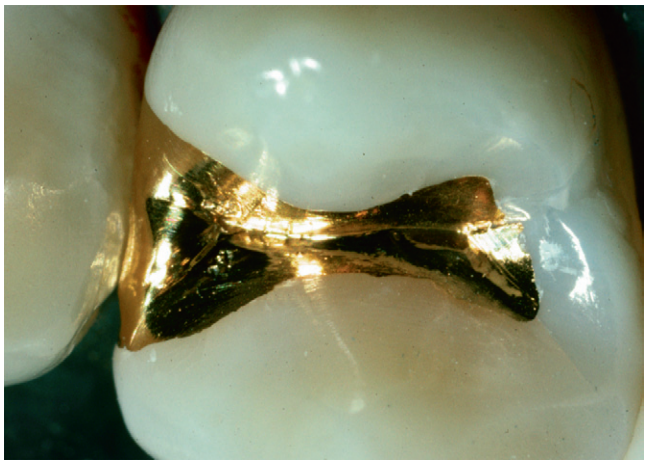


FIGURE 1-7 Direct-filling gold restoration illustrating the exceptional capability for marginal adaptation of this type of restoration. (Clinical procedures performed by Dr. Richard D. Tucker. Photo courtesy of Dr. John Sechena.)

We can conclude that some restorative materials became obsolete because of one or more of the following reasons: (1) their drawbacks overall far outweighed their known advantages, (2) material degradation led unacceptable margin adaptation, (3) material degradation led to unacceptable esthetics, (4) metallic appearance was generally unacceptable to patients, (5) alternative restoratives exhibited superior performance, (6) alternative materials were less technique-sensitive, (7) and alternative materials led to less costly patient treatment.

The following chapters present descriptions of the properties, technique characteristics, and performance potential of a wide variety of preventive, restorative, and auxiliary materials. These topics are arranged in one or more of the following categories: (I) General Classes and Properties of Dental Materials; (II) Auxiliary Dental Materials; (III) Direct Restorative Materials; and (IV) Indirect Restorative and Prosthetic Materials.

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CHAPTER 2

Structure of Matter and Principles of Adhesion

OUTLINE

Interatomic Bonds

Atomic Arrangement

Interatomic Bond Distance and Thermal Energy

Diffusion

Adhesion and Bonding

Bonding to Tooth Structure

KEY TERMS

Adherend—A material substrate that is bonded to another material by means of an adhesive.

Adhesion—A molecular or atomic attraction between two contacting surfaces promoted by the interfacial force of attraction between the molecules or atoms of two different species; adhesion may occur as chemical adhesion, mechanical adhesion (structural interlocking), or a combination of both.

Adhesive—Substance that promotes adhesion of one substance or material to another.

Adhesive bonding—Process of joining two materials by means of an adhesive agent that solidifies.

Cohesion—Force of molecular attraction between molecules or atoms of the same species.

Contact angle—Angle of intersection between a liquid and a surface of a solid that is measured from the solid surface through the liquid to the liquid/vapor tangent line originating at the terminus of the liquid/solid interface; used as a measure of wettability, whereby no wetting occurs at a contact angle of 180° and complete wetting occurs at an angle of 0°.

Diffusion coefficient—Proportionality constant representing the rate at which a substance is transported through a unit area and a unit thickness under the influence of a unit concentration gradient at a given temperature.

Glass transition temperature (T_g)—Temperature above which a sharp increase in the thermal expansion coefficient occurs, indicating increased molecular mobility.

Heat of vaporization—Thermal energy required to convert a solid to a vapor.

Latent heat of fusion—Thermal energy required to convert a solid to a liquid.

Melting temperature (melting point)—Equilibrium temperature at which heating of a pure metal, compound, or eutectic alloy produces a change from a solid to a liquid.

Metallic bond—Primary bond between metal atoms.

Micromechanical bonding—Mechanical adhesion associated with bonding of an adhesive to a roughened adherend surface.

Self-diffusion—Thermally driven transfer of an atom to an adjacent lattice site in a crystal composed of the same atomic species.

Stress concentration—State of elevated stress in a solid caused by surface or internal defects or by marked changes in contour.

Supercooled liquid—A liquid that has been cooled at a sufficiently rapid rate to a point below the temperature at which an equilibrium phase change can occur.

Surface energy—Same as surface tension but expressed in mJ/m^2.

Surface tension—A measurement of the cohesive energy present at an interface; in the case of a liquid, it is the liquid/air interface. This energy is the result of molecules on the surface of a liquid experiencing an imbalance of attraction between molecules. It has units of mN/m.

Thermal expansion coefficient—Relative linear change in length per unit of initial length during heating of a solid per K within a specified temperature range.

Wetting—The ability of a liquid to maintain contact with a solid surface; it reflects the intermolecular interactions when the two are brought in intimate contact.

Wetting agent—A surface-active substance that can be applied to a solid substrate to reduce the surface tension of the liquid to be placed on the solid; the purpose is to promote wetting or adhesion.

Vacancy—Unoccupied atom lattice site in a crystalline solid.

van der Waals forces—Short-range force of physical attraction that promotes adhesion between molecules of liquids or molecular crystals.

CRITICAL QUESTION

When the state of material (vapor, liquid and solid) changes, what happens between atoms or molecules that make up the material?

Around 460 B.C., the Greek philosopher Democritus proposed that all matter was composed of indivisible particles called *átomos* (*á* = "un"; *temno* = "to cut"; meaning "uncuttable"), which is the origin of the name *atoms*. We know that an atom consists of a nucleus surrounded by a cloud of negatively charged electrons, as depicted in the electron cloud model of an atom (Figure 2-1). Except for the hydrogen atom, where there are no neutrons, the nucleus contains a mix of positively charged protons and electrically neutral neutrons. The electrons of an atom exist in different clouds at the various energy levels. An atom becomes a negative ion when it gains electron(s) or a positive ion when it loses electron(s).

Two or more atoms can form an electrically neutral entity called a molecule. Attraction between atoms and between molecules result in materials we can see and touch. Consider water as an example. Chemically, the basic unit of water is a molecule made of two hydrogen atoms and one oxygen atom. If each molecule attains a kinetic energy that is higher than the attraction between these molecules, they appear in the vapor form. As the surrounding temperature decreases, the level of kinetic energy within individual molecules decreases and the attraction between them becomes more prominent, so that they condense to a liquid form. Further cooling yields a solid called ice, where the kinetic energy is so low that the molecules are immobilized by the attraction between them.

The transformation between vapor, liquid, and solid is called the change of state. A change from the solid to the liquid state will require additional energy—kinetic energy—to break loose from the force of attraction. This additional energy is called the **latent heat of fusion**. The temperature at which this change occurs is known as the **melting temperature** or fusion temperature. When water boils, energy is needed to transform the liquid to vapor, and this quantity of energy is known as the **heat of vaporization**. It is possible for some solids to change directly to a vapor by a process called sublimation as seen in dry ice; this, however, has no practical importance as far as dental materials are concerned.

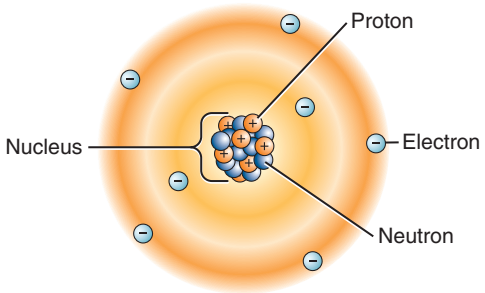


FIGURE 2-1 Electron cloud model of an atom. The neutrons (blue spheres) and protons (spheres with "+") occupy a dense central region called the nucleus. The orange cloud formation illustrates the trace of electrons (spheres with "–") as they move around the nucleus.

CRITICAL QUESTION

Which types of primary bonds control the properties of dental resins and cast alloys?

INTERATOMIC BONDS

The preceding brief focus on change of state raises a question concerning the types of forces holding these atoms and molecules together. The electronic structure of an atom is relatively stable if it has eight electrons in its outer valence shell, as noble gases do, except for helium, which has only two electrons. Other atoms must lose, acquire, or share electrons with yet other atoms to achieve a stable configuration—that is, eight electrons in the outer shell. These processes produce strong or primary bonds between atoms. The bonding of atoms within a molecule also creates new but much weaker forces holding the molecules together. These are often called secondary bonds.

PRIMARY BONDS

The formation of primary bonds depends on the atomic structures and their tendency to assume a stable configuration. The strength of these bonds and their ability to reform after breakage determine the physical properties of a material. Primary atomic bonds (Figure 2-2), also called chemical bonds, may be of three different types: (1) ionic, (2) covalent, and (3) metallic.

Ionic Bonds

The classic example of ionic bonding is the bond between the Na^+ and Cl^- of sodium chloride (Figure 2-2, *A*). Because the sodium atom contains one valence electron in its outer shell and the chlorine atom has seven electrons in its outer shell, the transfer of the sodium valence electron to the chlorine atom results in the stable compound Na^+Cl^-. In dentistry, ionic bonding exists in some dental materials, such as in gypsum structures and phosphate-based cements.

Covalent Bonds

In many chemical compounds, two valence electrons are shared by adjacent atoms (Figure 2-2, *B*). By virtue of sharing electrons, the two atoms are held together by covalent bonds to form a molecule that is sufficiently stable, and electrically neutral in a definite arrangement. The hydrogen molecule, H_2, exemplifies covalent bonding. The single valence electron in each hydrogen atom is shared with that of the other combining atom, and the valence shells become stable. Covalent bonding occurs in many organic compounds, such as in dental resins, where they link to form the backbone structure of hydrocarbon chains (Chapter 6).

Metallic Bonds

The third type of primary atomic interaction is the **metallic bond** (Figure 2-2, *C*). The outer shell valence electrons can be removed easily from metallic atoms and form positive ions. The free valence electrons can move about in the metal

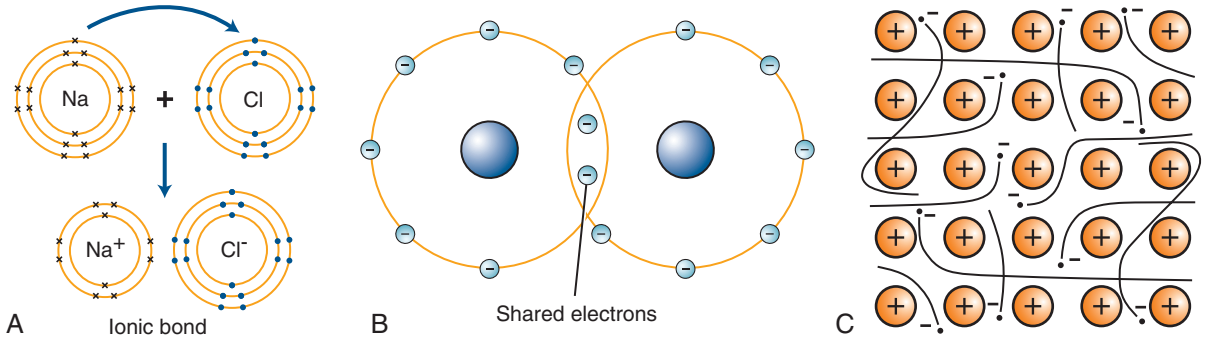


FIGURE 2-2 Primary bonds. **A**, Ionic bond, characterized by electron transfer from one element (Na) to another (Cl). **B,** Covalent bond, characterized by electron sharing and very precise bond orientations. **C,** Metallic bond, characterized by electron sharing and formation of a "cloud" of electrons that bonds to the positively charged nucleus in a lattice.

space lattice (Chapter 5) to form what is sometimes described as an electron "cloud" or "gas." The electrostatic attraction between the electron cloud and the positive ions in the lattice provides the force that bonds the metal atoms together as a solid.

The free electrons give the metal its characteristically high thermal and electrical conductivity. These electrons absorb light energy, so that all metals are opaque to transmitted light. The metallic bonds are also responsible for the ability of metals to deform plastically. The free electrons can move through the lattice, whereas their plastic deformability is associated with slip along crystal planes. During slip deformation, electrons easily regroup to retain the cohesive nature of the metal.

Combination of Primary Bonds

Although we can describe the three primary bonds separately, it is also possible to find more than one type of primary bond existing in one material. Consider calcium sulfate ($CaSO_4$), the main ingredient of gypsum products (Chapter 9), as an example (Figure 2-3). In the sulfate ion (SO_4^{2-}) the sulfur and oxygen atoms are held together covalently but they are short of two electrons. Calcium has two electrons in the outer orbit, which are easily removed and transferred to the SO_4. The result is a Ca^{2+} ion with attraction for an SO_4^{2-} ion.

? CRITICAL QUESTION

Is hydrogen bonding controlled by a van der Waals force?

SECONDARY BONDS

In contrast with primary bonds, secondary bonds do not share electrons. Instead, charge variations among atomic groups of the molecule induce dipole forces that attract adjacent molecules or parts of a large molecule.

van der Waals Forces

These **van der Waals** forces of attraction arise from dipole attractions (Figure 2-4). In the case of polar molecules, dipoles are induced by an unequal sharing of electrons (Figure 2-4, *A*). In the case of nonpolar molecules, random movement of electrons within the molecule creates fluctuating dipoles

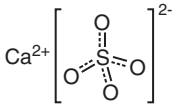


FIGURE 2-3 Combination of primary bonds. Ionic bond between Ca^{2+} and $[SO_4]^{2-}$, Covalent bonds between S and O.

(Figure 2-4, *B*). Dipoles generated within these molecules will attract other similar dipoles. Such interatomic forces are quite weak compared with the primary bonds.

Hydrogen Bond

The hydrogen bond is a special case of dipole attraction of polar compounds. It can be understood by studying a water molecule (Figure 2-5). Attached to the oxygen atom are two hydrogen atoms. These bonds are covalent. As a consequence, the protons of the hydrogen atoms pointing away from the oxygen atom are not shielded efficiently by the electrons. They become positively charged. On the opposite side of the water molecule, the electrons that fill the outer shell of the oxygen provide a negative charge. The positive hydrogen nucleus is attracted to the unshared electrons of neighboring water molecules. This type of bond is called a hydrogen bridge. Polarity of this nature is important in accounting for the intermolecular reactions in many organic compounds—for example, the sorption of water by synthetic dental resins.

ATOMIC ARRANGEMENT

All materials we use consist of trillions of atoms. As described earlier, they are attracted to each other and retain a particular physical appearance. The question is in which configuration they are held together. In 1665, Robert Hooke (1635–1703) explained crystal shapes in terms of the packing of their component parts, like stacking musket balls in piles. This is an exact model of the atomic structure of many familiar metals, with each ball representing an atom.

In the solid state, atoms combine in a manner that ensures minimal internal energy. For example, sodium and chlorine share one electron at the atomic scale. In the solid state, like grains of salt, they do not exist in individual pairs; in fact,

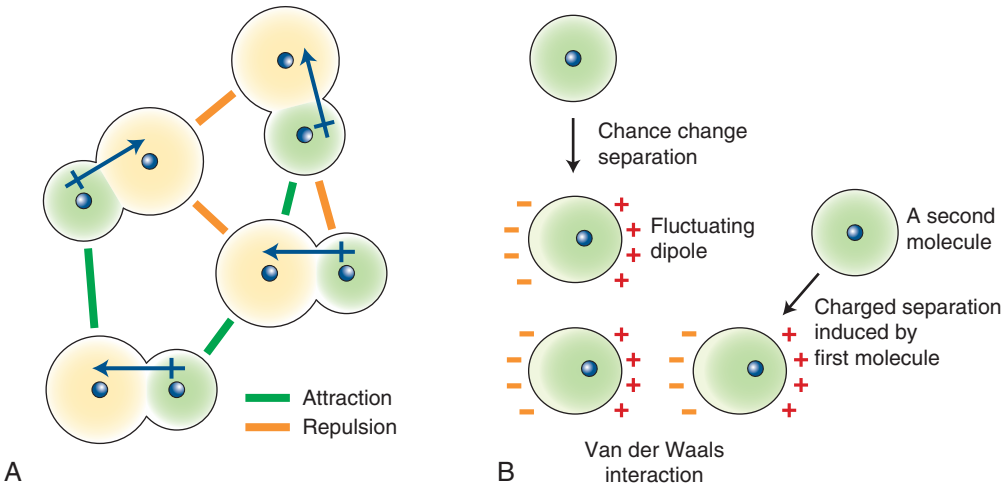


FIGURE 2-4 van der Waals forces by dipole attraction. **A,** Polar compound; the attraction and repulsion between molecules are induced by a permanent dipole moment resulting from asymmetrical electron distribution within the molecule. **B,** Nonpolar compound; a temporary dipole (fluctuating dipole) occurs when the symmetrical distribution of electrons in a molecule becomes asymmetrical temporarily; it then attracts the dipole to adjacent molecules, resulting in the eventual interaction.

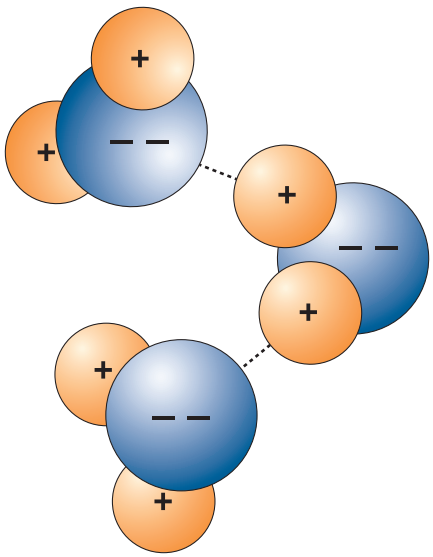


FIGURE 2-5 Hydrogen bond formation between water molecules. The polar water molecule bonds to adjacent water molecules via an H (*orange*) O (*blue*) interaction between molecules.

each sodium ion is attracted to six chlorine ions and vice versa (Figure 2-6). They form a regularly spaced configuration (long-range repetitive space lattice) known as a crystal. A space lattice can be defined as any arrangement of atoms in space in which every atom is situated similarly to every other atom.

There are structures where regularly spaced configurations do not occur in the solid state. For example, the molecules of some of the waxes used by a dentist or laboratory technician are distributed at random when solidified. This noncrystalline formation is also known as an amorphous structure.

? CRITICAL QUESTION

Which dental substances are examples of crystalline materials, noncrystalline materials, and combinations of crystalline and noncrystalline materials?

CRYSTALLINE STRUCTURE

There are 14 possible lattice types. The type of space lattice is defined by the length of each of three unit cell edges (called the axes) and the angles between the edges. The simplest and most regular lattice is a cubic, as shown in Figure 2-7, *A*; it is characterized by axes that are all of equal length and meet at 90-degree angles, representing the smallest repetitive volume of a crystal, which is called a unit cell. Each sphere represents the positions of the atoms. Their positions are located at the points of intersection of three planes, each plane (surface of the cube) being perpendicular to the other two planes. These planes are often referred to as crystal planes. However, the simple cubic arrangement shown in Figure 2-7, *A*, is hypothetical, as it leaves enough space to fit additional atoms per unit cell. Most crystalline lattices of atoms also contain sites of missing atoms. Each missing atom site is called a vacancy.

Most metals used in dentistry belong to the cubic system. For example, iron at room temperature has an atom at each corner of the cube and another atom at the body center of the cube (Figure 2-7, *B*). This crystal form is called a body-centered cubic cell. Copper, on the other hand, has additional atoms at the center of each face of the unit cell but none at the center of the cube. This form is called a face-centered cubic cell (Figure 2-7, *C*).

Other types of space lattices of dental interest are shown in Figure 2-8. The hexagonal close-packed arrangement (Figure 2-8, *G*) observed in titanium, zinc, and zirconium has become an important crystalline structure in dentistry. Note that each unit cell consists of three layers of atoms.

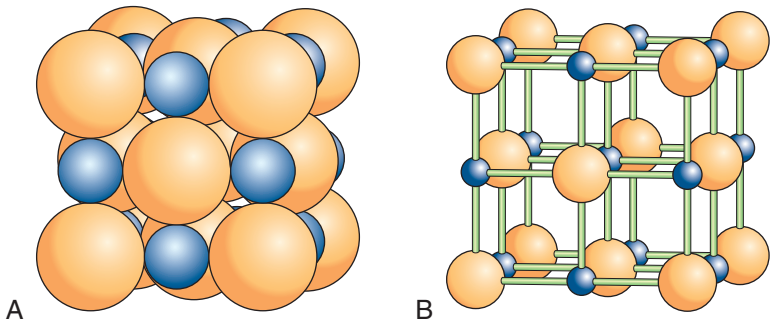


FIGURE 2-6 The atomic arrangement of table salt. **A,** Sphere model showing that atoms are actually closely packed together. **B,** Ball-and-stick model displaying the three-dimensional position of the atoms and bonds between them. The orange spheres are chlorine ions and the blue spheres are sodium ions.

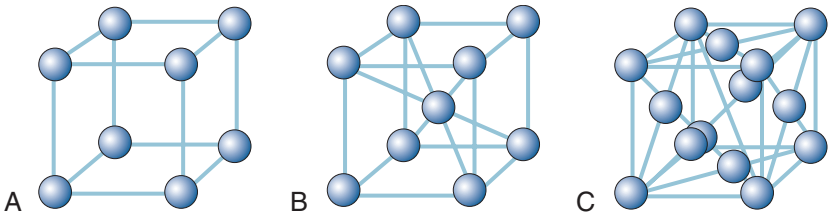


FIGURE 2-7 Unit cells of the cubic space lattices. **A,** Simple cubic. **B,** Body-centered cubic. **C,** Face-centered cubic.

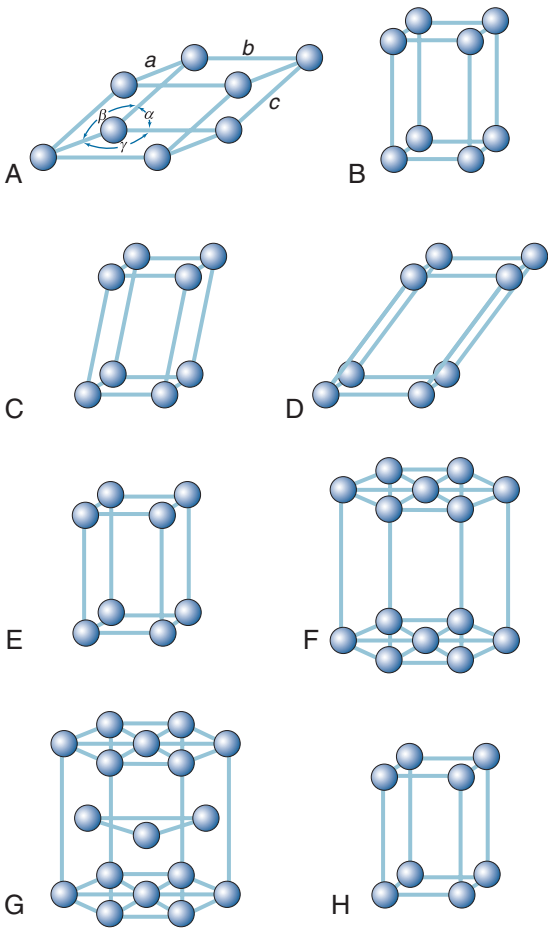


FIGURE 2-8 Other lattice types of dental interest. **A,** Rhombohedral; $a = b = c$; $\alpha = \beta = \gamma \neq 90°$. **B,** Orthorhombic; $a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$. **C,** Monoclinic; $a \neq b \neq c$; $\alpha \neq \beta = \gamma = 90°$. **D,** Triclinic; $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90°$. **E,** Tetragonal; $a = b \neq c$; $\alpha = \beta = \gamma = 90°$. **F,** Simple hexagonal; $a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$. **G,** Close-packed hexagonal; $a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$. H, Rhombic; $a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$.

All metallic-based dental materials are crystalline. Some pure ceramics, such as alumina and zirconia core materials, are entirely crystalline.

NONCRYSTALLINE STRUCTURE

Glass is a typical noncrystalline solid of SiO_2 because its atoms tend to be arranged in non-repeating units (Figure 2-9). The ordered arrangement of the glass is more or less locally interspersed with a considerable number of disordered units. Because this arrangement is also typical of liquids, such solids are sometimes called **supercooled liquids**. Because of the complexity of the physical configuration of polymer chains (Chapter 6), the molecules of resins are not favored to arrange in orderly repeating patterns. Therefore, polymeric-based materials used in dentistry are usually noncrystalline.

The structural arrangements of the noncrystalline solids do not represent such low internal energies as do crystalline arrangements of the same atoms and molecules. They do not have a definite melting temperature but rather gradually soften as the temperature is raised. The temperature at which there is an abrupt increase in the **thermal expansion coefficient**, indicating increased molecular mobility, is called the **glass transition temperature (T_g)**; it is characteristic of the particular glassy structure. Below T_g, the material loses its fluid characteristics and gains significant resistance to shear deformation. When set, synthetic dental resins are examples of materials that often have glassy structures with a T_g greater than body temperature.

Many dental materials often consist of a noncrystalline glassy matrix and crystalline inclusions (filler phase). Crystalline inclusions provide desired properties including color, opacity, increased thermal expansion coefficients, and, in some dental ceramics, increased radiopacity (Chapter 18). The filler phase of resin-based composite (Chapter 13), on the

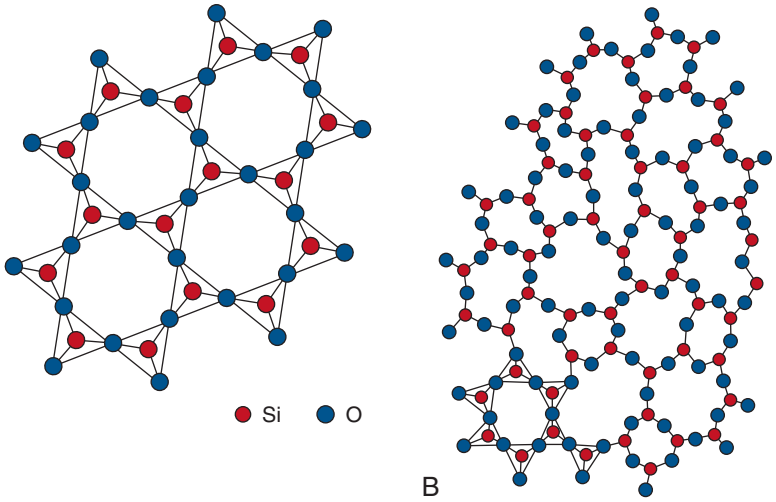


FIGURE 2-9 Two-dimensional illustration of crystalline (*left*) and noncrystalline (*right*) forms of SiO_2.

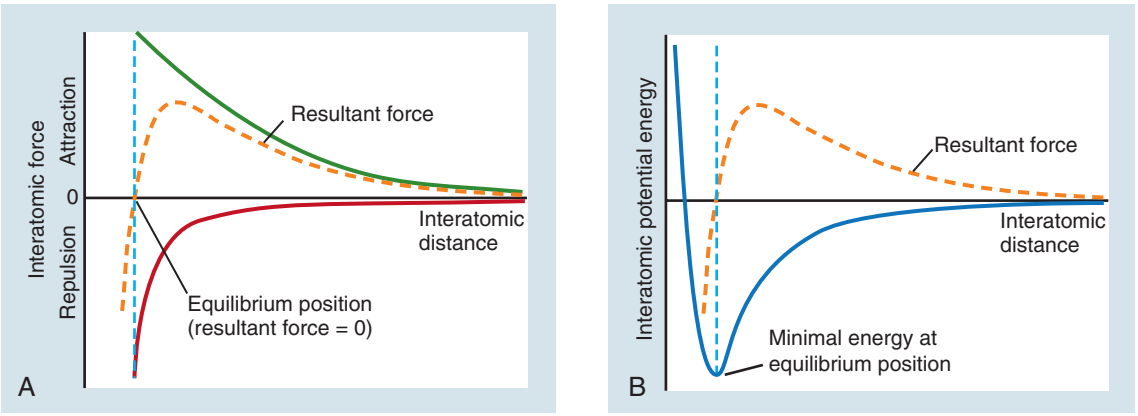


FIGURE 2-10 Interaction between two atoms. **A,** Relation of interatomic forces to interatomic distance. The resultant force (– –) is the sum of attraction (—) and repulsion (—) forces. At the equilibrium position (– –), either a negative (repulsive) or a positive (attractive) force is required to move the atom out of its equilibrium position. **B,** Integration of the interatomic force (– –) shown in (**A**) over the interatomic distance yields the interatomic energy (—). Note that the potential energy is at minimum when equilibrium (– –) is reached.

other hand, can be crystalline, such as quartz particles or noncrystalline glass spheres.

? CRITICAL QUESTION

How does the interatomic bond distance affect the thermal property of materials?

INTERATOMIC BOND DISTANCE AND THERMAL ENERGY

We can treat an atom as a discrete particle with definite boundaries and volume established by the electrostatic fields of the electrons. Between any two atoms, there are forces of attraction drawing them together and forces of repulsion pushing them apart. Both forces increase as the distance between the atoms decreases. The force of repulsion increases much more than the force of attraction as the atoms get closer (Figure 2-10, *A*). The balance between these two forces is essentially attractive when the two atoms are far apart, and becomes repulsive only when the atoms are much closer.

Bond Distance

The position at which both forces are equal in magnitude (but opposite in direction) is considered the equilibrium position of the atoms (Figure 2-10, *A*). The interatomic distance at equilibrium represents the distance between the centers of the two adjacent atoms.

Bonding Energy

Since the conditions of equilibrium are more nearly related to the energy factor than to interatomic distance, the relationships in Figure 2-10, *A*, can be more logically explained in terms of interatomic energy. Energy is defined as the product of force and distance. Integration of the interatomic force (dashed line in Figure 2-10, *A*) over the interatomic distance yields the interatomic energy (Figure 2-10, *B*). In contrast with the resultant force, the energy needed to keep them far apart does not change much initially as two atoms come closer together. As the resultant force approaches zero, the energy needed to keep them apart decreases as the repulsion force becomes significant (Figure 2-10, *B*). The energy finally

reaches a minimum when the resultant force becomes zero. Thereafter, the energy increases rapidly because the resultant repulsive force increases rapidly with little change in interatomic distance. The minimal energy corresponds to the condition of equilibrium and defines the equilibrium interatomic distance.

Thermal Energy

The atoms in a crystal at temperatures above absolute zero are in a constant state of vibration, and the average amplitude is dependent on the temperature: the higher the temperature, the greater the amplitude and, consequently, the greater the kinetic or internal energy. For a certain temperature, the minimal energy required to maintain equilibrium is denoted by the bottom of the trough in Figure 2-10, *B*. As the temperature increases, the amplitude of the atomic (or molecular) vibration increases. It follows also that the mean interatomic distance increases (Figure 2-11) as well as the internal energy. The overall effect is the phenomenon known as thermal expansion.

As the temperature increases from T_0 to T_5 in Figure 2-11, the mean interatomic distance increase is less with the deeper energy trough (Figure 2-11, *A*) than that in shallower energy trough (Figure 2-11, *B*). This means that the linear coefficient of thermal expansion (α) of materials with similar atomic or molecular structures tends to be inversely proportional to the melting temperature. If the temperature continues to increase, the increase of interatomic distance will result in change of state. A solid melts to a liquid, and the liquid subsequently vaporizes to a gas. For a solid with greater minimum energy, i.e., a deeper trough depth (Figure 2-11, *A*), greater amounts of energy are required to achieve melting and boiling, which corresponds to higher melting and boiling temperatures.

As shown in Figure 2-10, *A*, the net force on the atoms at the equilibrium distance is zero, but small displacements result in rapidly increasing forces to maintain the equilibrium distance. The stiffness or elastic modulus of the material (Chapter 4) is proportional to the rate of change of the force with a change in displacement that is measured by the slope of the net force curve near equilibrium. A greater slope of the force curve implies a narrower, deeper trough in the energy curve (Figure 2-11, *A*). Hence, a high melting point is usually accompanied by a greater stiffness.

The preceding principles represent generalities, and exceptions do occur. Nevertheless, they allow one to estimate the influence of temperature on the properties of most of the dental materials discussed in subsequent chapters.

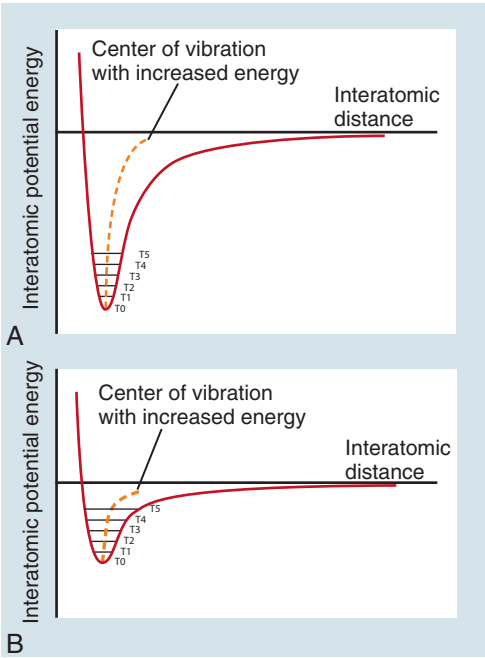


FIGURE 2-11 Thermal energy and bonding energy. As the temperature rises from T_0 to T_5, the interatomic distance increases. For the solid with a deeper potential energy trough (**A**), the actual increase in distance is less than that of the solid with a shallower potential energy trough (**B**). Therefore, less thermal expansion and a higher melting temperature are expected for (**A**). In addition, a high melting temperature usually is accompanied with a greater stiffness.

DIFFUSION

When we place a drop of ink in a bowl of water, we observe the spread of the ink in the water. It will eventually disperse through the entire body of the water. This process is called diffusion. The same process also occurs within solid materials but at a substantially slower rate. An understanding of diffusion in a solid requires two new concepts.

First, the atoms in a space lattice, as previously described, are constantly in vibration about their centers. At any temperature above the absolute zero temperature (–273.15 °C), atoms (or molecules) of a solid possess some kinetic energy. However, atoms in the material do not all possess the same level of energy. Rather, there is a distribution of atoms with a particular energy that varies from very low to high, with the average energy at equilibrium. If the energy of a particular atom exceeds the bonding energy, it can move to another position in the lattice.

Second, there are a finite number of missing atoms (called vacancies) within a solid formed during solidification. A noncrystalline structure, because of short-range order, also contributes some space. Both conditions represent pathways through which diffusion can occur. Atoms change position in pure, single-element solids even under equilibrium conditions; this process is known as **self-diffusion**. As with any diffusion process, the atoms or molecules diffuse in the solid state in an attempt to reach an equilibrium state. Just as ink disperses uniformly in water, a concentration of atoms in a solid metal can also be redistributed through the diffusion process.

Diffusion may also occur in the other direction to produce a concentration of atoms in a solid. For example, if the sugar in the water becomes supersaturated, the molecules of sugar diffuse toward each other and the sugar crystallizes out of solution. In the same manner, a solid copper-silver alloy with higher copper concentration may cause supersaturation of copper in silver, which forces diffusion of copper atoms to

increase the concentration of copper locally, causing them to precipitate.

Diffusion rates for a given substance increase as temperature, the chemical potential gradient, concentration gradient, or lattice imperfections increase. The diffusion rate will decrease with an increase in atom size and interatomic (or intermolecular) bonding. The diffusion constant that is uniquely characteristic of the given element in a compound, crystal, or alloy is known as the **diffusion coefficient**, usually designated as *D*. It is defined as the amount of a substance that diffuses across a given unit area (e.g., 1 cm^2) through a unit thickness of the substance (e.g., 1 cm) in one unit of time (e.g., 1 s).

CRITICAL QUESTION

Why are mercury and gallium of interest as components of direct restorative materials?

The diffusion coefficients of elements in most crystalline solids at room temperature are very low. Yet at temperatures that are a few hundred degrees higher, the bond energy between atoms decreases, thus allowing rapid atomic diffusion. For the same reason, the lower the melting point of a metal, the greater is its diffusion coefficient. Diffusion in a noncrystalline material may occur at a more rapid rate and often may be evident at room or body temperature. The disordered structure enables the molecules to diffuse more rapidly with less activation energy. Both mercury and gallium are liquid at room temperature because of their melting points at –38.36 °C (–7.05 °F) and 29.78 °C (85.60 °F), respectively. When either liquid metal is mixed with a suitable metal alloy, atoms in the alloy dissolve and diffuse rapidly within the liquid metal at intraoral temperature. The result is a new solid metal compound. This process has been utilized in dentistry for making metallic direct restorative materials (Chapter 15).

CRITICAL QUESTION

Why does a liquid that can adhere to one material not necessarily adhere to another material of a different composition?

ADHESION AND BONDING

So far, we have been exploring the attraction between atoms and molecules. Although we do not expect to observe a similar attraction between two nonmagnetized solid objects, we do notice that two solids can adhere to each other with or without the help of a third substance or device. As examples, an artificial denture stays attached to the soft tissue when saliva is present, plaque or calculus adheres to tooth structure, and a transmucosal abutment is fixed to the implant root by a screw (Figure 2-12). The first two examples involve bonding at the molecular scale and the last is achieved first by mechanical means and then by osseointegration (Chapter 20). Some of the dental materials you will be learning about are bonded to the hard tissue to replace the missing part of the tooth structure to restore its functions. Therefore, an understanding of the fundamental principles associated with bonding is important to the dentist.

When the molecules of one substrate adhere or are attracted to molecules of the other substrate, the force of attraction is called **adhesion** when unlike molecules are attracted and **cohesion** when the molecules involved are of the same kind. The material that is used to cause bonding is known as the **adhesive** and the material to which it is applied is called the **adherend**. In a broad sense, adhesive bonding is simply a surface attachment process, which is usually qualified by specifying the type of intermolecular attraction that may exist between the adhesive and the adherend.

CRITICAL QUESTION

Why is the potential energy of the atom on the surface higher than that of atoms within the bulk of the material?

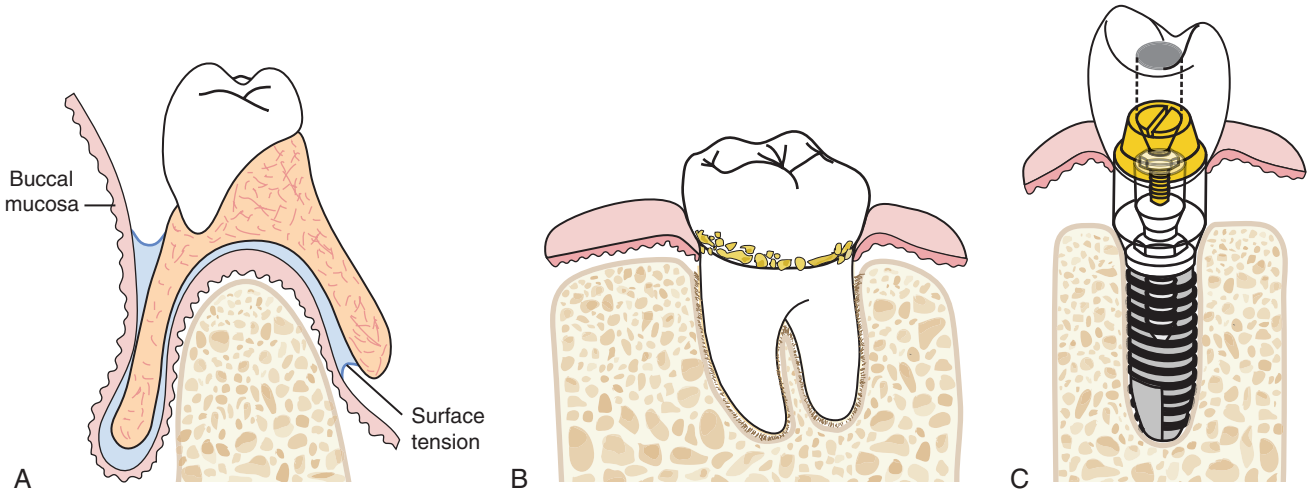


FIGURE 2-12 Examples of solid adhering to solid in dentistry. **A,** Retention of denture base; saliva fills in the space between the denture and soft tissue, providing retention through capillary attraction (see figure 2-14). The space between the denture and the soft tissue is exaggerated to show the capillary attraction. **B,** Plaque formation on the enamel surface, which converts to calculus by calcification. **C,** The implant root is first retained by the bone mechanically, followed by osseointegration for long-term implant stability. (Courtesy of Dr. Inchan Ko)

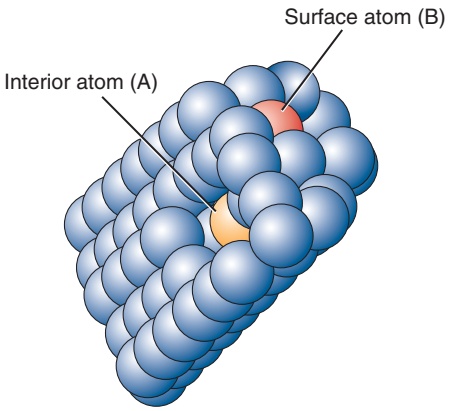


FIGURE 2-13 Comparing an atom under the surface (**A**) with one on the surface (**B**) reveals that a bond balance exists around the interior atom (**A**), while the surface atom (**B**) is free to develop bonds to atoms or molecules approaching the surface.

SURFACE AND SURFACE ENERGY

A surface is defined as the outmost layer of an object. We know that solids or liquids are made up of a finite number of atoms or molecules bonded by primary and/or secondary bonds. This means that their surface is populated by atoms or molecules that are ready to attract other atoms or molecules approaching the surface. It is the secondary bond formed between water molecules and the glass surface that makes a drop of water spread on a clean glass slide and keeps it from flowing when the glass slide is tilted. We can explain this phenomenon of attraction between atoms by the potential energy discussed in Figure 2-10. Consider the space lattice shown in Figure 2-13. Inside the lattice, all the atoms are equally attracted to each other. The interatomic distance for atom "A" has a balanced array of neighbors surrounding it and the energy is minimal. At the surface of the lattice, atom "B" is not equally attracted in all directions and the energy is greater. This energy quantifies the work needed to disrupt intermolecular bonds resulting a new surface. Thus, it is called the **surface energy**. The functional chemical groups available or the type of crystal plane of a space lattice present at the surface may affect the surface energy.

Molecules in air may be attracted to the surface and become adsorbed on the material surface. Initially the attraction between them is secondary bonding (van der Waals force). As the distance between the molecules from air and the surface diminishes, primary bonding may occur. Silver, platinum, and gold adsorb oxygen readily. Neither gold nor platinum forms stable oxides at room temperature; therefore, the bond between oxygen and metal remains secondary. In the case of silver, silver oxide may form as oxygen becomes bonded to silver by covalent bonding. This process is called chemisorption and is limited to the monolayer of oxide present on the surface. Both phenomena constitute adhesion, where oxygen is the adhesive and metals are the adherends.

The energy on the surface per unit area is referred to as the surface energy (in mJ/m^2) or **surface tension** (in mN/m). Falling liquid drops form spherical shapes, which have the smallest surface area of all known shapes, and they maintain the state of lowest energy. Any acquired surface impurity—such as an adsorbed gas, an oxide, or human secretions—can cause a reduction in the surface energy and adhesive qualities of a given solid as these impurities constitute the new surface. Table 2-1 lists the surface energy of selected solids and liquids.

TABLE 2-1 Surface Energy of Selected Materials

Material	Surface Energy (mJ/m^2)
Solids	
Enamel[1]	92
Dentin[1]	87
Teflon[2]	20
Gold alloy[3]	51–54
Ni-Cr[3]	48
Commercial pure titanium[3]	50
Acrylic denture resins[4]	46–54
Liquids	
Water[5]	72 @25°C
Mercury[5]	486 @25°C
Saliva[6]	53 @37°C
Dentin bonding agent[7]	34–55

Note: Depending on the measuring methods and the materials used, the values obtained are likely to be different among studies. The table is intended to give readers a general idea of surface energies of selected materials.
[1]Data from Weerkamp et al. (1988), *J Dent Res* 67:1483.
[2]Data from Janczuk (1999), *J Colloid Interface Sci* 211(1):96–103.
[3]Data from Sardin et al. (2002), *J Oral Rehab* 31:140.
[4]Data from Sipahi et al. (2001), *J Dent* 29:197.
[5]Data from Handbook of Chemistry and Physics (2011), 91st Edition, pp. 6–127.
[6]Data from Glantz (1970), *Odontol Rev* 21:119.
[7]Data from Gonçalves et al. (1997), *Braz Dent J* 8:43.

? CRITICAL QUESTION

What conditions are necessary to achieve the strongest level of bonding?

WETTING

When an impurity-free polished glass plate is placed on top of another similar plate and pressed together, they exhibit no tendency to adhere. Regardless of how smooth these glass surfaces may appear to be, they are likely to be rough on an atomic or molecular scale. Consequently, when they are placed in apposition, only the "hills" or high spots are in contact. Even if primary or secondary bonding occurs at these points of contact, these areas usually constitute only an insignificant portion of the total surface, and no perceptible adhesion takes place. In addition, no attraction is expected when the surface molecules of the attracting substances are separated by distances greater than 0.7 nm (0.0007 μm).

The examples of adhesives bonding to solid surfaces given earlier involved either a gas or liquid. It is obvious that gas and liquid can adapt to a solid surface by flowing into surface

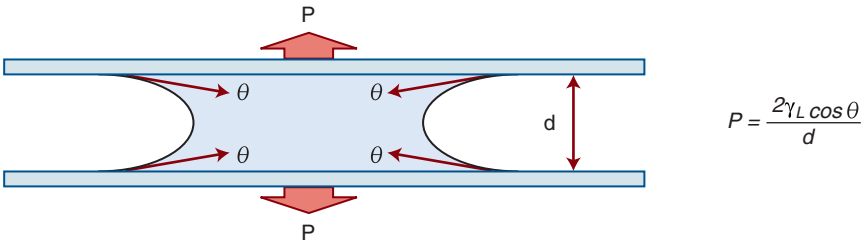


FIGURE 2-14 Two glass plates and water film. The liquid (water) between the two plates spreads because of good wetting. The attraction between the water molecule and glass surface is greater than the cohesive force between water molecules. Therefore, as water molecules spread, they also pull the two glass slides closer. Small arrows show the vector of surface tension and broad arrows show the force that pulls the slides apart. The surface tension of water is about 72 mN/m. For a space of 1 µm, the stress acting on the slide will be 140 kN/m^2 (0.14 MPa). You will learn in Chapter 4 that the value is relatively low. Therefore, if the glass slides cannot be separated in pure tension by hand it is likely that the water film (d) is only nanometers in thickness.

irregularities to provide contact over a greater part of the surface of the solid. If a drop of water is introduced between the same two glass plates before they are pressed together, considerable difficulty is encountered in separating the two plates (Figure 2-14). This is a result of the capillary action from intermolecular attractive forces between water and the glass plates

To produce adhesion on any targeted surface, the liquid must flow easily over the entire surface and adhere to the solid. This characteristic is known as **wetting**. If the liquid does not wet the surface of the adherend, adhesion between the liquid and the adherend will be negligible or nonexistent. The ability to wet the substrate is the dominating contributor to the adhesive bond when the adhesive sets from liquid to solid.

The ability of an adhesive to wet the surface of the adherend is influenced by a number of factors. The cleanliness of the surface is of particular importance. Impurities on the solid surface often yield a surface of lower energy than the clean surface and prevents any wetting by the adhesive, such as epoxy glue. A surface's surface energy can be so low, such as that of dental wax or Teflon (polytetrafluoroethylene), that it cannot be wet satisfactorily by most dental adhesives (Chapter 12). Impurity-free metal surfaces, on the other hand, because of their high surface energy, interact vigorously with liquid adhesives.

In general, the comparatively low surface energies of organic and inorganic liquids permit them to spread freely on solids of high surface energy. This is a prerequisite of good wetting and strong adhesive joints.

? CRITICAL QUESTION

Why does the wetting increase (higher wettability) if the adhesive attraction at the liquid/solid interface is greater than the cohesive attraction of the liquid molecules?

CONTACT ANGLE OF WETTING

How can we tell if a liquid can wet a solid satisfactorily for bonding, especially when the surface to be bonded is covered by that very liquid? When we place one drop of water on a clean glass slide and others on an acrylic plate and a sheet of Teflon, we will observe that the water drop on the acrylic plate does not spread out as much as the one on the glass slide and the water drop on the Teflon surface appears to bead up. If we observe this at the level of solid substrate, we will see the symmetrical profile of the former water drop resting on a flat surface (Figure 2-15). Both ends of the profile depict where three phases—vapor (air), liquid (water), and solid (glass, acrylic, or Teflon)—converge. We can draw a tangent relative to the curvature of the liquid profile from the vapor/liquid interface. The tangent line and the solid surface constitute an angle that defines the shape of the liquid; this is called the **contact angle**.

If the force of attraction between molecules of the adhesive and molecules of the substrate is stronger than the attraction between molecules of the adhesive, the liquid adhesive will spread much more broadly over the solid surface and result in a smaller contact angle (Figure 2-15, *A*). Thus, a small contact angle indicates that the adhesive forces at the interface are stronger than the cohesive forces holding the molecules of the adhesive together. If the adhesive beads up, it means that the force of adhesion is weaker than the cohesive force of the adhesive. Because the tendency for the liquid to spread increases as the contact angle decreases, the contact angle is a useful indicator of spreadability or wettability (Figure 2-15, *D*). Complete wetting occurs at a contact angle of 0° and no wetting occurs at an angle of 180°. Thus, the smaller the contact angles between an adhesive and an adherend, the better the ability of the adhesive to flow into and fill in irregularities within the surface of the adherend. The fluidity of the adhesive influences the extent to which these voids or irregularities are filled.

If oil drops or liquids other than water have been used instead, the observed contact angle will be different. Therefore, it is important to know the identity of the liquid that has been used to determine the contact angles. If none is identified, it is likely that distilled water has been used.

The profile of the liquid on a flat surface shows that there are three distinct interfaces: vapor/liquid, liquid/solid, and solid/vapor, and that each interface is characterized by an interfacial energy, γ_{VL}, γ_{LS}, and γ_{SV}, respectively. At

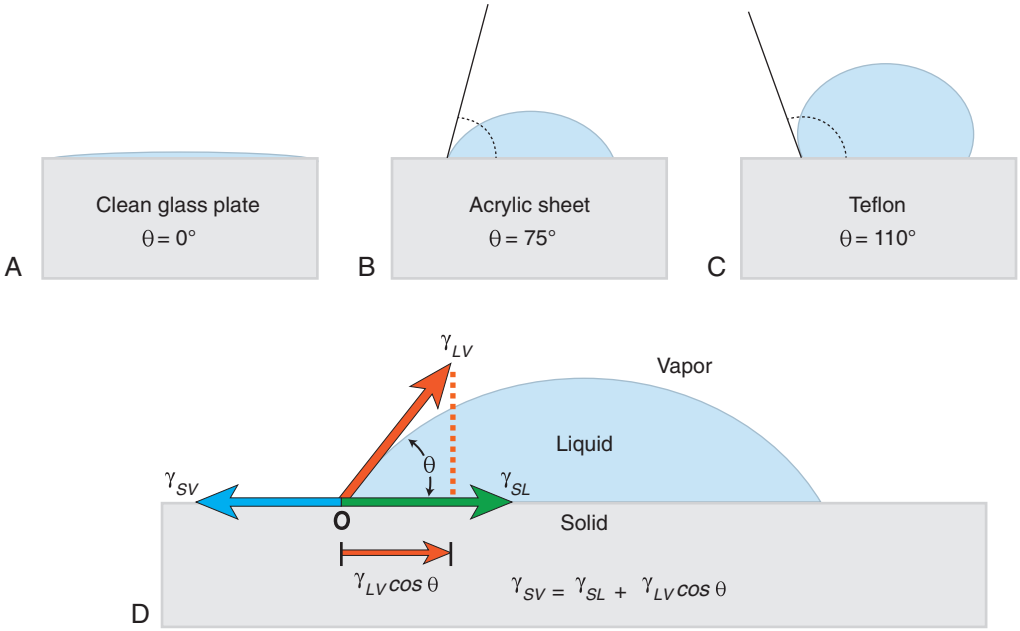


FIGURE 2-15 Contact angles of distilled water on three surfaces and relationship among interfacial energy. **A,** Water spreads freely on a flame-cleaned glass slide (good wetting). The profile depicted here is considered having 0° contact angle. **B,** Water on an acrylic surface. **C,** Water on a Teflon surface (poor wetting). **D**, Relationships between the interfacial energies at vapor/liquid (γ_{VL}), liquid/solid (γ_{LS}), and solid/vapor (γ_{SV}) interfaces with respect to contact angle at equilibrium; the relationship is also known as Young's equation.

equilibrium, the chemical potential in the three phases should be equal (Figure 2-15, *D*). It is important to point out that the Young's equation shown in Figure 2-15 assumes a perfectly flat surface at the molecular level, and any surface roughness and impurities can cause a deviation in the equilibrium contact angle from the contact angle predicted by Young's equation.

? CRITICAL QUESTION

You observe a lack of soft or hard tissue details in a gypsum model you have made from a hydrophobic impression material. What steps can be taken to eliminate this problem when you are using this impression material in the future?

Dental professionals encounter wetting issues on a daily basis. Issues involved with individual materials are discussed in later chapters. Here is one example of interest. When gypsum products (Chapter 9) are mixed with water to pour dental models in various types of impressions, wetting must occur between gypsum and the impression to ensure good surface quality of the gypsum model. The basic ingredient of the most popular silicone-based elastomeric impression material today is considered to be hydrophobic, because a contact angle of greater than 90° is observed when an aqueous medium is poured into this elastomeric mold. To improve the wettability of the set impression material by a gypsum-water mixture, the operator usually sprays a surfactant (also called debubblizer). The most direct approach by the manufacturer is to incorporate a **wetting agent** (also known as a surfactant) in the impression material during the manufacturing process (Chapter 8). The wetting agent migrates to the solid surface and accommodates surface wetting by the aqueous gypsum-forming mixture. Table 2-2 lists contact angles of probing liquids on selected materials.

? CRITICAL QUESTION

Micromechanical bonding of resin sealant to tooth enamel is usually quite effective in preventing pit and fissure areas from tooth decay. However, many factors can reduce the bonding effectiveness, resulting in partial or total loss of the sealant. Which of these factors are possible causes of debonding?

MECHANICAL BONDING

Strong attachment of one substance to another can also be accomplished by mechanical means rather than by molecular attraction. Such structural retention may be gross in nature, as evidenced by some non-dental applications involving the use of screws, bolts, or undercuts. Similar procedures that involve more subtle mechanisms are also used in restorative dentistry and called mechanical bonding or micromechanical retention.

Before resin-based adhesives were introduced to dentistry, various type of fluids or slightly viscous materials, like zinc phosphate cement (Chapter 14), were being used to retain cast gold alloy crowns or base metal endodontic posts and cores. These materials do not form a strong attraction to the substrate surface, but they provide the needed retention to hold the prostheses in place. In this scenario, the luting medium penetrates into irregularities that exist on the intaglio of the casting and those that are present on the adjoining tooth structure. Upon hardening, the numerous cementing material projections embedded in the adherend surface

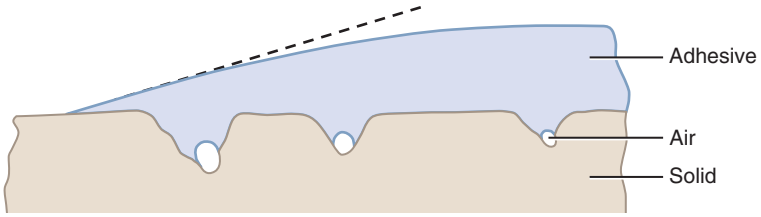


FIGURE 2-16 Air pockets form in a surface irregularity even when the contact angle of the adhesive is low. These voids contribute to the propagation of adhesive failure by concentration of stresses.

TABLE 2-2 Contact Angles of Probing Liquids on Solid Surfaces

Solid	Contact Angle (degree)	Probing Liquid
Amalgam[1]	145	Mercury
Amalgam[2]	77	Water
Acrylic denture resins[2]	75	Water
Dental ceramic (feldspathic core)[3]	71	Water
Dental ceramic (feldspathic core)[3]	54	Bonding resin
Teflon[2]	110	Water
Commercial pure titanium[4]	54	Water
Impression materials		
Polyether[5]	30–44	Water
Polysulfide[6]	76–85	Gypsum solution (0.2 gm/ml)
Addition silicone[5]	34–105	Water
Addition silicone (hydrophilic)[5]	20–78	Water
Condensation silicone[5]	82–103	Water

Note: Depending on the measuring methods and the materials used, the values obtained are likely to be different among studies. The table is intended to give readers a general idea of contact angle of various dental materials.
[1]Data from Baran & O'Brien (1977), *JADA* 94:898.
[2]Data from O'Brien (1967), PhD Dissertation, University of Michigan.
[3]Data from Oh et al. (2002), *J Prosthet Dent* 88:616.
[4]Data from Ponsonnet et al. (2003), *Mat Sci Eng C-Bio S* 23:551.
[5]Data from Cullen et al. (1991), *J Prosthet Dent* 66:261.
[6]Data from Pratten & Craig (1989), *J Prosthet Dent* 61:197.

provide the anchorage for mechanical retention. This process is often called **micromechanical bonding**.

The early formulation of resin-based filling materials did not form a strong attraction to tooth structure and leakage adjacent to the restoration occurred. Such leakage patterns contribute to marginal stain, secondary caries, and irritation of the pulp. This drawback was brought under control only when acid etching of enamel had been accepted as a routine procedure. Before insertion of the resin, the enamel of the adjoining tooth structure is exposed to phosphoric acid for a short period and then rinsed to remove any residual acid. The acid produces minute pores in the enamel surface into which the resin subsequently flows when it is placed into the preparation. On hardening, these resin projections provide improved mechanical retention of the restoration, thereby reducing the possibility of interfacial leakage. In fact, the etching procedure cleans the enamel surface and creates more surface area, facilitating greater wettability of the enamel by the adhesive and subsequently a stronger bond.

It is important to note that whereas surface imperfections provide sites for mechanical bonding, there are areas that adhesives may not fill because of trapped air pockets (Figure 2-16). When the adhesive interfacial region is subjected to thermal changes and mechanical stresses, **stress concentrations** develop around these voids. The stress may become so great that it initiates a separation in the adhesive bond adjacent to the void. This crack may propagate from one void to the next, and the joint may separate under stress.

CRITICAL QUESTION

What are the main challenges involved in bonding to tooth structure?

BONDING TO TOOTH STRUCTURE

Adhesive bonding to tooth structure and other dental materials has become a major component of restorative dentistry. So far, we have used an ideal adherend that has a clean surface with uniform composition and certain surface irregularities in our discussion of bonding. The tooth structure to which we plan to bond certainly does not fall in that category. Tooth composition is not homogeneous. Both organic and inorganic components are present in different amounts in dentin as compared with enamel. A material that can adhere to the organic components may not adhere to the inorganic components, and an adhesive that bonds to enamel may not adhere to dentin to the same extent.

The instruments used to prepare the tooth for bonding leave a rough surface and debris, which promote air entrapment at the interface. We routinely treat prepared surfaces with appropriate agents to remove this debris and continue to face the task of removing new debris with each additional procedure, in addition to dealing with saliva contamination. Furthermore, there is a fluid exchange through certain components of the tooth. The dental adhesive must compete with water for wetting the tooth surface by displacing or incorporating it. Then, too, the adhesive must sustain long-term adhesion to the tooth structure in an aqueous environment. Attempts are being made to use more hydrophilic resins that are not as sensitive to the presence of moisture as materials currently in use. To further enhance adhesive bonding to tooth structure or other dental materials, the incorporation

of functional groups that have the potential of chemically reacting with the bonding substrate has also been explored. Perhaps there will be no need of mechanical retention in the cavity preparation in the future. These subjects are discussed in detail in the chapters dealing with materials for bonding applications.

More intriguing is the possibility of developing a material capable of forming a thin, durable film on the tooth surface that could be topically applied to the intact enamel. Such a film with low surface energy could serve as a barrier to the formation of plaque, the development of caries, and possibly the deposition of calculus.

SELECTED READINGS

Buonocore MG: *The Use of Adhesives in Dentistry*. Springfield, IL, 1975, Charles C Thomas.
The problems associated with dental adhesives are nicely illustrated. It is of interest that many of the procedures using bonding technology discussed in this text have become commonplace.

Callister WD, Jr, Rethwisch DG: *Materials science and engineering: an introduction*, ed 8, Hoboken, NJ, 2010, John Wiley & Sons.
An excellent text on materials science for a more in-depth coverage of materials structure and properties.

Glantz P: On wettability and adhesiveness: a study of enamel, dentine, some restorative dental materials, and dental plaque. *Odontol Revy* 20(Suppl 17):1–132, 1969.
The author proposed that the reduction of dental caries by topical fluorides resulted from lowering the surface energy of the tooth structure and thereby reducing plaque accumulation over a given interval.

Good RJ: Contact angle, wetting, and adhesion: a critical review. *J Adhes Sci Technol* 6:1269–1302, 1992.
An excellent review on the fundamentals of contact angle and wetting and their relationship to adhesion.

Gordon JE: *The New Science of Strong Materials, or Why You Don't Fall Through the Floor?* ed 2, Princeton, NJ, 1984, Princeton University Press.
A general discussion of the strength of materials from a fundamental base. The sections on biological structural materials, timber, cellulose, teeth, and bone are particularly interesting.

Phillips RW, Ryge G, editors: *Proceedings on Adhesive Restorative Dental Materials*. Spencer, IN, 1961, Owen Litho Service.
The recommendations for critically important areas of research have provided an impetus for investigations in this area.

Zisman WA: Influence of constitution on adhesion. *Ind Eng Chem* 55:18–38, 1963.
One of the pioneers in surface phenomena discusses parameters that influence wetting.

CHAPTER 3

Physical and Chemical Properties of Solids

OUTLINE

Terminology

Rheology

Structural Relaxation

Color and Optical Effects

Thermal Properties

Electrochemical Properties

Magnetic Materials

KEY TERMS

RHEOLOGY

Dilatant—Resistance to flow increases as the rate of deformation (shear strain rate) increases. The faster that fluids are stirred or forced through a syringe, the more viscous and more resistant to flow they become.

Pseudoplastic—Viscous character that is opposite from dilatant behavior in which the rate of flow decreases with increasing strain rate until it reaches a nearly constant value. Thus, the more rapidly that pseudoplatic fluids are stirred or forced through a syringe, the more easily they flow.

Rheology—Study of the deformation and flow characteristics of matter (see also *viscosity*, Chapter 6).

Thixotropic—Property of gels and other fluids to become less viscous and flow when subjected to steady shear forces through being shaken, stirred, squeezed, patted, or vibrated. When the shear force is decreased to zero, the viscosity increases to the original value. Also known as *shear thinning*, in which the greater the applied shear force, the less the resistance to flow.

Viscosity—Resistance of a fluid to flow (see also *rheology*).

STRUCTURAL RELAXATION

Creep—Time-dependent plastic strain of a solid under a static load or constant stress.

Sag—Irreversible (plastic) deformation of metal frameworks of fixed dental prostheses in the firing temperature range of ceramic veneers.

COLOR AND OPTICAL EFFECTS

Absorption—The extent to which light is absorbed by the material in an object.

Chroma—Degree of saturation of a particular hue (dominant color).

Color—Sensation induced from light of varying wavelengths reaching the eye.

Esthetics—Principles and techniques associated with development of the color and appearance required to produce a natural, pleasing effect in the dentition (Chapter 19). *Aesthetics* is an alternative spelling with the same meaning.

Hue—Dominant color of an object; for example, red, green, or blue.

Metamerism—Phenomenon in which the color of an object under one type of light source appears to change when illuminated by a different light source.

Opacity—The extent to which light does not pass through a material. No image and no light can be seen through an opaque object.

Reflection—The amount of light that reflects from the surface of an object.

Refract/Refraction—The degree to which light is bent when it passes from one medium to another. This makes a spoon appear bent in a glass of drinking water when light passes from air through glass into water, reflects off of the spoon, and then passes back through water and glass into air. The index of refraction is a measure of this effect.

Translucency—The quality of light passing through an object in a diffuse manner, only to reveal a distorted image that can be viewed through the material.

Transmit/Transmittance—The amount of light passing through an object.

Transparency—The extent to which light passes through a material and to which an undistorted image can be seen through it.

Value—Relative lightness or darkness of a color. Also known as the gray scale.

THERMAL PROPERTIES

Coefficient of thermal expansion (linear coefficient of expansion)—Change in length per unit of the original length of a material when its temperature is raised by 1 K (1 °C).

K—The **kelvin (K)** temperature scale extends the degree Celsius scale such that zero degrees K is defined as absolute zero (0 K = –273.15 °C). Temperatures on this scale are called "kelvins," *not* "degrees kelvin," kelvin is *not* capitalized, and the symbol (capital K) stands alone with *no* degree symbol. 1 K = 1 °C, K = °C + 273.15.

Thermal conductivity (coefficient of thermal conductivity)—Property that describes the thermal energy transport in watts per second through a specimen 1 cm thick with a cross-sectional area of 1 cm^2 when the temperature differential between the surfaces of the specimen perpendicular to the heat flow is 1 K (1 °C).

Thermal diffusivity—Measure of the speed with which a temperature change will proceed through an object when one surface is heated.

ELECTROCHEMICAL PROPERTIES

Concentration cell—Electrochemical corrosion cell in which the potential difference is associated with the difference in concentration of a dissolved species, such as oxygen, in solution along different areas of a metal surface. Pitting corrosion and crevice corrosion are types of concentration cell corrosion.

Crevice corrosion—Accelerated corrosion in narrow spaces caused by localized electrochemical processes and chemistry changes, such as acidification and depletion in oxygen content. Crevice corrosion commonly occurs when microleakage takes place between a restoration and the tooth.

Corrosion—Chemical or electrochemical process in which a solid, usually a metal, is attacked by an environmental agent, resulting in partial or complete dissolution.

Electromotive series—Arrangement of metals by their equilibrium values of electrode oxidation potential. Used to judge the tendency of metals and alloys to undergo electrochemical (galvanic) corrosion.

Galvanic corrosion (electrogalvanism)—Accelerated attack occurring on a less noble metal when electrochemically dissimilar metals are in electrical contact within a liquid corrosive environment.

Galvanic shock—Pain sensation caused by the electrical current generated when two dissimilar metals are brought into contact in the oral environment.

Pitting corrosion—Highly localized corrosion occurring at metal surface defects such as pits, scratches, and cracks in which the region at the bottom is oxygen-deprived and becomes the anode while the surface around it becomes the cathode. Thus metal at the base preferentially ionizes and goes into solution, causing the defects to enlarge.

Stress corrosion—Degradation caused by the combined effects of mechanical stress and a corrosive environment, usually exhibited as cracking.

Tarnish—Process by which a metal surface is dulled or discolored when a reaction with a sulfide, oxide, chloride, or other chemical causes surface discoloration through formation of a thin oxidized film.

MAGNETIC MATERIALS

Magnet—Metallic material in which the component atoms are so ordered that it can attract iron-containing objects or align itself in an external magnetic field.

Tesla—Unit of flux density (T) of the magnetic field produced by a magnet.

TERMINOLOGY

This chapter provides brief descriptions of physical and chemical properties as background and preparation for more detailed discussion in later chapters in which these properties are used to describe the characteristics of specific dental materials.

Physical properties are based on the laws of mechanics, acoustics, optics, thermodynamics, electricity, magnetism, radiation, atomic structure, and nuclear phenomena. Hue, value, and chroma relate to **color** and perception and are physical properties based on the laws of optics, which is the science that deals with the phenomena of light, vision, and sight. Thermal conductivity, diffusivity, and expansion are physical properties based on the laws of thermodynamics. Mechanical properties, a subset of physical properties based on the laws of mechanics, are discussed in Chapter 4.

Chemical properties are based on the ways in which substances interact, combine, and change, as governed by their outer orbital electrons. The outer electrons are responsible for binding atoms together in molecules and for the electrical, thermal, optical, and magnetic properties of solids.

As examples, the physical properties of color and thermal expansion are of particular importance to the performance of

dental ceramics (Chapter 18). Flow and viscosity (the resistance of a fluid to flow) are essential properties of impression materials (Chapter 8). Creep (slow deformation under a static load) is relevant to the clinical performance of amalgam (Chapter 15). Tarnish and corrosion are electrochemical properties that strongly affect the performance of metals and their alloys.

RHEOLOGY

Rheology is the study of the deformation and flow characteristics of matter, whether liquid or solid. Viscosity is the resistance of a fluid to flow. Dental professionals must manipulate a wide variety of dental materials in a fluid state in order to achieve successful clinical outcomes. Moreover, the success or failure of a given material may be as dependent on its manipulation and handling properties in the liquid state as it is on its performance properties as a solid. Most dental materials are initially in a fluid state so that they can be placed and shaped as required; then they undergo transformation to a solid state, in which they are durable and perform their function. Cements and impression materials undergo a fluid-to-solid transformation in the mouth. Gypsum products used in the fabrication of models and dies are transformed extraorally from fluid slurries into solids (see Chapter 9). Amorphous materials such as waxes and resins appear solid but actually are supercooled liquids that can flow plastically (irreversibly) under sustained loading or deform elastically (reversibly) under small stresses (see Chapters 6 and 10). The ways in which these materials flow or deform when subjected to stress are important to their use in dentistry. The study of flow characteristics of materials is the basis for the science of rheology (also see Chapter 6).

Although a liquid at rest cannot support a shear stress (shearing force per unit shearing area), most liquids, when placed in motion, resist imposed forces that cause them to move. This resistance to fluid flow (viscosity) is controlled by internal frictional forces within the liquid. Thus **viscosity** is a measure of the consistency of a fluid and its resistance to flow. A highly viscous fluid flows slowly. Dental materials have different viscosities depending on their intended clinical application. Dental assistants, dentists, and dental students who have observed the more viscous nature of zinc polycarboxylate and resin cements compared with zinc phosphate cement when these materials have been properly mixed as luting cements, are familiar with these viscosity differences. In everyday life we find wide differences in viscosities among such fluids as water, syrup, ketchup, moisturizing cream, and toothpaste.

This concept is illustrated in Figure 3-1. A liquid occupies the space between two flat surfaces, as, for example when a spatula is moved through a pasty fluid such as a dental cement to blend two components on a mixing pad. The mixing surface is fixed, and the upper surface (e.g., a spatula blade) moves to the right at a given velocity (V). A force (F) is required to overcome the frictional resistance within the fluid (i.e., the viscosity) and cause the fluid to flow. As discussed

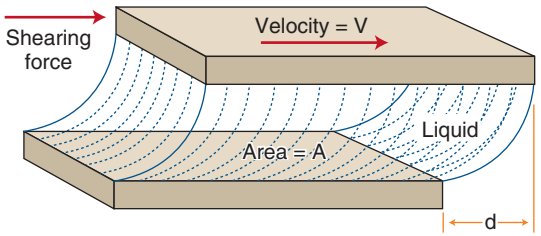


FIGURE 3-1 Shear strain, ε(V/d) of a viscous liquid between two plates caused by translation of the top plate at a velocity, V, relative to the rigid lower plate (i.e., a spatula blade mixing dental cement on a mixing pad).

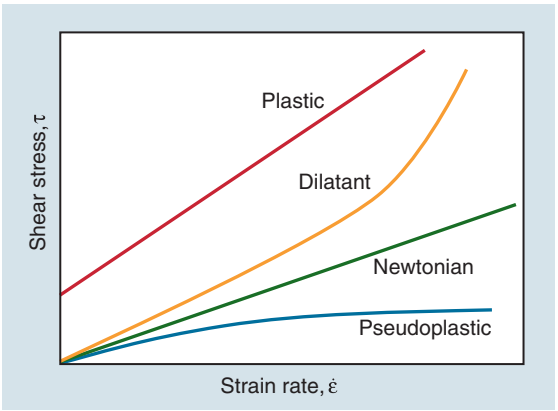


FIGURE 3-2 Shear stress versus shear strain rate for fluids exhibiting different types of rheologic behaviors.

in Chapter 4, stress is the force per unit area that develops within a structure when an external force is applied. This stress causes a deformation, or strain, to develop. Strain is calculated as a change in length divided by the initial reference length. If the two surfaces have an area (A) in contact with the liquid, a shear stress (τ) can be defined as $\tau = F/A$. The shear strain rate, or rate of change of deformation, is $\varepsilon = V/d$, where d is the shear distance of the upper surface relative to the fixed lower surface and V is the velocity of the moving surface. As the shear force F increases, V increases, and a curve can be obtained for force versus velocity. This type of curve is analogous to the load-versus-displacement curves discussed in Chapter 4, which are derived from static measurements on solids.

Curves depicting shear stress versus shear strain rate are used to characterize the viscous behavior of fluids. The rheologic behaviors of four types of fluids are shown in Figure 3-2. An "ideal" fluid produces a shear stress proportional to the strain rate. That is, the greater the force applied, the faster the fluid flows and the plot is a straight line. This is known as Newtonian viscosity. Because viscosity (h) is defined as the shear stress divided by the strain rate, τ/ε, a Newtonian fluid has a constant viscosity and exhibits a constant slope of shear stress plotted against strain rate, as seen in Figure 3-2. The plot is a straight line and resembles the elastic portion of a stress-strain curve (see Chapter 4), with viscosity the analog of the elastic modulus (elastic stress divided by elastic strain). Viscosity is measured in units of megapascals (MPa) per

second, or centipoise (cP). Pure water at 20°C has a viscosity of 1.0 cP, whereas the viscosity of molasses is approximately 300,000 cP. This value is similar to that of tempered agar hydrocolloid impression material (281,000 cP at 45 °C). Of the elastomeric impression materials, light-body ("thin" consistency) polysulfide has a viscosity of 109,000 cP, compared with 1,360,000 cP for heavy-body ("thick" consistency) polysulfide at 36 °C.

The viscosity of many dental materials decreases with increasing strain rate until it reaches a nearly constant value. That is, the faster they are stirred, forced through a syringe, or squeezed, the less viscous and more fluid they become. This is **pseudoplastic** viscosity and is illustrated by the change in slope of the plot in Figure 3-2. Liquids that show the opposite behavior are **dilatant** and become more rigid as the rate of deformation (shear strain rate) increases. That is, the faster they are stirred, etc., the more viscous and resistant to flow they become.

Finally, some classes of materials behave like a rigid body until some minimum value of shear stress is reached. This is represented by the offset along the shear-stress axis. These fluids, which exhibit rigid behavior initially and then attain constant viscosity, are referred to as "plastic." Ketchup is a familiar example—a sharp blow to the bottle is usually required to produce an initial flow.

The viscosity of most fluids decreases rapidly with increasing temperature. Viscosity may also depend on previous deformation of the liquid. Such fluids become less viscous and more flowable upon repeated applications of pressure and are termed **thixotropic**. Dental prophylaxis pastes, plaster of Paris, resin cements, and some impression materials are thixotropic. The thixotropic nature of impression materials is beneficial because the material does not flow out of a mandibular impression tray until it is placed over dental tissues, and a prophylaxis paste does not flow out of a rubber cup until it is rotated against the teeth to be cleaned. If these materials are stirred rapidly and the viscosity is measured, a value is obtained that is lower than the value for a sample that has been left undisturbed.

The viscosity of a dental material may determine its suitability for a given application. Likewise, the nature of the curve representing shear stress versus shear strain rate can be important in determining the best way to manipulate a material. As explained in more detail later, the viscosity as a function of time can also be used to measure the working time of a material that undergoes a liquid-to-solid transformation.

STRUCTURAL RELAXATION

STRESS RELAXATION

After a substance has been permanently deformed (plastic deformation), there are trapped internal stresses. For example, in a crystalline substance such as a metal, the atoms in the crystal structure are displaced and the system is not in equilibrium. Similarly, in amorphous structures, some molecules are too close together and others too far apart when the substance is permanently deformed.

The displaced atoms are not in equilibrium positions and are therefore unstable. Through a solid-state diffusion process driven by thermal energy, the atoms can slowly return to their equilibrium positions. The result is a change in the shape or contour of the solid as the atoms or molecules change positions. The material warps or distorts. Such stress relaxation is a problem with elastomeric impression materials and can lead to distortions in the impression and subsequent lack of fit, as discussed in Chapter 8.

The rate of relaxation increases with an increase in temperature. For example, if a wire is bent, it may tend to straighten out if it is heated to a high temperature. At room temperature, any such relaxation caused by rearrangement of metal atoms may be negligible. On the other hand, there are many noncrystalline dental materials (such as waxes, resins, and gels) that, when manipulated and cooled, can then undergo relaxation (with consequent distortion) at an elevated temperature. Considerable attention is given to this phenomenon in succeeding chapters because such dimensional changes by relaxation may result in an inaccurate fit of dental appliances.

CREEP AND FLOW

If a metal is held at a temperature near its melting point and is subjected to a constant applied stress, the resulting strain will increase over time. **Creep** is defined as the time-dependent plastic strain of a material under a static load or constant stress. The related phenomenon of sag occurs in the permanent deformation of long-span metal bridge structures at porcelain-firing temperatures under the influence of the mass of the prosthesis. For a given thickness, a greater bridge mass is related to greater flexural stress and greater flexural creep. Metal creep usually occurs as the temperature increases to within a few hundred degrees of the melting range. Metals used in dentistry for cast restorations or substrates for porcelain veneers have melting points (for pure metals) or melting ranges (for alloys) that are much higher than mouth temperatures, and they are not susceptible to creep deformation intraorally. However, some alloys used for metal-ceramic prostheses can creep at porcelain veneering temperatures. This phenomenon is discussed further in Chapter 18.

Dental amalgams contain from 42% to 52% of mercury by weight and begin melting at temperatures only slightly above room temperature. (The melting range of an alloy is discussed in Chapter 5.) Because of its low melting range, dental amalgam can undergo creep at a restored tooth site under periodic sustained stress, such as would be imposed by patients who clench their teeth. Because creep produces continuing plastic deformation, the process can, over time, be very destructive to a dental amalgam filling. The relationship of this property to the behavior of amalgam restorations is discussed in Chapter 15. A creep test is required in American National Standards Institute/American Dental Association Specification No. 1 for amalgam alloy and in International Organization for Standardization (ISO) standard No. 1559.

The term *flow*, rather than *creep*, has generally been used in dentistry to describe the rheology of amorphous materials

such as waxes. The flow of wax is a measure of its potential to deform under a small static load, even that associated with its own mass. Although creep or flow may be measured under any type of stress, compression is usually employed in the testing of dental materials. A cylinder of prescribed dimensions is subjected to a given compressive stress for a specified time and temperature. The creep or flow is measured as the percentage decrease in length that occurs under these testing conditions. Creep may cause unacceptable deformation of dental restorations (such as low-copper dental amalgam) made from a material that is used clinically at a temperature near its melting point for an extended period. Creep may also lead to an unacceptable fit of fixed dental prosthesis frameworks when a cast alloy with poor creep (**sag**) resistance is veneered with porcelain at relatively high temperatures (about 1000 °C; see Chapter 18).

COLOR AND OPTICAL EFFECTS

The preceding sections have focused on those properties that are necessary to permit a material to restore the function of damaged or missing natural tissues. Another important goal of dentistry is to restore or improve **esthetics**—the color and appearance of natural dentition. Esthetic considerations in restorative and prosthetic dentistry have received increasingly greater emphasis in recent decades, and the challenges have grown even greater in the past few years following the widespread use of bleaching and whitening technologies. Thus, the development of a general-purpose, technique-insensitive, direct-filling, tooth-colored, color-stable restorative material remains one of the more serious challenges of current dental materials research.

Since esthetic dentistry imposes severe demands on the artistic abilities of the dentist and technician, knowledge of the underlying scientific principles of color and other optical effects is essential. This is especially true for the increasingly popular restorations that involve ceramic materials (see Chapter 18). More comprehensive treatments of this subject can be found in the "Selected Readings" at the end of this chapter.

NATURE OF LIGHT AND THE ROLE OF HUMAN VISION

Light is electromagnetic radiation that can be detected by the human eye. The eye is sensitive to wavelengths from approximately 400 nm (violet) to 700 nm (dark red), as shown in Figures 3-3 and 3-4. The reflected light intensity and the combined intensities of the wavelengths present in incident and reflected light determine the appearance properties of hue, value, and chroma, which are shown in Figure 3-5 and discussed in the next section. For an object to be visible, it must reflect or **transmit** light incident on it from an external source. The incident light is usually polychromatic; that is, a mixture of the various wavelengths, commonly known as "white" light. Incident light is selectively absorbed

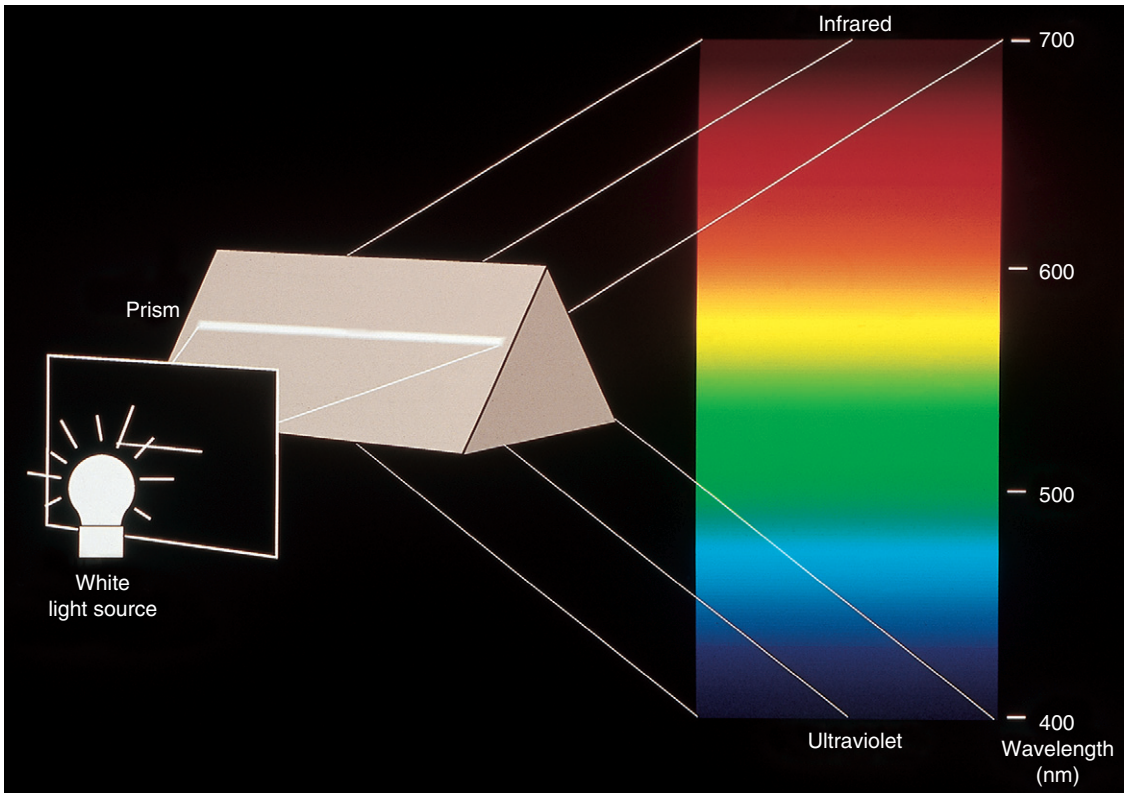


FIGURE 3-3 Spectrum of visible light ranging in wavelength from 400 nm (violet) to 700 nm (red). The most visually perceptible region of the equal energy spectrum under daylight conditions is between wavelengths of 540 and 570 nm, with a maximum value of visual perceptibility at 555 nm (see Figure 3-4).

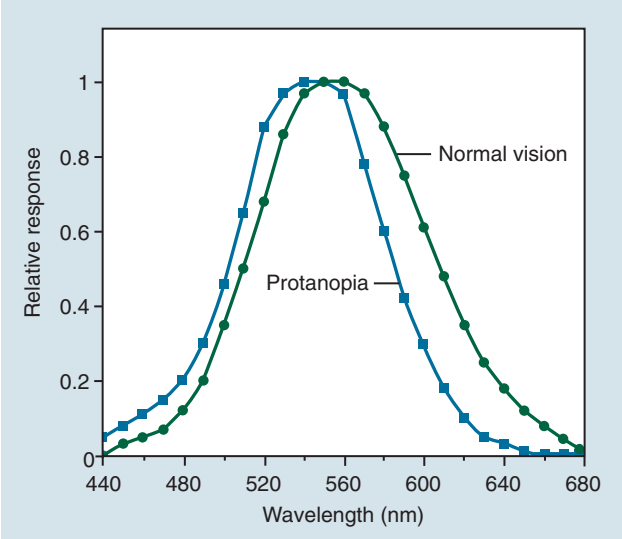


FIGURE 3-4 Relative visual response of humans to wavelength of light for a normal observer and one with protanopia (red-green) color blindness. Protanopia is experienced by 1% of the male population and 0.02% of the female population.

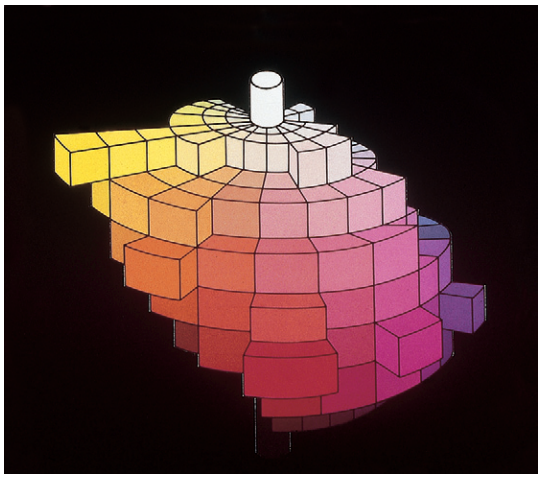


FIGURE 3-5 The three dimensions of color space. Value increases from black at the bottom center to white at the top center. Chroma increases from the center radially outward, and changes in hue occur in a circumferential direction. **A,** 3-D Munsell Color Space. **B,** Partial color space revealing hue, value, and chroma regions. (Courtesy of Minolta Corporation, Instrument Systems Division, Ramsey, NJ.)

or scattered (or both) at certain wavelengths. The spectral distribution of the transmitted or reflected light resembles that of the incident light, although certain wavelengths are reduced in magnitude.

The phenomenon of vision, and certain related terminology, can be illustrated by considering the response of the human eye to light reflected from an object. Light from an object that is incident on the eye is focused in the retina and is converted into nerve impulses, which are transmitted to the brain. Cone-shaped cells in the retina are responsible for color vision. These cells have a threshold intensity required for color vision and respond to wavelengths as shown in Figure 3-4 for both normal color vision and color-deficient vision. Someone with normal vision has maximum sensitivity in the green-yellow region at about 550 nm and is least sensitive in the red and blue-violet regions of the spectrum.

The signals from the retina are processed by the brain to produce the psychophysiological perception of color. Because a neural response is involved in color vision, constant stimulation by a single color may result in color fatigue and a decrease in the eye's response. Defects in certain portions of the color-sensing receptors result in the different types of color blindness; thus humans vary greatly in their ability to distinguish colors. In a scientific sense, one might liken the normal human eye to an exceptionally sensitive differential colorimeter, a scientific instrument that measures the intensities and wavelengths of light. Although colorimeters are more precise than the human eye in measuring slight differences in colored objects, they are inaccurate for rough or curved surfaces. The eye is highly sensitive in comparing two colors seen side by side, whether on rough, smooth, flat, or curved surfaces.

The Nature of the Object under View

Esthetics is critically important in dealing with dental restorative materials. For good esthetics, the interaction of light with restorative materials must mimic the interaction of light with natural teeth. The nature of the restorative material, or that of any object under view, determines how that object will appear. Electromagnetic radiation in the visible region interacts with an object through **reflection** from its surface, **absorption**, **refraction,** or **transmission** (i.e, by passing through unchanged.) These phenomena determine the **opacity**, **translucency**, or **transparency** of an object. Light reflected from rough surfaces *scatters* in many directions because it is reflected at many angles by the uneven surface. This leads to an appearance that ranges from mirrorlike for a perfectly smooth surface (termed *specular reflectance*) to the flat, dull appearance (termed *diffuse reflectance*) of a surface such as chalk.

The opacity of a material is related to the amount of light it can absorb and/or scatter. The opposite of opacity is translucency. For example, if 1-mm thicknesses of each of two materials absorb 20% and 50%, respectively, of the light passing through them, the former is less opaque or more translucent than the latter. Transparent materials are at the far end of the translucency scale, absorb no light, and transmit 100% of the light that passes through them.

Enamel is a composite material consisting of hydroxyapatite crystals in a protein matrix. When light strikes enamel, some is reflected, some refracted, some absorbed, and some transmitted. Enamel has a refractive index of 1.65 and is translucent.

CRITICAL QUESTION

How is color described objectively and quantitatively?

THREE DIMENSIONS OF COLOR

Verbal descriptions of color are not precise enough to describe the appearance of teeth. For example, the definition of *puce* is "a brilliant purplish-red color," according to Microsoft's *Encarta World English Dictionary*, while *Webster's Third New International Dictionary* defines it as "a dark red that is yellower and less strong than cranberry, paler and slightly yellower than average garnet, bluer, less strong, and slightly lighter than pomegranate, and bluer and paler than average wine." These definitions are too variable, complex, and imprecise to describe a desired color of a dental crown to a laboratory technician. Such a written description is subjective and does not clearly and unambiguously allow one to perceive the color. To overcome this problem, color perception is described by three objective variables: hue, value, and chroma. These three parameters constitute the three dimensions of "color space," as shown in Figure 3-5.

- **Hue**: The dominant color of an object, for example red, green, or blue. This refers to the dominant wavelengths present in the spectral distribution. The continuum of these hues creates the 3-D color solid shown in Figure 3-5.
- **Value**: Value is also known as the gray scale. It is the vertical, or Z-axis, of Figure 3-5. Value increases toward the high end (lighter) and decreases toward the low end (darker). Value is also expressed by the "lightness" factor (L* in Figure 3-6), with varying levels of gray between the extremes of white and black. Teeth and other objects can be separated into lighter shades (higher value) and darker shades (lower value). For example, the yellow of a lemon is lighter than the red of a cherry. For a light-diffusing and light-reflecting object such as a tooth or dental crown, value identifies the lightness or darkness of a color, which can be measured independently of the hue.

The components of a color space can be more easily visualized by its individual parts in Figure 3-5, *B*, here seen as discs stacked along the value axis (lightness, L*) on a scale of 0 to 10 from black to white. Around the periphery are 10 basic hues (dominant wavelength/color). Chroma (strength, saturation) radiates out from the value axis like the spokes of a wheel (illustrated by green).

Figure 3-6 represents a horizontal plane, perpendicular to the L* (value) axis, through the color solid in Figure 3-5. This color chart is based on the Commission Internationale de l'Éclairage L*a*b* color space, in which L* represents the value of an object, a* is the measurement along the red-green axis, and b* is the measurement along the yellow-blue axis. The color of a red apple is shown by the letter A in the upper and lower charts. Its color appearance can be expressed by L* = 42.83, a* = 45.04, and b* = 9.52. In comparison, a dental body (gingival) porcelain of shade A2 can be described by a higher (lighter) L* of 72.99, a lower a* of 1.00, and a higher b* of 14.41.

- **Chroma**: Chroma is the degree of saturation of a particular hue. For example, red can vary from "scarlet" to light pink, where scarlet has a high saturation and pink has a low saturation. The yellow color of a lemon is a more saturated, "vivid," color than that of a banana, which is a less saturated, "dull" yellow. Chroma varies radially, perpendicular to the value/L* axis (see Figure 3-6, *A*, near the bottom right). Colors in the center are dull (gray). In other words, the higher the chroma, the more intense the color. Chroma is not considered separately in dentistry. It is always associated with the hue and value of dental tissues, restorations, and prostheses. One can see the relationship among these dimensions of color in the adjustments on a color television set, which use the same principles of hue, value, and chroma.

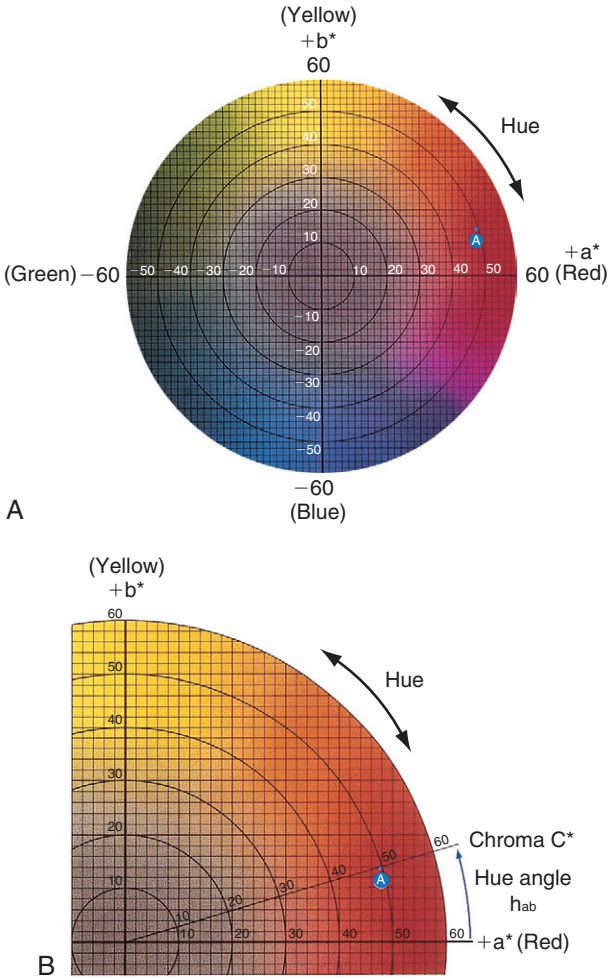


FIGURE 3-6 L*a*b* color chart showing the color of a red apple at point A (*top and bottom*). For this chart, the appearance is expressed by L* (value) = 42.83; a* (red-green axis) = 45.04; and b* (yellow-blue axis) = 9.52. In contrast, the color of shade A2 porcelain can be described by L* = 72.99; a* = 1.00; and b* = 14.41. (Courtesy of Minolta Corporation, Instrument Systems Division, Ramsey, NJ.)

COLOR MATCHING

In dental practice, color matching is most often performed with the use of a shade guide, such as the one shown in Figure 3-7, to select the color of ceramic veneers, inlays, or crowns. Shade guide tabs are used in much the same way as paint chips to match the color of house paint. The individual shade



FIGURE 3-7 Tab arrangements of the Vitapan classical shade guide. **A,** Manufacturer's arrangement No. 1: group division according to hue. **B,** Manufacturer's arrangement No. 1: "value scale," no group division. **C,** Alternative arrangement: according to color difference in relation to the lightest tab, group division. (From Paravina RD, Powers JM: *Esthetic color training in dentistry,* St. Louis, Mosby, 2004.)

tabs shown in the upper portion of Figure 3-7 are grouped according to hue (A, B, C, and D, where A = red-brown, B = red-yellow, C = gray, D = red-gray), followed by value (1 to 4, or lightest to darkest). This arrangement follows the "classical" order originated by Vita for porcelain. Recently, however, the trend is to arrange shade guides in decreasing order of value (lightest to darkest: B1, A1, B2, D2, A2, C1, C2, D4, A3, D3, B3, A3.5, B4, C3, A4, C4). Matching tooth shades is simplified by the arrangement of tabs by value; this arrangement has been found to be easier and more reliable to use (see R. D. Paravina, Dental Color Matcher, listed in the "Selected Readings"). Unfortunately, although a reasonable match can be achieved between a tooth (or restoration) and one of the shade guide tabs, it is usually insufficient to simply select a shade from a shade guide and transfer the information to a lab or technician. To ensure esthetic results, additional information such as drawings, descriptions, and photographs (e.g., Figure 3-8) should also be sent. Obviously if the technician can see the actual teeth, the probability of achieving an acceptable color match will be even greater.

Further, the subjective preference of the patient must be taken into account. An exact match between a crown or bridge and the remaining sound teeth is not always sufficient. Patients usually prefer a lighter shade (higher value) in a restoration as compared with the color of the natural teeth. Figure 3-8, *A*, shows the result of shade matching in which the two central incisor crowns were selected to be somewhat higher in value than the lateral incisors. Even though there is a slight mismatch, it is perceptible only under close observation (Figure 3-8, *B*), and the patient was quite satisfied with the overall effect.



FIGURE 3-8 **A,** Two central incisor metal-ceramic crowns with porcelain margins. The value (L*) of these crowns is higher than that of the adjacent lateral incisor teeth. **B,** Closeup view of the metal-ceramic crowns on the left.

THE EFFECT OF THE OBSERVER

Signals of color are sent to the human brain from three sets of receptors in the retina called cones, which are especially sensitive to red, blue, and green. Factors that interfere with the true perception of color generally include low or high light levels, fatigue of the color receptors, sex, age, memory, and cultural background. However, according to a 1995 study (Anusavice and Barrett, 1995), there appears to be no effect related to observer age, gender, or clinical experience relative to the accuracy of dental shade matching.

At low light levels, the rods in the retina of the human eye are more dominant than the cones, and color perception is

lost. As the brightness becomes more intense, color appears to change (Bezold-Brucke effect). Also, if an observer looks at a red object for a reasonably long time, receptor fatigue causes a green hue to be seen when he or she then looks at a white background. For this reason, if a patient is observed against an intense-colored background, the dentist or clinician may select a tooth shade with a hue that is shifted somewhat toward the complementary color of the background color. For example, a blue background shifts color selection toward yellow, and an orange background shifts the color selection toward blue-green. Unfortunately, 8% of men and 0.5% of women exhibit color blindness (see Figure 3-4). Most commonly, these people cannot distinguish red from green because of the lack of either green-sensitive or red-sensitive cones. However, this deficiency may not affect the shade selection of natural teeth.

The ranges of hue, chroma, and value ordinarily found in human teeth represent only a small portion of the standard color space. For example, compare Figure 3-5 with in the subset of color space shown in Figure 3-6. The selectivity of the human eye is such that accurate color matching is difficult even when one is using a shade guide that contains only a small number of shades (see Figure 3-7).

? CRITICAL QUESTION

Why are some objects color matched under one type of illumination but mismatched under another illumination source?

THE EFFECT OF THE LIGHT SOURCE

Because the spectral distribution of the light reflected from or transmitted through an object is dependent on the spectral content of the incident light, the appearance of an object is dependent on the nature of the light in which the object is viewed. Daylight, incandescent, and fluorescent lamps are common sources of light in the dental operatory or laboratory, and each of these has a different spectral distribution. Objects that appear to be color-matched under one type of light may appear different under another type. This phenomenon is called **metamerism**. Thus, if possible, color matching should be done under two or more different light sources, one of which should be daylight, and the laboratory shade-matching procedures should be performed under the same lighting conditions.

? CRITICAL QUESTION

Why do some tooth-colored restorations appear to be missing when viewed under "black light" illumination, such as that used in nightclubs and at rock concerts?

FLUORESCENCE

In addition to the processes already discussed, natural tooth structure absorbs light at wavelengths too short to be visible to the human eye. These wavelengths between 300 and 400 nm are referred to as near-ultraviolet radiation. Natural sunlight, photoflash lamps, certain types of vapor lamps, and ultraviolet lights used in decorative lighting ("black lights") are sources containing substantial amounts of near-ultraviolet radiation. The energy that the tooth absorbs is converted into light with longer wavelengths, in which case the tooth actually becomes a light source. This phenomenon is called fluorescence. The emitted light, a blue-white color, is primarily in the 400- to 450-nm range. Fluorescence makes a definite contribution to the brightness and vital appearance of a human tooth. As an example, ceramic crowns or composite restorations that lack a fluorescing agent appear as missing teeth when viewed under a black light.

A more detailed discussion of color and color perception, the use of shade guides, and other aspects of the science of color matching and its use in the art of restoring a natural, pleasing dentition, can be found under Color and Optical Effects in the "Selected Readings" section.

RADIOPACITY

X-rays, a form of electromagnetic radiation, lie at the high-energy end of the spectrum. Hence the interaction of dental biomaterials with x-radiation may be classified as an optical property. There are numerous circumstances where it is necessary to be able to distinguish a dental material radiographically from the surrounding tissue. For example, sufficient radiographic contrast is required in an x-ray image in order to assess restorations for marginal defects or breakdown, help differentiate composite restorations from dental caries, and detect microleakage. In case of accidental ingestion or traumatic impaction of dentures or other appliances, a delay in the detection, location, and removal of the appliance and its fragments may be life-threatening. A significant number of foreign bodies of dental origin, with many injuries and deaths, are reported each year, particularly among the elderly.

The amount of x-ray energy absorbed by an object depends on the density and thickness of the material and the energy of the radiation. Generally, the higher the atomic number of the component atoms, the greater the x-ray absorbance and the larger the contrast produced. Polymers and resins are inherently radiolucent, whereas metals with atomic numbers above about 19 (potassium) are inherently radiopaque. To impart radiopacity, restorative resins often utilize strontium- or barium-containing glass reinforcing particles (see Chapter 13); denture polymers may (but rarely) contain barium-sulfate or other heavy-metal compound additives to render them radiopaque. Radiopacity similar to that of hard tissue provides the optimal contrast for dental restorations. When radiopacity is too low, the resin will not be visible on an x-ray image; when it is too high, it may block out and obscure details of adjacent anatomy. Dentin has approximately the same radiodensity as that of aluminum, while enamel has approximately twice the radiodensity of dentin and aluminum. To claim that a composite is radiopaque, the American Dental Association requires commercial dental restorative resins to have a radiopacity at least equal to that of aluminum. To be adequately detectable on medical chest x-ray images, it has been found that a denture resin fragment of 2 mm should have a radiopacity equal or

greater than that of 0.2 mm of copper. This requires the resin to have sufficient additive to produce a radiopacity about three times that of aluminum.

THERMAL PROPERTIES

When restorative materials are placed in deep cavities, the heat transmitted to vital dental pulp must be limited so as to prevent thermal shock and trauma. In other circumstances, as with denture bases in contact with mucosal surfaces, the transmission of a certain amount of thermal energy is desirable to convey the sensations of heat and cold associated with food and beverages. Such attributes are governed by the properties of thermal conductivity and thermal diffusivity. Another category of thermal behavior is the expansion when heated and contraction when cooled. If, for example, a dental restoration expands and contracts at a rate different from that of the adjacent hard tissues, marginal failures and leakage can result. This attribute is governed by the coefficient of thermal expansion.

THERMAL CONDUCTIVITY

Thermal conductivity (κ) is the physical property that governs heat transfer through a material by conductive flow. The conduction of heat within a solid involves the transfer of thermal energy from one part of a material to another across a temperature gradient. It is defined as the quantity of heat in calories per second passing through a material 1 cm thick with a cross section of 1 cm^2 having a temperature difference of 1 K (1 °C) and is measured under steady-state conditions in which the temperature gradient does not change. According to the second law of thermodynamics, heat flows from points of higher temperature to points of lower temperature. The International System (SI) unit or measure for thermal conductivity is watts per meter per kelvin ($W \times m^{-1} \times K^{-1}$). In general, thermal conductivities increase in the following order: *polymers* < *ceramics* < *metals,* although there are exceptions.

Materials that have a high thermal conductivity are called *conductors*, whereas materials of low thermal conductivity are called *insulators*. The higher its thermal conductivity, the greater the ability of a substance to transmit thermal energy, and vice versa. If the thermal gradient does not change (i.e., heat is supplied at one end and withdrawn at the other end at a steady rate), the thermal conductivity is a measure of the heat transferred. If, however, the temperature gradient does change with time, which is invarably the case in the mouth, thermal diffusivity will determine the amount of heat transferred and, consequently, the change in temperature experienced.

? CRITICAL QUESTION

What is the difference between thermal conductivity and thermal diffusivity, and why does it matter in dentistry?

THERMAL DIFFUSIVITY

Thermal diffusivity is a measure of the speed with which a temperature change will spread through an object when one surface is heated. It is calculated from the thermal conductivity divided by the product of density and heat capacity:

$$h = \frac{\kappa}{c_p \times \rho} \quad (1)$$

where h is thermal diffusivity, κ is thermal conductivity, c_p is heat capacity at constant pressure, and ρ is the temperature-dependent density in grams per cm^3. (c_p is numerically equal to the more commonly used term, *specific heat*, which is the quantity of heat needed to raise the temperature of a unit mass by 1 °C).

A material with a high density and high specific heat will likely have a low thermal diffusivity. Such a material changes its temperature very slowly. Low heat capacity and high thermal conductivity lead to high diffusivity, and temperature changes transmit rapidly through the material. As shown in Table 3-1, gold has about one tenth the heat capacity of dentin, about 500 times the thermal conductivity, and about 600 times the thermal diffusivity. Thus a pure gold filling would provide the tooth pulp with very little protection against thermal shock as compared with natural dentin.

When the product of heat capacity and density ($c_p \times \rho$) is high, the thermal diffusivity may be low, even though the

TABLE 3-1 Density and Thermal Properties of Water, Enamel, Dentin, and Dental Materials

Material	Density ($g\ cm^{-3}$)	Specific Heat ($cal\ g^{-1}\ K^{-1}$)	Thermal Conductivity ($W\ m^{-1}\ K^{-1}$)	Thermal Diffusivity ($cm^2\ s^{-1}$)
Water	1.00	1.00	0.44	0.0014
Dentin	2.14	0.30	0.57	0.0018–0.0026
Glass ionomer	2.13	0.27	0.51–0.72	0.0022
Zinc phosphate	2.59	0.12	1.05	0.0030
Composite	1.6–2.4	0.20	1.09–1.37	0.0019–0.0073
Enamel	2.97	0.18	0.93	0.0047
Amalgam	11.6	0.005	22.6	0.96
Pure gold	19.3	0.03	297	1.18

thermal conductivity is relatively high. Therefore both thermal conductivity and thermal diffusivity are important parameters in predicting the transfer of thermal energy through a material. Because of the rapid changes in temperature that can occur during ingestion of hot or cold foods and liquids, the thermal diffusivity of a dental restorative material may be more important than its thermal conductivity. Enamel and dentin are effective thermal insulators, as shown in Table 3-1. The thermal conductivities and thermal diffusivities of cementing materials (glass ionomer, zinc phosphate, and composite) compare favorably with these tissues, in contrast with the markedly higher values for metallic restorative materials. Thus when the remaining dentin between the cavity and the pulp is too thin to provide sufficient thermal protection, an additional layer of an insulating base material should be placed, as discussed in Chapter 14, on dental cements.

COEFFICIENT OF THERMAL EXPANSION

When materials undergo a temperature increase, the vibrational motion of atoms and mean interatomic (bond) distances increase. This results is an increase in volume—an expansion. The increase is described by the **coefficient of thermal expansion, α,** which is defined as the change in length per unit of the original length of a material when its temperature is raised 1 °C (1 K). (See the discussion of thermal energy in Chapter 2):

$$\alpha = \frac{\Delta L}{L \times \Delta T} \qquad (2)$$

where L is the original length, ΔL is the change in length and ΔT is the temperature change. Values for α of some materials of interest in dentistry are presented in Table 3-2. The units are typically expressed as either mm/m K or ppm/K.

TABLE 3-2 Coefficients of Thermal Expansion (α) of Dental Materials Compared with Those of Tooth Enamel and Dentin

Material	α (ppm K^{-1})	$\alpha_{material}/\alpha_{tooth\ enamel}$
Aluminous porcelain	6.6	0.58
Dentin	8.3	0.75
Commercially pure titanium	8.5	0.77
Type II glass ionomer	11.0	0.96
Tooth enamel	11.4	1.00
Gold-palladium alloy	13.5	1.18
Gold (pure)	14.0	1.23
Palladium-silver alloy	14.8	1.30
Amalgam	25.0	2.19
Composite	14–50	1.2–4.4
Denture resin	81.0	7.11
Pit and fissure sealant	85.0	7.46
Inlay wax	400.0	35.1

This parameter is extremely important in dental applications as broad ranging as producing cast restorations that fit and maintaining the seal at a restoration margin. Its influence often dictates the procedures that have been developed for using wax patterns, casting metal crowns, placing amalgam and composite resin restorations, and preparing metal-ceramic crowns and bridges. A tooth restoration may expand or contract more than the tooth during a change in temperature; thus there may be marginal microleakage adjacent to the restoration, or the restoration may debond from the tooth. According to the values in Table 3-2, direct restorative materials may change in dimension up to 4.4 times more than the tooth enamel for every degree of temperature change.

The high thermal expansion coefficient of inlay wax is also important because it is highly susceptible to temperature changes. For example, an accurate wax pattern that fits a prepared tooth contracts significantly when it is removed from the tooth or a die in a warmer area and then stored in a cooler area. This dimensional change is transferred to a cast metal restoration that is made from the lost-wax process. Similarly, denture teeth that have been set in denture base wax in a relatively warm laboratory may shift appreciably in their simulated intraoral positions after the denture base is moved to a cooler room before the processing of a denture.

Thermal stresses produced from a thermal expansion or contraction difference are also important in the production of metal-ceramic restorations. Consider a porcelain veneer that is fired to a metal substrate (coping). It may contract to a greater extent than the metal during cooling and induce tangential tensile stresses or tensile hoop (circumferential) tensile stresses in the porcelain, which may cause immediate or delayed crack formation. Although these thermal stresses cannot be eliminated completely, they can be reduced appreciably by selection of materials whose expansion or contraction coefficients are matched fairly closely (within 4%). This is discussed more fully in Chapter 18, on ceramics.

? CRITICAL QUESTION

Which factors in the oral environment promote the corrosion of metallic dental restorations and prostheses?

ELECTROCHEMICAL PROPERTIES

Dentistry uses a wide variety of metals for restorations and prosthetic devices, the successful clinical performance and long-term durability of which require adequate corrosion resistance in the oral environment. **Corrosion** is an electrochemical process and is dependent on the ability to conduct electrical current, either by means of free electrons in metals or via ions in solution. Corrosion and its influence on durability and appearance are the major ways in which electrochemistry affects oral well-being. Pulpal pain caused by an electrical current produced when two dissimilar metals are brought into contact, known as galvanic shock, is another. The most important electrochemical effects are toxic and allergic responses to metal ions released by corrosion, which may affect both

nearby tissues and distant organs. In most cases corrosion is undesirable. However, a limited amount of corrosion at the margins of dental amalgam restorations may be beneficial, since the corrosion products tend to seal the marginal gap and inhibit the ingress of oral fluids and bacteria.

The oral environment is highly conducive to electrochemical action. It is warm, moist, and subjected to wide fluctuations in temperature and pH. Thus, an understanding of corrosion and the underlying electrochemical properties is essential in order to control electrochemical effects and thereby minimize corrosion and corrosion-induced problems in dentistry.

TARNISH AND CORROSION

Tarnish is a surface discoloration on a metal or a slight loss or alteration of the surface finish or luster. In the oral environment, tarnish often occurs from the formation of deposits on the surface of a restoration. Tarnish also arises from the formation of thin films, such as oxides, sulfides, or chlorides. The latter phenomenon may be only a simple surface deposit, and such a film may even be protective, as discussed subsequently. However, it is often an early indication and precurser of corrosion.

Corrosion is a process whereby deterioration of a metal is caused by reaction with its environment. In due course, corrosion can cause severe and catastrophic disintegration of metals. Even if highly localized, corrosion may cause mechanical failure of a structure even though the actual volume of material lost is quite small. Corrosive disintegration can take place through the action of moisture, atmosphere, acid or alkaline solutions, and certain chemicals. Tarnish is often the forerunner of corrosion because the tarnish film accumulates components that chemically attack the metallic surface. For example, eggs and certain other foods contain significant amounts of sulfur. Various sulfides, such as hydrogen or ammonium sulfide, initially tarnish and eventually corrode silver, copper, tin, mercury, and other metals present in their alloys. Also, water, oxygen, and chlorine ions are present in saliva and contribute to the corrosive attack. Various acidic solutions—such as phosphoric, acetic, and lactic acids—are present at times and, at the proper concentration and pH, can promote corrosion.

FUNDAMENTAL BASIS OF CORROSION

Corrosion occurs because most commonly used metals and alloys are not in their lowest energy state (thermodynamically the most stable state), For example, iron (Fe) is not available in nature as pure Fe. Instead, it exists in the form of various oxides of iron, from which metallic Fe is extracted by metallurgical techniques. Similarly, aluminum (Al) is extracted from aluminum oxide (Al_2O_3), and copper (Cu) from Cu sulfides. Oxidized compounds such as Fe_3O_4, Al_2O_3, or CuS (commonly classified as minerals) are thermodynamically stable and consequently occur in nature in these fully reacted forms. Thus, pure metals spontaneously convert to a highly reacted, oxidized state by reacting with, for example, oxygen, sulfur, or chlorine in order to revert to their lowest energy state. This, in essence, is the process of corrosion. Gold is unique: it does not corrode and is available in nature in pure forms. Ceramics, on the other hand, do not corrode because they are already fully oxidized and in their lowest energy states. However, glass-phase ceramics and feldspathic porcelains, and glazes can dissolve in acidic and basic media.

Corrosion of a metal is either a chemical or an electrochemical process, in each of which the first step is the loss of an electron.

Chemical corrosion is the direct combination of metallic and nonmetallic elements to yield a chemical compound through oxidation reactions. A good example is the discoloration of silver by sulfur, where silver sulfide forms by chemical corrosion. It can also be a corrosion product of dental gold alloys that contain silver. This mode of corrosion is also referred to as dry corrosion, since it occurs in the absence of water or another fluid electrolyte. Another example is the oxidation of silver-copper alloy particles that are mixed with mercury to prepare certain dental amalgam products. These alloy particles contain a silver-copper eutectic phase; oxidation limits their reactivity with mercury, thereby affecting the setting reaction of the dental amalgam product. This is why it is prudent to store the alloy in a cool, dry location to ensure an adequate shelf life.

Electrochemical corrosion, also known as **galvanic** corrosion, requires the presence of water or some other fluid electrolyte and a pathway for the transport of electrons (i.e., an electrical current). It is also referred to as wet corrosion, since it requires a fluid electrolyte. Electrochemical corrosion is seldom isolated and almost invariably is accompanied by chemical corrosion. However, the electrochemical mode of corrosion is the more important for dental materials and is the focus in this chapter.

? CRITICAL QUESTION

Which mechanisms of electrochemical corrosion are possible for metallic dental restorations and prostheses?

ELECTROCHEMICAL MECHANISM OF CORROSION

When a metal is in contact with a fluid electrolyte, the chemical potential causes enough ions to dissolve to form a saturated solution and produce an equal number of free electrons. The loss of electrons by a metal is known as oxidation and is the initial electrochemical event in the corrosion process. The ease with which a metal gives up electrons in solution and oxidizes can be expressed in terms of the *oxidation potential*. An electrochemical cell is illustrated schematically in Figure 3-9.

An electrochemical cell is composed of three essential components: an anode, a cathode, and an electrolyte; it is a battery, since it produces a voltage and current between the two electrodes. In this example the anode could be an amalgam restoration and the cathode a gold alloy restoration, with saliva serving as the electrolyte.

The *anode* is the surface or site on a surface where positive ions (M^+) are formed (i.e., the metal surface that is undergoing an oxidation reaction and corroding) with the production

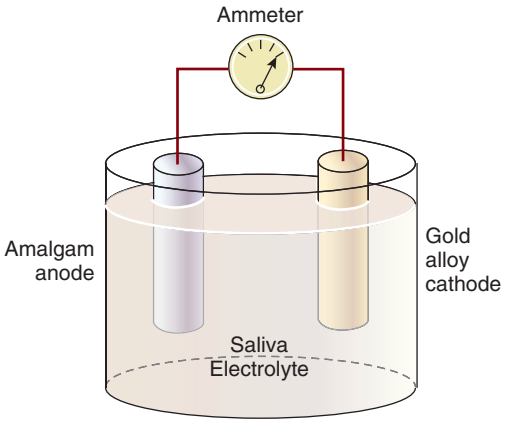


FIGURE 3-9 Diagram of an electrochemical cell consisting of a simulated amalgam anode, a gold alloy cathode, and saliva as the electrolyte.

of free electrons, as illustrated by the following anodic/oxidation reaction:

$$M^{o} \rightarrow M^{+} + e^{-} \quad (3)$$

Once the solution is saturated with metal ions the reverse reaction, reduction, can occur. The *cathode* is the surface or sites on a surface where metal ions are deposited from a saturated solution and consume free electrons produced at the anode. Several reduction reactions can take place, depending on the environment. For example, metal ions may be removed from the solution to form metal atoms (reaction 4) as occurs in metal plating; hydrogen ions may be converted to hydrogen gas (reaction 5); or hydroxyl ions may be formed (reaction 6).

Cathodic/reduction reaction:

$$M^{+} + e^{-} \rightarrow M^{o} \quad (4)$$

$$2H^{+} + 2e^{-} \rightarrow H_2\uparrow \quad (5)$$

$$2H_2O + O_2 + 4e^{-} \rightarrow 4(OH)^{-} \quad (6)$$

The electrolyte supplies the ions needed at the cathode and carries away the corrosion products at the anode. The external circuit serves as a conduction path to carry electrons (the electrical current) from the anode to the cathode. An electrical potential difference—that is, a voltage (V)—can be measured, which has considerable importance in that it is capable of producing a physiological sensation such as pain. This difference in electrical potential is also known as electromotive force (EMF).

In order for electrochemical corrosion to be an ongoing process, the production of electrons by the oxidation reactions at the anode must be exactly balanced by the consumption of electrons in the reduction reactions at the cathode. Often the cathodic reactions can be considered to be the primary driving force for electrochemical corrosion. This is a very important consideration in determining the rate of a corrosion process, and it can be used to advantage in order to reduce or eliminate corrosion.

Different metals have different tendencies for oxidation because of their differences in electronic structure; this tendency to oxidize (ionize) is measured by the *electrode potential* expressed in volts or millivolts. The more negative the electrode potential, the easier it is for any particular metal to ionize and oxidize, and the more susceptible it is to tarnish and corrosion. The more positive its electrode potential, the less the metal's susceptibility to tarnish and corrosion. Recall that noble metals have their full complement of eight outer electrons and that they have very low tendencies to give up electrons and oxidize. Therefore, noble metals have a very positive electrode potential and are highly resistant to corrosion. Noble metals include gold, platinum, palladium, iridium, rhodium, osmium, and ruthenium. Their presence in alloys can confer varying levels of corrosion resistance.

TABLE 3-3 Electromotive Series of the Metals

Metal	Ion	Electrode Potential (V)
Gold	Au^{+}	+1.50
Gold	Au^{3+}	+1.36
Platinum	Pt^{2+}	+0.86
Palladium	Pd^{2+}	+0.82
Mercury	Hg^{2+}	+0.80
Silver	Ag^{+}	+0.80
Copper	Cu^{+}	+0.47
Bismuth	Bi^{3+}	+0.23
Antimony	Sb^{3+}	+0.10
Hydrogen	H^{+}	–0.00
Lead	Pb^{2+}	–0.12
Tin	Sn^{2+}	–0.14
Nickel	Ni^{2+}	–0.23
Cadmium	Cd^{2+}	–0.40
Iron	Fe^{2+}	–0.44
Chromium	Cr^{2+}	–0.56
Zinc	Zn^{2+}	–0.76
Aluminum	Al^{3+}	–1.70
Sodium	Na^{+}	–2.71
Calcium	Ca^{2+}	–2.87
Potassium	K^{+}	–2.92

The basis for judging the tendency of metals and alloys to undergo electrochemical corrosion is the **electromotive (or galvanic) series**, which arranges metals by their equilibrium values of electrode potential. Table 3-3 presents an electromotive series useful for dental metals and alloys in water at 25 °C. Each of these standard half-cell potentials may be considered as the voltage of an electrochemical cell in which one electrode is the hydrogen electrode (reaction 5), designated arbitrarily as zero potential, and the other electrode is the element of interest. The sign of the electrode potential in Table 3-3 indicates the polarity in such a cell. Metals with a more positive potential have a lower tendency to dissolve and are therefore more resistant to becoming oxidized and corroded in aqueous environments.

If two pure metals are immersed in an electrolyte and connected by an electrical conductor to form a galvanic cell, the metal with the lower (more negative) electrode potential in Table 3-3 becomes the anode and undergoes oxidation, that is, its ions go into solution. As an example, in a galvanic cell composed of copper (−0.46 V) and zinc (−0.76 V) electrodes in an aqueous acidic solution, the zinc electrode becomes the anode and undergoes surface dissolution.

In general the relative position of any element in the electromotive series depends not only on its inherent solution tendencies but also on its ionic concentration. As the ionic concentration increases, the tendency for that element to dissolve decreases. Thus, an increase in metal ion content may eventually prevent further corrosion because the metal's ions have saturated the immediate environment. However, this would be unusual for metallic dental materials because dissolving ions are continually removed by food, fluids, and toothbrushing. Thus, corrosion in the mouth is typically an ongoing process. Many types of electrochemical corrosion are possible in the oral environment because saliva, with the salts it contains, is a weak electrolyte. The electrochemical properties of saliva depend on the concentrations of its components, pH, surface tension, and buffering capacity. Each of these factors may influence the strength of any electrolyte. Thus, the magnitude of the resulting corrosion process will be controlled by these variables.

In an environment in which a metal is corroding, both anodic and cathodic reactions take place simultaneously on the surface of the metal. Metal ions go into solution or form corrosion products because of the anodic reactions and other ions are reduced in the cathodic reactions. These two reactions may occur at randomly distributed sites on the metal surface or, more frequently, there are anodic areas at which mostly the metal dissolves and cathodic areas at which mostly other ions are discharged. Several forms of electrochemical corrosion are based on the mechanisms that produce these inhomogeneous areas; they are discussed below.

DISSIMILAR METALS

An important type of electrochemical reaction occurs when combinations of dissimilar metals are in direct physical contact. Here two adjacent metal restorations where the metal surfaces have different compositions. The alloy combinations that may produce galvanic corrosion or electrogalvanism through the flow of galvanic currents may be in either continuous or intermittent contact. An example would be a dental amalgam restoration placed on the occlusal surface of a tooth directly opposing a gold inlay. Because both restorations are wet with saliva, an electrical circuit exists with a difference in potential between the dissimilar restorations (Figure 3-10). When the two restorations are brought into contact, there is a sudden short-circuit through the two alloys. This can result in a sharp pain, called **galvanic shock**, which is well known in dentistry. An undetected piece of aluminum foil in a baked potato can produce the same effect.

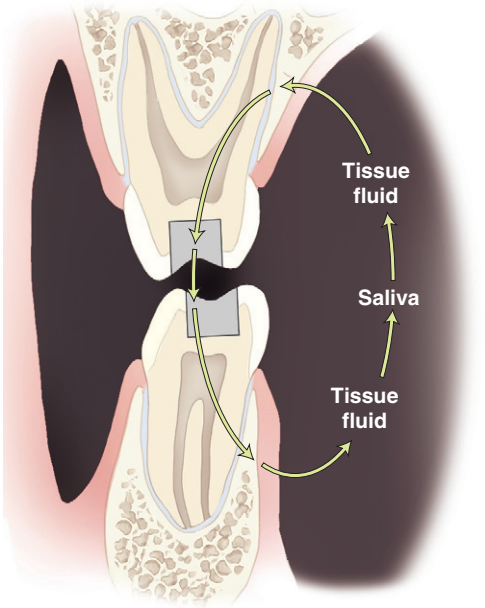


FIGURE 3-10 Possible path of a galvanic current in the mouth.

When the teeth are not in contact, there is still an electrical circuit associated with the difference in potential or electromotive force (EMF) between the two restorations. The saliva forms the electrolyte and the hard and soft tissues can constitute the external circuit, although the electrical resistance of the external circuit is considerable in comparison with that which exists when the two restorations are brought into contact. The current generated is inversely related to the electrical resistance of the metal of interest. The electrical currents measured under these conditions between a gold crown and an amalgam restoration in the same mouth, but not in contact, appear to be approximately 0.5 to 1 microampere (μA) with a corresponding potential difference of approximately 500 millivolts (mV). These oral galvanic currents are somewhat greater when dissimilar alloys are present, but they also occur between restorations of similar alloys, which never have exactly the same surface composition or structure.

A current is present even in a single isolated metallic restoration, although it is less intense. In this situation the electrochemical cell is generated as a result of the electrical potential differences created by the two electrolytes: saliva and tissue fluids. The term *tissue fluid* is used to denote the dentinal fluid, soft tissue fluid, and blood that provide the means for completing the external circuit. Because the chloride ion concentration is seven times higher than that of saliva, it is assumed that the interior surfaces of a dental restoration exposed to dentinal fluid will have a more active electrochemical potential. Possible current pathways are diagrammed in Figure 3-11.

Although the magnitude of these currents usually diminishes somewhat as the restoration ages, it remains indefinitely at the approximate value cited. The clinical significance of these currents, other than their influence on corrosion, will be discussed later in this chapter. Coating with a varnish helps to eliminate galvanic shock.

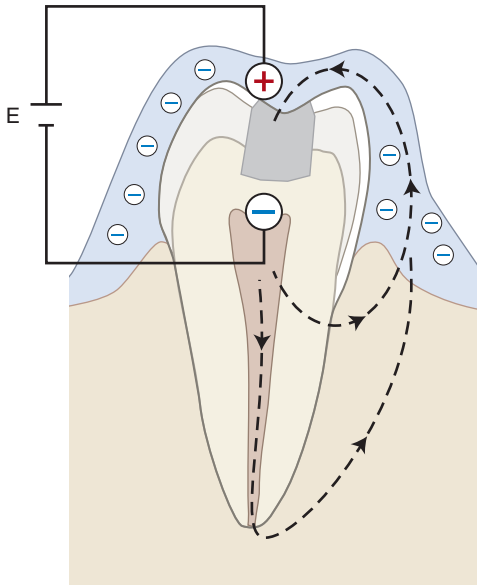


FIGURE 3-11 Schematic illustration of a single metallic restoration showing two possible current pathways between an external surface exposed to saliva and an interior surface exposed to dentinal fluid. Because the dentinal fluid contains a higher Cl^- concentration than saliva, it is assumed that the electrode potential of the interior surface exposed to dentinal fluid is more active; it is therefore given a negative sign (–). The potential difference between the two surfaces is represented by E. (From *Metals Handbook,* 9th ed, Vol. 13. Metals Park, OH, American Society for Metals, 1978, p 1342.)

HETEROGENEOUS SURFACE COMPOSITION

Another type of galvanic corrosion is associated with the heterogeneous composition of the surfaces of dental alloys, whose microstructures have been described in the preceding two chapters. Examples include the eutectic alloys and peritectic alloys (see Chapter 5). Commercial dental alloys generally contain more than three elements, and they can have complex microstructures that result in even more heterogeneous surface compositions. For example, when an alloy containing a two-phase eutectic microstructural constituent is immersed in an electrolyte, the lamellae of the phase with the more negative electrode potential are attacked, and corrosion results.

In an alloy that is a single-phase solid solution, any cored structure is less resistant to corrosion than is the homogenized solid solution because of differences in electrode potential caused by microsegregation and variations in composition between individual microstructural elements (see Chapter 5). Even a homogenized solid solution is susceptible to corrosion at the grain boundaries, which are anodic to the cathodic grain interiors, because atomic arrangements at the grain boundaries are less regular and have higher energies (see Chapter 5). Solder joints (Chapter 16) between dental alloys also corrode because of differences in compositions of the alloy and solder.

Impurities in alloys enhance corrosion, and these impurities are typically segregated at the grain boundaries, as described in Chapter 5. Mercury impurities that can inadvertently contaminate gold alloys during handling by dental personnel have electrode potentials different from those of the bulk grains of the gold alloys. Finally, it follows from the preceding discussion that nominally pure metals, which do not contain significant quantities of impurities or secondary microstructural phases acting as miniature electrodes with different potentials, corrode at much slower rates than alloys do.

STRESS CORROSION

Since the imposition of stress increases the internal energy of an alloy, either through the elastic displacements of atoms or the creation of microstrain fields associated with dislocations (when permanent deformation occurs, as described in Chapter 17), the tendency to undergo corrosion will be increased. It is plausible that, for most metallic dental appliances, the deleterious effects of stress and corrosion, called **stress corrosion**, are most likely to occur during fatigue or cyclic loading in the oral environment. Small surface irregularities, such as notches or pits, act as sites of stress concentration so that ordinary fatigue failure (in the absence of corrosion) occurs at nominal stresses below the normal elastic limit of the alloy. Thus any cold working of an alloy by bending, burnishing, or malleting causes localized permanent deformation in some parts of the appliance. Electrochemical cells consisting of the more deformed metal regions (anodic), saliva, and undeformed or less deformed metal regions (cathodic) are created, and the deformed regions will experience corrosion attack. This is one reason why excessive burnishing of the margins of metallic restorations is contraindicated.

CRITICAL QUESTION

How can a small pit in the surface of a metallic restoration or a gap between a metal restoration and a tooth become susceptible to and sustain aggressive, localized corrosive attack?

CONCENTRATION CELL CORROSION

An important type of electrochemical corrosion is called **concentration cell** corrosion, which occurs whenever there are variations in the electrolytes or in the composition of the given electrolyte within the system. For example, there are often accumulations of food debris in the interproximal areas between the teeth, particularly if oral hygiene is poor. This debris then produces an electrolyte in that area, which is different from the electrolyte that is produced by normal saliva at the occlusal surface. Electrochemical corrosion of the alloy surface underneath the layer of food debris will take place in this situation.

A similar type of attack may occur from differences in the oxygen concentration between parts of the same restoration, with the greatest attack at the areas containing the least oxygen (the anode). Irregularities—such as pits, scratches, and cracks—in restoration surfaces are important examples of this phenomenon. The region at the bottom of such a defect is oxygen-deprived and becomes the anode because it will

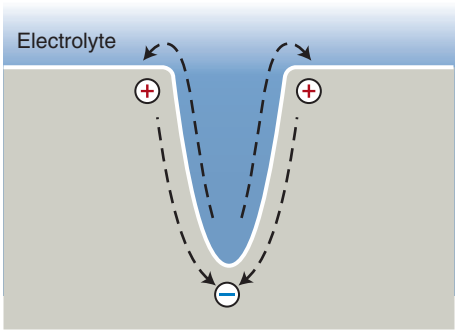


FIGURE 3-12 A pit on a dental alloy as a corrosion cell. The region at the bottom of the pit is an anode, and the surface around the rim of the pit is the cathode. The ionic current flows through the electrolyte and the electronic current flows through the metal. (With permission from Richman, MH: *An Introduction to the Science of Metals.* Ginn Custom Publishers, 1974.)

typically be covered with food debris and mucin, while the alloy surface around the rim of a scratch or pit becomes the cathode, as diagrammed in Figure 3-12. Consequently metal atoms at the base of the pit ionize and go into solution, causing the pit to deepen. The rate of such corrosion may be very rapid, since the area of the anodic region is much smaller than that of the cathodic region and there must be a balance of charge transport in both regions. Consequently failure may occur much more rapidly than would be expected from a uniform surface attack. Thus, to protect against such **pitting corrosion**, all metallic dental restorative materials should be polished. A closely related category of concentration cell corrosion is "**crevice corrosion**," in which preferential attack occurs at crevices and marginal gaps of crowns, bridges, and cavity restorations because of the presence of food debris and other deposits.

Seldom is any one of the preceding types of electrochemical corrosion found alone. Generally two or more types act simultaneously, thereby compounding the problem. This phenomenon can be illustrated by considering the dissimilar metal corrosion between a cast gold inlay and an amalgam restoration. Because surface deposits can form during this type of electrochemical corrosion, differences in oxygen concentration will arise. Moreover, if the corrosion product layer is incomplete or porous, as is usually the case with metallic dental restorations, the resulting inhomogeneous surface will produce new electrochemical cells for continued corrosion. It should be obvious that good oral hygiene helps to prevent the accumulation of surface deposits and is essential for minimizing corrosion.

PROTECTION AGAINST CORROSION

Gold coating is employed to enhance the appearance of many commercial nondental products. However, this noble metal is soft, and when its surface becomes scratched or pitted to such a depth that the base metal is exposed, the base metal will be corroded at a very rapid rate because concentration cells have been created and two dissimilar metals are in direct contact. Attempts to use metallic and nonmetallic coatings to provide corrosion protection for dental gold alloys have generally been ineffective because such coatings: (1) were too thin, (2) were incomplete, (3) did not adhere to the underlying metal, (4) were readily scratched, or (5) were attacked by oral fluids.

However, in the case of two dissimilar metals in contact, paint or another nonconductive film can be used to advantage if it is applied to the more noble metal. The corrosion rate of the more active metal will be reduced because the surface area available for the reduction reaction has been decreased, and a scratch in the coating over the noble alloy will not lead to rapid attack of the active metal.

A highly effective protection utilizes certain metals that develop a thin, adherent, highly protective film by reaction with the environment; such a metal is said to be passive. A thin surface oxide forms on chromium, which is a good example of a passivating metal. The most common example is stainless steel, which contains sufficient amounts of chromium added to iron and its alloys to passivate the alloy, as described in Chapters 16 and 17. Iron, steel, and certain other metals that are subject to corrosion may also be electroplated with nickel followed by chromium for corrosion protection and esthetic reasons. However, it should be pointed out that tensile stress and certain ions, such as chloride ions, can disrupt the protective oxide film, leading to rapid corrosion. Chromium-passivated metals can be susceptible to stress corrosion and pitting corrosion; therefore patients should be warned against using household bleaches for cleaning partial denture frameworks or removable orthodontic appliances that are alloyed with chromium. Titanium (Ti) also forms a passivating titanium oxide film, which is of interest, since both commercially pure Ti and alloys in which Ti is a major component are used for a variety of dental applications, such as cast restorations, orthodontic wires, endodontic instruments, and implants (see Chapters 16 and 20). Titanium and its alloys are widely used in dentistry because of their favorable combination of chemical, physical, and biological properties as well as their resistance to corrosion. Their consequent biocompatibility is among their major advantages. Nevertheless, corrosion can occur and the long-term accumulation of corrosion products can lead to fractures of the alloy-implant interface, implant abutment, or implant body. The combination of stress, corrosion, and bacteria contributes to implant failure.

Noble metals resist corrosion because their electromotive force is positive with regard to any of the common reduction reactions found in the oral environment. In order to corrode a noble metal under such conditions, an external current (overpotential) is required. A guideline that has been employed by the manufacturers of many dental alloys is that at least half the atoms should be noble metals (gold, platinum, and palladium) so as to ensure against corrosion. Palladium has been found to be effective in reducing the susceptibility to sulfide tarnishing for alloys containing silver. If noble metals are used to avoid corrosion, it is important that the more active constituents of the alloy be uniformly dispersed in a random solid solution, since the formation of a second phase that is enriched in an active metal will produce a galvanic corrosion cell.

CLINICAL SIGNIFICANCE OF GALVANIC CURRENTS

Small galvanic currents associated with electrogalvanism are known to be continually present in the mouth, promoting corrosion, as discussed earlier. As long as metallic restorative materials are employed, it is unlikely that these galvanic currents can be eliminated. Although postoperative pain caused by galvanic shock is not common, it can be a source of discomfort to an occasional patient. However, such postoperative pain usually occurs immediately after insertion of a new restoration and generally subsides and disappears in a few days. It is likely that the physiological condition of the tooth is the primary factor responsible for the pain resulting from this current flow. Once the tooth has recovered from the injury of preparing the cavity and has returned to a more normal physiological condition, the current flow produces no response. Currently the most practical method for reducing or eliminating galvanic shock is a varnish coating on the surface of the metallic restoration. As long as the varnish remains, the restoration is insulated from saliva and no electrochemical cell is established. By the time the varnish has worn away, the pulp has usually healed sufficiently that no pain persists.

The balance of evidence shows that galvanic currents are deleterious only from the standpoint of patient discomfort, and even then only rarely. Nevertheless, dentists should avoid clinical procedures that exacerbate the condition, such as insertion of an amalgam restoration directly in contact with a gold crown. Mercury released from the corroding amalgam (the anode) may interact with the gold alloy (the cathode) and weaken it. A discoloration of both restorations may also occur, and often a metallic taste develops that can persist indefinitely.

For further information, consult the articles listed in the "Selected Readings" under Electrochemical Properties.

MAGNETIC MATERIALS

Magnetic materials are ubiquitous, being found in a wide range of everyday items from magnetic bulletin boards to compasses to electrical generators. In dentistry they are primarily used for retention of implant-borne prostheses and for orthodontic tooth movement. The force that magnets deliver is biologically safe and can be directed and exerted both within the mouth and through soft and hard tissues.

Magnetism occurs in nature in *magnetite,* a magnetic iron oxide, and in the synthetic alloys aluminium-nickel-cobalt (AlNiCo), platinum-cobalt (PtCo), samarium-cobalt (SmCo), and neodymium-iron-boron (NdFeB). Magnetism develops from circulating electrical currents. In magnetic materials the circulation is due to electrons orbiting within the atoms. In most materials the magnetic effects among the electrons cancel out, but in iron and the alloys mentioned above, a net magnetic field is induced when the atoms are properly aligned. This alignment produces a magnetic field, which emerges from one pole (north pole) and returns to the other (south) pole. A magnetic field induces changes in the surrounding medium in proportion to its flux density, the unit of which is the **Tesla** (T), and the flux density is proportional to the size of the magnet. Attraction or repulsion between two magnets is dependent on their pole orientation and is inversely proportional to the square of the distance between them. These properties result in a dramatic reduction in attractive or repulsive force when magnets are not optimally aligned and not in close proximity.

A major shortcoming of magnets is their susceptibility to corrosion and need to be protected by a highly durable coating. This is often done by electroplating. Another problem is loss of magnetic flux over time or in the presence of elevated temperatures. In dentistry, magnetic materials are used that generate a constant field that is permanent at mouth temperatures. However, heating to relatively modest temperatures can cause irreversible magnetic loss. For example, this can occur in applications where magnets are embedded in acrylic appliances that, during curing, reach temperatures of 80 °C to 90 °C from the exothermic setting reaction of the methylmethacrylate resin (see Chapter 20, "Denture Base Resins").

Within their range of current dental uses, magnets and static magnetic fields have been found to be biologically safe if the flux is less than 40 mT, according to the guidelines of the International Commission on Non-Ionizing Radiation Protection and the World Health Organization. According to these organizations, vertigo and nausea are experienced when the head moves rapidly in a field greater than 2 T, as might occur during medical magnetic resonance imaging. These symptoms derive from the disturbance of vestibular function by induced current in the central nervous system. There is little evidence of other effects including carcinogenesis, although experimental data are still sparse. Magnetic fields developed near the gingiva by magnetic attachments for removable partial dentures have been reported to be well below 40 mT—in the 10- to 15-mT range.

ACKNOWLEDGEMENT

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Physical Properties

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An especially useful explanation of complementary colors is given in Chapter 5 http://www.applepainter.com/Chap05/

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CHAPTER

4

Mechanical Properties of Dental Materials

OUTLINE

What Are Mechanical Properties?

Stresses and Strains

Elastic Properties

Strength Properties

Weibull Statistics

Other Important Properties

Stress Concentration Effects

Clenching and Mastication Forces

Criteria for Selection of Restorative Materials

KEY TERMS

Brittleness—Relative inability of a material to deform plastically before it fractures.

Compressive stress—Compressive force per unit area perpendicular to the direction of applied force.

Compressive strength—Compressive stress at fracture.

Ductility—Relative ability of a material to elongate plastically under a tensile stress. This property is reported quantitatively as percent elongation.

Elastic strain—Amount of deformation that is recovered instantaneously when an externally applied force or pressure is reduced or eliminated.

Elastic modulus (also modulus of elasticity and Young's modulus)—Stiffness of a material that is calculated as the ratio of elastic stress to elastic strain.

Flexural strength (bending strength or modulus of rupture)—Force per unit area at the instant of fracture in a test specimen subjected to flexural loading.

Flexural stress (bending stress)—Force per unit area of a material that is subjected to flexural loading.

Fracture toughness—The critical stress intensity factor at the point of rapid crack propagation in a solid containing a crack of known shape and size.

Hardness—Resistance of a material to plastic deformation, which is typically produced by an indentation force.

Malleability—Ability to be hammered or compressed plastically into thin sheets without fracture.

Percent elongation—Amount of plastic strain, expressed as a percent of the original length, which tensile test specimen sustains at the point of fracture (*Ductility*).

Plastic strain—Irreversible deformation that remains when the externally applied force is reduced or eliminated.

Pressure—Force per unit area acting on the surface of a material (compare with *Stress*).

Proportional limit—Magnitude of elastic stress above which plastic deformation occurs.

Resilience—The amount of elastic energy per unit volume that is sustained on loading and released upon unloading of a test specimen.

Shear stress—Ratio of shear force to the original cross-sectional area parallel to the direction of the applied force.

Shear strength—Shear stress at the point of fracture.

Stress—Force per unit area within a structure subjected to a force or pressure (see *Pressure*).

Stress concentration—Area or point of significantly higher stress that occurs because of a structural discontinuity such as a crack or pore or a marked change in dimension.

Strain—Change in dimension per unit initial dimension. For tensile and compressive strain, a change in length is measured relative to the initial reference length.

Stress intensity (stress intensity factor)—Relative increase in stress at the tip of a crack of given shape and size when the crack surfaces are displaced in the opening mode (also *Fracture Toughness*).

Strain hardening (work hardening)—Increase in strength and hardness and decrease in ductility of a metal that results from plastic deformation.

Strain rate—Change in strain per unit time during loading of a structure.

Strength—(1) Maximum stress that a structure can withstand without sustaining a specific amount of plastic strain (yield strength); (2) stress at the point of fracture (ultimate strength).

Tensile stress—Ratio of tensile force to the original cross-sectional area perpendicular to the direction of applied force.

Tensile strength (ultimate tensile strength)—Tensile stress at the instant of fracture.

Toughness—Ability of a material to absorb elastic energy and to deform plastically before fracturing; measured as the total area under a plot of tensile stress versus strain.

True stress—Ratio of applied force to the actual (true) cross-sectional area; however, for convenience, stress is often calculated as the ratio of applied force to the initial cross-sectional area.

Yield strength—The stress at which a test specimen exhibits a specific amount of plastic strain.

By the end of this chapter you will have developed a conceptual foundation of the reasons for fracture of restorative materials and a basic framework of design features that will enhance your ability to increase the fracture resistance of restorative materials in the oral environment. This knowledge will allow you to differentiate the potential causes of clinical failures that may be attributed to material deficiencies, design features, dentist errors, technician errors, or patient factors such as diet, biting force magnitude, and force orientation. However, a familiarity with the key terms is essential to understand the principles involved in the load-versus-deformation behavior of dental biomaterials.

? CRITICAL QUESTION

Why is strength not a true property of brittle dental materials?

WHAT ARE MECHANICAL PROPERTIES?

Elastic solids may be stiff or flexible, hard or soft, brittle or ductile, and fragile or tough. However, these are qualitative mechanical properties that do not describe how similar or dissimilar dental materials of the same type may be. Mechanical properties are defined by the laws of mechanics—that is, the physical science dealing with forces that act on bodies and the resultant motion, deformation, or stresses that those bodies experience. This chapter focuses primarily on static bodies—those at rest—rather than on dynamic bodies, which are in motion. However, fatigue properties, determined from cyclic loading, are also important for brittle materials, as discussed later. Mechanical properties of importance to dentistry include **brittleness**, **compressive strength**, **ductility**, **elastic modulus**, fatigue limit, flexural modulus, **flexural strength**, **fracture toughness**, hardness, impact strength, **malleability**, **percent elongation**, Poisson's ratio, **proportional limit**, shear modulus, **shear strength**, **tensile strength**, torsional strength, **yield strength**, and Young's modulus.

All mechanical properties are measures of the resistance of a material to deformation, crack growth, or fracture under an applied force or pressure and the induced stress. An important factor in the design of a dental prosthesis is strength, a mechanical property of a material, which ensures that the prosthesis serves its intended functions effectively and safely over extended periods of time. In a general sense, strength is the ability of the prosthesis to resist induced stress without fracture or permanent deformation **(plastic strain)**. Plastic deformation occurs when the elastic **stress** limit (proportional limit) of the prosthesis material is exceeded. Although **strength** is an important factor, it is not a reliable property for estimating the survival probabilities over time of prostheses made of brittle material because strength increases with specimen size and stressing rate, decreases with the number of stress cycles, and is strongly affected by surface processing damage. Thus, strength is not a true property of a material compared with fracture toughness, which more accurately describes the resistance to crack propagation of brittle materials.

Why do dental restorations or prostheses fracture after a few years or many years of service? The simplest answer is that the mastication force exerted by the patient during the final mastication cycle (loading and unloading) has induced a failure level of stress in the restoration. But why did the fracture not occur during the first month or year of clinical service? One can assume that the stress required to fracture a restoration must decrease somehow over time, possibly because of the very slow propagation of minute flaws to become microcracks through a cyclic fatigue process. The failure potential of a prosthesis under applied forces is related to the mechanical properties and the microstructure of the prosthetic material. Mechanical properties are the measured responses, both elastic (reversible upon force reduction) and plastic (irreversible or nonelastic), of materials under an applied force, distribution of forces, or **pressure**. Mechanical properties are expressed most often in units of stress and/or **strain**. The stressing rate is also of importance since the strength of brittle materials increase with an increase in the rate at which stress is induced within their structures. They represent measures of (1) elastic or reversible deformation (e.g., proportional limit, **resilience**, and modulus of elasticity); (2) plastic or irreversible deformation (e.g., percent elongation and hardness); or (3) a combination of elastic and plastic-deformation (e.g., toughness and yield strength). To discuss these properties, one must first understand the concepts of stress and strain and the differences between force, pressure, and stress.

? CRITICAL QUESTION

How can two different compressive forces applied to the same ceramic crown produce different stresses within the crown surface?

STRESSES AND STRAINS

When a force or pressure is exerted on an elastic solid, the atoms or molecules respond in some way at and below the

area of loading, but the applied force has an equal and opposite reaction at the area at some other point in the structure (e.g., an area that supports the solid and resists its movement). Although we assume for simplicity that the stress induced in the material structure is uniform between the loaded surface and the resisting surface, this is clearly not the case. In fact, the stress induced near the surface decreases with distance from the loading point and increases as the supporting surface is approached. This pattern is called a stress distribution or stress gradient.

For the elastic solid in question, the atoms may be compressed in such a way that their interatomic equilibrium distances are decreased temporarily until the force is decreased or eliminated. However, if the force is increased further, it is possible that the atoms will be displaced permanently or their bonds ruptured. Dental restorations should be designed such that permanent displacement of atoms or rupture of interatomic bonds does not occur except possibly at surface areas where normal wear may occur.

The physical process by which atoms or molecules become displaced from their equilibrium positions under the application of an external force or pressure is related to yielding or plastic deformation on a broader scale. Stress is the force per unit area acting on millions of atoms or molecules in a given plane of a material. Except for certain flexural situations, such as four-point flexure, and certain nonuniform object shapes, stress typically decreases as a function of distance from the area of the applied force or applied pressure. Thus, stress distributions in an elastic solid are rarely uniform or constant. However, for purposes of determining mechanical properties, we assume that the stresses are uniformly distributed.

For dental applications, there are several types of stresses that develop according to the nature of the applied forces and the object's shape. These include tensile stress, shear stress, and compressive stress. The strength of a material is defined as the average level of stress at which it exhibits a certain degree of initial plastic deformation (yield strength) or at which fracture occurs (ultimate strength) in test specimens of the same shape and size. Strength is dependent on several factors, including the (1) stressing rate, (2) shape of the test specimen, (3) size of the specimen, (4) surface finish (which controls the relative size and number of surface flaws), (5) number of stressing cycles, and (5) environment in which the material is tested. However, the clinical strength of brittle materials (such as ceramics, amalgams, composites, and cements) is reduced when large flaws are present or if **stress concentration** areas exist because of improper design of a prosthetic component (such as a notch along a section of a clasp arm on a partial denture). Under these conditions a clinical prosthesis may fracture at a much lower applied force because the localized stress exceeds the strength of the material at the critical location of the flaw (stress concentration).

When one chews a hard food particle against a ceramic crown, the atomic structure of the crown is slightly deformed elastically by the force of mastication. If only elastic deformation occurs, the surface of the crown will recover completely when the force is eliminated. Elastic stresses in materials do not cause permanent (irreversible) deformation. On the other hand, stresses greater than the proportional limit cause permanent deformation and, if high enough, may cause fracture. For brittle materials that exhibit only elastic deformation and do not plastically deform, stresses at or slightly above the maximal elastic stress (proportional limit) result in fracture. These mechanical properties of brittle dental materials are important for the dentist to understand in designing a restoration or making adjustments to a prosthesis.

Based on Newton's third law of motion (i.e., for every action there is an equal and opposite reaction), when an external force acts on a solid, a reaction occurs to oppose this force which is equal in magnitude but opposite in direction to the external force. The stress produced within the solid material is equal to the applied force divided by the area over which it acts. A tensile force produces **tensile stress**, a compressive force produces compressive stress, and a shear force produces **shear stress**. A bending force can produce all three types of stresses, but in most cases fracture occurs because of the tensile stress component. In this situation, the tensile and compressive stresses are principal axial stresses, whereas the shear stress represents a combination of tensile and compressive components.

When stress is induced by an external force or pressure, deformation or strain occurs. As an illustration, assume that a stretching or tensile force of 200 newtons (N) is applied to a wire 0.000002 m^2 in cross-sectional area. The tensile stress (σ), by definition, is the tensile force per unit area perpendicular to the force direction:

$$\sigma = \frac{200\ \text{N}}{2\times10^{-6}\ \text{m}^2} = 100\frac{\text{MN}}{\text{m}^2} = 100\ \text{MPa} \qquad (1)$$

The SI unit of stress or pressure is the pascal, which has the symbol Pa, that is equal to 1 N/m^2, 0.00014504 lbs/in^2 in Imperial units, or 9.9×10^{-6} atmospheres. Because the wire has fractured at a stress of 100 megapascals (MPa), its tensile strength is 100 MPa, where 1 MPa = 1 N/mm^2 = 145.04 psi.

In the English or Imperial system of measurement, the stress is expressed in pounds per square inch. However, the megapascal unit is preferred because it is consistent with the SI system of units. SI stands for Systéme Internationale d' Unités (International System of Units) for length, time, electrical current, thermodynamic temperature, luminous intensity, mass, and amount of substance.

The pound-force (lbf) is not an SI unit of force or weight. It is equal to a mass of 1 pound multiplied by the standard acceleration of gravity on earth (9.80665 m/s^2). The newton (N) is the SI unit of force, named after Sir Isaac Newton. To illustrate the magnitude of 1 MPa, consider a McDonald's quarter-pound hamburger (0.25 lbf or 113 g before cooking) suspended from a 1.19-mm-diameter monofilament fishing line. The stress per unit area within the line is 1 N/mm^2, or 1 MPa. If the line is 1.0 m long and if it stretches 0.001 m under the load, the strain (ε) is the change in length, Δl, per unit original length, l_o, or

$$\varepsilon = \frac{\Delta l}{l_o} = \frac{0.001\ \text{m}}{1.0\ \text{m}} = 0.001 = 0.1\% \qquad (2)$$

We can conclude that the line reaches a stress of 1 MPa at a tensile strain of 0.1%. Note that although strain is a dimensionless quantity, units such as meter per meter or centimeter per centimeter are often used to remind one of the system of units employed in the actual measurement. The accepted equivalent in the English system is inch per inch, foot per foot, and so forth.

CRITICAL QUESTION

Why is the maximum **elastic strain** of a cast alloy used for an inlay or crown an important factor in burnishing a margin? Use a sketch of a gap (e.g., Figure 4-4) between a crown and the tooth margin or a stress-strain diagram (e.g., Figure 4-3) to explain your answer.

Burnishing of a cast metal margin is a process sometimes used to reduce the width of a gap between the crown margin and the tooth surface. For a metal with relatively high ductility and moderate yield strength, application of a high pressure against the margin will plastically deform the margin and reduce the gap width. However, because elastic deformation has also occurred, the margin will spring back as elastic strain decreases during the decrease in pressure. Thus, burnishing the margin will close the gap only to the extent of the plastic deformation (strain) that is induced during burnishing.

Strain, or the change in length per unit length, is the relative deformation of an object subjected to a stress. Strain may be either elastic, plastic, elastic and plastic, or viscoelastic. Elastic strain is reversible. The object fully recovers its original shape when the force is removed. Plastic strain represents a permanent deformation of the material; it does not decrease when the force is removed. When a prosthetic component such as a clasp arm on a partial denture is deformed past the elastic limit into the plastic deformation region, elastic plus plastic deformation has occurred, but only the elastic strain is recovered when the force is released. Thus, when an adjustment is made by bending an orthodontic wire, a margin of a metal crown, or a denture clasp, the plastic strain is permanent but the wire, margin, or clasp springs back a certain amount as elastic strain recovery occurs.

Viscoelastic materials deform by exhibiting both viscous and elastic characteristics. These materials exhibit both properties and a time-dependent strain behavior. **Elastic strain** (deformation) typically results from stretching but not rupturing of atomic or molecular bonds in an ordered solid, whereas the viscous component of viscoelastic strain results from the rearrangement of atoms or molecules within amorphous materials.

Stress is described by its magnitude and the type of deformation it produces. Three types of "simple" stresses can be classified: tensile, compressive, and shear. Complex stresses, such as those produced by applied forces that cause flexural or torsional deformation, are discussed in the section on **flexural stress**.

TENSILE STRESS

A tensile stress is always accompanied by tensile strain, but it is very difficult to generate pure tensile stress in a body—that is, a stress caused by a load that tends to stretch or elongate a body. The reason is that if a slight amount of bending (flexure) occurs during tensile loading, the resulting stress distribution will consist of tension, compression, and shear components. The microtensile test is designed to load a test specimen along its long axis and the testing machine fixtures often have a toggle or freely rotating attachment that minimizes the misalignment of loaded specimen with the loading axis of the testing machine.

There are few pure tensile stress situations in dentistry. However, a tensile stress can be generated when structures are flexed. The deformation of a bridge and the diametral compression of a cylinder described later represent examples of these complex stress situations. In fixed prosthodontics clinics, a sticky candy (e.g., Jujube, a sticky/gummy candy) can be used to remove crowns by means of a tensile force when patients try to open their mouths after the candy has mechanically bonded to opposing teeth or crowns. However, tensile, compressive, and shear stresses can also be produced by a bending force, as shown in Figure 4-1 and as discussed in the following sections. Because most dental materials are quite brittle, they are highly susceptible to crack initiation in the presence of surface flaws when subjected to tensile stress, such as when they are subjected to flexural loading. Although some brittle materials can be strong, they fracture with little warning because little or no plastic deformation occurs to indicate high levels of stress.

COMPRESSIVE STRESS

When a body is placed under a load that tends to compress or shorten it, the internal resistance to such a load is called a **compressive stress**. A compressive stress is associated with a compressive strain. To calculate compressive stress, the applied force is divided by the cross-sectional area perpendicular to the axis of the applied force.

CRITICAL QUESTION

Although the shear bond strength of dental adhesive systems is often reported in manufacturers' advertisements, most dental prostheses and restorations are not likely to fail by the development of pure shear stresses. Which two factors tend to prevent the occurrence of pure shear failure?

SHEAR STRESS

This type of stress tends to resist the sliding or twisting of one portion of a body over another. Shear stress can also be produced by a twisting or torsional action on a material. For example, if a force is applied along the surface of tooth enamel by a sharp-edged instrument parallel to the interface between the enamel and an orthodontic bracket, the bracket may debond by shear stress failure of the resin luting agent. Shear

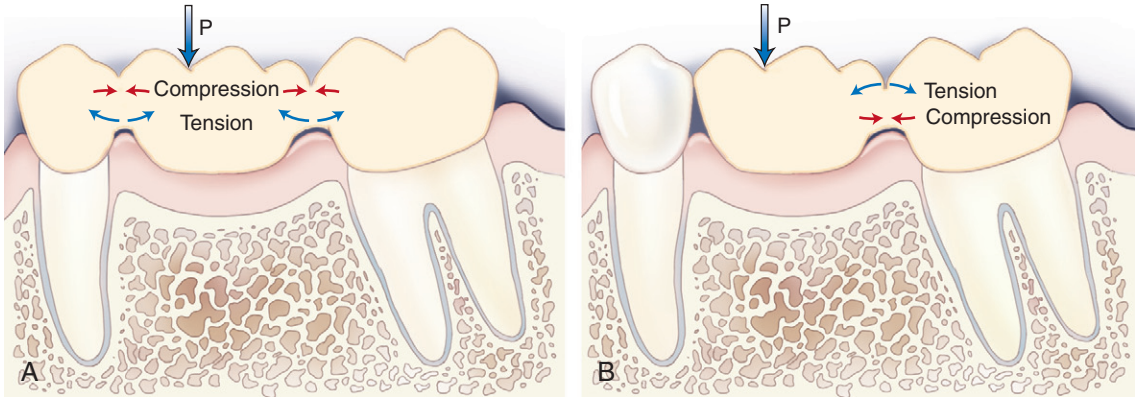


FIGURE 4-1 **A,** Stresses induced in a three-unit bridge by a flexural force (P). **B,** Stresses induced in a two-unit cantilever bridge. Note that the tensile stress develops on the gingival side of the three-unit bridge and on the occlusal side of the cantilever bridge.

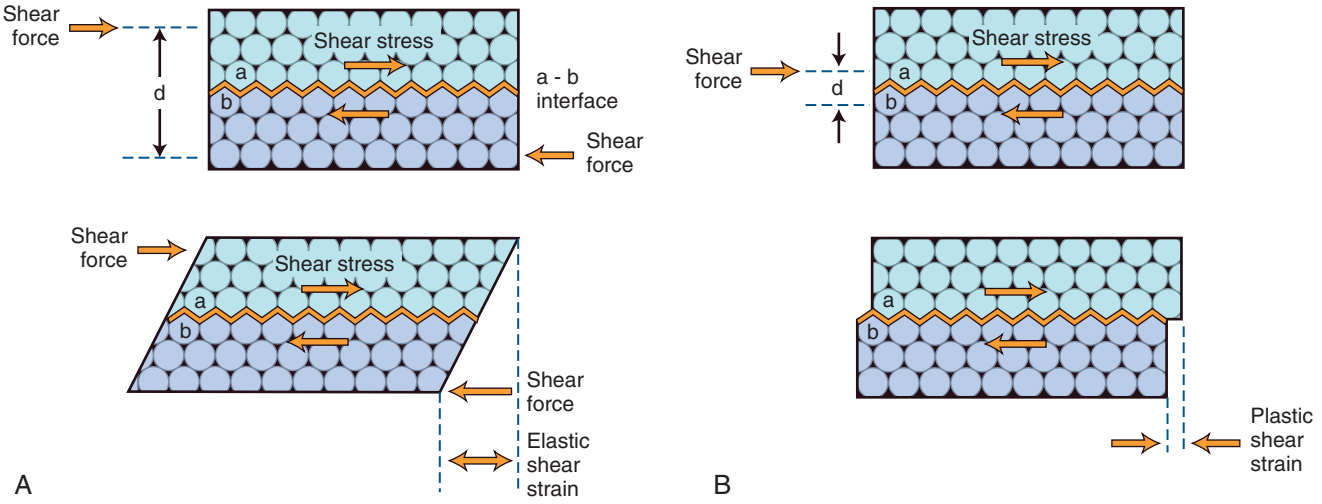


FIGURE 4-2 Atomic model illustrating elastic shear deformation (**A**) and plastic shear deformation (**B**) for the unit length of a material structure.

stress is calculated by dividing the force by the area parallel to the force direction.

In the mouth, shear failure is unlikely to occur for at least four reasons: (1) Many of the brittle materials in restored tooth surfaces generally have rough, curved surfaces. (2) The presence of chamfers, bevels, or changes in curvature of a bonded tooth surface would also make shear failure of a bonded material highly unlikely. (3) To produce shear failure, the applied force must be located immediately adjacent to the interface, as shown in Figure 4-2, *B*. This is quite difficult to accomplish even under experimental conditions, where polished, flat interfaces are used. The farther away from the interface the load is applied, the more likely it is that tensile failure rather than shear failure will occur because the potential for bending stresses would increase. (4) Because the tensile strength of brittle materials is usually well below their shear strength values, tensile failure is more likely to occur.

? CRITICAL QUESTION

Why do brittle structures that are flexed usually fail on the surface that exhibits increasing convexity?

FLEXURAL (BENDING) STRESS

Examples of flexural stresses produced in a three-unit fixed dental prosthesis (FDP) and a two-unit cantilever FDP are illustrated in Figures 4-1, *A*, and 4-1, *B*, respectively. These stresses are produced by bending forces in dental appliances in one of two ways: (1) by subjecting a structure such as an FDP to three-point loading, whereby the endpoints are fixed and a force is applied between these endpoints, as in Figure 4-1, *A*; and (2) by subjecting a cantilevered structure that is supported at only one end to a load along any part of the unsupported section, as in Figure 4-1, *B*. Also, when a patient

bites into an object, the anterior teeth receive forces that are at an angle to their long axes, thereby creating flexural stresses within the teeth.

As shown in Figure 4-1, *A*, tensile stress develops on the tissue side of the FDP, and compressive stress develops on the occlusal side. Between these two areas is the neutral axis that represents a state with no tensile stress and no compressive stress. For a cantilevered FDP such as that shown in Figure 4-1, *B*, the maximum tensile stress develops within the occlusal surface area since it is the surface that is becoming more convex (indicating a stretching action). If you can visualize this unit bending downward toward the tissue, the upper surface becomes more convex or stretched (tensile region) and the opposite surface becomes compressed. As explained in the section on stress concentration, these areas of tension represent potential fracture initiation sites in most materials, especially in brittle materials that have little or no plastic deformation potential.

Shown in Figure 4-2 is a bonded two-material system with the white atoms of material A shown above the interface and the shaded atoms of material B shown below the interface. The atoms are represented over six atomic planes, although dental structures have millions of atomic planes. However, the principles of stress and strain apply in both cases. In the upper section of Figure 4-2, *A*, a shear force is applied at distance d/2 from interface A-B. As this force increases in magnitude, it first produces an elastic shear strain (lower section of Figure 4-2), which will return to zero strain when the shear force is removed. As shown in Figure 4-2, *B*, if the shear force on the external surface is increased sufficiently, a permanent or plastic deformation will be produced.

For the case in Figure 4-2, *B*, the force is applied along interface A-B and not at a distance away, as shown in Figure 4-2, *A*. Because of this application of force along the interface, pure shear stress and shear strain develop only within the interfacial region. Because atoms have been displaced at near-neighbor locations, localized plastic deformation has also occurred. In the lower section of Figure 4-2, *B*, the force has been released and a permanent strain of one atomic space has occurred. For Figure 4-2, *A*, the stress induced is not pure shear since the force is applied at a distance from the interface. This is the reason why most shear bond tests do not actually measure shear strength but a tensile component of bending stress. These strength values are reported erroneously as shear strength rather than "apparent shear strength," which indicates that pure shear was unlikely.

ELASTIC PROPERTIES

Mechanical properties and parameters that are measures of the elastic strain or plastic strain behavior of dental materials include **elastic modulus** (also called **Young's modulus** or modulus of elasticity), dynamic Young's modulus (determined by the measurement of ultrasonic wave velocity), shear modulus, flexibility, resilience, and Poisson's ratio. Other properties that are determined from stresses at the highest stress end of the elastic region of the stress-strain graph or within the initial plastic deformation region (proportional limit, elastic limit, and yield strength) are described in the following section on strength properties.

ELASTIC MODULUS (YOUNG'S MODULUS OR MODULUS OF ELASTICITY)

The word *stiffness* should come to mind upon reading one of these three terms in the dental literature. Elastic modulus describes the relative stiffness or rigidity of a material, which is measured by the slope of the elastic region of the stress-strain graph. Shown in Figure 4-3 is a stress-strain graph for a stainless steel orthodontic wire that has been subjected to a tensile force. The ultimate tensile strength, yield strength (0.2% offset), proportional limit, and elastic modulus are shown in the figure. This figure represents a plot of true stress versus strain because the force has been divided by the changing cross-sectional area as the wire was being stretched. The straight-line region represents reversible elastic deformation, because the stress remains below the proportional limit of 1020 MPa, and the curved region represents irreversible plastic deformation, which is not recovered when the wire fractures at a stress of 1625 MPa. However, the elastic strain (approximately 0.52%) is fully recovered when the force is released or after the wire fractures. We can see this easily by bending a wire in our hands a slight amount and then reducing the force. Assuming that the induced stress has not exceeded the proportional limit, it straightens back to its original shape as the force is decreased to zero.

This principle of elastic recovery is illustrated in Figure 4-4 for a burnishing procedure of an open metal margin (top,

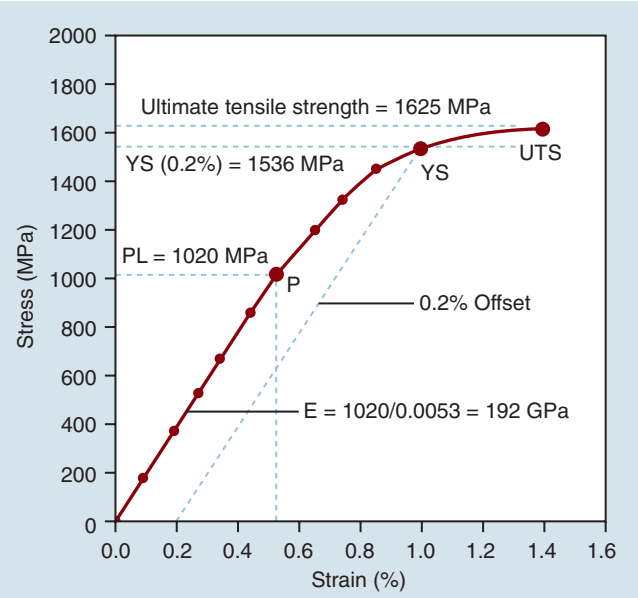


FIGURE 4-3 Stress-strain plot for a stainless steel orthodontic wire that has been subjected to tension. The proportional limit (PL) is 1020 MPa. Although not shown, the elastic limit is approximately equal to this value. The yield strength (YS) at a 0.2% strain offset from the origin (O) is 1536 MPa and the ultimate tensile strength (UTS) is 1625 MPa. An elastic modulus value (E) of 192,000 MPa (192 GPa) was calculated from the slope of the elastic region.

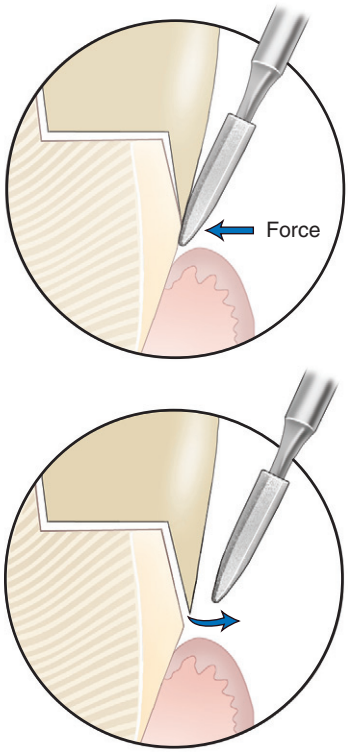


FIGURE 4-4 Schematic illustration of a procedure to close an open margin of a metal crown by burnishing with a rotary instrument. Note that after the rotating stone is removed (*bottom*), the elastic strain has been recovered and a slight marginal discrepancy remains.

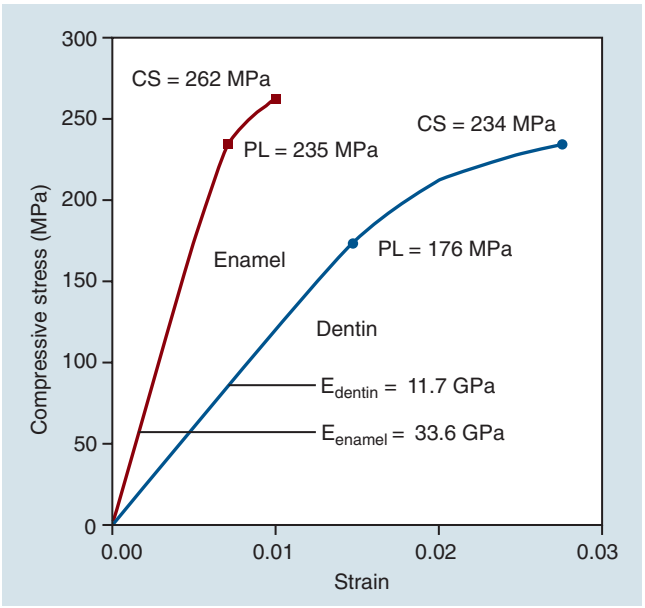


FIGURE 4-5 Stress-strain plot for enamel and dentin that have been subjected to compression. The ultimate compressive strength (CS), proportional limit (PL), and elastic modulus (E) values are shown. (Data from Stanford JW, Weigel KV, Paffenbarger GD, and Sweeney WT: Compressive properties of hard tooth tissue. *J Am Dent Assoc* 60:746, 1960.)

left), where a dental abrasive stone is shown rotating against the metal margin (top, right) to close the marginal gap as a result of elastic plus plastic strain. However, after the force is removed, the margin springs back an amount equal to the total elastic strain. Only by removing the crown from a tooth or die can total closure be accomplished. Because we must provide at least 25 µm of clearance for the cement, total burnishing on the tooth or die is usually adequate since the amount of elastic strain recovery is relatively small.

Shown in Figure 4-5 is a stress-strain graph for enamel and dentin that have been subjected to compressive stress. These curves were constructed from typical values of elastic moduli, proportional limit, and ultimate compressive strength reported in the scientific literature. If the tensile stress below the proportional limit in Figure 4-3 or the compressive stress (below the proportional limit) in Figure 4-5 is divided by its corresponding strain value, that is, tensile stress/tensile strain or compressive stress/compressive strain, a constant of proportionality will be obtained that is known as the elastic modulus, modulus of elasticity, or Young's modulus. These terms are designated by the letter E. The units of E are usually expressed as MPa for highly flexible materials or GPa for most stiffer restorative materials. The slope of the straight-line region (elastic range) of the stress-strain graph is a measure of the relative rigidity or stiffness of a material. Although the stiffness of a dental prosthesis can increase by increasing its thickness, the elastic modulus does not change. The elastic modulus has a constant value that describes a material's relative stiffness as determined from a stress-strain graph, which compensates for differences in cross-sectional area and length by plotting force per unit area by the relative change in dimension, usually length, relative to its initial value.

Variations in values of proportional limit, elastic modulus, and ultimate compressive strength have been reported for enamel and dentin relative to the area of the tooth from which the test specimens were obtained. Note that the proportional limit, ultimate compressive strength, and elastic modulus of enamel are greater than the corresponding values for dentin (Figure 4-5). In fact, the elastic modulus of enamel is about three times greater than that of dentin and, depending on the study considered, it can be as much as seven times higher. Dentin is capable of sustaining significant plastic deformation under compressive loading before it fractures. Thus, enamel is a stiffer and more brittle material than dentin and unsupported enamel is more susceptible to fracture. Conversely dentin is more flexible and tougher.

Because the elastic modulus of a material is a constant, it is unaffected by the amount of elastic or plastic stress induced in the material. It is independent of the ductility of a material, since it is measured in the linear region of the stress-strain plot. Thus, elastic modulus is not a measure of its plasticity or strength. Materials with a high elastic modulus can have either high or low strength values. Although a compressive test was selected to measure the properties of tooth structures in Figure 4-5, the elastic modulus can also be measured by means of a tensile test.

Because the elastic modulus represents the ratio of the elastic stress to the elastic strain, it follows that the lower the strain for a given stress, the greater the value of the modulus. For example, if one wire is much more difficult to bend than another of the same shape and size, considerably higher stress must be induced before a desired strain or deformation can be produced in the stiffer wire. Such a material would possess a comparatively high modulus of elasticity. A polyether impression material has a greater stiffness (elastic modulus) than all other elastomeric impression materials. Thus, a greater force is needed to remove an impression tray from undercut areas in the mouth. The modulus of elasticity of most dental biomaterials is given in units of giganewtons per square meter (GN/m^2), also referred to as gigapascals (GPa). This property is indirectly related to other mechanical properties. For example, two materials may have the same proportional limit but their elastic moduli may differ considerably.

The elastic modulus (E) of a tensile test specimen can be calculated as follows:

$$\text{Stress} = P / A = \sigma \tag{3}$$

$$\text{Strain} = \Delta l / l_o = \varepsilon \tag{4}$$

where P = the applied force or load
A = the cross-sectional area of the material under stress
Δl = the increase in length
l_o = the original length
Thus,

$$\Delta E = \frac{\text{Stress}}{\text{Strain}} = \frac{\sigma}{\varepsilon} = \frac{P/A}{\Delta l/l_o} \tag{5}$$

DYNAMIC YOUNG'S MODULUS

Elastic modulus can be measured by a dynamic method as well as the static techniques described in the previous section. Since the velocity at which sound travels through a solid can be readily measured by ultrasonic longitudinal and transverse wave transducers and appropriate receivers, the velocity of the sound wave and the density of the material can be used to calculate the elastic modulus and Poisson's ratio. This method of determining dynamic elastic moduli is less complicated than conventional tests of tensile or compressive strength, but the values are often found to be higher than those obtained by static measurements. For most purposes, however, these values are acceptable.

If a shear stress was induced instead of uniaxial tensile or compressive stress, the resulting shear strain could be used to define a shear modulus for the material. The shear modulus (G) can be calculated from the elastic modulus (E) and Poisson's ratio (ν) using Eq. 6:

$$G = \frac{E}{2(1+\upsilon)} = \frac{E}{2(1+0.3)} = 0.38E \tag{6}$$

A value of 0.25 to 0.30 for Poisson's ratio is typical. Thus, the shear modulus is usually about 38% of the elastic modulus value.

FLEXIBILITY

For materials used to fabricate dental appliances and restorations, a high value for the elastic limit (the stress above which a material will not recover to its original state when the force is released) is a necessary requirement because the structure is expected to return to its original shape after it has been stressed and the force is removed (elastic recovery). Usually a moderately high modulus of elasticity is also desirable because only a small deformation will develop under a considerable stress, as in the case of an inlay or an impression material.

However, there are instances where a larger strain or deformation may be needed with a moderate or slight stress. For example, in an orthodontic appliance, a spring is often bent a considerable distance under the influence of a small stress. In such a case, the structure is said to be flexible and to possess the property of flexibility. The maximum flexibility is defined as the flexural strain that occurs when the material is stressed to its proportional limit.

RESILIENCE

As interatomic spacing increases, internal energy increases. As long as the stress is not greater than the proportional limit, this energy is known as **resilience**. Popularly, the term *resilience* is associated with springiness, but it means precisely the amount of energy absorbed within a unit volume of a structure when it is stressed to its proportional limit. The resilience of two or more materials can be compared by observing the areas under the elastic region of their stress-strain plots assuming that they are plotted on the same scale. The material with the larger elastic area has the higher resilience.

Shown in Figure 4-6 is a stress-strain diagram illustrating the concepts of resilience and **toughness**. The area bounded by the elastic region is a measure of resilience and the total area under the stress-strain curve is a measure of toughness. This figure is explained further in the following section. Work is the product of the force times the distance through which the force acts. When work is performed on a body, energy is imparted to it. Consequently, when a dental restoration is deformed, it absorbs energy. If the induced stress is not greater than the proportional limit (the oral structure is not permanently deformed), only elastic energy is stored in the structure until the applied force is removed.

When a dental restoration is deformed during mastication, the chewing force may act on the tooth structure, the restoration, or both and the magnitude of the structure's strain (deformation) is determined by the induced stress. In most dental restorations, large strains are precluded because of the proprioceptive response of neural receptors in the periodontal ligament. The pain stimulus causes the biting force to be decreased and the induced stress to be reduced, thereby preventing damage to the teeth or restorations. For example, a proximal inlay might cause excessive movement of the adjacent tooth if large proximal strains developed during compressive loading on the occlusal surface. Hence the restorative material should exhibit a moderately high elastic modulus

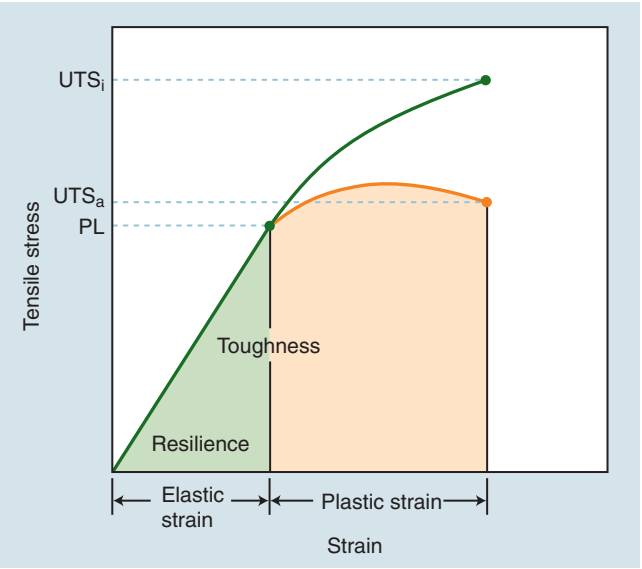


FIGURE 4-6 Conventional tensile stress-strain curve (*orange line*) in the plastic deformation region calculated on the basis of the initial cross-sectional area of a rod. The solid line (*above the orange line*) represents the calculated stress values based on the actual reduced area of the rod as deformation increases. The resilience can be calculated by measuring the area within the elastic region. The toughness is related to the total area within the elastic and plastic regions. In this case, the proportional limit (PL) remains constant, but the toughness and ultimate strength (UTS_i) are different.

and relatively low resilience, thereby limiting the elastic strain produced.

POISSON'S RATIO

Because of the conservation of mass, an object, such as a cylinder, becomes longer and thinner when a tensile force is applied to it. Conversely, a compressive force acts to make such an object shorter and thicker. An axial tensile stress, σ_z, along the z (long axis) of a mutually perpendicular xyz coordinate system produces an elastic tensile strain and an accompanying elastic contraction in the x and y directions (ε_x and ε_y, respectively). The ratio of $\varepsilon_x / \varepsilon_z$ or $\varepsilon_y / \varepsilon_z$ is an engineering property of the material called the Poisson's ratio (ν).

$$\nu = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\varepsilon_y}{\varepsilon_z} \qquad (7)$$

Poisson's ratio can be similarly determined in an experiment involving an axial compressive stress. Poisson's ratio is related to the nature and symmetry of the interatomic bonding forces described in Chapter 2. For an ideal isotropic material of constant volume, the ratio is 0.5. Most engineering materials have values between 0.25 and 0.30.

CRITICAL QUESTIONS

How can two identical forces produce two different stresses in an all-ceramic crown? Is it possible for a stiff material with a high modulus of elasticity to fail with no plastic deformation and at a lower strength than a more flexible material? Explain your answers.

STRENGTH PROPERTIES

How much strength do we need in materials for dental restorations to resist fracture for the lifetimes of our patients? An engineer would answer this question with another question. How large can the restorations be and still provide adequate aesthetics and masticatory function? Obviously for restorations to last forever without fracture we would have to build excessively large structures for some materials, such as pure glass or unfilled acrylic resin. For other materials with great ductility and/or high fracture toughness and high flexural strength, the prostheses or restorations could be designed with approximately the same dimensions and anatomic form as existed for the original teeth. For the latter materials, we could assume the strength properties to be adequate if we followed some well-established engineering principles. **Strength** is equal to the degree of stress necessary to cause either fracture (ultimate strength) or a specified amount of plastic deformation (yield strength). When we describe the strength of an object or a material, we are most often referring to the maximum stress that is required to cause fracture. Keep in mind, however, that strength values reported by manufacturers usually represent mean values, which means that 50% of the tested specimens have failed below this strength. Both types of deformational behavior can be described by strength properties, but we should use proper strength terms to differentiate between the stress causing permanent deformation and that required to produce fracture.

For specific dental materials, particularly metals, we are equally interested in the maximum stress that a structure can sustain before it becomes permanently or plastically deformed. This stress can be described either by the proportional limit or elastic limit. At stresses above these limits, plastic deformation occurs. The strength of a material can be described by one or more of the following properties: (1) proportional limit, the stress above which stress is no longer proportional to strain; (2) elastic limit, the maximum stress a material can withstand before it becomes plastically deformed; (3) yield strength or proof stress, the stress required to produce a given amount of plastic strain; and (4) ultimate tensile strength, shear strength, compressive strength, and flexural strength, each of which is a measure of stress required to fracture a material. When a force is applied to a ceramic crown, the magnitude of stress that develops within the surface of the crown will depend on how the force was applied and the orientation of the force. If the force is well distributed over an area, the stress that is induced in the crown will be reduced compared with a much more concentrated force of the same magnitude. Strength is not a measure of individual atom-to-atom attraction or repulsion but rather of the interatomic forces collectively over the entire wire, cylinder, implant, crown, pin, or whatever structure is stressed. Furthermore, the ultimate strength may not necessarily be equal to the actual instantaneous average stress at fracture, since the original cross-sectional area has changed in size.

CRITICAL QUESTION

How can the ultimate tensile stress (ultimate strength) sometimes be less than the maximum tensile stress?

Shown in Figure 4-6 is a stress-strain plot of a metal rod that has been subjected to a tensile test. The stress is calculated by dividing the applied force at any instant by the original cross-sectional area and is represented by the bold dashed line above the lightly shaded area. However, the diameter actually decreases as the metal is stretched.

The **true stress** is calculated as the force divided by the actual cross-sectional area at each measured strain value and is represented in Figure 4-6 by the bold line in the plastic deformation region above the dashed curve. It is evident that the cross section of the wire decreases as it lengthens under tensile stress. Because of the reduction in area, the force required to increase deformation actually decreases. Thus the stress calculated for testing purposes (force per unit initial area) decreases, and the ultimate tensile strength based on the initial area (lower UTS value) as indicated in Figure 4-6 is less than the maximum tensile stress that occurs at the peak of the curve.

Although the true stress-strain curve represents the situation more accurately, the stress-strain curve as indicated by the dashed line in Figure 4-6 is commonly used. When we calculate the tensile strength of a certain wire, we wish to know the maximum stress it supports in tension without regard to the small changes that may occur in the cross-sectional area. Therefore, the ultimate tensile strength is defined as the **tensile stress** within a structure at the point of rupture.

PROPORTIONAL LIMIT

When a wire is stretched steadily in tension, the wire eventually fractures. However, in dentistry we are interested also in the stress at which plastic deformation begins to develop. One method by which to determine this point is to plot a stress-strain diagram similar to that in Figures 4-3, 4-5, or 4-6. If the material obeys Hooke's law, the elastic stress will be proportional to elastic strain. For such a material, the stress-strain diagram shown in Figure 4-3 starts from the origin (O) as a straight line. Along this line the material behaves elastically, and it springs back to its initial shape and size at the instant the force is removed. When a certain stress value corresponding to point P is exceeded, the line becomes nonlinear and stress is no longer proportional to strain. When a straight edge is laid along the straight-line portion of the curve from O to P, the stress value at P, the point above which the curve deviates from a straight line, is known as the proportional limit.

For a material to satisfy Hooke's law, the elastic stress must be directly proportional to the elastic strain. The initial region of the stress-strain plot must be a straight line. Because direct proportionality between two quantities is graphically represented by a straight line, the linear portion of the graph in Figures 4-3, 4-5, and 4-6 satisfies this law. Because the proportional limit (stress corresponding to point P) is the greatest elastic stress possible in accordance with this law, it represents the maximum stress above which stress is no longer proportional to strain. For the stress-strain curve of dentin that is shown in Figure 4-5, the strain corresponding to the proportional limit is important because it represents the percent deformation that can be sustained in dentin before it becomes deformed permanently.

ELASTIC LIMIT

When a small tensile stress is induced in a wire, the wire will return to its original length when the load is removed. If the load is increased progressively in small increments and then released after each increase in stress, a stress value will be reached at which the wire does not return to its original length after it is unloaded. At this point the wire has been stressed beyond its elastic limit. The elastic limit of a material is defined as the greatest stress to which the material can be subjected such that it returns to its original dimensions when the force is released. Although tensile stress was used in the example, similar elastic limit measurements can be made for any type of stress, although different values of elastic limit are obtained in tension, compression, and shear.

CRITICAL QUESTION

Yield strength is a commonly reported property for metals and alloys but not for ceramics. Why is it not possible to measure the yield strength of ceramics or other purely brittle materials? Use a stress-strain plot to explain your answer.

YIELD STRENGTH (PROOF STRESS)

Irregularities along the straight-line region of the stress-versus-strain plot may represent minor deviations from Hooke's law and cause some uncertainty in determining the precise point at which the selected line deviates from linearity (proportional limit). Thus a different property, **yield strength**, is used in cases where the proportional limit cannot be determined with sufficient accuracy.

Yield strength often is a property that represents the stress value at which a small amount (0.1% or 0.2%) of plastic strain has occurred. A value of either 0.1% or 0.2% of the plastic strain is often selected and is referred to as the percent offset. The yield strength is the stress required to produce the particular offset strain (0.1% or 0.2%) that has been chosen. As in Figure 4-3, the yield strength for 0.2% offset is greater than that associated with an offset of 0.1%. If yield strength values for two materials tested under the same conditions are to be compared, identical offset values should be used. To determine the yield strength for a material at 0.2% offset, a line is drawn parallel to the straight-line region (Figure 4-3), starting at a value of 0.002, or 0.2% of the plastic strain, along the strain axis and is extended until it intersects the stress-strain curve. The stress corresponding to this point is the yield strength. Although the term *strength* implies that the material has fractured, it is actually intact but has sustained a specific amount of plastic strain (deformation). For brittle materials such as dental ceramics, the stress-strain plot is a straight line with no plastic region. Thus, a determination of

yield strength is not practical at either a 0.1% or 0.2% strain offset because there is no plastic strain. The material has actually fractured at a lower strain value.

Elastic limit, proportional limit, and *yield strength* are defined differently, but their values (of stress) are fairly close to each other in many cases. Elastic and proportional limits are usually assumed to be identical, although their experimental values may differ slightly. As shown in Figure 4-3, the yield strength (proof stress) is greater than the proportional limit. These values are important in the evaluation of dental materials because they represent the stress at which permanent deformation of the structure begins. If they are exceeded by mastication stresses, the restoration or appliance may no longer function as originally designed.

PERMANENT (PLASTIC) DEFORMATION

As shown in Figure 4-3, the stress-strain graph is no longer a straight line above the proportional limit (PL); instead, it curves until the structure fractures. The stress-strain graph shown in Figure 4-3 is more typical of actual stress-strain curves for ductile materials. Unlike the linear portion of the graph at stresses below the proportional limit, it is not possible to extrapolate the shape of the curve above P because stress is no longer proportional to strain.

If the material is deformed by stress at a point above the proportional limit before fracture, removal of the applied force will reduce the stress to zero, but the plastic strain (deformation) remains. Thus the object does not return to its original dimension when the force is removed. It remains bent, stretched, compressed, or otherwise plastically deformed.

COLD WORKING (STRAIN HARDENING OR WORK HARDENING)

When most metal alloys have been stressed beyond their proportional limits, their hardness and strength increase at the area of deformation, but their ductility decreases. As dislocations move and pile up along grain boundaries, further plastic deformation in these areas becomes more difficult. As a result, repeated plastic deformation of the metal, as occurs during the bending of orthodontic wire or adjustment of a clasp arm on a removable dental prosthesis, can lead to embrittlement of the deformed area of the wire, and it may fracture when further permanent adjustment is attempted. Since the elastic modulus remains constant, the stress-strain curve of the deformed area would extend above the level of ultimate strength of the metal, but the plastic deformation part of the curve would be decreased progressively with each bend of a wire or clasp arm. The key to minimizing the risk of reduced plasticity (embrittlement) is to deform the metal in small increments so as not to plastically deform the metal excessively.

DIAMETRAL TENSILE STRENGTH

Tensile strength can generally be determined by subjecting a rod, wire, or dumbbell-shaped specimen to tensile loading (a uniaxial tension test). Since this test is quite difficult to perform for brittle materials because of alignment and gripping problems, another test can be used to determine this property for brittle dental materials. It is referred to as the diametral compression test, which is represented schematically in Figure 4-7. This test should be used only for materials that exhibit elastic deformation primarily and little or no plastic deformation. In this method, the compressive load is placed by a flat plate against the side of a short cylindrical specimen (disk), as illustrated in Figure 4-7. The vertical compressive force along the side of the disk produces a tensile stress that is perpendicular to the vertical plane passing through the center of the disk. Fracture occurs along this vertical plane (the dashed vertical line on the disk). In such a situation, the tensile stress is directly proportional to the compressive load applied. It is calculated by the following formula:

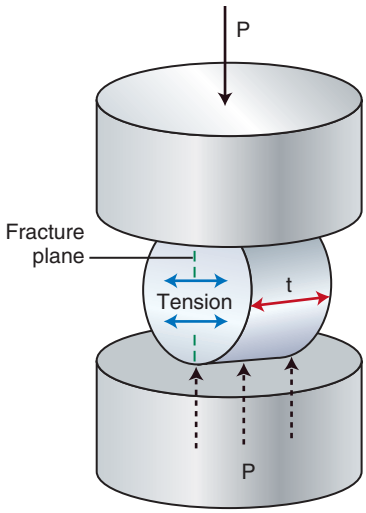


FIGURE 4-7 Diametral compression test. Although a compressive force is applied along the side of the disk, a tensile fracture is produced. The tensile strength is calculated from the fracture load P, the disk diameter D, and the thickness t.

$$\text{Tensile Stress} = \frac{2F}{\pi Dt} \quad (8)$$

where F = applied force
D = diameter
t = thickness

This test is simple to conduct and provides excellent reproducibility of results. However, use of this test on materials that exhibit appreciable plastic deformation before fracture results in erroneously high tensile strength values. Fracture of the specimen into several pieces rather than the ideal fragmentation into two segments suggests an unreliable test result.

FLEXURAL STRENGTH

Flexural strength, which is also called transverse strength and **modulus of rupture**, is essentially a strength test of a bar supported at each end or a thin disk supported along a lower support circle under a static load. For the disk specimen, the failure stress value is referred to as the biaxial flexural strength; the theory involved is beyond the scope of this textbook. For

a bar with a rectangular cross section subjected to three-point flexure (upper central loading in Figure 4-8), the following equation may be used to calculate the flexural strength (maximum flexural stress at the lower midpoint surface):

$$\sigma = \frac{3PL}{2wt^2} \quad (9)$$

where σ = maximum flexural stress (MPa)
P = load at fracture (N)
L = distance between two supports (mm)
w = width of specimen (mm)
t = thickness or height of specimen (mm)

Typical specimen dimensions are a minimum span length of 20 mm, a width of 4 mm and a thickness of 1.2 to 2.0 mm.

One of the limitations of the three-point flexural test is that if the bar specimen does not fracture at the midpoint directly under the applied force (F), a correction must be made to calculate the fracture stress at the actual point of fracture. If the fracture occurs in the middle of the lower span, Eq. 9 may be used.

The four-point flexural test shown in Figure 4-9 is preferred over the three-point test because the stress within the central loading span is constant. Therefore no correction is required for specimens that fracture within the central loading span but that do not fracture precisely at the midpoint. The flexural stress within the midspan area can be calculated from Eq. 10 as follows:

$$\sigma = \frac{3PL}{4wt^2} \quad (10)$$

where σ = flexural strength
P = total applied load
L = distance between lower supports
w = width of specimen
t = thickness or height of specimen

The units of stress are force per unit area, most often given in the SI unit of megapascal (MPa). This test is, in a sense, a collective measurement of tensile, compressive, and shear stresses simultaneously. However, for sufficiently thin specimens, it is usually dominated by the tensile stress that develops along the lower surface. When the load is applied, the specimen bends. For a flat bar specimen, the resulting strain is represented by a decrease in the length of the top surface (compressive strain) of the specimen and an increase in the length of the lower surface (tensile strain). Consequently the principal stresses on the upper surface are compressive whereas those on the lower surface are tensile. Obviously the stresses change direction within the specimen between the top and bottom surfaces, with both stress and strain being zero at the region of change. This neutral surface does not change in dimension and is known as the neutral axis. Shear stress is also produced near the supported ends of the specimen, but it does not play a significant role in the fracture process. For brittle materials such as ceramics, flexural tests are preferred to the diametral compressive test because they more closely simulate the stress distributions in dental prostheses such as cantilevered bridges and multiple-unit fixed dental prostheses (FDPs or bridges) as well as the clasp arms of removable dental prostheses (RDPs).

BIAXIAL FLEXURAL TEST

This test is preferred by some scientists to avoid the problem of edge fractures, which can occur in flexural tests of bar specimens. For the typical biaxial flexural tests, disk-shaped specimens 12 mm in diameter and 1.2 mm in thickness are used. The biaxial flexure test based on the piston-on-three-ball design is shown schematically in Figure 4-10. The load is applied by means of a piston with a slightly curved contact surface and the disk is supported by steel balls, which have a

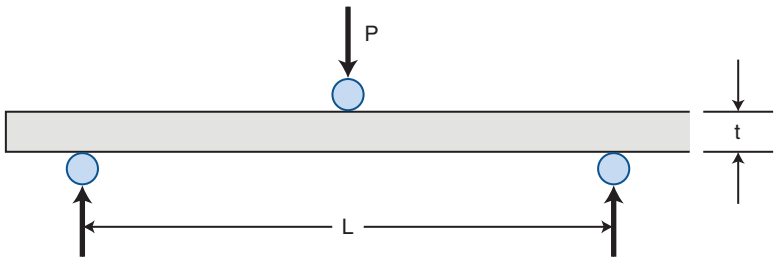


FIGURE 4-8 Three-point flexure test design.

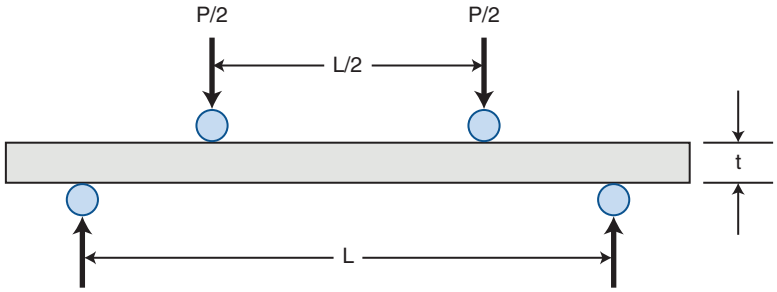


FIGURE 4-9 Four-point flexure test design.

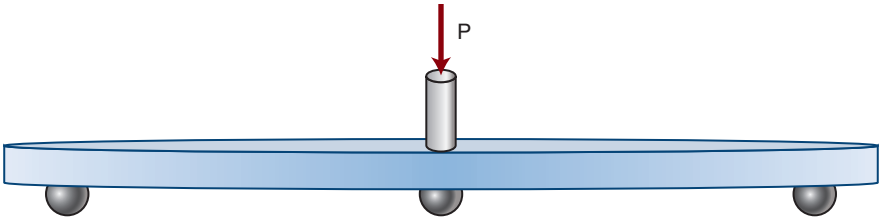


FIGURE 4-10 Schematic illustration of the piston-on-three-ball test for the biaxial flexure test.

diameter of approximately 3.2 mm. These are arranged at an angle of 120° relative to each other on a circle of approximately 10 to 12 mm in diameter. The biaxial flexural strength is calculated from a complex equation that is beyond the scope of this book.

Strength values obtained from a measurement of the failure load described earlier are misleading if they are used to design a structure that is subjected to repeated or cyclic loading. Few clinical fractures occur during a single-load application. If such fractures were common, these products would be withdrawn from the market soon after their introduction. This is a good reason why one should not be the first to buy a new restorative material but rather allow sufficient time for clinical data to be reported. Most prosthesis and restoration fractures develop progressively over many stress cycles after initiation of a crack from a critical flaw and subsequently by propagation of the crack until a sudden, unexpected fracture occurs. Stresses well below the ultimate tensile strength can produce premature fracture of a dental prosthesis because microscopic flaws grow slowly over many cycles of stress. This phenomenon is called fatigue failure. Normal mastication induces several thousands of stress cycles per day within a dental restoration. For glasses and certain glass-containing ceramics, the induced tensile stress and the presence of an aqueous environment further reduce the number of cycles to cause fatigue failure.

Fatigue behavior is determined by subjecting a material to a cyclic stress of a maximum known value and determining the number of cycles required to cause fracture. As shown in Figure 4-11, a plot of the failure stress versus the number of cycles to failure enables calculation of a maximum service stress or an endurance limit—the maximum stress that can be maintained without failure over an infinite number of cycles. For brittle materials with rough surfaces, the endurance limit is lower than it would be if the surfaces were more highly polished (Figure 4-11). For a given applied stress, the rougher material would fail in fewer cycles of stress.

Some materials or prosthetic appliances exhibit static fatigue, a phenomenon attributed to the interaction of a constant tensile stress with structural flaws over time. The influence of flaw size on the stress to cause failure is shown in Figure 4-12. Note that for a given flaw size, less stress is required to produce failure if the stress is cycled between high and low values. Furthermore, aqueous solutions are known to corrosively degrade dental ceramics by converting surface flaws to one or more cracks over time in the presence of tensile stress. This environmental factor further reduces the magnitude of tensile stress that can be sustained by ceramics over time.

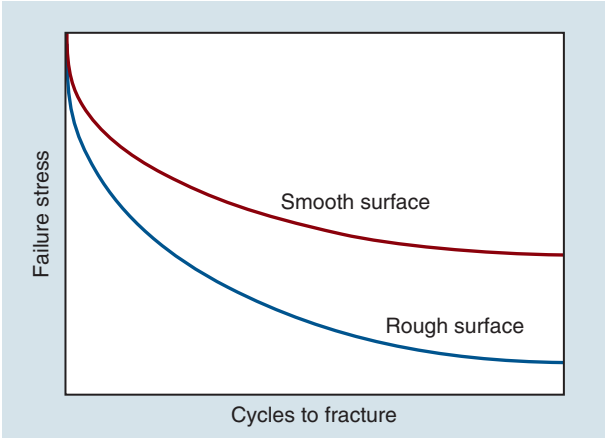


FIGURE 4-11 Dynamic fatigue failure stress for a brittle material as a function of surface roughness and number of stress cycles.

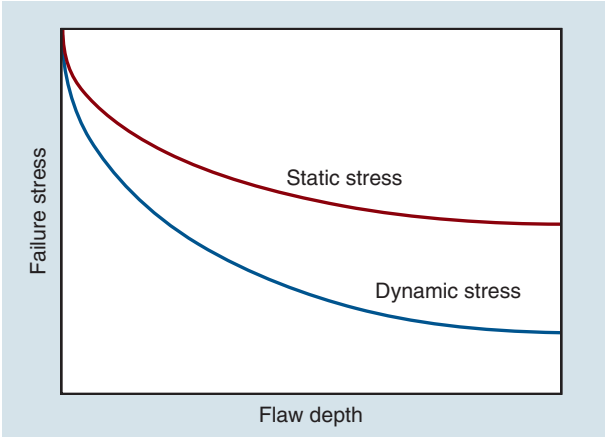


FIGURE 4-12 Dynamic and static fatigue failure stress for a brittle material as a function of flaw depth.

Ceramic orthodontic brackets and activated wires within the brackets represent a clinical system that can exhibit static fatigue failure in which a sustained stress in the presence of water causes cracks to develop and progress over time. The delayed fracture of molar ceramic crowns subjected to periodic cyclic forces may be caused by fatigue failure. Thus dental restorative materials can exhibit either static or

dynamic fatigue failure depending on the nature of the loading or residual stress situation. In either case, the failure begins as a flaw that propagates until catastrophic fracture occurs.

IMPACT STRENGTH

This property may be defined as the energy required to fracture a material under an impact force. The term *impact* is used to describe the reaction of a stationary object to a collision with a moving object. A Charpy-type impact tester is usually used to measure impact strength. A pendulum is released that swings down to fracture the center of a bar specimen supported at both ends. The energy lost by the pendulum during the fracture of the specimen can be determined by a comparison of the length of its swing after the impact with that of its free swing when no impact occurs. The energy units are joules, foot-pounds, inch-pounds, and so forth. Unlike the case in most mechanical tests, the dimensions, shape, and design of the specimen to be tested should be identical for uniform results.

For another impact device, called the Izod impact tester, the specimen is clamped vertically at one end. The blow is delivered at a certain distance above the clamped end instead of at the center of the specimen, which is supported at both ends, as described for the Charpy impact test.

With appropriate values for the velocities and masses involved, a blow by a fist or other object to the lower jaw can be considered an impact situation. In the impact process, the external forces and resulting stresses change rapidly, and a static property such as the proportional limit is not useful in predicting the resulting deformations. However, a moving object possesses a known amount of kinetic energy. If the struck object is not permanently deformed, it stores the energy of the collision in an elastic manner. This ability is reflected by the resilience of a material, which is measured by the area under the elastic region of the stress-strain diagram. Thus a material with a low elastic modulus and a high tensile strength is more resistant to impact forces. A low elastic modulus and a low tensile strength suggest low-impact resistance. For dental materials of low-impact resistance, the elastic moduli and tensile strengths, respectively, are as follows:

Resin-based composite:	17 GPa and 30–90 MPa
Dental porcelain:	40 GPa and 50–100 MPa
Poly(methylmethacrylate):	3.5 GPa and 60 MPa
Amalgam:	21 GPa and 27–55 MPa
Alumina ceramic:	350–418 GPa and 120 MPa

Thus, if one simply calculates the area under the stress-versus-strain graph, the greatest resilience is associated with the composite, followed in decreasing order by the porcelain, PMMA, amalgam, and alumina.

WEIBULL STATISTICS

When a manufacturer reports the strength of a restorative material, one might assume that a restoration made with that material would have the reported strength. Unfortunately such a restoration could have a strength lying in the lowest 5% of test values. In some cases such extreme values are called outliers. The reported strength typically represents the mean value of a range of strengths determined from a specific test such as a tensile test, a compression test, a shear test, a flexure test, or an impact test. Thus it would be more useful if we knew the 95% stress level—that is, the stress level below which 95% of specimens of identical shape, size, and processing conditions would survive a given fracture test. However, it would be even more useful if we knew the 95% stress level for cyclic fatigue test conditions, which would more closely simulate clinical conditions. Nevertheless, for brittle materials such as some dental restorative materials (e.g., resin-based composites and ceramics), the distribution of strength values tends to be non-normal or non-Gaussian. If the strength distribution does not exhibit a normal or symmetrical distribution with values clustered uniformly around a mean value, the distribution may be better described by the use of Weibull statistics, which is based on the concept of the weakest link.

Ceramic strength data are typically asymmetrical. Thus, they are better described using the Weibull distribution than the Gaussian distribution function. Weibull plots of log fracture probability as a function of fracture stress can be used as a factor in the design of dental restorations that are produced from brittle biomedical materials. A Weibull plot can be used to determine the cumulative probability that a sample will fail under a given load or induced stress. These plots are based on data obtained on a representative population (ideally 30 or more) of specimens tested in a manner similar to that which the materials will experience during clinical service. If a dental practice specifies that less than one ceramic restoration in 100 should fracture during use, the Weibull distribution data can be analyzed to estimate the stress that would cause this 1% level of failure. With a knowledge of this 99% survival stress, the design of restorations can be optimized by changing dimensions or restricting use conditions such that no location within the restoration sustains stresses above the failure stress.

Another important Weibull parameter is the Weibull modulus (designated by m), which represents the distribution of flaws in brittle materials or the distribution of strength determined from a plot of log fracture probability versus failure stress. The failure strengths of brittle materials are statistically distributed as a function of the homogeneity of the material. The Weibull distribution is described by Eq. 11:

$$Pf = 1 - \exp[-(\sigma/\sigma_o)^m] \quad (11)$$

where Pf = fracture probability defined by the relation $Pf = i/(N + 1)$
i = rank in strength
N = total number of specimens in the sample
m = shape parameter or Weibull modulus
σ = fracture stress
σ_o = scale parameter or characteristic strength (63.2% failure level)

A low Weibull modulus reflects a high variation in measured strength values and an increase in the probability that flaws will interact to weaken a brittle material. A low Weibull modulus suggests that products with strength that is substantially lower than the mean will exhibit a greater inconsistency in strength. The use of these products for prostheses will result in a greater variation in fracture force and decreased reliability. Higher values of Weibull modulus correspond to a higher level of homogeneity of the material and greater reliability as a structural material. Most ceramics exhibit m values in the range of 5 to 15, and metals, which are ductile, have m values above 20.

OTHER IMPORTANT PROPERTIES

TOUGHNESS

Toughness is defined as the amount of elastic and plastic deformation energy required to fracture a material. Fracture toughness is a measure of the energy required to propagate critical flaws in the structure. Toughness is measured as the total area under the stress-strain graph (such as shown in Figure 4-6) from zero stress to the fracture stress. Toughness increases with increases in strength and ductility. The greater the strength and the higher the ductility (total plastic strain), the greater the toughness. Thus, it can be concluded that a tough material is generally strong, although a strong material is not necessarily tough. In comparison, the modulus of resilience is the energy required to stress a structure to its proportional limit. It can be measured as the area under the linear elastic portion of the stress-strain curve.

FRACTURE TOUGHNESS

The strength of ductile materials such as gold alloys and certain resin-based composites is useful for determining the maximum stress that restorations of these materials can withstand before a certain amount of plastic deformation or fracture occurs. For brittle materials such as dental ceramics, strength is of only limited value in the design of ceramic prostheses. Small defects (porosity and microcracks) are randomly distributed in location and size throughout a ceramic, causing large strength variations in otherwise identical ceramic specimens. Furthermore, surface flaws caused by grinding—as from coarse-, medium-, or fine-grit diamond particles—can greatly weaken an otherwise strong ceramic, especially in the presence of tensile stress in the area of the flaws. Strength is inversely proportional to the square root of the flaw depth within the surface.

Fracture toughness, or the critical **stress intensity**, is a mechanical property that describes the resistance of brittle materials to the catastrophic propagation of flaws under an applied stress. Fracture toughness is given by the symbol K_{Ic} in units of stress times the square root of crack length; that is, $MPa \cdot m^{1/2}$ or the equivalent form, $MN \cdot m^{-3/2}$. Thus, the fracture resistance of a porcelain veneer with a K_{Ic} of 0.75 $MPa \cdot m^{1/2}$ is much lower than that of the tougher supporting core ceramics used for all-ceramic prostheses, such as alumina and yttrium-stabilized zirconia with K_{Ic} values of 3.4 $MPa \cdot m^{1/2}$ and 7.9 $MPa \cdot m^{1/2}$, respectively.

CRITICAL QUESTION

Is a stiff material (high elastic modulus) stronger than a more flexible material? Explain your answer by sketching a stress-strain plot.

BRITTLENESS

Materials that are very brittle have a tensile strength markedly lower than their corresponding compressive strength because of their inability to plastically deform and reduce the tensile stress at flaw tips. This is true of all brittle dental materials, such as amalgams, composites, cements, ceramics, and some base metal alloys. The failure of these materials in clinical usage is most often associated with their low tensile strengths and the presence of flaws within the tensile stress region.

Shown in Figure 4-13 are three stress-strain curves of materials with variable strength, elastic modulus, and percent elongation. Material A is stronger, stiffer, and more ductile than materials B and C. Material B has less ductility than material A and thus, is more brittle. Material C has no ductility and is perfectly brittle; it is also the weakest of the three materials. **Brittleness** is the relative inability of a material to sustain plastic deformation before fracture of a material occurs. For example, amalgams, ceramics, and composites are brittle at oral temperatures (5 to 55 °C). They sustain little or no plastic strain before they fracture. In other words, a brittle material fractures at or near its proportional limit. This behavior is shown by material C in Figure 4-13.

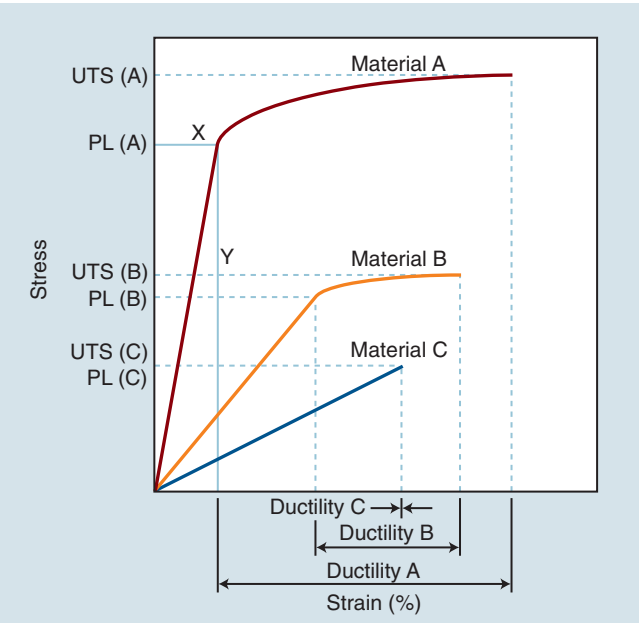


FIGURE 4-13 Stress-strain plots of materials that exhibit different mechanical properties. UTS, ultimate tensile stress; PL, proportional limit.

However, a brittle material is not necessarily weak. For example, a cobalt-chromium partial denture alloy may have a percent elongation of less than 1.5% but an ultimate tensile strength of 870 MPa. The tensile strength of a glass-infiltrated alumina core ceramic (In-Ceram Alumina) is moderately high (450 MPa), but it has 0% elongation.

If a glass is drawn into a fiber with very smooth surfaces and insignificant internal flaws, its tensile strength may be as high as 2800 MPa (400,000 psi), but it will have no ductility (0% elongation). Thus, dental materials with low or zero percent elongation—including amalgams, composites, ceramics, and nonresin luting agents—will have little or no burnishability because they have no plastic deformation potential.

CRITICAL QUESTION

What is the difference in appearance between a stress-strain graph for a material that has high strength, high stiffness, and high ductility and one for a material that is weak, flexible, and more brittle?

DUCTILITY AND MALLEABILITY

When a cast dental alloy is stressed beyond its proportional limit, it becomes permanently deformed. If it sustains tensile stress and considerable permanent deformation without rupture, it is classified as a ductile alloy. **Ductility** represents the ability of a material to sustain a large permanent deformation under a tensile load up to the point of fracture. For example, a metal that can be drawn readily into a long thin wire is considered to be ductile.

Examples of three materials with different degrees of ductility (percent elongation) are shown in Figure 4-13. Material A is the most ductile as shown by the longest plastic strain range (curved region). Material C is typical of brittle materials because no plastic deformation is possible and fracture occurs at the proportional limit.

Malleability is the ability of a material to sustain considerable permanent deformation without rupture under compression, as in hammering or rolling into a sheet. Gold is the most ductile and malleable pure metal, and silver is second. Of the metals of interest to the dentist, platinum ranks third in ductility, and copper ranks third in malleability.

Ductility is the relative ability of a material to be stretched plastically at room temperature without fracturing. Its magnitude can be assessed by the amount of permanent deformation indicated by the stress-strain curve. For example, the plastic strain indicated in Figure 4-13 is a relative measure of the ductility of the solid material. After fracture, the mechanical stress decreases instantly to zero, and the residual strain represents the amount of permanent deformation that has been produced in the object.

WHICH TESTS ARE USED FOR DUCTILITY?

Three common methods are used to determine ductility: (1) the percent elongation after fracture, (2) the reduction in area of tensile test specimens, and (3) the maximum number of bends performed in a cold bend test. Probably the simplest and most commonly used method is to compare the increase in length of a wire or rod after fracture in tension to its length before fracture. Two marks are placed on the wire or rod a specified distance apart and this distance is designated as the gauge length. For dental materials, the standard gauge length is usually 51 mm. The wire or rod is then pulled apart under a tensile load. The fractured ends are fitted together and the gauge length is again measured. The ratio of the increase in length after fracture to the original gauge length, expressed in percent, is called the percent elongation and represents the quantitative value of ductility.

The second method that can determine ductility involves the necking or cone-shaped constriction that occurs at the fractured end of a ductile metal wire after rupture under a tensile load. The percent decrease in cross-sectional area of the fractured end in comparison with the original area of the wire or rod is referred to as the relative reduction in area.

The third method for the measurement of ductility is known as the cold bend test. The material is clamped in a vise and bent around a mandrel of a specified radius. The number of bends to fracture is counted, and the greater the number, the greater the ductility. The first bend is made at 90 degrees from the vertical to the horizontal, but all subsequent bends are made through angles of 180°.

CRITICAL QUESTION

Hardness is a property used to predict the wear resistance of a material and its ability to abrade opposing dental structures. What other factors may be responsible for excessive wear of natural tooth enamel or prosthetic surfaces by a hard material?

HARDNESS

Except for comparing one material with another, this term is difficult to define. In mineralogy the relative hardness of a substance is based on its ability to resist scratching. In metallurgy and most other disciplines, the concept that is most generally accepted is that of "resistance to indentation." It is on the basis of this process that most modern hardness tests are designed.

An indentation produced on the surface of a material from the applied force of a sharp point or abrasive particle results from the interaction of numerous properties. Among the properties that are related to the hardness of a material are compressive strength, proportional limit, and ductility.

Hardness data for dental materials are useful to the dentist and materials scientist. Hardness tests are included in numerous specifications for dental materials developed by the American Dental Association (ADA) and standards promoted by the International Organization for Standardization (ISO). There are several types of surface hardness tests. Most are based on the ability of the surface of a material to resist penetration by a diamond point or steel ball under a

specified load. The tests most frequently used in determining the hardness of dental materials are known by the names Barcol, Brinell, Rockwell, Shore, Vickers, and Knoop. Selection of the test should be determined on the basis of the material being measured.

The Brinell hardness test has been used extensively for determining the hardness of metals and metallic materials used in dentistry. The Brinell hardness number is related to the proportional limit and the ultimate tensile strength of dental gold alloys. Because the test is a relatively simple one, it may often be conveniently used as an index of properties that involve more complex test methods. The Brinell hardness test is one of the oldest tests employed for determining the hardness of metals. In this test, a hardened steel ball is pressed under a specified load into the polished surface of a material, as diagrammed in Figure 4-14. The load is divided by the area of the projected surface of the indentation, and the quotient is referred to as the Brinell hardness number, usually abbreviated as HB or BHN, or more recently, HBW. Thus, for a given load, the smaller the indentation, the larger is the number and the harder the material.

The Rockwell hardness test is somewhat similar to the Brinell test in that a steel ball or a conical diamond point is used, as diagrammed in Figure 4-14. Instead of measuring the diameter of the impression, the depth of penetration is measured directly by a dial gauge on the instrument. A number of indenting points of different sizes are available for testing a variety of different materials. The Rockwell hardness number (abbreviated as RHN) is designated according to the particular indenter and load employed. The convenience of the Rockwell test, with direct reading of the depth of the indentation, has led to its wide usage in industry. However, neither the Brinell test nor the Rockwell test is suitable for brittle materials.

The Vickers hardness test employs the same principle of hardness testing that is used in the Brinell test. However, instead of a steel ball, a square-based pyramid is used (Figure 4-14). Although the impression is square instead of round, the method for calculating the Vickers hardness number (usually abbreviated as HV or VHN) is the same as that for the BHN in that the load is divided by the projected area of indentation. The lengths of the diagonals of the indentation are measured and averaged. The Vickers test is employed in the standard testing of dental casting gold alloys. The test is suitable for determining the hardness of brittle materials; therefore, it has also been used for measuring the hardness of other cast dental alloys as well as of tooth structure.

The Knoop hardness test employs a diamond-tipped tool that is cut in the geometric configuration shown in Figure 4-14. The impression is rhombic in outline, and the length of the largest diagonal is measured. The load is divided by the projected area to give the Knoop hardness number (usually abbreviated as HK or KHN). When the indentation is made and the indenter is subsequently removed, the shape of the Knoop indenter causes elastic recovery of the projected

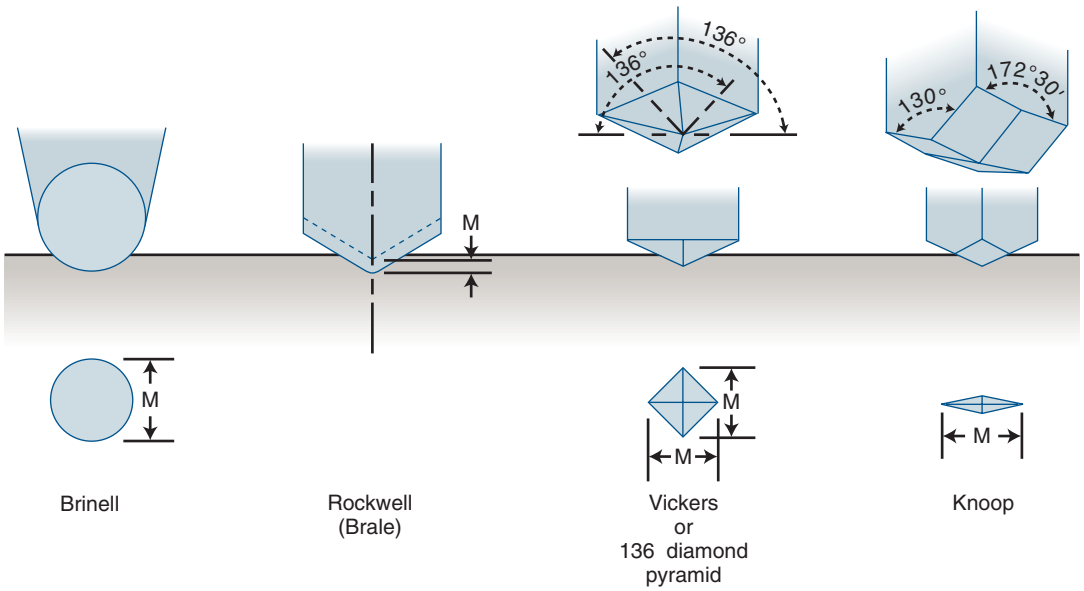


FIGURE 4-14 Shapes of hardness indenter points (*upper row*) and the indentation depressions left in material surfaces (*lower row*). The measured dimension M that is shown for each test is used to calculate hardness. The following tests are shown: Brinell test—a steel ball is used, and the diameter of the indentation is measured after removal of the indenter. Rockwell test—a conical indenter is impressed into the surface under a minor load (*dashed line*) and a major load (*solid line*), and M is the difference between the two penetration depths. In the Vickers or 136° diamond pyramid test, a pyramidal point is used, and the diagonal length of the indentation is measured. In the Knoop test, a rhombohedral pyramid diamond tip is used and the long axis of the indentation is measured.

impression to occur primarily along the shorter diagonal. The stresses are distributed in such a manner that only the dimensions of the minor axis are subject to change by relaxation. Thus, the hardness is virtually independent of the ductility of the tested material. The hardness of tooth enamel can be compared with that of gold, porcelain, resin, and other restorative materials. Also, the load may be varied over a wide range, from 0.1 kgf to more than 1 kgf, so that values for both exceedingly hard and very soft materials can be obtained by this test.

The Knoop and Vickers tests are classified as microhardness tests in comparison with the Brinell and Rockwell macrohardness tests. Both Knoop and Vickers tests employ loads less than 9.8 N. The resulting indentations are small and limited to depths of less than 19 μm. Hence they are capable of measuring the hardness in small regions of thin objects. The Rockwell and Brinell tests give average hardness values over much larger areas. Other less sophisticated measurement methods, such as the Shore and the Barcol tests, are sometimes employed for measuring the hardness of rubber and plastic types of dental materials. These tests use compact portable indenters of the type generally used in industry for quality control. The principle of these tests is also based on resistance to indentation. The equipment generally consists of a spring-loaded metal indenter point and a gauge from which the hardness is read directly. The hardness number is based on the depth of penetration of the indenter point into the material.

? CRITICAL QUESTION

Why do prostheses sometimes fail under a very small force even though the strength of the prosthetic material is relatively great?

STRESS CONCENTRATION EFFECTS

Unexpected fractures of dental prostheses and restorations occur occasionally even when high-quality materials have been used. These failures result from locally high stresses in specific areas even though the average stress in the structure is low. The cause of this strength reduction is the presence of small microscopic flaws or microstructural defects on the surface or within the internal structure. These flaws are especially critical in brittle materials in areas of tensile stress because tensile stress tends to open cracks; therefore the stress at the tips of these flaws is greatly increased and may lead to crack initiation and broken bonds. Shown in Figure 4-15 is a theoretical tensile stress distribution in brittle and ductile materials. Although the tensile stress has increased at the flaw tip in each case, it has increased by a smaller amount in the ductile material (right-side illustration of Figure 4-15), in which plastic deformation has occurred with subsequent widening of the flaw tip, thereby reducing the magnitude of localized tensile stress. As shown on the left side of Figure 4-15, the tensile stress in a brittle material cannot be relieved by plastic deformation at the flaw tip and a crack develops as the stress increases to a critical level. Note the increased level of tensile stress at the tip of the flaw. However, the stress at areas far away from these flaws will be much lower if flaws are absent in these areas.

The flaw does not play a significant role when the material is subjected to an external compressive force, as shown in the center of Figure 4-15. In this case the compressive stress that develops in the material tends to close the crack, and this stress distribution is more uniform. There are two important aspects of these flaws: (1) the stress intensity increases with the length of the flaw, especially when it is oriented perpendicular to the direction of tensile stress, and (2) flaws on the surface are associated with higher stresses than are flaws of the same size in interior regions. Thus, surface finishing of brittle materials—such as ceramics, amalgams, and composites—is extremely important in areas subjected to tensile stress.

Reduced strength of a brittle restorative material may be caused by localized areas of stress enhancement can also

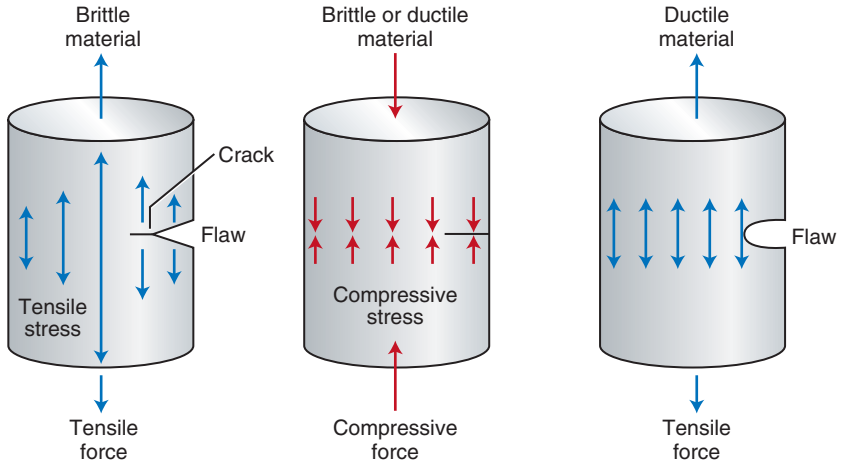


FIGURE 4-15 Influence of tensile and compressive stresses on flaws in brittle and ductile materials.

result from factors other than the inherent microscopic flaws on the surface of a material. Areas of high stress concentration are caused by one or more of the following factors:

1. Surface defects, such as porosity, grinding roughness, and machining damage
2. Interior flaws, such as voids or inclusions
3. Marked changes in contour, such as the point of attachment of a clasp arm to a partial denture framework or a sharp internal angle at the pulpal-axial line angle of a tooth preparation for an amalgam or composite restoration
4. A large difference in elastic moduli or thermal expansion coefficient across a bonded interface
5. A Hertzian load (or point contact)

HOW CAN WE MINIMIZE STRESS CONCENTRATIONS?

Relative to factor 1 above, the surface can be polished to reduce the depth of the defects. Little can be done for interior flaws (factor 2) other than to ensure the highest quality of the structure or to increase the size of the object. For factor 3, the design of any prosthesis should vary gradually rather than abruptly. Notches should be avoided. Internal line angles of tooth preparations should be well rounded to minimize the risk of cusp fracture. For factor 4, the most brittle material should have the lower elastic modulus so that more stress is transferred to the material with the higher elastic modulus. If this is not possible, the elastic moduli of the two materials should be more closely matched. For factor 4, the materials must be closely matched in their coefficients of expansion or contraction. If a thermal mismatch cannot be avoided, the weaker, more brittle material should have a slightly lower expansion or contraction coefficient so that a protective compressive stress is sustained in its structure next to the interface. Relative to factor 5, the cusp tip of an opposing crown or tooth should be well rounded such that occlusal contact areas in the brittle material are large. In addition, the internal line angle of the tooth preparation should have as large a radius of curvature as possible. However, this stress concentration effect increases the risk of tooth fracture, which may or may not cause fracture of the restorative material but it will likely require replacement of the restorative material, assuming that the tooth fracture does not require tooth extraction.

CRITICAL QUESTIONS

Fracture toughness is a more precise measure of the fracture resistance of a brittle material, than its tensile strength. Why is the tensile strength of brittle materials—such as dental amalgam, composite, ceramic, and inorganic cements—so variable? Which one of a series of reported tensile strength values should be used in considering the selection of a new product made of one of these materials?

STRENGTH OF TOOTH STRUCTURE

The relatively wide variation in mechanical properties of human tooth structure are attributed to the technical problems associated with preparing and testing such small specimens, which in some instances are less than 1 mm in length. The results reported in one study are shown in Table 4-1. This study explored the effect of enamel rod orientation by propagating cracks in the occlusal surface and in axial sections in directions parallel and perpendicular to the occlusal surface. The cracks in the axial enamel section were longer in the direction perpendicular to the occlusal surface rather than parallel to the surface. The cracks that propagated toward the dentinoenamel junction (DEJ) were arrested and did not penetrate the DEJ into dentin. The fracture toughness of dentin varied by a factor of 3 as a function of enamel rod orientation. The elastic modulus of enamel also varied between the occlusal surface and the axial section. The results of this study demonstrate that the mechanical properties of tooth structure are a function of microstructural orientation. Indentation energy is a recently introduced property that is used to predict the machinability and wear behavior of ceramics. Research data suggest that during indentation or cutting, brittle enamel may be removed by microfracture, whereas dentin may be removed by forming ductile chips.

Although the data in Table 4-1 indicate a variation in the properties of enamel and dentin from one type of tooth to another, the difference is more likely the result of variations within individual teeth than between teeth. The properties of enamel vary somewhat with its position on the tooth, that is, cuspal enamel is stronger than enamel on other surfaces of the tooth. Also, the properties of enamel vary according to

TABLE 4-1 Properties of Tooth Structure (Human Third Molars)

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Please refer to the printed publication.

the microscopic structure. For example, enamel is stronger under longitudinal compression than when subjected to lateral compression. On the other hand, the properties of dentin appear to be independent of structure regardless of the direction of compressive stress.

The tensile properties of tooth structure have also been measured. Dentin is considerably stronger in tension (50 MPa) than is enamel (10 MPa). Although the compressive strengths of enamel and dentin are comparable, the proportional limit and modulus of elasticity of enamel are greater than the corresponding values for dentin. The higher modulus of elasticity of enamel results in less resilience compared with dentin.

CLENCHING AND MASTICATION FORCES

Because of their dynamic nature, biting stresses that are exerted during mastication are difficult to analyze. A number of studies have been made to determine the maximum biting force and maximum clenching force. The *Guinness Book of Records* (1994) lists the highest biting force as 4337 N (975 lbf) sustained for 2 s. This study was performed by Gibbs et al. (1986). The average maximum sustainable biting force is approximately 756 N (170 lbf). The biting force in some dental patients may be greater than previously believed. The biting force of bruxer-clenchers may be underestimated by a factor of six compared with non-bruxers. However, the range of biting forces varies markedly from one area of the mouth to another and from one individual to another. Maximum bite forces range from 400 to 890 N (90 to 200 lbf) for molar teeth; from 222 to 445 N (50 to 100 lbf) for premolars; from 133 to 334 N (30 to 75 lbf) for canines; and from 89 to 111 N (20 to 55 lbf) for incisors. Although there is considerable overlap, biting force generally is greater for males than for females and for young adults than for children.

Gibbs et al. (2002) reported a mean clenching force of 462 N (104 lbf), with a range of 98 to 1031 N (22 to 232 lbf) for individuals between the ages of 28 and 76 (mean age = 46) who had lost their posterior teeth. In comparison, subjects with a complete dentition exerted a mean clenching force of 720 N (162 lbf) with a range of 244 to 1243 N (55 to 280 lbf). A two-tailed t-test showed that the average difference of 258 N (58 lbf) between the two groups was significant ($P<\leq 0.01$). If one assumes that if a force of 756 N (170 lbf) is applied to a cusp tip over an area equivalent to 3.9 mm^2 (0.006 in^2), the compressive stress would be 193 MPa (28,000 psi). If the area is smaller, then the stress within the cusp would be proportionately greater.

Typically, the energy of a biting or chewing event is absorbed by the food bolus during mastication as well as by the teeth, periodontal ligament, and bone. Also, the design of the tooth enables it to absorb significant static as well as dynamic (impact) energies. As can be seen in Figure 4-5, the modulus of resilience of dentin is greater than that of enamel and it is better able to absorb impact energy. Enamel is a brittle substance with a comparatively high modulus of elasticity, a low proportional limit in tension, and a low modulus of resilience.

CRITERIA FOR THE SELECTION OF RESTORATIVE MATERIALS

A brittle material is highly susceptible to surface flaws and internal defects when tensile stresses are present. Because it cannot plastically deform to reduce stress concentrations, and its tensile strength is far lower than its compressive strengths. The compressive strength of brittle materials is often reported even though most brittle materials rarely fail under compressive stresses. However, when tensile strength values are not available, flexural strength values should be used, since they reflect a tensile mode of fracture. When tensile strength, flexural strength, or fracture toughness data are not available, the compressive strength can be useful for comparisons of the fracture resistance of a similar family of brittle materials, such as groups of amalgams, composites, ceramics, or cements.

The physical properties described earlier have been obtained using specimen shapes and sizes that are quite different from those of tooth restorations. Thus, material products must be selected intuitively on the basis of property comparisons. Engineers employ similar criteria for the selection of materials to be used for the construction of large structures. Engineers have an advantage over dentists in this respect because they know beforehand the maximum "average" stresses that structures are expected to sustain before fracture occurs. Furthermore, these expected stresses are multiplied by a "safety factor" to ensure that the structure will be able to withstand a certain amount of excess stress. However, the tensile strength values reported for restorative materials represent the mean stress values below which 50% of the test specimens have fractured and above which only 50% had survived. Because this is an unacceptable failure rate for restorative dentistry, the range of measured values should be known. From an ultraconservative viewpoint, the lowest 5 or 10% of a strength distribution, not mean values, should be used to design a prosthesis intended to resist fracture at a high level of confidence. We can also use the 95% survival stress as determined from Weibull analyses of the data.

It is unfortunate that the magnitudes of mastication forces are not known for individual patients to the extent that the dentist can predict the stresses that will be induced in dental restorations. However, patients who exhibit evidence of extreme bruxism represent a higher risk population for the fracture of brittle restorative materials. The knowledge of the relationships between the properties of restorative materials known to exhibit excellent long-term survival performance is reinforced by clinical experience. As is true for the field of engineering, the dental profession is aware that the best test of a successful restorative material is the test of time under actual clinical conditions.

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CHAPTER 5

Structure and Properties of Cast Dental Alloys

OUTLINE

History of Metal Development in Dentistry

Metallic Bonding

Classification of Alloys

Effects of Alloy Elements on Properties of High Noble and Noble Metal Alloys

Solidification and Microstructure of Cast Dental Alloys

Solid Solutions

Conditions for Solid Solubility

Equilibrium-Phase Diagrams

Eutectic Alloys

Peritectic Alloys

Solid-State Reactions in High Noble and Noble Alloy Systems

Color of Cast Metal Alloys

KEY TERMS

Alloy—A crystalline solid with metallic properties that is composed of two or more chemical elements at least one of which is a metal and all of which are mutually soluble in the molten state.

Alloy system—All possible alloyed combinations of two or more elements at least one of which is a metal. For example, the binary gold-silver system includes all possible alloys of gold and silver, varying from 100% gold and 0% silver to 100% silver and 0% gold.

Binary metal alloy—An alloy that contains two chemical elements at least one of which is a metal.

Coring—A microstructure in which a composition gradient exists between the center and the surface of cast dendrites, grains, or particles.

Dendritic microstructure—A cast alloy structure of highly elongated crystals with a branched morphology.

Equiaxed grain microstructure—A cast alloy microstructure with crystal (grain) dimensions that are similar along all crystal axes.

Grain—A single crystal in the microstructure of a metal.

Grain boundary—The interface between adjacent grains in a polycrystalline metal. Dental alloys are polycrystalline solids consisting of many individual grains (crystals) separated by grain boundaries.

Heterogeneous nucleation—Formation of solid nuclei on the mold walls or on particles within a solidifying molten metal.

Homogeneous nucleation—Formation of nuclei that occur at random locations within a supercooled molten metal in a clean, inert container.

Metal—(1) An element or alloy whose atoms readily lose electrons to form positively charged ions. (2) A metallic material composed of one or more chemical elements that is opaque, ductile, relatively malleable, a good conductor of electricity, a good thermal conductor, and usually lustrous when light is reflected from its polished surface.

Microstructure—Structural features of a metal, including grains, grain boundaries, phases, and defects such as porosity, revealed by microscopic imaging of the chemically or electrolytically etched surface of a flat, polished specimen.

Nucleus—A stable cluster of atoms in a new phase that forms within a parent matrix phase during the solidification of a microstructure.

Phase—A homogeneous, physically distinct, and mechanically separable portion of a metal microstructure.

Phase diagram (constitution diagram)—A graph of equilibrium phases and solubility limits for an alloy system as a function of composition and temperature.

Quaternary alloy—An alloy that contains four elements at least one of which is a metal.

Solid solution (metallic)—A solid crystalline phase containing two or more elements at least one of which is a metal and whose atoms share the same crystal lattice.

Tarnish—Superficial discoloration or dulling of a metal surface that is often caused by a reaction with oxygen or sulfur.

Ternary alloy—An alloy that contains three elements at least one of which is a metal.

Cast metals are used for the construction of many types of metallic prostheses, including inlays, onlays, partial crowns, full crowns, bridges, endodontic posts, partial denture frameworks, and implant abutments. Cast **metal** substructures are also used as frameworks for metal-ceramic and metal-resin prostheses. Thus, an understanding of the structure and properties of cast metals is essential to ensure the optimal quality and performance of metallic-based prostheses and restorations. This chapter provides an overview of cast metal technology and the science of physical metallurgy, the discipline that investigates the effects of composition, casting processes, deformation, and heat treatment on the physical and mechanical properties of metals.

Although the use of cast metals has decreased in recent years because of increased consumer demand for esthetics over durability, a knowledge of the structure and properties of cast metals and **alloys** is essential to ensure proper handling of these materials in clinical practice and to diagnose clinical failures of cast restorations should they occur. Furthermore, cast metals are used as copings or substructures for metal-ceramic restorations, one of the most common types of esthetic crown and bridge prostheses, and the most durable of esthetic restorations, especially when used to restore posterior teeth. The principles of molten metal solidification and equilibrium **phase** formation during the casting of metals are presented in this chapter. The key terms above will facilitate an understanding of the phase transformations and structures formed in cast dental alloys.

HISTORY OF METAL DEVELOPMENT IN DENTISTRY

In the seventh century B.C. the Etruscans used ivory and bone supported by gold frameworks as tooth forms. In the 1800s, over 2500 years later, metal restorations were made by compacting aluminum, amalgam, gold, lead, platinum, and silver in tooth cavities. Although prostheses and restorations have been made from metals for centuries, precision casting technology was not available until the 20th century. The concepts of producing gold castings using the lost-wax process and a melting torch were introduced in 1903 at a meeting of the Society of Stomatology of Paris. In 1907 Taggert introduced a method for producing precise cast metal crown and bridge forms. Electricity-driven furnaces and casting machines became available in the early 1900s and casting technology advanced rapidly soon thereafter. However, the successful casting of titanium, one of the most biocompatible metals available for dentistry, was not achieved until the 1970s because of its reactivity with oxygen and the technique sensitivity of this metal. Since then, several technological advances such as CAD-CAM technology, electroforming, laser sintering, and laser welding have been introduced to facilitate the processing of metals for dental applications.

In dentistry, metals, ceramics, polymers, and composites are the four major material groups used for dental prostheses and restorations. It is not easy to define the word *metal* because of the wide variation in properties and characteristics of metallic materials. The *Metals Handbook* (1992) defined a metal as "an opaque lustrous chemical substance that is a good conductor of heat and electricity and, when polished, is a good reflector of light." From the standpoint of dental restorations, this definition leaves a lot to be desired because dentists are concerned about plaque adhesion to metal surfaces, the ability to form bonds to porcelain, the ability to join components of a metal or metal-ceramic prosthesis accurately to ensure proper fit on prepared teeth, wear of opposing teeth, and the biocompatibility aspects of the component metallic elements.

METALS AND ALLOYS

CRITICAL QUESTION

Why is the word *metal* difficult to define?

Pure metals have properties that can be markedly different when alloyed with other metals or nonmetals. For example, the element iron alloyed with relatively small amounts of carbon produces much stronger and harder metals called steels, which can be used for high-stress applications. When chromium is alloyed with iron and carbon, the corrosion resistance of this alloy, called stainless-steel, is greatly enhanced because of the formation of an adherent oxide of chromium (Cr_2O_3). Certain carbon steels are electroplated with chromium to produce corrosion-resistant instruments.

Since an alloy is a material with metallic properties consisting of two or more chemical elements at least one of which is a metal, the choice of elements depends on which properties are required for specific clinical conditions. Characteristics such as castability, ability to be soldered (or brazed), solidification shrinkage, expansion coefficient, corrosion resistance, biocompatibility, and color are important for a variety of clinical applications,

Gallium and mercury, elements commonly used in dental alloys, are liquid at body temperature but when alloyed, they become a component of the solid alloy at oral temperatures. With the exception of pure gold foil, commercially pure titanium, and endodontic silver points, metals used for dental restorations, implants, partial denture frameworks, orthodontic wires, and endodontic instruments are alloys. All pure metals and alloys used as restorative materials in dentistry are crystalline solids when used to produce their functional prosthesis or restoration forms. Because the metals are crystalline, the microstructural changes that occur during processing or heat treatment control desired properties for dental applications.

Compared with the properties of ceramics, composites, and polymers, the unique characteristics of metal alloys are described qualitatively and quantitatively by properties and characteristics such as brittleness, color, ductility, electrical and thermal conductivity, hardness, luster, malleability, melting temperature, specific gravity, solderability, wear

resistance, and weldability. In addition, the ability of most alloys to make a ringing sound when struck by a hard object can provide evidence that they are metals. Thus, no single property or characteristic defines a metal completely.

The wide range of dental alloy compositions is described briefly in this chapter and they are discussed further in Chapter 16. Dental casting alloys are associated with the following groups:

1. Dental amalgams, which contain mercury (Hg), silver (Ag), tin (Sn), and copper (Cu).
2. High noble (HN) alloys, which contains at least 40 wt% gold (Au) and 60 wt% of noble metals.
3. Noble (N) metal alloys, which are typically based on palladium (Pd) as the main noble metal with a total noble metal content of at least 25 weight percent. Noble metal alloys may also contain gold, silver, copper, gallium (Ga), indium (In), platinum (Pt), and tin (Sn).
4. Predominantly base (PB) metal alloys, which contain less than 25 wt% of noble metals, are most commonly composed of one of the following groups: nickel and chromium (Ni-Cr); cobalt and chromium (Co-Cr); iron, carbon, and chromium (Fe-C-Cr); commercially pure titanium (CP-Ti); and titanium-aluminum and vanadium (Ti-Al-V).

CP titanium, which is classified in four different grades, can technically be considered as an alloy because small percentages of other impurity elements are allowed as specified by a standard that has been established by the American Society for Testing and Materials (ASTM) for each grade. Grade 2 titanium is used widely in aerospace, marine, and medical applications because of its ease of forming, its moderately high strength (equal to or greater than 275 MPa), and its excellent corrosion resistance. Although it is classified as commercially pure, grade 2 CP-Ti may contain up to 0.10% C, 0.30% Fe, 0.015% H, 0.03% N, 0.25% O, and 0.40% of other elements.

Two nonwhite metals in the periodic table of the elements (Table 5-1) are gold and copper, both of which are important components of cast dental alloys. Alloys with a relatively high gold content are yellow in hue and those containing significant concentrations of copper are reddish-yellow in hue. Most cast dental alloys, which are based on either cobalt, nickel, palladium, or silver, are "white" or silver in appearance, although these alloys may exhibit slight differences in hue and chroma. There is one exception, however. In the late 1970s a palladium-indium (Pd-In) alloy was introduced that exhibited a yellow hue. This color was attributed to an optical effect involving the intermetallic compound Pd-In. Argenco

TABLE 5-1 Physical Properties of Alloy-Forming Elements

Element	Symbol	Atomic Weight	Melting Point (°C)	Boiling Point (°C)	Density (g/cm^3)	Thermal Expansion Coefficient (10^{-6}/K)
Aluminum	Al	26.98	660.3	2450	2.70	23.6
Carbon	C	12.01	630.5	4830	2.22	6.0
Chromium	Cr	52.00	271.3	2665	7.19	6.2
Cobalt	Co	58.93	1495.0	2900	8.85	13.8
Copper	Cu	63.54	1083.0	2595	8.96	16.5
Gold	Au	196.97	1063.0	2970	19.32	14.2
Indium	In	114.82	156.2	2000	7.31	33.0
Iridium	Ir	192.20	2454.0	5300	22.50	6.8
Iron	Fe	55.85	1527.0	3000	7.87	12.3
Magnesium	Mg	24.31	650.0	1107	1.74	25.2
Mercury	Hg	200.59	–38.9	357	13.55	40.0
Molybdenum	Mo	95.94	2619.0	5560	10.22	4.9
Nickel	Ni	58.71	1453.0	2730	8.90	13.3
Palladium	Pd	106.40	1552.0	3980	12.02	11.8
Platinum	Pt	195.09	1769.0	4530	21.45	8.9
Rhodium	Rh	102.91	1966.0	4500	12.44	8.3
Silicon	Si	28.09	1410.0	2480	2.33	7.3
Silver	Ag	107.87	960.8	2216	10.49	19.7
Tin	Sn	118.69	231.9	2270	7.30	23.0
Titanium	Ti	47.90	1668.0	3260	4.51	8.5
Tungsten	W	183.85	3410.0	5930	19.30	4.6
Zinc	Zn	65.37	420.0	906	7.133	0.4

Data from Lyman T, editor: *Metals Handbook*, ed 8, vol 1. Cleveland OH, American Society for Metals, 1964.

Y+ (Argen Corporation, San Diego, CA) is an example of such an alloy. Another alloy of this type, Castell (Jensen Dental, North Haven, CT) is marketed as a yellow type III alloy. This alloy contains 20% Au, 20% Pd, 17% In, 38% Ag, 17% In, 4% Zn, 1% Cu and other minor elements. Because it contains more than 25% by weight of noble metals, it would be classified as a noble alloy. Alloys of this type exhibit a pale yellow to gold color derived from the interaction of two white metals, palladium and indium. Alloying additions are included to improve castability, ductility, strength, hardness, **tarnish** resistance, and corrosion resistance. These alloys have recently gained in popularity because of the high price of gold. The tarnish resistance of the alloy is highly dependent on the composition and quality of the casting. Any porosity or contamination will result in rapid discoloration of the alloy. Once lab technicians learn how to use the alloy correctly, it can have great success clinically.

A clean, polished, metallic surface exhibits a luster that cannot be duplicated by other types of solids. Most metals emit a metallic sound ("ring") when they are struck by another metal, although some silica compounds can also emit a similar sound. A unique characteristic of metals is that they are generally excellent thermal and electrical conductors. Compared with ceramics, polymers, and composites, metals have greater fracture toughness (K_{Ic})—that is, the ability to absorb energy and inhibit crack extension under an applied tensile stress. Fracture toughness is a measure of the resistance of a material to crack propagation when a microcrack exists in its structure. For example, the fracture toughness (K_{Ic}) of metals ranges from 25 to 60 MPa·$m^{1/2}$ compared with a range of 0.75 to 12 MPa·$m^{1/2}$ for dental ceramics. The latter value was reported for Ce-TZP/Al_2O_3, which contained 10 mol% CeO_2 as a stabilizer. Although higher K_{Ic} values have been reported for similar ceramics, these values were derived from the indentation crack method, which is known to be unreliable, especially when residual stresses are present.

Generally metal alloys are stronger and more dense than nonmetallic structures. Most metals are also far more ductile and malleable than nonmetals, which are generally brittle. Three elements of dental alloys—iron, nickel, and cobalt—can be magnetic, but they can also be produced in a nonmagnetic state. Although many metals are resistant to chemical attack in air at room temperature, some metals require alloying elements to resist tarnish and corrosion in the oral environment and to optimize their passivity when they are in contact with dissimilar metals in the mouth. As mentioned above, chromium is required as an alloying element in iron-nickel-cobalt alloys to provide passivation of the alloy through the formation of a thin surface layer of chromium oxide.

Noble metals [gold (Au), iridium (Ir), osmium (Os), palladium (Pd), platinum (Pt), rhodium (Rh), and ruthenium (Ru)] are highly resistant to corrosion and oxidation and do not require alloying elements for protection in corrosive environments. Pure noble metals must be alloyed to provide sufficient resistance to deformation and fracture when they are used for cast implants, endodontic posts and cores, and crown and bridge restorations. Small additions of oxidizable elements—such as iron, tin, and indium—are added to high noble (HN) and noble (N) alloys used for metal-ceramic prostheses to promote bonding between the ceramic veneer and the metal oxide on the metal surface.

Of the 118 elements currently listed in the periodic table, about 88 (74.6%) can be classified as metals. No element having an atomic number higher than 92 occurs naturally in large quantities. It is of scientific interest that the metallic elements can be grouped according to density, ductility, melting point, and nobility. This indicates that the properties of metals are closely related to their valence electron configuration. The groups of pure metal elements can be seen in Figure 5-1, the periodic chart of the elements. All elements in the same group—for example, the alkali metals in group 1—have the same number of outer electrons, which results in similar chemical properties. The halogens within group 17 also have similar properties. For example, when halogen atoms react, they gain an electron to form negatively charged ions. Each ion has the same electron configuration as the other noble gases in the same period. Thus, the ions formed are more chemically stable than the elements from which they were formed.

The elements in groups 3 to 12 comprise the transition metals. These elements have variable valences and are sometimes used as catalysts. Nonmetals are listed in groups 14 to 16. The lanthanide series of elements (58 to 71) are called the rare earth elements. The actinide series of elements (90 to 103) participate in or are produced by nuclear reactions. Several metals of importance for dental alloys are transition elements (typically 21 to 80, although groups 89 to 112 are also included), in which the outermost electron shells are occupied before the interior shells are filled.

? CRITICAL QUESTION

Why are the general physical and mechanical properties of metallic dental materials different from those of ceramic and polymeric dental materials?

All metal elements have loosely bound outer electrons around the neutral atom. If two different metals form the electrodes of a galvanic cell, the more easily oxidized metal becomes the anode and supplies electrons to an external circuit. The formation of positive ions (cations) from metals in solution is a consequence of the ionic cores that are associated with metallic bonding.

The properties of the pure elements do not change abruptly from metallic to nonmetallic as viewed from the left to the right side of the periodic chart in Figure 5-1. The boundary between metals and nonmetals is indistinct, and the elements near the boundary exhibit characteristics of both metals and nonmetals. The elements boron, carbon, and silicon are often combined with metals to form commercially important engineering materials. Silicon is termed a semiconductor because its electrical conductivity is intermediate between that of a metal and that of an insulator. However, in dentistry the most common casting alloys used for dental appliances and prostheses are based on a majority of one or more of the following

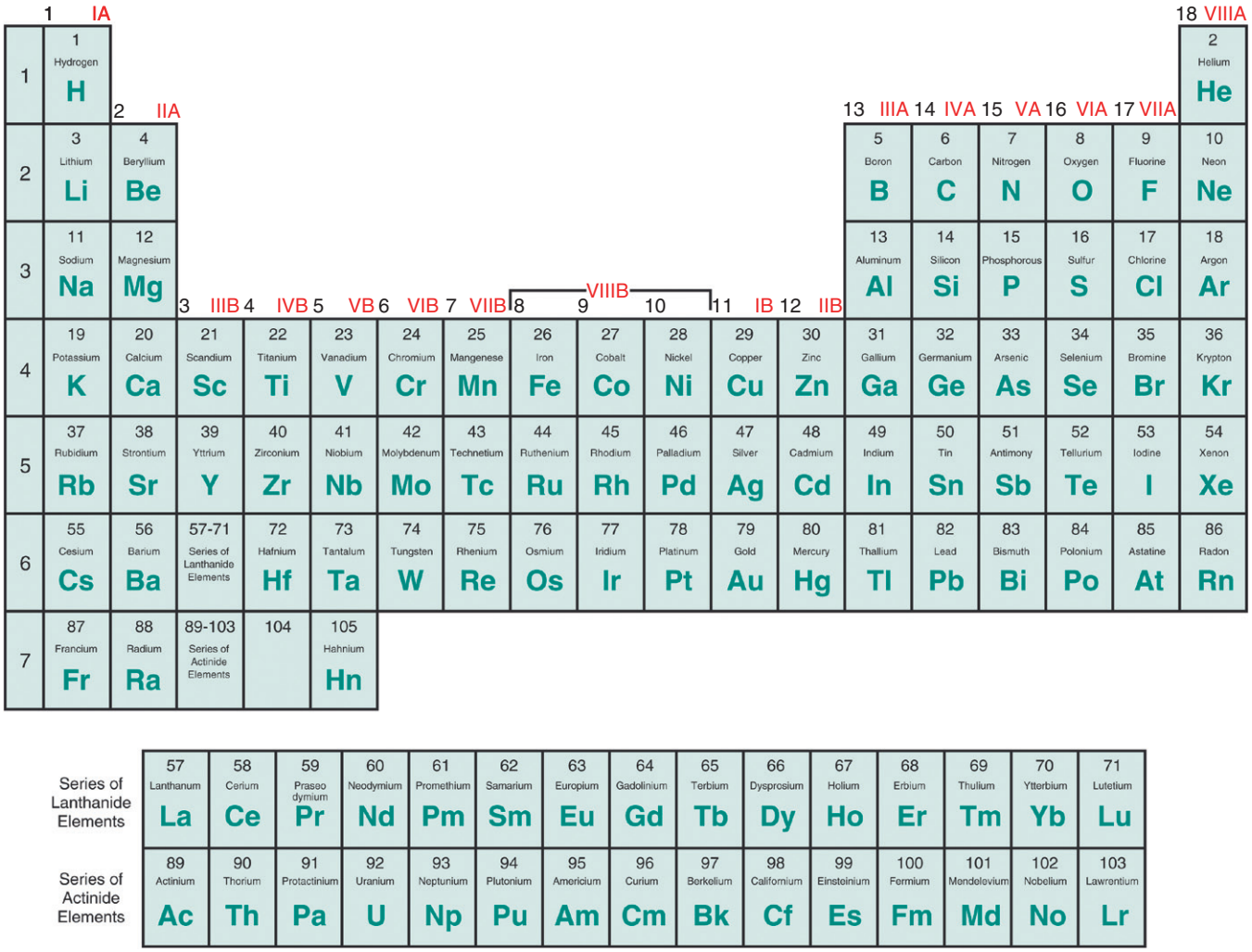


FIGURE 5-1 Periodic chart of the elements. (Adapted from Burtis CA, Ashwood ER: *Tietz Fundamentals of Clinical Chemistry*, ed 5, Philadelphia, 2001, Saunders.)

metallic elements: cobalt (Co), gold (Au), iron (Fe), nickel (Ni), palladium (Pd), silver (Ag), and titanium (Ti).

METALLIC BONDING

Metals have the ability to conduct heat and electricity. These properties are associated with the mobility of its free valence electrons. Since the outer valence electrons can be removed easily from metal atoms, the nuclei containing the balance of the bound electrons form positively charged ionic cores. In addition to covalent bonds (primarily elements in groups II to VII) and ionic bonds, atoms in solid metals are held together primarily by metallic bonding, which is based on a "cloud," "gas," or "sea" of free electrons. Because the cloud of electrons is shared among many atoms, the metallic bonds are nondirectional. Also, the difference in electronegativity between atoms is small and the valence electron orbitals are spherical, so electron sharing between atoms is minimal. Hence, the valence electrons in the cloud tend to be shared among many metal atoms rather than just between adjacent atoms. In this regard the metal atoms are ionic in nature. However, compared with metallic bonding, ionic and covalent bonding is typically associated with valence electrons localized near their central atoms.

Free electrons act as conductors of both thermal energy and electricity. They transfer energy by moving readily from bands of higher energy to those of lower energy under the influence of either a thermal gradient or the potential gradient of an electrical field. Metallic bonding is also responsible for the luster of polished metals and their typical ability of undergoing significant permanent deformation (associated with the properties of ductility and malleability) under mechanical stresses above their elastic limits or yield points. These characteristics are not typical of ceramics and polymers, whose atoms and molecules are bonded by covalent and ionic mechanisms.

? CRITICAL QUESTION

Why are pure metals not useful for most dental applications?

Pure metals, in common with other chemical elements, can be identified by their specific melting and boiling points and by their basic physical and chemical properties. Some of these properties for metals of dental interest are listed in Table 5-1. Pure metals have limited uses in dental and engineering applications, because they are too soft and some may corrode excessively. To optimize properties, most metals used in engineering and dental applications are either mixtures of two or more metallic elements or mixtures of one or more metals and nonmetallic elements. These alloys are generally prepared by fusion of the elements above their melting points. For example, a small amount of carbon is added to iron to form steel. A certain amount of chromium is added to iron, carbon, and other elements to form stainless steel, an alloy that is highly resistant to corrosion. As previously noted, chromium is also used to impart corrosion resistance to nickel or cobalt alloys, which comprise two of the major groups of base metal alloys used in dentistry. Chromium provides this corrosion resistance by forming a very thin, adherent surface oxide (Cr_2O_3) that prevents the diffusion of oxygen or other corroding species to the underlying metal. Although pure gold is also highly resistant to corrosion, copper is added to gold for many dental alloys to increase their strength and resistance to permanent deformation. In this chapter, the term *metal* is used to describe alloys as well as pure metals.

CLASSIFICATION OF ALLOYS

Cast dental alloys can be classified according to the following five categories: (1) use (all-metal inlays, crowns and bridges, metal-ceramic prostheses, posts and cores, removable partial dentures, and implants); (2) major elements (gold-based, palladium-based, silver-based, nickel-based, cobalt-based, and titanium-based); (3) nobility (high noble, noble, and predominantly base metal); (4) three principal elements (such as Au-Pd-Ag, Pd-Ag-Sn, Ni-Cr-Be, Co-Cr-Mo, Ti-Al-V, and Fe-Ni-Cr); and (5) dominant phase system (single phase, eutectic, peritectic, and intermetallic types). To specify the type of a particular alloy for dental applications, we can use a simple classification system such as the revised classification that was proposed by the American Dental Association in 2003 (high noble, HN; titanium and titanium alloys; noble, N; and predominantly base metal, PB), or we can be much more specific by listing the concentration of the most abundant and/or the most important elements contained in the alloy. The IdentAlloy system also provides certificates for high noble alloys (HN), noble alloys (N), titanium (TI), predominantly base alloys (PB), and cobalt-base alloys (cobalt base PB).

If two metals are present during solidification of a molten metal, a binary alloy is produced; if three or four metals are present, ternary and **quaternary alloys**, respectively, are produced. As the number of metals increases beyond two, the alloy structure becomes more complex. For simplicity's sake, only binary alloys are described in this chapter.

The simplest alloy is a solid solution, in which atoms of two metals are mutually completely soluble and dispersed in specific arrays within the same crystal structure, such as face-centered cubic (FCC) as shown in Figure 5-1, body-centered cubic (BCC), and hexagonal close-packed (HCP). When observed with an optical microscope, the individual grains and the **microstructures** overall of solid solution alloys may resemble those of pure metals. The structure will appear to be entirely homogeneous, since only one phase is formed during solidification. The temperature-versus-composition graphs for such alloys are sometimes referred to as "isomorphous phase diagrams." Most gold alloys used in clinical dentistry are predominantly solid solutions, although they usually contain more than two metals.

When two metals are not completely soluble in each other, the solid state is a mixture of two or more phases. Important examples are the eutectic alloys and peritectic alloys, which are discussed in the following sections. Alloys can have intermediate phases, which have a range of compositions different from the solid solutions formed by the nearly pure metals. In some alloy systems, intermetallic compounds with a fixed composition can also be formed.

CRITICAL QUESTIONS

How do gold, platinum, palladium, and silver concentrations affect the color of gold alloys and the thermal expansion coefficient of high noble and noble metal alloys? Which of these elements strengthen and harden noble metal alloys? Which three alloy elements promote bonding to porcelain?

EFFECTS OF ALLOY ELEMENTS ON PROPERTIES OF HIGH NOBLE AND NOBLE METAL ALLOYS

Pure gold lacks sufficient strength and stiffness for any dental application except as direct filling gold (also known as gold foil). Alloys with high gold contents have been used in dentistry for centuries. Gold is inert in the oral environment, extremely malleable, and does not cause excessive wear of tooth structure. Cast gold prostheses have proven to be the most durable compared with all other materials used for indirect restorations.

A high gold concentration provides a warm, esthetically attractive hue, superb tarnish and corrosion resistance, excellent ductility, minimal abrasiveness, and superb wear resistance for its alloys. Gold is useful to raise the thermal expansion coefficient (TEC) of palladium alloys. Palladium has a higher melting point than gold and a higher modulus of elasticity. The thermal expansion coefficient (TEC) of palladium is too low for it to be used with most commercial porcelains, so elements such as silver are needed to raise the TEC of palladium alloys. On the other hand, palladium is used to lower the TEC of gold-based PFM alloys.

Palladium whitens gold alloys markedly. It raises the melting range of gold alloys as well as their elastic modulus, strength, and hardness. Palladium lowers the density of gold alloys. Small amounts of palladium improve the tarnish and corrosion resistance of Au-Ag-Cu crown and bridge alloys, especially of alloys containing less than 68% Au. Gold and palladium are completely soluble in one another and they are

common components in many noble PFM alloys because they offset each other's limitations. Gallium is used primarily in Pd-based PFM alloys. Gallium strengthens these alloys and decreases their melting range.

Platinum (Pt) is used primarily in yellow-gold PFM alloys to increase the melting range, hardness, strength, and elastic modulus. Like palladium (Pd), it also decreases the TEC of gold alloys. Additions of Pt affect the properties of gold alloys to a lesser extent compared with Pd. However, Pt has less of an effect on changes in the color of alloys with high gold content.

Silver is added to Au-Ag-Cu casting alloys to offset the reddish hue contributed by Cu. However, Ag-rich Au-Ag-Cu alloys tend to have a slightly greenish hue. In Pd-based PFM alloys, Ag is used primarily to raise the thermal expansion coefficient (TEC). Silver decreases the melting range of both Pd and Au alloys. It also tends to improve the flow of casting alloys and solders. However, Ag has been reported to cause a greenish-yellow discoloration of some dental porcelains, although this phenomenon of "greening" does not appear to be a problem with current porcelains.

Copper strengthens and reddens Au-Ag-Cu crown and bridge alloys. However, it is not used in alloys with high gold contents because, like Ag, it also tends to discolor porcelain. It is added to Pd-based PFM alloys to increase their TECs. However, higher Cu contents produce dark-colored oxide layers that may adversely affect the esthetics of metal-ceramic (PFM) restorations. Copper does not seem to cause porcelain discoloration if it is alloyed primarily with Pd. Cobalt has been used as an alternative to Cu in Pd-based PFM alloys. However, like Cu, it also forms dark-colored oxides.

Zinc is added to crown and bridge alloys as an oxygen scavenger, thereby reducing gas porosity in castings. For PFM alloys, zinc can be added also to strengthen and harden the alloys and/or to increase the TEC. It also decreases the melting range.

Indium (In) is used in some Au-Ag-Cu casting alloys to improve their castability. In Au- and Pd-based alloys, it strengthens and hardens the alloys, increases their TECs, and decreases their melting temperature range. It also contributes to the formation of a bonding oxide in PFM alloys. Tin also contributes to the formation of a bonding oxide and it strengthens and hardens Au- and Pd-based PFM alloys. It also decreases the melting range of Au-based and Pd-based alloys and increases the TECs of these alloys.

Iron is used primarily to strengthen Au-Pt alloys for PFM applications. Like Sn and In, it also forms a bonding oxide.

Three noble elements that are used to refine the **grain** structure of alloys are iridium (Ir), rhenium (Re), and ruthenium (Ru). Grain refinement restricts the growth of grains during solidification. Smaller grains block dislocation movement from grain to grain, resulting in increased yield strength.

? CRITICAL QUESTION

Why do dental alloys begin freezing by **heterogeneous nucleation** rather than by **homogeneous nucleation**?

SOLIDIFICATION AND MICROSTRUCTURE OF CAST DENTAL ALLOYS

If a pure metal is melted and cooled to room temperature, a graph of its temperature-versus-time behavior during cooling would look similar to that in Figure 5-2. The temperature decreases steadily from point A to point B′. An increase in temperature then occurs from point B′ to point B, at which time the temperature remains constant until the time indicated at point C is reached. Subsequently, the temperature of the metal decreases steadily to room temperature (D).

The temperature, T_f, indicated by the straight or "plateau" portion of the curve at BC is the solidification temperature of the pure metal. This is also the melting point or fusion temperature. During melting, the temperature remains constant. During freezing or solidification, heat is released as the metal changes from a high-energy liquid to a low-energy solid. This energy difference is the latent heat of solidification and is equal to the heat of fusion. It is defined as the number of calories of heat liberated from 1 g of a substance when it transforms from a liquid to a solid.

At temperatures above T_f (i.e., above the plateau BC), the metal is molten. Below point C, all temperatures are associated with the solid metal. The initial cooling of the liquid metal from T_f to point B′ is termed *supercooling*. During the supercooling process, crystallization of the pure metal begins. Once the crystals begin to form, the release of the latent heat of fusion causes the temperature to rise to T_f, where it remains until crystallization is completed at point C. Supercooling of pure metals occurs only in clean, inert containers under circumstances in which heterogeneous nucleation of metal crystals is not possible.

The fusion temperatures of metals and alloys and their solidification behavior are important to the dentist and the dental laboratory technician. Typically, an exact wax or plastic replica of the prosthesis form is prepared initially. Using a highly accurate dental investment, an expanded mold is

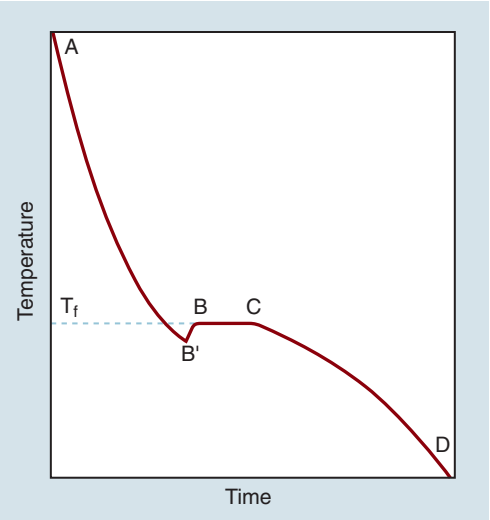


FIGURE 5-2 A time-temperature cooling curve for a pure metal, illustrating supercooling.

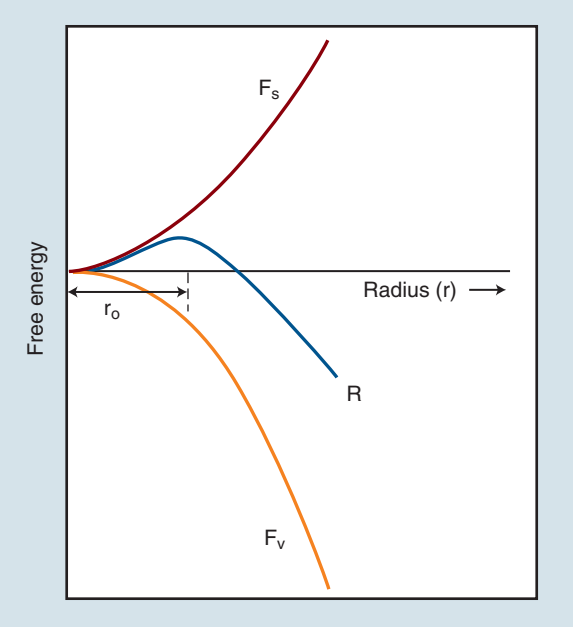


FIGURE 5-3 Free energy of formation of a nucleus as a function of its radius. F_V is the volume free energy of the embryo, F_S is the free surface energy, and R is the resultant free energy.

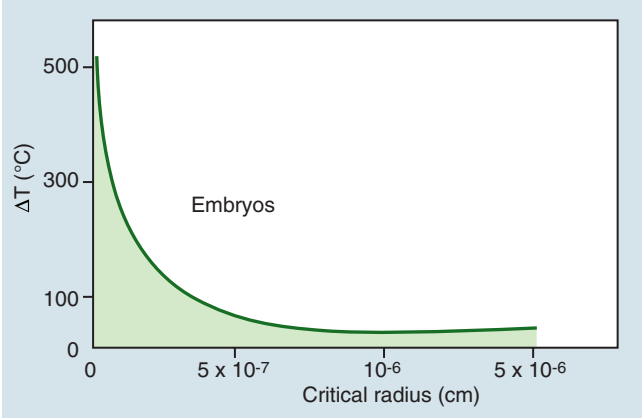


FIGURE 5-4 The critical nucleus radius of copper as a function of the degree of supercooling. ΔT denotes the number of degrees of supercooling below T_f (584 °C). The shaded area represents nuclei; the unshaded area represents the embryos. (From Chalmers B: Principles of Solidification, Wiley New York, 1964).

prepared from the pattern, into which the molten alloy is cast under pressure. When the alloy solidifies, it shrinks and the original pattern is precisely reproduced as a cast metal structure.

NUCLEUS FORMATION

Although the surface tension of liquid metals is approximately 10 times greater than that of water, the structures of liquid metals do not differ significantly from those of other liquids. Atoms of a metal migrate in the liquid state at a rapid rate that is related to its diffusion coefficient of approximately 10^{-5} cm^2/s. Liquid metals do not differ in structure from one another as much as do solid metals, and these relationships change. Figure 5-3 illustrates this solidification process from the viewpoint of thermodynamics. Solidification begins with the formation of embryos in the molten metal—i.e., small clusters of atoms that form nuclei of crystallization that have the same arrangement as the long-range atomic order found in the solidified metal. At temperatures above the fusion temperature (T_f), these embryos will also form spontaneously in the molten metal, but they are unstable, since the liquid state has a lower free energy than the solid state.

CRITICAL QUESTION

What are the contributions of the surface free energy and the volume free energy to the overall free energy of these embryos as a function of the embryo size?

The surface free energy (F_S) of an embryo is greater than its internal energy because the unequal attraction of the surface atoms tends to draw these atoms closer together and the surface tension increases. Thus work is required to create the surface of an embryo (atom cluster), which is the basis of the surface energy contribution. This surface free energy increases as the square of the embryo radius. The volume free energy contribution (F_V) is the difference between the free energies of the solid and liquid states, and the solid state has a lower free energy when the temperature is below the equilibrium freezing (solidification) temperature (T_f). Thus F_V becomes increasingly negative and more energetically favorable as the temperature of the supercooled liquid is decreased below T_f. For a given temperature below T_f, F_V varies as the third power of the spherical embryo radius.

At a specific temperature of the supercooled liquid metal, the overall, resultant (R) free energy of an embryo as a function of its radius is the sum of the surface free energy (positive) and the volume free energy change (negative) contributions. For small values of the embryo radius, the curve for R in Figure 5-3 illustrates that small F_S dominates and the overall free energy for the formation of the embryo is positive or energetically unfavorable. As the embryo radius increases, F_V dominates and the overall free energy of the embryo is negative (i.e., energetically favorable). There is a critical **nucleus** size, designated as r_o in Figure 5-3, which corresponds to the maximum point in total free energy of the embryos as a function of the radius. For an embryo of radius (r_o), the overall free energy (R) decreases upon the addition of another atom and continues to decrease as the embryo grows. Thus, embryos with radii smaller than r_o are unstable and spontaneously form and disappear in the liquid metal, whereas embryos with radii larger than r_o become stable nuclei and continue to grow during the solidification process.

The greater the amount of supercooling, or the greater the rate of cooling below T_f, the smaller is the critical radius r_o because the value of F_V for a given embryo size becomes increasingly negative. The value of F_S per unit area is not greatly affected by the amount of supercooling. This effect is shown in Figure 5-4, which illustrates the small values of r_o

that occur during the solidification of metals. Hence, an increasing number of embryos become stable as supercooling increases, and these embryos have reduced surface energy because of their decreased radii. If the molten metal is cooled so rapidly that solidification occurs at a much lower temperature than T_f, there is a tendency for many small, stable nuclei of solidification to form. This process of nucleus formation in the bulk liquid metal is called homogeneous nucleation, since it occurs in the absence of a surface that would promote heterogeneous nucleation.

Homogeneous nucleation is a random process, having an equal probability of occurring at any point in the molten metal. The surface energy of the embryos must be reduced for the atoms to contact and wet the surface of particles in the molten metal or areas on the mold surface. During this process the surface area of the embryo in contact with the molten metal is reduced, the surface energy decreases, and stable embryos are formed. This mechanism is controlled by seeding the nuclei with impurities on the mold wall. When pure gold solidifies, fine particles of gold diffuse into the molten metal and cause nucleation. In this way, imperfections in the mold walls, particles of dust, and other impurities in the molten metal can produce heterogeneous nucleation of crystals.

? CRITICAL QUESTION

Why does the grain size of a cast dental alloy significantly decrease when the rates of cooling and solidification increase?

LIQUID-TO-SOLID TRANSFORMATION OF CAST METALS

Pure metals crystallize from nuclei in an elongated, dendritic pattern that resembles the branches of a tree. As liquid metal cools and solidifies, crystals are formed by diffusion of atoms from the molten metal to existing nuclei of crystallization. The crystals also grow by atomic diffusion in random patterns within the crystal structure, and structural imperfections are formed randomly throughout the structure. Extensions form spontaneously on the advancing front of the solidifying metal that grow into cooler regions of the mold cavity, typically along areas of the mold wall that cool the fastest. The temperature is higher in the liquid adjacent to the solidifying metal. Extensions of the solid grow rapidly in the adjacent supercooled regions that lie farther away in the molten metal, and such growth occurs along certain crystallographic directions. The heat that is released by the solidifying metal lowers the amount of supercooling at the liquid-solid interface. This heat impedes growth in regions adjacent to the solid extensions and highly elongated crystals are formed. Subsequently a similar growth process occurs at lateral sites along the extensions, and later growth extends to lateral sites along the secondary branches, resulting in a three-dimensional dendritic structure.

Dendrite formation occurs during solidification of alloys because of constitutional supercooling, which is discussed in a subsequent section. Shown in Figure 5-5 is a dendritic structure of a polished and etched cast palladium-based alloy. The light areas are the dendrites, and the dark areas are

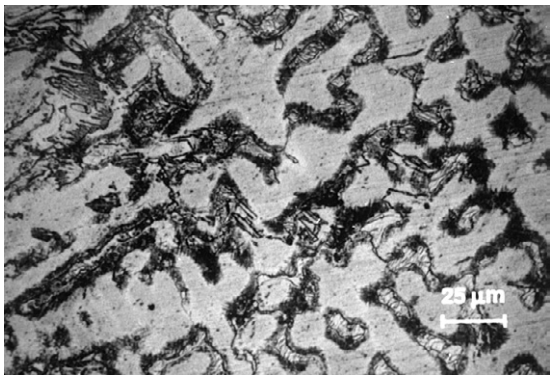


FIGURE 5-5 Optical microscopic image of a polished and etched palladium-based alloy with a dendritic as-cast microstructure. (From Carr AB, Brantley WA: New high-palladium casting alloys: Part 1. Overview and initial studies. *Int J Prosthodont* 4:265, 1991. Reproduced with permission from Quintessence Publishing Company, Inc.)

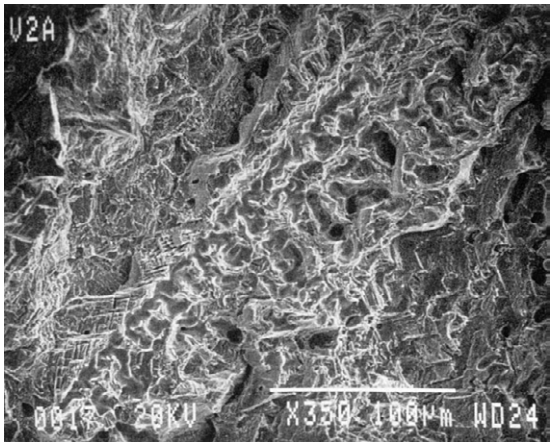


FIGURE 5-6 SEM image of the fracture surface of a cast base metal alloy for removable partial denture frameworks, showing the pattern of crack propagation in the dendritic microstructure. (From Bridgeport DA, Brantley WA, Herman PF: Cobalt-chromium and nickel-chromium alloys for removable prosthodontics, Part 1. Mechanical properties of as-cast alloys. *J Prosthodont* 2:144, 1991. Reproduced with permission.)

interdendritic regions. These **dendritic microstructures** are not desirable in cast dental alloys because interdendritic regions serve as sites for crack formation and propagation. Illustrated in Figure 5-6 is the fracture surface of a cast tensile test specimen of a base metal alloy. Microcracks, called "hot tears," form at elevated temperatures in thin cast areas of these alloys. This process occurs when there is insufficient metal thickness to resist the stresses caused by the casting investment during solidification. To avoid hot tears, castings must have adequate thickness, and alloys should have equiaxed grains in the as-cast condition rather than a dendritic structure. A lower burnout temperature can also minimize hot tearing because the alloy will have greater strength at lower mold temperatures.

Although predominantly base metal (PB) alloys for dental prostheses typically solidify with a dendritic microstructure, most high noble (HN) and noble (N) metal casting alloys

solidify with an equiaxed polycrystalline microstructure, such as that shown in Figure 5-7. The microstructural sections in this figure are called grains (crystals), and the term *equiaxed* means that the three dimensions of each grain are similar, in contrast to the elongated shape and size of the dendrites in Figures 5-5 and 5-6. The grains in Figure 5-7 have dimensions ranging from approximately 10 to 20 μm (micrometers or microns).

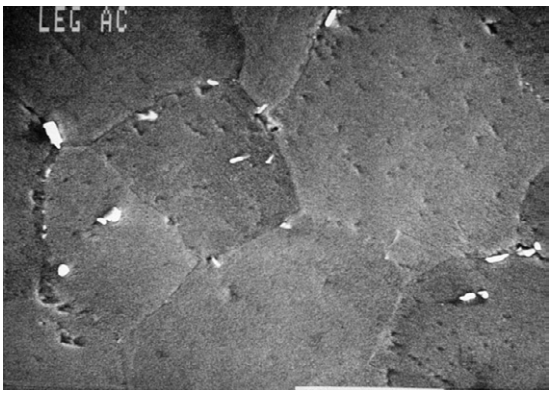


FIGURE 5-7 SEM image of a polished and etched high-palladium alloy with an equiaxed fine-grain as-cast microstructure. The white-appearing particles are ruthenium-rich and arise from the use of ruthenium as a grain-refining element. (From Brantley WA, Cai Z, Foreman DW, et al: X-ray diffraction studies of as-cast high-palladium alloys. *Dent Mater* 11:154, 1995. Reproduced with permission.)

Shown in Figure 5-8, *A*, is a schematic illustration of the coalescence of individual grains to form an equiaxed grain structure. Solidification starts from isolated nuclei in the molten metal, and these crystals gradually grow by the clustering of atoms and the crystals extend toward each other. When the adjacent crystals eventually contact one another, their growth stops, as shown in Figure 5-8, *E*. The final microstructure is shown in Figure 5-8, *F*.

The grain boundaries in a solidified metal are revealed by polishing and etching of the cast metal surface by a specific solution for a given time. Successively finer abrasives (typically aluminum oxide or silicon carbide) are used following the initial rough grinding stage. Abrasive particles embedded in polishing papers are used initially and subsequent polishing stages are performed with slurries made from a mixture of water and abrasive powders. For the final polishing stage, an abrasive with a particle size of 0.05 μm is often used, since the width of the resulting scratches will be about an order of magnitude smaller than the wavelength of visible light. Thus these fine scratches will not be visible in the optical microscope. The chemical or electrolytic etching solution preferentially removes atoms and creates grooves at the grain boundaries, because these atoms have a higher energy compared with atoms in the interiors of grains. Thus, the grain boundaries have a darker appearance than the bulk grains in the optical microscope because of light scattering by these grooves. Similarly, differences in electron scattering by the

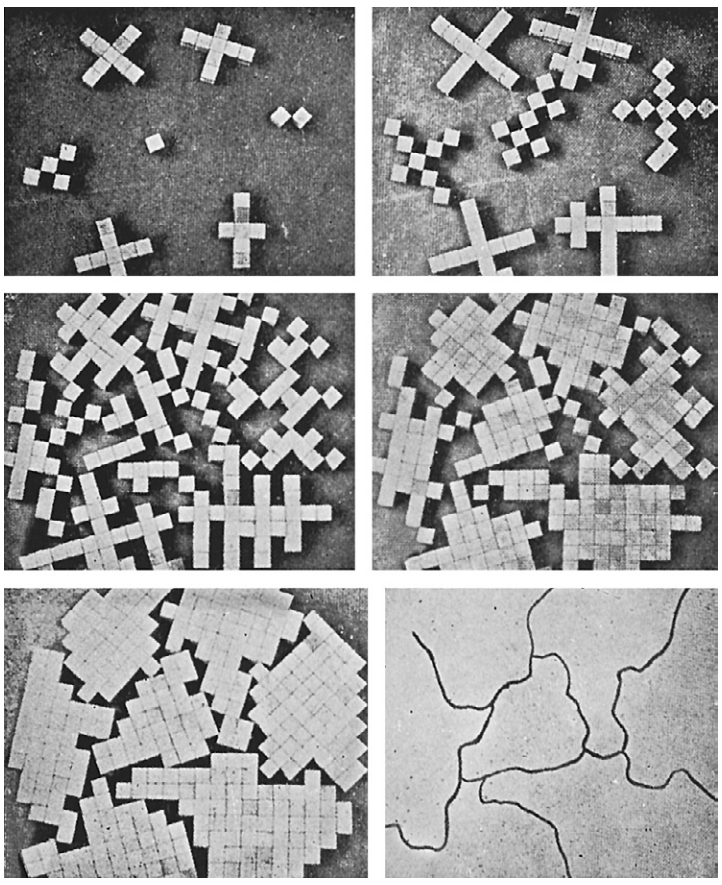


FIGURE 5-8 Stages in the formation of metallic grains during the solidification of a molten metal. (From Rosenhain W: *Introduction to Physical Metallurgy*, ed 3, London, 1935, Constable and Co, Reproduced with permission.)

grain boundaries and bulk grains in etched metals can be seen in a scanning electron microscope. Each grain represents a microscopic single crystal that has a different orientation from those of adjacent grains.

As shown in Figure 5-8, *E*, the regular atom arrangement in a cast metal becomes discontinuous at a **grain boundary**. As is true also for wrought metals, the movement of dislocations along their atomic slip planes during permanent deformation of ductile dental alloys continues until the dislocations meet a grain boundary. Since dislocations cannot progress along atom planes into adjacent grains because of their misalignment of the planes with those of adjacent grains, they will subsequently accumulate at the grain boundaries. When this occurs, further deformation in these regions will require greater stress, and strain hardening will occur. Strain hardening, also called work hardening, leads to increased strength and decreased ductility (increased brittleness). The grain boundaries are the final sites at which a molten metal solidifies during the formation of an equiaxed grain structure. The grain boundaries also accumulate low-melting phases, precipitates, and porosity. These structural features also appear in the interdendritic regions of dental alloys with a cast dendritic microstructure such as that shown in Figure 5-5.

? CRITICAL QUESTION

How does the grain size affect the properties of cast dental alloys?

GRAIN REFINEMENT AND GRAIN SIZE

Noble metal casting alloys for dental prostheses generally have equiaxed fine-grain microstructures because they contain small concentrations of iridium (Ir), ruthenium (Ru), or rhenium (Re) as grain-refining elements. The grain size of high noble (HN) and noble (N) metal casting alloys controls the yield strength of engineering alloys, which varies inversely with the square root of grain size (Hall-Petch relationship). Fine grain sizes of noble metal alloys are promoted by rapid solidification conditions that occur during dental casting because the time during which solidification occurs is inadequate for the growth of large crystals. The compositional uniformity and corrosion resistance of a cast dental alloy will be superior for a fine grain size because there is less opportunity for microsegregation.

Dental base metal (PB) and titanium-based casting alloys, in which nickel (Ni), cobalt (Co), iron (Fe), and titanium (Ti) are the principal elements, typically have dendritic as-cast microstructures. Dendritic microstructures form during the freezing of pure metals by thermal supercooling. During such processes, crystals are nucleated along the investment walls and dendrites grow perpendicular to the walls toward the center of the mold cavity.

? CRITICAL QUESTION

Why should a dentist or lab technician consider both the weight percent and the atomic percent of potentially toxic elements when selecting an alloy for dental prostheses?

Most dental casting alloys solidify from a liquid to a liquid-plus-solid phase at a lower temperature i.e., the liquidus temperature, and then to a solid phase at the solidus temperature. The liquidus temperature is the lowest temperature at which all components of an alloy can be in a liquid state. In a specific temperature range, the solid and liquid phases coexist in equilibrium rather than at a single temperature, as in a pure metal. The concentration of each element can be expressed as a weight percentage (wt%) or as an atomic percentage (at%). As an example, the $AuCu_3$ phase, which can form during slow cooling of molten Au-Cu alloys in a specific composition range, contains 51 wt% Au and 49 wt% Cu, but on an atomic basis, it contains 25 at% Au and 75 at% Cu. The compositions of the principal elements in dental alloys as listed on material safety data sheets (MSDS) or on IdentAlloy certificates are usually specified in weight percent.

Another example of the difference between atomic and weight percentages occurs with predominantly nickel-based alloys that contain a small amount (1.8 wt%) of beryllium (Be), which is a relatively toxic element. However, these Ni-Cr-Mo-Be alloys contain approximately 11 at% when reported on an atom basis. For alloys with elements that differ considerably in atomic weight, the weight percentage composition and atomic percentage composition will differ substantially. Usually, the properties of an alloy relate more directly to the atomic percentage rather than the weight percentage of each element.

SOLID SOLUTIONS

The majority of noble metal casting alloys for dental restorations are based on solid solutions. An important example is the palladium-silver (Pd-Ag) **alloy system**. When this alloy is solidified, the silver atoms are distributed randomly in the FCC structure of pure palladium, thereby forming a solid solution. Because the silver atoms become integrated into the crystal structure of palladium, no microstructural features can be mechanically separated into two or more phases, so only one solid phase is present. However, the atoms of silver may not be randomly located in the palladium crystal structure when a dental casting is cooled rapidly and the atom species may be segregated. To produce a homogeneous structure, heat treatment at elevated temperatures for sufficiently long times promotes solid-state diffusion that ensures the uniform distribution of palladium and silver atoms.

SOLUTES AND SOLVENTS

When two metals are mutually soluble in the solid state, the solvent is that metal whose crystal structure is retained over the composition range of interest. In palladium-silver (Pd-Ag) alloys, the two metals are completely soluble in all proportions and the same type of crystal structure occurs throughout the alloy system (i.e., all compositions of the two elements). In such a case, the solvent is defined as the metal whose atoms occupy the majority of the total number of positions in the crystal structure.

There are two principal atomic arrangements for binary solid solutions. One of these is the substitutional solid solution in which the atoms of the solute metal occupy the positions in the crystal structure that are normally occupied by the solvent atoms in the pure metal. For a Pd-Ag alloy in which Pd is the solvent metal, Ag atoms replace the Pd atoms randomly in the crystal structure. Another type of solid solution is the interstitial solid solution. In this case, the solute atoms are present in random positions (interstices) between the atoms in the crystal structure of the solvent metal. This type of solid solution usually requires that the solute atoms be much smaller in diameter than the solvent atoms, and these solid solutions are usually limited to relatively small concentrations of solute. The interstitial solid solution of carbon in iron is important, since it forms the basis for the family of carbon steels. Commercially pure titanium (CPTi), which is important for implants and restorative dentistry, consists of high-purity (99 wt% or higher) titanium, with oxygen, carbon, nitrogen, and hydrogen atoms dissolved interstitially. These concepts can also be extended to solid solutions in which atoms of several solute metals are randomly located in the crystal structure of the solvent metal.

In Au-Cu substitutional solid solutions, the solvent and solute atoms have some affinity for each other at lower temperatures, such that a random arrangement of Au and Cu atoms represents a higher energy state than if the atoms were ordered with like nearest neighbors. At high temperatures, Au-Cu alloys are disordered solid solutions with an FCC crystal structure (Figure 5-9, *A*). If an alloy containing 50.2 wt% Au and 49.8 wt% Cu is allowed to cool slowly below 400 °C, the $AuCu_3$ structure forms, in which the Au atoms are located at the corners of the FCC unit cells and the Cu atoms are located at the centers of the faces (Figure 5-9, *B*). This unit cell is equivalent to $AuCu_3$, since two adjacent unit cells share each of the six Cu atoms at the centers of each of the six faces of the cube and eight unit cells share each of the eight Au corner atoms. This ordered structure is called a superlattice.

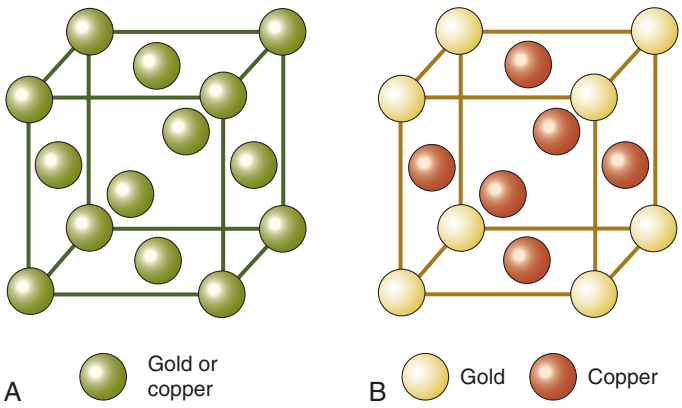


FIGURE 5-9 Structure of $AuCu_3$. In a unit cell of the face-centered cubic crystal structure for a disordered gold-copper substitutional solid solution (**A**), the positions of the gold atoms cannot be distinguished from the positions of the copper atoms. In the superlattice or ordered arrangement (**B**), the gold atoms are situated at the corners and the copper atoms are on the faces of the cube.

The structure of $AuCu_3$ has a simple cubic structure rather than an FCC structure because the symmetry of the Au crystal structure is lost because of the presence of the Cu atoms.

CONDITIONS FOR SOLID SOLUBILITY

For two or more species to be mutually soluble in solid solution, several conditions must be satisfied, including atom size difference, valence, type of crystal structure, and the potential for solvent atoms to become ordered. The average distance between solvent atoms in a substitutional solid solution changes in response to the diameters of the solute atoms. If the sizes of two metallic atoms differ by less than approximately 15%, they possess a favorable size factor for solid solubility. If the size is greater than 15%, multiple phases appear during solidification.

Solid solutions are more likely to form when the metal elements have the same valence. When the valences are different, the electron/atom ratio for the alloy is different. An alloy structure typically can tolerate only a small change in the value of the electron/atom ratio before transforming to a different, lower energy structure. For example, alloys of copper with metallic elements of higher valence have a lower maximum solid solubility as the solute valence increases.

If elemental species have a high degree of chemical affinity, they tend to form an intermetallic compound during solidification rather than a solid solution. Metals such as Au and Cu, which have some chemical affinity for each other, form ordered structures at lower temperatures.

Solid solutions in an alloy can form metals only when they contain the same type of crystal structure. For example, the Au-Cu and Pd-Ag alloy systems for cast metal prostheses form a continuous series of solid solutions, in which all alloys have the FCC structure.

Although the diameter of a Cu atom differs as much as 12% from that of Au, Ag, Pd, and Pt atoms in dental gold casting alloys for all-metal prostheses (Table 5-2), Cu promotes significant strengthening of these alloys. Copper forms a limited series of solid solutions with silver. Complete solid solubility of Cu in Au and Pd occurs at high temperatures. During cooling to a lower temperature range, ordering takes place for some Au-Cu compositions, as occurs in the $AuCu_3$ superlattice.

According to Table 5-2, the difference between the atomic diameters of Ag and Sn is approximately 4%. However, these two metals differ in valence and have different crystal structures, so there is limited solid solubility for Sn in Ag. As the Sn content increases, an intermetallic compound (Ag_3Sn) forms, which is an important residual phase in high-copper dental amalgams.

PHYSICAL PROPERTIES OF SOLID SOLUTIONS

If a larger solute atom is substituted for a solvent atom in the atomic structure of a metal, localized distortion occurs and dislocation movement is impeded, as discussed for wrought alloys in 17. As a result, strength, proportional limit, and hardness are increased and ductility is usually decreased. The

effects of this solid-solution strengthening are similar to those achieved by cold working.

Pure Au is not useful for low-stress areas of restorations unless it is strain-hardened, as occurs when direct-filling gold is formed into a prepared tooth preparation. Although pure gold in the cast condition is too weak for restorations, adding only 5% of copper will provide adequate strength and hardness to the Au-Cu alloy that are sufficient for the casting to be used for small inlays. Solid solution strengthening of an alloy increases with greater concentrations of the solute atoms and with increasingly dissimilar sizes of the solvent and solute atoms up to the solid solubility limit. For binary alloys that form solid solutions, the maximum hardness is reached at concentrations of approximately 50% for each metal.

TABLE 5-2 **Atom Size and Unit Cell Structure of Dental Alloy Elements**

Element	Atom Radius (angstroms)	Crystal Structure
Aluminum	1.431	Face-centered cubic
Cobalt	1.253	Hexagonal close-packed
Copper	1.278	Face-centered cubic
Chromium	1.249	Body-centered cubic
Gallium	1.360	Orthorhombic
Gold	1.442	Face-centered cubic
Iron	1.241	Body-centered cubic Face-centered cubic
Molybdenum	1.263	Body-centered cubic
Nickel	1.246	Face-centered cubic
Platinum	1.387	Face-centered cubic
Palladium	1.375	Face-centered cubic
Silicon	1.175	Diamond cubic
Silver	1.445	Face-centered cubic
Tin	1.508	Body-centered tetragonal
Titanium	1.445	Body-centered cubic
Tungsten	1.371	Body-centered cubic
Zinc	2.665	Hexagonal close-packed

CRITICAL QUESTION

Why is the study of binary-phase diagrams important, even though dental alloys contain more than three elements and conditions during solidification and cooling after casting are far removed from equilibrium?

EQUILIBRIUM-PHASE DIAGRAMS

Equilibrium- or constitution-phase diagrams are useful to identify the phases present in an alloy system for different compositions and temperatures. The diagrams shown in this chapter are primarily for two-element alloys. For three-component alloy systems, a 3-D phase diagram would be much more complex. Nevertheless, binary-phase diagrams are useful for understanding the structure of dental alloys and they can provide microstructural predictions when cast dental alloys are subjected to heat treatment.

For a solid solution alloy system made of proportions of metal A combined with metal B, all possible combinations of A and B, ranging from 100% A to 100% B, A and B are completely soluble at all compositions in both the solid and liquid states. Figure 5-10 represents the Pd-Ag phase diagram. These two metals exhibit complete solubility in both liquid and solid

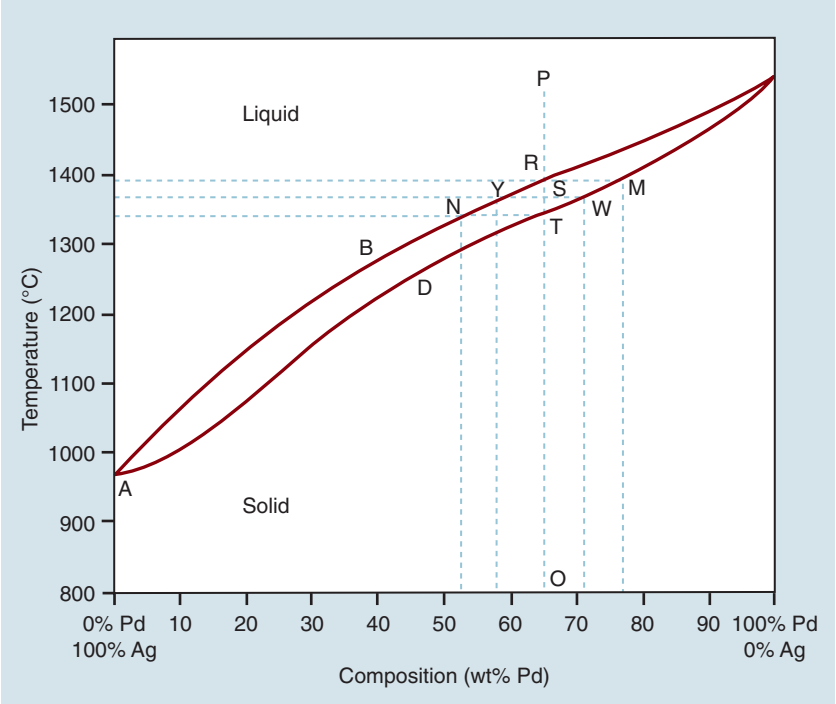


FIGURE 5-10 Equilibrium-phase diagram for the palladium-silver system showing percentages by weight. Only the percentage composition for palladium is given; the percentage composition for silver is determined by subtracting the palladium composition from 100.

states. Note the liquid, liquid-plus solid, and solid regions separated by the liquidus and solidus curves.

INTERPRETATION OF THE PHASE DIAGRAM

Consider the cooling of an alloy containing 65% Pd and 35% Ag, as indicated by the dashed line PO, which is perpendicular to the baseline or composition axis (Figure 5-10). At the point where PO corresponds to the temperature of 1500 °C, the alloy is in the liquid state. When the temperature decreases to approximately 1400 °C, line PO intersects the liquidus curve at point R and the first solid forms. However, the composition of these first crystals is different from the 65% Pd and 35% Ag parent alloy. To determine the composition of the first solid that forms, observe tie line RM extending from point R on the liquidus curve to point M on the solidus curve. Thus, the composition of the first solid that forms at point M is 77% Pd, compared with the composition of 65% Pd for the liquid phase at point R.

When the temperature decreases to approximately 1370 °C, denoted by point S, the alloy is about midway through its solidification temperature range (1340 to about 1400 °C). The compositions of the solid and liquid may be determined by drawing the line YW and locating its points of intersection (Y and W) with the liquidus and solidus curves, respectively. The approximate composition of the liquid is 57% Pd, as shown by the projection of point Y on the baseline, and that of the solid is 71% Pd, determined by projecting point W to the baseline. At the temperature corresponding to point T (approximately 1340 °C), the last portion of liquid that solidifies has the composition of 52% Pd (point N). The solid phase contains 65% Pd (point T). In the absence of grain-refining elements, the alloy will solidify in a dendritic structure.

When the temperature decreases below point T, the liquid-plus-solid phases become a solid with a Pd composition of 65%. When an alloy composition undergoes solidification, the percentages of the liquid and solid phases that are present at a given temperature can be calculated by the lever rule. For example, at 1370 °C, the weight percentage of liquid phase is calculated by dividing segment length SW by the length of the tie line YW, expressed as a percentage of approximately 44%. Thus, the amount of solid phase that forms at this temperature under equilibrium conditions is 56%.

To determine the percentages of two phases in equilibrium at a given temperature, the point of intersection of the vertical line for the alloy composition with the tie line across the two-phase field becomes the fulcrum. Then the ratio of the length of the tie line segment opposite a given boundary curve to the total length of the tie line connecting the two boundary curves is the percentage of the phase whose composition limit is defined by the given boundary curve. For example, in the liquid-plus-solid phase region at about 1370 °C, the fulcrum is at point S and the weight percentage of the solid phase at this temperature is the length YS divided by length YW.

Because Figure 5-10 represents an equilibrium-phase diagram, the calculated weight percentages are based on the assumption that the alloy has been held at sufficient times and temperatures for atomic diffusion to achieve equilibrium conditions. If this condition is satisfied, the composition of the alloy crystals (grains) is the same at any point in the alloy.

? CRITICAL QUESTION

Why is the development of microsegregation in cast alloys more pronounced when there is a greater difference between the liquidus and solidus temperatures?

CORING AND HOMOGENIZATION HEAT TREATMENT

It is evident from Figure 5-10 and Table 5-3 that the composition of a rapidly cooled dendrite will not be uniform. For example, the first stable nucleus that forms at the temperature R (or slightly below) in Figure 5-10 contains 77 wt% palladium (Pd). As the temperature decreases, the Pd content decreases in each succeeding "layer" that solidifies on this nucleus, and the silver (Ag) content increases as the solidification temperature (on the solidus curve) is reached.

At the solidus temperature T in Figure 5-10, the composition of the outermost layer of the dendrite is 65% Pd and 35% Ag. In the **coring** process, the last liquid to solidify is richer in Ag (point N) as it solidifies between the dendrites. Thus, under rapid solidification conditions, the alloy has a cored structure. The core consists of dendrites composed of compositions that developed at higher solidus temperatures, and the matrix is the portion of the microstructure between the dendrites that contains compositions that developed at lower solidus temperatures.

A cored structure is shown in Figure 5-11, *A*, for an as-cast Cu-Ag alloy. The light, relatively broad microstructural features are the dendrites (core) that have higher melting temperatures. The dark, narrow features are the interdendritic regions (matrix), which have lower melting temperatures. Compare the structural features of Figure 5-11, *A*, with those of Figure 5-5. A homogenization heat treatment, which promotes atomic diffusion, can eliminate as-cast compositional difference and produce equiaxed grains as shown in Figure 5-11, *B*. Also shown are small dark spots, which are casting porosity defects and precipitate particles that formed during the heat treatment. The microstructure of Figure 5-11, *A*, is

TABLE 5-3 Liquid and Solid Phases in a Palladium-Silver Alloy as a Function of Temperature*

	PALLADIUM CONCENTRATION (WT%)	
Temperature (°C)	**Liquid Phase**	**Solid Phase**
1500	65	Not present
1400	65	77
1370	57	71
1340	52	65
900	Not present	65

*Palladium 65% and silver 35% by weight. Refer to Pd-Ag phase diagram in Figure 5-10.

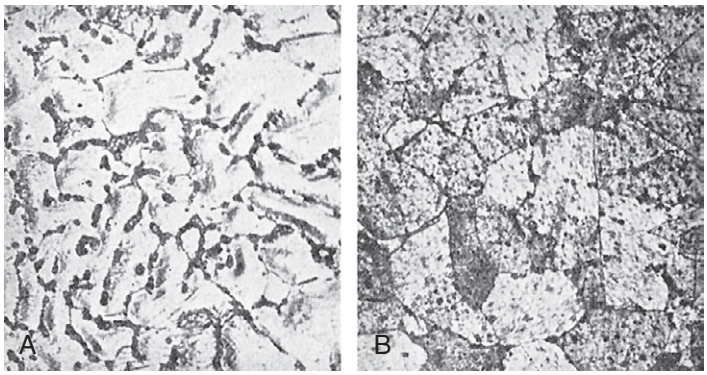


FIGURE 5-11 **A,** Copper-silver alloy (1%) as cast. **B,** The same cast alloy after homogenization heat treatment (×100).

typical of dental base metal alloys, which generally have dendritic as-cast microstructures. Some noble alloys for metal-ceramic applications, which have equiaxed polycrystalline as-cast microstructures, show substantial microsegregation, in which the solidified grains have nonuniform compositions and the grain boundaries have an indistinct form in the etched microstructure. Homogenization heat treatment will reduce microsegregation as can be confirmed by the appearance of distinct grain boundaries in the microstructure.

To homogenize the cast structure, it must be heated near its solidus temperature to promote the most rapid diffusion without melting. The alloy in Figure 5-11, *B*, was homogenized for 6 hours. Little grain growth occurs when a casting receives this type of heat treatment because the grain boundaries are immobilized by secondary or impurity elements and phases. Higher temperatures are employed than would be used for isothermal heat treatment (annealing) of a wrought alloy.

An inhomogeneous dental gold alloy is more subject to tarnish and corrosion than the same alloy after homogenization. This is also important for Ag-Pd alloys, since silver-rich phases tend to tarnish readily in the oral environment. Alloys with heterogeneous microstructures have greater resistance to permanent deformation than alloys with homogeneous microstructures. Consequently the ductility of an alloy usually increases with a corresponding decrease in brittleness after a homogenization heat treatment.

CRITICAL QUESTIONS

What are the advantages and disadvantages of eutectic alloys? How do alloy compositions of binary eutectic systems affect their properties?

EUTECTIC ALLOYS

Eutectic alloys have several important applications in dentistry because they correspond to a composition with the lowest melting point in an alloy system. They are used in joining metal components through processes of brazing or soldering. The Ag-Cu eutectic composition is also used to produce spherical particles that are combined with Ag_3Sn lathe-cut particles to be reacted with mercury to form a dispersed-phase dental amalgam. Another example of the potential importance of eutectic compositions occurs near the pure Au end of the Au-Ir system, in which the eutectic composition at approximately 0.005% Ir has been considered important for grain refinement of dental gold casting alloys by iridium, one of the seven noble metal elements.

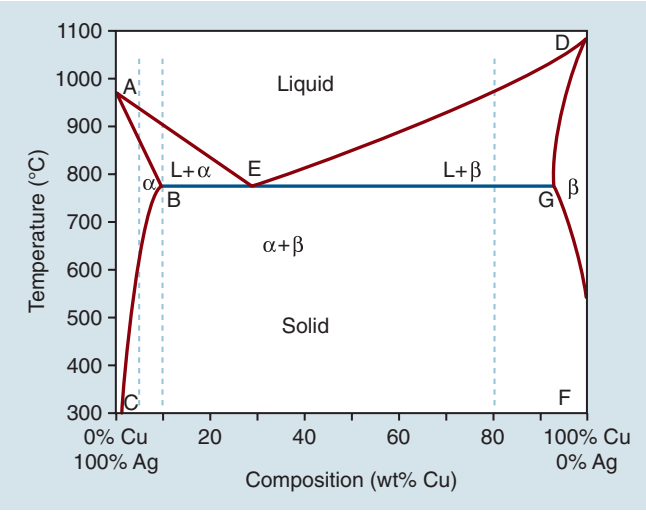


FIGURE 5-12 Equilibrium-phase diagram for the silver-copper system showing percentages by weight.

The eutectic system exemplifies alloys for which the component metals have limited solid solubility. Two metals, A and B, that are completely insoluble in each other in the solid state, provide an illustration of a eutectic alloy. In this case, some grains are composed solely of metal A and the remaining grains are composed of metal B. However, both metals are usually soluble in one another at least to some extent in the solid state. Therefore a binary eutectic system, in which the two metals are partially soluble in each other, is used for purposes of illustration. Such a system of interest in dentistry is the Ag-Cu system.

THE SILVER-COPPER SYSTEM

The phase diagram for the Ag-Cu system is shown in Figure 5-12, where three phases can be observed: (1) a liquid phase (L); (2) a silver-rich substitutional solid solution phase (α) containing a small percentage of copper atoms; and (3) a copper-rich substitutional solid solution phase (β)containing

a small percentage of silver atoms. The α and β phases are referred to as terminal solid solutions because of their locations at the left and right sides of the phase diagram. The solidus curve is the boundary line ABEGD. Note that no liquid phase exists below this line. The liquidus curve is AED, since there are no solid phases above this line. The major portion of the diagram below 780 °C is composed of a two-phase α-plus-β region, which represents a mixture of the silver-rich and copper-rich phases in the alloy microstructures.

The first difference to be noted in comparing Figure 5-12 with the solid solution system of Figure 5-10 is that the liquidus and solidus phases meet at composition E rather than at the pure metal composition in Figure 5-10. This composition, of 72% Ag and 28% Cu by weight, which corresponds to point E, is known as the eutectic composition, sometimes called simply the eutectic.

The temperature at which the eutectic composition melts (779 °C, corresponding to line BEG) is lower than the fusion temperature of 100% silver or 100% copper (*eutectic* means "lowest melting") and is the lowest temperature at which any alloy of silver and copper is entirely liquid.

There is no solidification range for composition E. The eutectic liquid composition solidifies at a single temperature even though the solid consists of two phases (α and β). Eutectic alloys are often used when a lower fusion temperature is desired, as for dental solders. However, as discussed later, eutectic alloys are inferior in other important respects to solid solution alloys.

A layered or lamellar structure is typically formed (Figure 5-13, *A*) when a binary eutectic solidifies because a minimal amount of diffusion is required to produce atom segregation, although rod-shaped eutectic structures have been observed for some alloys.

The eutectic reaction during cooling can be written schematically as follows:

$$\text{Liquid} \rightarrow \alpha \text{ solid solution} + \beta \text{ solid solution} \quad (1)$$

Another important aspect of the phase diagram in Figure 5-12 is the manner in which two portions (AB and DG) of the solidus slope toward the third portion, the horizontal line BEG. At the left side of the diagram, from A to B, the copper content of the silver-rich α phase varies from 0% to nearly 9%. At the right side of the diagram, from D to G, the silver content of the copper-rich β phase varies from 0% to approximately 8%. The phase diagram in Figure 5-12 contains solvus lines CB and FG, which are not present in phase diagrams for solid solution systems. Solvus line CB shows that under equilibrium conditions, the solid solubility of copper in the α phase increases from about 1% at 300 °C to nearly 9% at B. Solvus line FG shows that the equilibrium solid solubility of silver in the β phase increases from an extremely small value at 300 °C to a maximum of approximately 8% at point G.

The compositions of the phases that form during equilibrium cooling for the various alloys of silver and copper can be determined in the same manner as for solid solutions of silver and palladium (see Figure 5-10). As shown in Figure 5-12, if an alloy containing 10% Cu is melted at a temperature

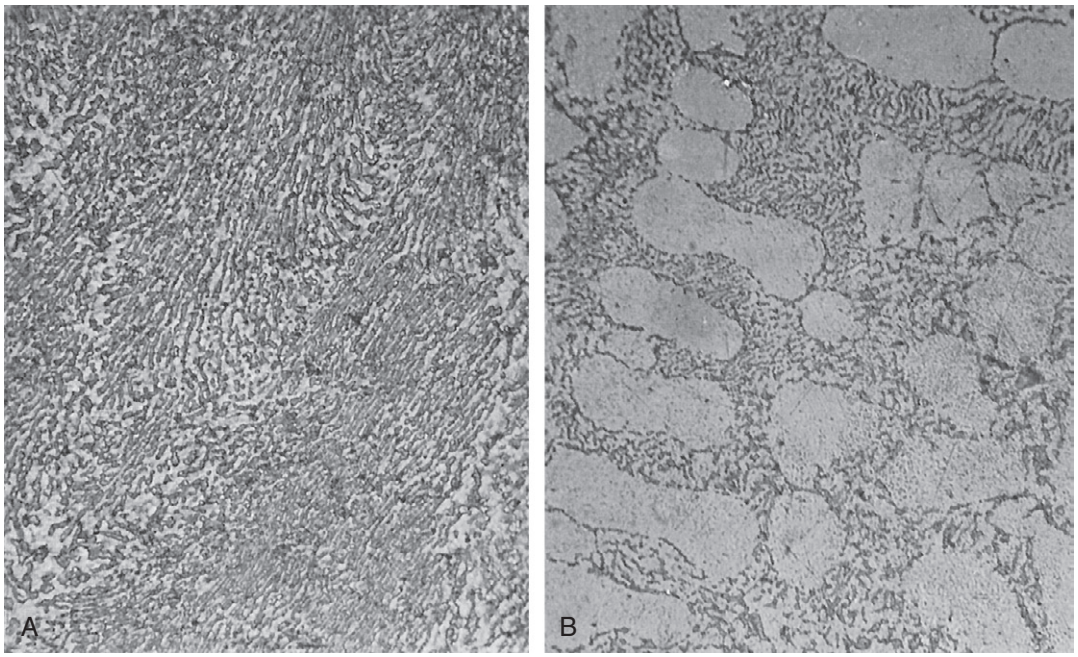


FIGURE 5-13 Microstructure of two lead-tin alloys. **A,** The alloy has the eutectic composition 62% Sn–38% Pb. The structure is composed of alternating layers (lamellae) of solid solution (*dark*) that is Pb-rich and β solid solution (*light*) that is Sn-rich (×1280). **B,** The alloy has a high tin content (75% Sn–25% Pb). The light islands are primary β phase, which solidified first. They are surrounded by the eutectic structure, which solidified when the eutectic temperature was reached (×560). (Courtesy of P. G. Winchell.)

above the liquidus and allowed to cool under equilibrium conditions (along the second dashed vertical line from the left of Figure 5-12), crystals of the first solid form in the liquid phase at approximately 900 °C at point B. If a horizontal tie line is drawn from the liquidus (AE) to the solidus (AB) from the point at which the dashed line crosses AE, one can see that this first solid is the α solid solution, which has an approximate composition of 4% Cu and 96% Ag.

When the temperature of this alloy decreases to 850 °C, another tie line drawn at this temperature between the solidus and liquidus indicates that all α solid solution crystals under equilibrium conditions have the approximate composition of 5% Cu and the remaining liquid has a uniform composition of approximately 15% Cu. When the temperature of the alloy reaches the eutectic temperature of 779 °C, the tie line becomes BE. The last liquid to solidify has the eutectic composition of 72% Ag and 28% Cu. During this last phase of solidification, alternating layers of α and β phases have been formed, similar to those shown in Figure 5-13, *A*.

If the starting liquid alloy composition contains a greater percentage of copper than that for the eutectic, the changes in composition during cooling are similar except that now the first solid to form as crystals in the liquid phase is the β solid solution. The changes in composition of the liquid and β phases during the equilibrium cooling of an alloy containing 80% Cu and 20% Ag (represented by the right dashed vertical line in Figure 5-12) can be determined by constructing tie lines (including EG) at several temperatures across the (L plus β) phase field.

In summary, the first crystals to form during the equilibrium freezing of Ag-Cu alloys with compositions between points B and G are either the solid solution α phase or the solid solution β phase. The final portion of the molten alloy to freeze will form regions of the eutectic structure. The primary grains that form by the growth of these starting primary α or β crystals are large compared with the dimensions of the alternating layers of α and β phases of the eutectic. As described previously for the Ag-Pd solid solution system, application of the lever rule will yield percentages of the two phases at any temperature in the L-plus-α or L-plus-β phase fields during the equilibrium cooling process.

Equilibrium cooling of molten 5% Cu alloy below the eutectic temperature is indicated by the first vertical dashed line at the left in Figure 5-12. This alloy solidifies as the α solid solution at approximately 860 °C, where the vertical dashed line intersects AB. As the temperature continues to decrease below the eutectic temperature of 779 °C, the composition of this solid solution phase remains unchanged until a temperature of approximately 630 °C is reached (intersection of the vertical dashed line with CB). Then the Cu-rich β phase begins to precipitate from the α solid solution because the solid solubility limit of Cu in the latter solid solution has been exceeded. This condition occurs only if slow cooling has allowed equilibrium to be achieved. However, rapid cooling of the 5% Cu alloy will not allow sufficient time for atomic diffusion and will result in an alloy consisting of almost all of the α phase at room temperature.

If the starting molten alloy contains between approximately 9% and 92% Cu (compositions lying between vertical lines passing through B and G), the lamellar eutectic structure will form during equilibrium solidification. Alloy compositions lying to the left of B or to the right of G will form either primary α-phase or primary β-phase crystals, respectively, during solidification, which is completed when the temperature decreases below AB or DG, respectively. Then, as the solidified alloy cools under equilibrium conditions to room temperature, precipitates of the other solid solution phase will form (typically at the grain boundaries) when the temperature decreases below the solvus line (CB or FG, respectively). The molten eutectic alloy composition (point E) solidifies at a single temperature of 779 °C to yield the two-phase α-plus-β structure that is similar to that shown in Figure 5-13, *A*.

PROPERTIES OF HYPOEUTECTIC AND HYPEREUTECTIC ALLOYS

The mechanical properties of the Pd-Ag solution alloys vary nearly linearly with small to moderate changes in composition. In comparison, more complex relationships occur for alloy compositions in eutectic systems. Alloys in these systems with a composition less than that of the eutectic are called hypoeutectic alloys and those with a composition greater than the eutectic are known as hypereutectic alloys. The primary crystals of the hypoeutectic alloys in the Ag-Cu system of Figure 5-12 consist of the α solid solution, whereas those of the hypereutectic alloys consist of the β solid solution. Hypoeutectic or hypereutectic alloys that contain the eutectic constituent in their microstructures (compositions between B and G) are relatively brittle, whereas alloys with microstructures lacking this constituent (compositions to the left of B or to the right of G) are ductile. Alloy embrittlement occurs because the alternating lamellae of the α and β phases inhibit the movement of dislocations, which increases strength and hardness but decreases ductility (or increases brittleness). The tarnish resistance of these alloys without the eutectic is superior to that of the alloys containing the eutectic constituent.

PERITECTIC ALLOYS

Another example of the limited solid solubility of two metals is the peritectic transformation. The Ag-Sn system, which is the basis for the original dental amalgam alloys, is a peritectic system. A peritectic phase transformation also occurs in the Ag-Pt system, which is associated with many gold casting alloys. Also, the Pd-Ru alloy system has a peritectic reaction at 16.5% Ru. Ruthenium is an important grain-refining element for palladium casting alloys.

Like the eutectic transformation, the peritectic reaction is an invariant reaction that occurs at a particular composition and temperature. The reaction during the cooling process can be written as:

$$\text{Liquid} + \beta \text{ solid solution} \rightarrow \alpha \text{ solid solution} \quad (2)$$

Figure 5-14 is the phase diagram for the Ag-Pt alloy system. The α phase is silver-rich, the β phase is

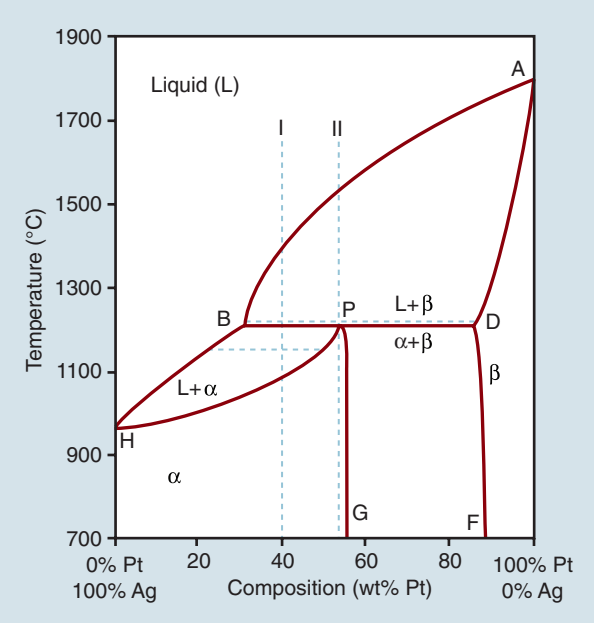


FIGURE 5-14 Equilibrium-phase diagram of the platinum-silver system showing percentages by weight.

platinum-rich, and the two-phase (α-plus-β) region results from the limited solid solubility of less than approximately 12% Ag in Pt at 700 °C (point F) of silver in platinum. Figure 5-14 shows that the equilibrium solid solubility of Pt in Ag is approximately 56% at 700 °C. The peritectic transformation occurs at point P, where the liquid composition at B and the platinum-rich β phase (composition at point D) transform into the silver-rich α phase (composition at point P). For a hypoperitectic composition, such as exists for alloy I, cooling through the peritectic temperature results in the following transformation:

$$\text{Liquid} + \beta \rightarrow \text{liquid} + \alpha \qquad (3)$$

As shown in Figure 5-14, the two liquid phases involved in transformation (3) have different compositions. For transformations (2) and (3), the α phase forms at the interface between the liquid and β phase. Because extensive diffusion is required in these phases for transformation, peritectic alloys are susceptible to coring during rapid cooling. This cored structure has inferior corrosion resistance and is more brittle than the homogeneous solid solution phase.

SOLID-STATE REACTIONS IN HIGH NOBLE AND NOBLE ALLOY SYSTEMS

Solid-state reactions provide important mechanisms that can strengthen some dental alloys. The best-known example is the ordering of Au-Cu alloys, which is relevant for Types III and IV gold casting alloys for full metal restorations. Although the Au and Cu atoms are completely soluble in the liquid state and at high temperatures in the solid state, at lower temperatures the attraction between these two atom species can convert regions with a random solid solution into an ordered solid phase for some compositions.

CRITICAL QUESTION

By which two mechanisms does copper provide strengthening and hardening of gold casting alloys?

GOLD-COPPER SYSTEM

Shown in Figure 5-15 is the Au-Cu phase diagram. The melting range between solid and liquid is narrow for all compositions, and the liquidus and solidus curves meet at 80.1% Au. At the right side of this diagram, the addition of 10% Cu to Au lowers the liquidus temperature markedly. These points are useful to understand the nature of Au-Cu alloy compositions used for casting dental prostheses.

At temperatures below the solidus temperature and above 410 °C, Au and Cu have complete mutual solid solubility and all alloys initially solidify as the disordered α solid solution, in which the atoms of each species are randomly located in the FCC crystal structure. However, when alloys of appropriate compositions are subsequently cooled under equilibrium conditions, solid-state ordering transformations occur.

As shown in Figure 5-15, the ordered α′ phase forms when alloys containing between 40% and 65% Au are cooled below 390 °C at equilibrium. This is the Au-Cu_3 structure, whose unit cell was shown in Figure 5-9. As previously noted, because of the different atomic weights of Au and Cu, the Au-Cu_3 structure contains approximately 50% Au. On the other hand, when alloys containing between 65% and 85% Au are cooled below 410 °C under equilibrium conditions, a different ordered α''_2 structure, also known as Au-Cu II, is formed. Upon further equilibrium cooling below 385 °C, the α''_2 structure transforms to the α''_1 ordered structure, which is referred to as Au-Cu I. Under normal slow cooling conditions for Au-Cu alloys in this composition range, the α''_1 structure is formed. It is interesting to note that the equiatomic Au-Cu structure contains approximately 75% Au.

The gold and copper atoms, which are randomly located in the FCC structure of the α phase at higher temperatures, occupy alternating planes in the α''_1 superlattice (Figure 5-16). This ordered structure has a face-centered tetragonal unit cell because the lattice parameter in the vertical direction shown in Figure 5-16 is different from that in the other two directions owing to the unequal atomic radii of gold and copper. The α''_2 superlattice has an unusual orthorhombic unit cell. The unit cell for Au-Cu II may be visualized in Figure 5-16 as five tetragonal Au-Cu I unit cells similar to the one illustrated and joined to five additional tetragonal Au-Cu I unit cells, in which the copper atoms are located at the midplane location rather than at the top and bottom faces.

Strengthening of dental gold casting alloys occurs through ordered structures as well as strengthening associated with several solute atom species in the disordered FCC gold solid solution matrix. Because the crystal structure of the ordered phase differs from that of the gold solid solution, each region of the ordered phases is surrounded by a localized elastic strain field, which is necessary to maintain continuity of atomic bonds across the interface between the ordered phase and the matrix phase. As a result, the movement of

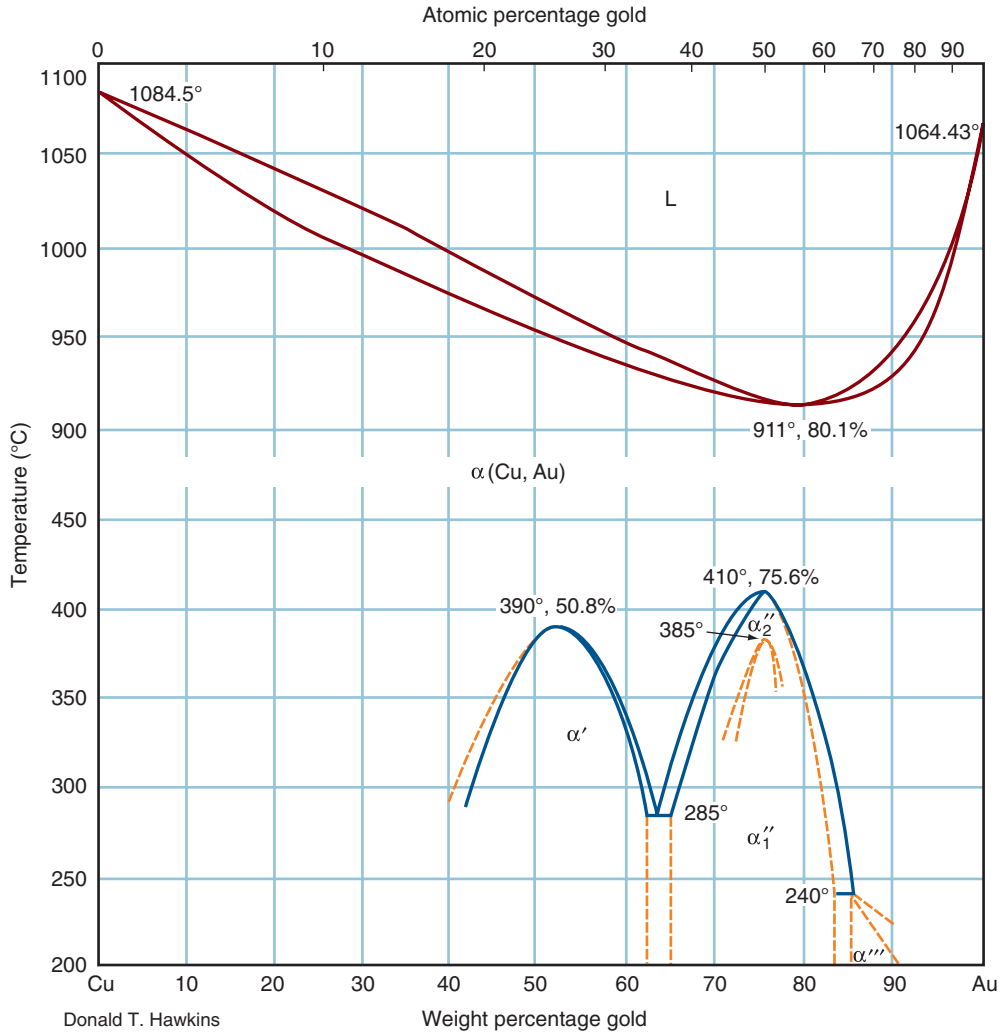


FIGURE 5-15 Equilibrium-phase diagram for the gold-copper system. (With permission from *Metals Handbook*, ed 8, vol 8. Metals Park, OH, 1973, American Society for Metals, pp 267.) (The temperature range between 450 and 900 °C has been condensed to save space.)

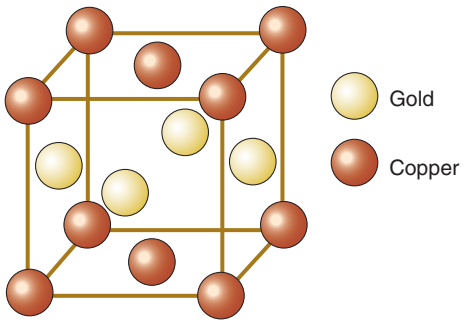


FIGURE 5-16 Unit cell of the face-centered tetragonal superlattice of Au-Cu.

dislocations is restricted through gold casting alloys that contain regions of ordered structure.

Rapid cooling of a molten alloy in a room-temperature water bath or an ice-water bath does not allow sufficient time for atomic movement to form the ordered structure. The disordered solid solution is retained at room temperature and the gold alloy is relatively soft and ductile, which facilitates adjustments of the cast margins in the dental laboratory or at the chair side with the patient. Bench-cooling of Type III or IV gold alloy castings through the ordering temperature range allows enough atomic movement for partial transformation. After adjustments have been completed on a Type III or IV gold alloy cast in the quenched condition, the casting can be age-hardened through a specific heat treatment. The alloy is heated to a temperature within the ordering range for a period of time as recommended by the manufacturer and then quenched. This procedure is not commonly performed because of the additional time involved. For commercial Type III and IV dental gold casting alloys, the Vickers hardness increases after age hardening. Because the amount of copper in the Type I and II gold alloys is insufficient, age hardening does not occur.

To restore hardened Type III or IV gold alloy castings to their softened condition, a solution heat treatment can be performed. This process involves heating the casting to a temperature below the solidus temperature (e.g., 700 °C), holding for approximately 10 minutes to convert the alloy to a random substitutional solid solution, and then quenching the casting to retain this atomic arrangement at room

temperature. The softened casting can subsequently be given the previously described age-hardening heat treatment and quenched, yielding a stronger but less ductile alloy.

OTHER GOLD ALLOYS

Dental gold casting alloys may contain at least three principal solute metals (Cu, Pd, and Pt), which provide solid solution strengthening. Other elements in amounts less than 1%, such as zinc (Zn) and iridium (Ir), are present as well. Because many of these metals in binary combinations can form precipitates leading to age hardening, it is useful to study the Pt-Au, Pd-Cu, and Pt-Cu binary systems. Comparisons of these diagrams provide information about phases that might be present in the multicomponent commercial gold alloys.

In the Pt-Au system at temperatures below the solidus, a large two-phase region develops in a manner similar to a eutectic structure. The Pd-Cu system exhibits two superlattice transformations that lead to the formation of Pd-Cu and Pd-Cu_3 phases. The Pt-Cu system exhibits at least two intermediate phases, Pt-Cu and Pt-Cu_3. These phase diagrams and their potential relevance to alloy properties can be related through the same approaches that have been discussed previously. Because of elemental microsegregation during rapid solidification and cooling, phases may be observed in cast dental alloys that would not occur under equilibrium conditions for the same alloy compositions. Furthermore, the compositions of phases in multicomponent alloys will generally be more complex than those for binary compositions.

An effective age-hardening constituent in gold alloys is the $FePt_3$ intermetallic compound, which is useful in strengthening high-gold alloys for metal-ceramic prostheses (Smith et al., 1970). Platinum is used to increase the melting range and lower the TEC of the alloy.

? CRITICAL QUESTION

Why are there substantial differences between the microstructures and strengthening mechanisms for the high-palladium alloys and the palladium-silver alloys?

PALLADIUM-BASED ALLOYS

Alloys based on a high palladium content have been used for metal-ceramic prostheses since their introduction in the early 1980s because of their lower cost compared with gold-based alloys, their excellent mechanical properties, and their proven adherence to dental porcelain. These alloys should not be confused with the silver-palladium alloys (with silver as the majority element) that must not be used for casting frameworks for metal-ceramic prostheses. Although the unit cost of palladium was higher than that of gold between 2001 and 2003, the cost of gold has increased progressively to a value more than twice that of palladium in 2012. In fact, the cost of gold ($1555/troy ounce in May 2012) has exceeded the cost of palladium ($602/troy ounce in February 2012). In comparison, the cost of platinum was $1424 per troy ounce.

Because of the escalating cost of gold during the decade, palladium-based alloys, base metal alloys, and ceramics have become more attractive. Although the unit metal cost of palladium-based alloys was approximately half that of alternative gold alloys by the end of 2010, their clinical use has diminished somewhat because of the price volatility of palladium and the increased acceptance of all-ceramic prostheses.

Some of the high-palladium alloys are based on the Pd-Ga system, in which there is a eutectic composition at the high-palladium-content side of the phase diagram and complex precipitation reactions at lower temperatures. For Pd-Cu-Ga alloys, both the rapid cooling rate during solidification and the addition of copper shift the eutectic composition to higher percentages of palladium that result in formation of a Pd_2Ga eutectic phase in the cast microstructure. Both Pd-Cu-Ga alloys and the Pd-Ga alloys have a fine submicron "tweed" structure that can be observed by TEM. This structure appears to form by a martensitic phase transformation in the FCC cell structure of the palladium solid solution matrix and remains stable during the firing cycles for dental porcelain. Strengthening of these alloys occurs by the solid solution mechanism and by the formation of Pd_5Ga_2 precipitates in some Pd-Cu-Ga alloy compositions.

Although the reference for Pd-based alloys is the Pd-Ag phase diagram in Figure 5-10, the presence of additional elements yields desirable mechanical properties and metal oxides for porcelain bonding. The corresponding binary diagrams may be useful for predicting the occurrence of these phases. Because the precipitate sizes are generally too small for accurate determination of their compositions using scanning electron microscopy or electron microprobe microanalysis, elemental analysis using a transmission electron microscope is required.

MULTICOMPONENT ALLOY SYSTEMS

Up to this point we have described primarily the characteristics of binary alloys and palladium-based **ternary alloys**. Although most high noble (HN) dental gold alloys are ternary alloys of gold, silver, and copper, they also contain minor additions of platinum, palladium, and zinc. These alloys, which form single-phase solid solutions when quenched immediately after solidification, can be strengthened and hardened by heat treatment. A variety of age-hardening mechanisms have been identified by alloy manufacturers, which may vary significantly depending on the alloy composition. There are many possible ternary alloys, quaternary alloys, and higher-order multicomponent alloy systems that can be used for restorative dentistry. Such systems are complex, and the phase diagram data available are limited. Thus binary-phase diagrams are often used to estimate the effect of individual elements on the phases formed and the resulting microstructures of these cast alloys. However, such equilibrium diagrams should be interpreted carefully since actual casting and cooling processes reflect nonequilibrium conditions.

BASE METAL ALLOYS

This chapter has focused primarily on the principles of the solidification, microstructure, and effects of alloy elements on important properties of noble metal casting alloys. The

principles of alloy solidification, phase formation and phase transformation as a function of composition and thermal processing for predominantly base metal (PB) alloy systems are essentially the same as those described for HN and N alloy systems. The characteristics and properties of these alloys are described in Chapter 16.

COLOR OF CAST METAL ALLOYS

The trend over the past several decades has been to choose porcelain-fused-to-metal (PFM, also known as metal-ceramic) or all-ceramic crowns and bridges rather than full-metal prostheses. There are several reasons for this, including the unstable costs of noble metals (Figure 5-17), a general increasing trend for esthetics over durability, the recent (2000 to 2010) moderate success of all-ceramic restorations, and the lack of patient information on the risks and benefits of all prosthetic choices. Although PFM (metal-ceramic) restorations can be made with excellent esthetics, the fact that metal occasionally may be visible directly or indirectly is a negative factor that affects the choices of restorative materials by both dentists and patients. Although this adverse esthetic result may be associated with white high noble and noble alloys, the use of high noble yellow-gold alloys for PFM restorations has also declined over time. Even the introduction of ultra–low-fusing porcelains whose expansion coefficients are comparable to those of lower-melting rich-yellow ceramic alloys has not reversed this trend significantly.

To achieve a rich yellow color, a gold content of 84% or more is typically required in PFM alloys in order to maintain the desirable "yellow" color of pure gold. Although high noble (HN) alloys should contain at least 40% Au and a total of 60% of noble metals, HN alloys with gold contents of approximately 40% are "white" in color. Shown in Figure 5-18

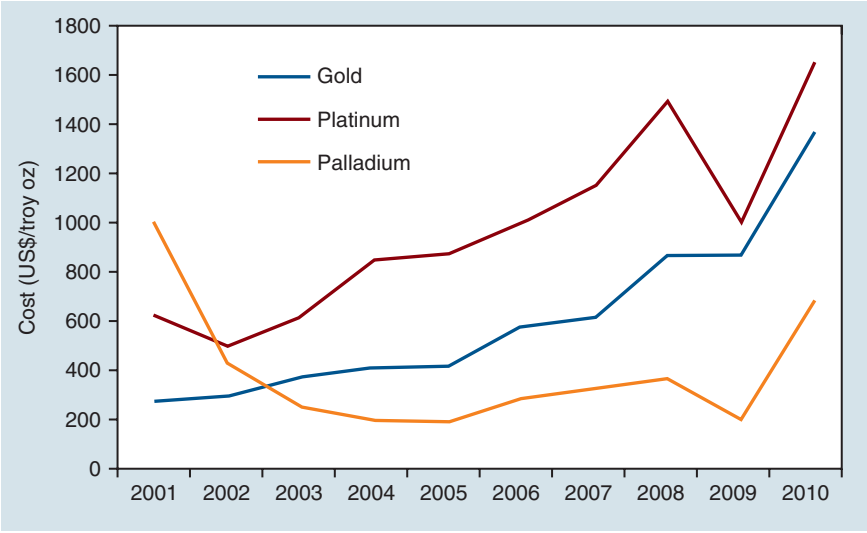


FIGURE 5–17 Cost of noble metals (U.S. dollars per troy ounce) between 2001 and 2011.

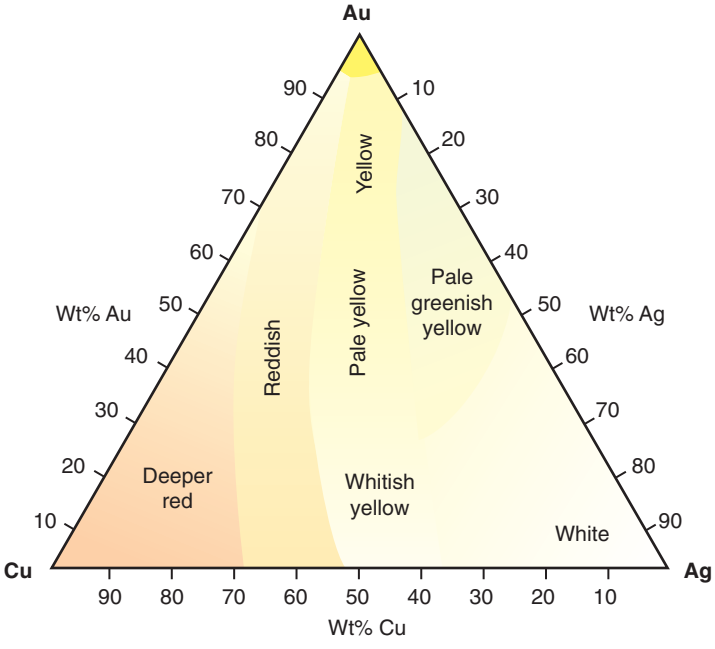


FIGURE 5–18 Color range of Au-Ag-Cu alloys.

is a schematic representation of the range of hues that result from various concentrations of Au, Cu, and Ag in ternary alloys. The transition areas from one color to another are more or less continuous rather than segmented as shown in this illustration. The areas are merely intended to indicate approximate changes in hue as Cu and/or Ag are added to a gold matrix.

Virtually all of the noble palladium-based alloys for metal-ceramic applications are "white" (silver) in color. One of the challenges of encouraging patients to accept treatment with the relatively high cost of high noble PFM metals is that they cannot see the difference between the color of N alloys and predominantly base metal (PB) alloys. Thus, some education is required so that the patients are aware of the benefits of HN and N alloys compared with PB alloys.

Since 1990, ultralow-firing veneering ceramic and matched gold alloys with a reduced platinum and palladium content have been available to provide all-metal or metal-ceramic restorations in which the metal displays a deep rich-yellow color. Such systems allow dentists and patients to clearly see that the restorations display the expected gold color.

Laboratory technicians can select from dozens of alloys available for all-metal and PFM restorations. The color of the alloys they select does not always confirm the noble metal content. For example, a full crown that contains 62% gold by weight may show an attractive yellow color compared with a "white" PFM alloy that also contains 62% gold. The appearance of yellow-colored metals is highly desirable and preferred by many dentists and patients, although the overall treatment cost sometimes controls the selection of an all-ceramic prosthesis or a base metal PFM prosthesis compared with prostheses prepared with HN yellow-gold alloys. Further details on dental casting alloys are presented in Chapter 16.

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CHAPTER

6

Dental Polymers

OUTLINE

History of Dental Polymeric Materials

Dental Uses of Polymeric Materials and Resins

Components and Composition

Performance Criteria for Dental Resins

Mechanical and Physical Properties of Polymers

Chemistry of Polymerization

Copolymerization

Acrylic Dental Resins

KEY TERMS

Backbone—The main chain of a polymer.

Block copolymer—Polymer made of two or more monomer species and identical monomer units ("mers") occurring in relatively long sequences along the main polymer chain. See also *random copolymer* and *graft or branched copolymer*.

Chain transfer—Stage of polymerization in which the free radical on the growing end of one polymer chain is transferred to either a monomer or a second polymer chain. This terminates chain growth in the first chain and initiates chain growth in the monomer or second polymer chain (see also Figures 6-10 and 6-11).

Curing—Chemical reaction in which low-molecular-weight monomers (or small polymers) are converted into higher-molecular-weight materials to attain desired properties (see also the closely related terms *polymerization* and *setting*).

Crosslink—A difunctional or multifunctional monomer that forms a link between two polymer chains. Crosslinked polymers have many such crosslinks between neighboring chains such that a three-dimensional interconnected polymer network results. See Figures 6-2 and 6-3.

Denture base—The part of the denture that rests on the soft tissues overlying the maxillary and mandibular jawbone and that anchors the artificial teeth.

Elastic recovery—Reduction or elimination of elastic strain (deformation per unit length) when an applied force is removed; elastic solids recover elastic strain immediately on removal of the applied force, whereas viscoelastic materials recover elastic strain over time. The greater the viscous nature of an elastomer, the more incomplete the recovery.

Final set—Stage at which the curing process is complete.

Free radical—An atom or group of atoms (R) with an unpaired electron (•). R•-producing reactions that initiate and propagate polymerization and eventually lead to a final set.

Glass transition temperature (T_g)—The temperature at which macromolecule molecular motion begins to force the polymer chains apart. Thus, polymeric materials soften when heated above this temperature.

Graft or branched copolymer—Polymer in which a sequence of one type of mer unit is attached as a graft (branched) onto the backbone of a second type of mer unit.

Initial set (of a polymer)—The stage of polymerization during which the polymer retains its shape.

Induction—Activation of free radicals, which in turn initiates growing polymer chains.

Macromolecule—A large high-molecular-weight compound usually consisting of repeating units in a chainlike configuration (see also *polymer*).

Mer—The term used to designate the repeating unit or units in a polymer chain; thus, mers are the "links" in the chain.

Methacrylate polymers—Type of macromolecule derived from monomers with the chemical structure $CH_2=C(CH_3)–COOR$.

Monomer—Chemical compound that is capable of reacting to form a polymer.

Plastic flow (of a polymer)—Irreversible deformation that occurs when polymer chains slide over one another and become relocated within the material.

Polymer—Chemical compound consisting of a large organic molecule ("macromolecule") formed by the union of many smaller repeating units (mers).

Polymerization—Chemical reaction in which monomers of a low molecular weight are converted into chains of polymers with a high molecular weight.

$$\text{Monomer} + \text{Monomer} + \text{Monomer} + \text{Monomer} \xrightarrow{\text{Polymerization}} -\text{Mer}-\text{Mer}-\text{Mer}-\text{Mer}-$$

PMMA and MMA—Poly(methylmethacrylate), a commonly used acrylic thermoplastic dental material derived by polymerization of the monomer, methylmethacrylate (MMA).

Propagation—Stage of polymerization during which polymer chains continue to grow to high molecular weights.

Random copolymer—Polymer made of two or more monomer species but with no sequential order between the mer units along the polymer chain. See also *block copolymer* and *graft or branched copolymer*.

Resin or synthetic resin—Blend of monomers and/or macromolecules with other components, which form a material with a set of useful properties.

Resin-based composite—A highly crosslinked resin reinforced by a dispersion of amorphous silica, glass, crystalline, or organic resin filler particles and/or fibers bonded to the polymer matrix by a coupling agent.

Setting (of a polymer)—Extent to which polymerization has progressed.

Thermoplastic polymer—Macromolecule material made of linear and/or branched chains that softens when heated above the glass-transition temperature (T_g), at which molecular motion begins to force the chains apart and soften the polymer. Thermoplastics can be heated above the T_g, molded to a new shape, and then cooled below the T_g to retain the new configuration.

Thermosetting polymer—Polymeric material that becomes permanently hard when heated above the temperature at which polymerization occurs and that does not soften again on reheating to the same temperature.

Termination—Stage of polymerization during which polymer chains no longer grow.

Viscoelastic—Term describing a polymer that combines the spring-like behavior of an elastic solid (such as a rubber band) with that of the puttylike behavior of a viscous, flowable fluid (such as honey).

Polymers are formed through chemical reactions that convert large numbers of low-molecular-weight molecules, known as **monomers**, into large, very high-molecular-weight long-chain **macromolecules**. *Resins* are compositions of either monomers or macromolecules blended with other components to provide a material with a useful set of properties. The particular form and morphology of the macromolecule determine whether it is a fiber, a rigid solid, or an *elastomer* (rubberlike) material. Monomer resins are useful in dentistry because they can be shaped and molded and then transformed to a solid to take on a permanent shape when they polymerize. Synthetic polymer resins are often called *plastics,* which are substances that, although dimensionally stable in normal use, can be permanently reshaped by *irreversible* deformation. The utility of plastics is derived from their ability to be permanently formed and molded into complex shapes, either by the application of heat and pressure or by a chemical reaction. Based on their thermal behavior, they can be divided either into **thermoplastic polymers** if they undergo a reversible change or **thermosetting polymers** if they undergo an irreversible change when heated. Elastomers readily undergo extensive *reversible* deformation under small applied stresses; that is, they exhibit elastic behavior.

HISTORY OF DENTAL POLYMERIC MATERIALS

The modern era's use of dental polymers began with natural rubber for dentures. Vulcanized rubber, a plant-derived latex **crosslinked** with sulfur, was introduced as a *denture base* material in 1853. At about the same time, celluloid, a nitrocellulose material used to make billiard balls and detachable shirt collars, was adapted as a **denture base** material. Both materials offered advantages over the wood, bone, ivory, and ceramics used at the time, but each also had substantial drawbacks. An early advance was a combination of the two materials as a "composite" structure (see Chapter 13) in order to gain a better balance among the advantages and drawbacks of each material. Vulcanized rubber was used as the denture base and celluloid formed the gingival area around porcelain teeth. This denture was flexible, allowed easy fabrication of denture bases, and simulated the look of gingival tissue. Unfortunately the celluloid portion absorbed stains, gradually became grossly discolored, developed odors, and was flammable. Thus, substantial improvements in both appearance and functional durability were still needed.

During the 1890s, gutta-percha, a plant exudate containing trans-polyisoprene, came into use for temporary crowns and cavity fillings, permanent restorations, and root canal (endodontic) filling materials. Interestingly, gutta-percha, which is closely related to natural latex rubber (cis-polyisoprene), remains in wide use as an endodontic material to this day. Gutta-percha is a *thermoplastic* polymer. Vulcanized latex is an *elastomeric* polymer, which is now used in dentistry in examination gloves and rubber dams. During the 20th century a wide variety of synthetic elastomers—polysulfides, silicone rubber, polyethers, and polyvinylsiloxanes—were developed, some of which were adapted for use as dental impression

materials (Chapter 8). At about the same time, during the 1930s and 1940s, phenol-formaldehyde, polystyrene, polyvinylchloride (PVC), vinyl acetate, and other synthetic polymers were developed. Many were evaluated as denture materials but with limited success until the introduction in 1936 of polymethylmethacrylate **(PMMA)**, as a heat-processed thermosetting material. By 1940, PMMA was also being used to make inlays, crowns, and fixed dental prostheses. Beginning in the mid 1940s, room-temperature polymerizing methacrylates became available that were quickly adapted for dentistry as self-**curing** prosthetic and restorative resins (also known as cold- and chemical-curing resins). Low-temperature curing has made possible directly placed esthetic restorative materials. Sevriton (LD Caulk Inc., Milford, DE), introduced in the 1950s, was the first such tooth-colored **resin** for anterior teeth. It was composed of methylmethacrylate **(MMA)** monomer blended with powdered PMMA.

Methylmethacrylate/PMMA resins were soon replaced by the more durable difunctional **methacrylate** monomers based on either bis-GMA (bisphenol-A glycidylmethacrylate, see Figure 6-16) or urethane dimethacrylate (see Figure 6-17). These innovations were pioneered by Dr. Ray Bowen of the ADA Research Foundation, who introduced self-curing dimethacrylates reinforced by a dispersed phase ceramic particle "filler" in the late 1950s. Such **resin-based "composites"** form a highly crosslinked, durable, and esthetically pleasing polymer network (Chapter 13).

Self-curable resins were later replaced by ultraviolet photocured materials, which were in turn replaced by blue-light photo-polymerizable resins. These latter "light-curable" resin materials remain in use today, although they have evolved through many innovations in the initiator, reinforcing filler, and monomer components. In the past few years, new resins have been introduced that utilize highly esthetic nanometer-sized reinforcing particles. Most recently, a new monomer system based on a ring-opening polymerization mechanism has been introduced to reduce the problems associated with curing shrinkage (Chapter 13).

The dimethacrylate resins have had an enormous impact on dentistry; they are now used to seal fissures against cariogenic bacteria, as adhesives for both enamel and dentin bonding (Chapter 12), as luting and adhesive cements (Chapter 14), as veneering materials, and as direct and indirect restoratives (Chapter 13). Because the field is dynamic, and new types of polymeric materials are continually being developed, a dentist's knowledge must include basic concepts of polymer materials science to critically evaluate new developments in the field and to make informed choices on the uses of new dental products. This chapter provides a brief review of the fundamentals of polymer materials for this purpose.

DENTAL USES OF POLYMERIC MATERIALS AND RESINS

As described above, polymeric materials are used in a variety of dental applications. Hardly a single clinical procedure is accomplished without the use of one or more of these products, typical applications of which include the following:

- *Prosthodontics*: denture bases and teeth, soft liners, custom trays, impression materials, core buildup materials, temporary restoratives, cementing/luting materials, and maxillofacial prostheses
- *Operative Dentistry*: dentin bonding agents, cavity fillings, resin and glass-ionomer cements, pit and fissure sealants, splinting materials, and veneers
- *Orthodontics*: brackets, bracket bonding resins and cements, and spacers
- *Endodontics*: gutta-percha points, root canal sealants, and rubber dams
- *Equipment*: mixing bowls and spatulas, mouth guards (sports equipment), and protective eyewear

Polymeric resins are increasing in use for restoring and replacing tooth structure and missing teeth. These resins can be bonded with other resins, directly to tooth structure, or to other restorative materials such as amalgam. If all teeth are missing, a denture base with attached denture teeth can be made to restore chewing ability. Most of these restorative and prosthetic applications are based on methacrylate resins. More recently, epoxy resins and related silorane materials, based on ring-opening **polymerization** mechanisms, have been introduced. These resins are discussed in a later section.

? CRITICAL QUESTION

How do the mechanical properties of a polymer change as the molecular weight increases?

COMPONENTS AND COMPOSITION

FUNDAMENTAL NATURE OF POLYMERS

The two most significant features of polymers are that they consist of very large macromolecules and that their chainlike molecular structure is capable of virtually limitless configurations and conformations. Chain length, the extent of chain branching and crosslinking, and the organization of the chains among themselves, determine the properties of polymers as illustrated in Figures 6-1 and 6-2 and as explained below. Polymerization is a repetitive intermolecular chain growth reaction that can proceed almost indefinitely, sometimes reaching molecular weights as high as 50 million.

In addition to the carbon-chain organic polymers, macromolecules may also consist of inorganic polymer networks such as those formed by silicon dioxide repeating units. As discussed in later chapters, these polymers are found in glass, silicate ceramics, the reinforcing components of dental resin composites, and in glass-ionomer cements. However, in this chapter the discussion is limited to organic (carbon-carbon repeating units in the **backbone** chain) polymers.

CHAIN LENGTH AND MOLECULAR WEIGHT

The longer the polymer chain, the greater are the numbers of entanglements (temporary connections) that can form along

it. Therefore, the longer the chain, the more difficult it is to distort the polymeric material; thus, such properties as rigidity, strength, and melting temperature increase with increasing chain length (Figure 6-1). Consider the analogy between the behavior of a group of polymer molecular chains and a plate of spaghetti. The longer the strands or chains, the more difficult it is to separate (disentangle) them. Cutting them up—that is, reducing the chain length—makes them easier to separate.

Synthetic resins polymerize randomly from activated local sites. Thus, depending on the ability of the chains to grow from their local activation sites, the molecular chains that form within a polymeric material will vary in length. Therefore, an average value is needed to express the overall molecular weight of polymers. Two types of averages are commonly used: the number average, $\overline{M}_n$, based on the average number of **mer** repeating units in a chain, and the weight average, $\overline{M}_w$, based on the molecular weight of the average chain. For example, the number average molecular weight for various commercial dental denture polymers typically varies from 8,000 to 39,000. Denture teeth with crosslinked resin (see below) may have a much higher molecular weight.

In a biological context, it is important to realize that polymerization progresses to completion and that residual monomer can be leached out. These low-molecular-weight compounds may cause adverse reactions, such as an allergic response. Residual monomer also has a pronounced effect on the average molecular weight of the polymer. For example, only 0.9% of residual monomer in a polymer, which theoretically has an $\overline{M}_n$ of 22,400 if completely cured, will reduce the average molecular weight to 7,300.

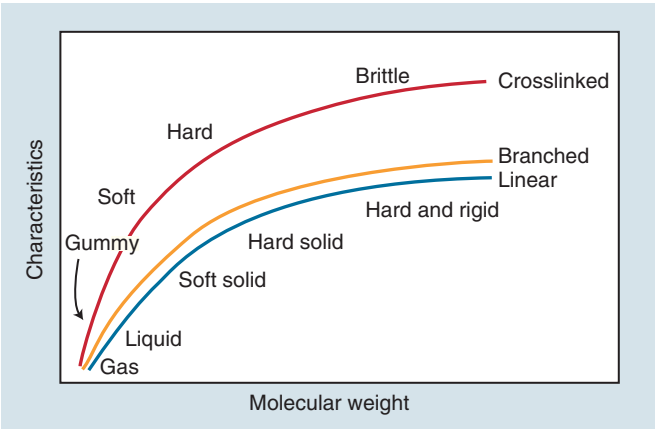


FIGURE 6-1 Effect of polymer chain length, branching, and crosslinking on mechanical and physical properties. Rigidity, strength, and melting temperature increase as polymer chain length grows and molecular weight increases.

The expression $\overline{M}_w$ implies that larger molecules are weighted more in the calculation. Therefore, $\overline{M}_w$ is always greater than $\overline{M}_n$ except when all molecules are of the same length; then $\overline{M}_w = \overline{M}_n$. Considering the concepts just discussed, the ratio $\overline{M}_w/\overline{M}_n$ (called the polydispersity) is a measure of the range and distribution of chain sizes. Polymers with equal value of $\overline{M}_w$ but different values of polydispersity will exhibit somewhat different properties. For example, polymers of higher polydispersity will begin to melt at a lower temperature and have a larger temperature range of melting.

CHAIN BRANCHING AND CROSSLINKING

In addition to linear macromolecules, polymer chains are often connected together to form a nonlinear, branched, or crosslinked polymer (Figures 6-1 and 6-2). Branching is analogous to extra arms growing out of a polymer chain; thus, the probability of entangled, physical connections among chains increases. Various consequences of chain branching are discussed later in this chapter (e.g., in the section below on internal plasticizers). While the entangled interchain connections formed by chain branches are temporary in the sense that they can be disentangled with relatively low-energy, crosslinks that are chemical bond connections between chains and require a relatively high energy to break. Because of interlinking a large number of chain *backbones*, a highly crosslinked polymeric material can consist of just a few giant molecules or even a single giant molecule.

In crosslinked polymers, some of the structural units must have at least two sites where reactions can occur. For example, as described in Chapter 8, during curing of polysulfide impression material, linear polymers are joined, or bridged, through reactive side chains to form crosslinked molecular networks (see Figure 8-3 which shows crosslinking of poly(methylmethacrylate) by ethylene glycol dimethacrylate during copolymerization).

Crosslinking forms bridges between chains and dramatically increases molecular weight. Consequently, physical and mechanical properties vary with the composition and extent of crosslinking for a given polymer system. The three-dimensional network of crosslinked polymers increases

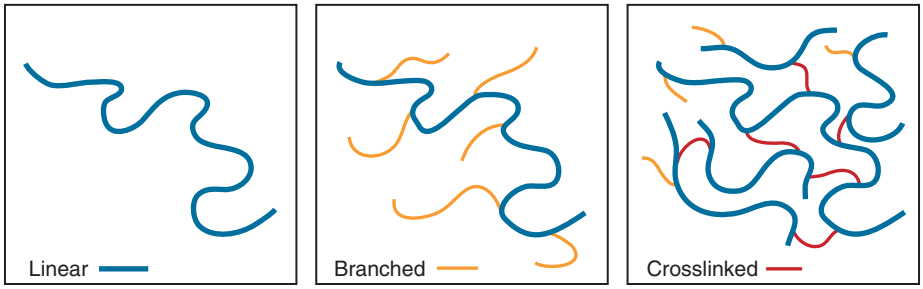


FIGURE 6-2 Schematic diagrams of linear, branched, and crosslinked polymers.

rigidity and resistance to solvents. Crosslinking of a low-molecular-weight polymer increases the softening temperature, known as the **glass-transition temperature** (T_g), compared with that of a high-molecular-weight polymer (see Figure 6-1). On the other hand, crosslinking has only a modest influence on strength.

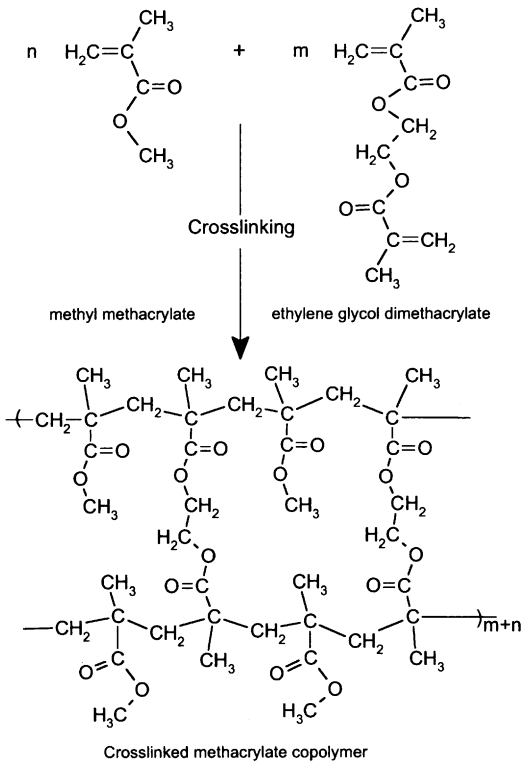


FIGURE 6-3 A crosslinked structure is formed by copolymerization, where at least one comonomer is multifunctional. Here methylmethacrylate is copolymerized with ethylene glycol dimethacrylate.

Copolymer Structures

Polymers that have only one type of repeating unit (mer) are homopolymers; those with two or more types of mer units are known as copolymers. There are three different types of copolymers:

- ***Random copolymer***—No sequential order exists among the two or more mer units along the polymer chain.

  … ABBABABAAABAAAABABBBBABAAAABABABB …

- ***Block copolymer***—Identical monomer units occur in relatively long sequences (blocks) along the main polymer chain.

  … AAAAABBBBBBBAAAABBBBBBBAAABBBAAAA …

- ***Graft or branched copolymer***—Sequences of one type of mer unit (B) are "grafted" onto a backbone chain of a second (A) type of mer unit to form a branched configuration (see Figure 6-2).

```
... AAAAAAAAAAAAAA ...
      |     |
      B     B
      B     B
      B     B
```

MOLECULAR ORGANIZATION

In some polymers the chains are randomly coiled and entangled in a very disordered or random pattern known as an amorphous structure (Figure 6-4, left side). In others, the chains align themselves to form a highly ordered, or crystalline, structure (Figure 6-4, right side). Most polymeric materials combine these two forms of organization in greater or lesser proportions. Characteristically, the linear dental polymers are predominantly amorphous with little or no

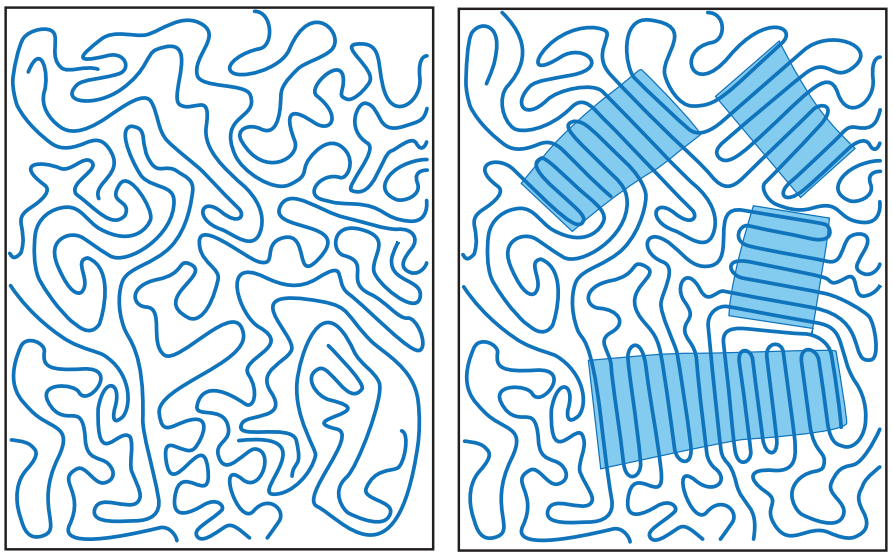


FIGURE 6-4 Schematic diagram of polymers that contain only amorphous intermolecular and intramolecular organization (*left*) and combinations of both amorphous and crystalline regions (*shaded areas on right*).

crystallinity. The polymer chains form a tangled mass, comparable with cooked spaghetti, in which each string is a mile or so long. Such polymer segments have little chance to migrate and are immobile in the solid state. As in the case of glass, a short-range order results.

However, many polymers have regions of long-range ordering that produce a degree of crystallinity depending on the secondary bonds that can be formed, the structure of the polymer chain, the degree of ordering, and the molecular weight (Figure 6-4). Polymer crystallinity usually increases strength, rigidity, hardness, and melting temperature, but at the price of reduced ductility—that is, increased brittleness.

Factors that reduce or prevent crystallinity include the following:

- Copolymer formation, which inhibits polymer chain alignment
- Polymer-chain branching, which also interferes with chain alignment
- Random arrangement of substituent groups, particularly large side groups that keep polymer chains separated
- Plasticizers, which tend to separate the chains (see Solvation Properties, below)

PERFORMANCE CRITERIA FOR DENTAL RESINS

For dental applications, polymeric materials should be mechanically strong and physically stable, easily manipulated as needed, have excellent esthetic qualities, be chemically stable both in storage and in the mouth, have biological compatibility, and have a reasonable cost. Although current dental polymers approach these requirements, none meets them all; consequently each commercial example of a particular material tends to display a different balance among the various performance characteristics.

MECHANICAL AND PHYSICAL PROPERTIES

Dental resins should have sufficient strength and resilience to resist the forces developed by biting, chewing, and impact and sufficient toughness as well as fracture and fatigue resistance to maintain form and function for many years. The material should also be dimensionally stable under all conditions of service, including thermal changes and variations in loading. When used as a denture base for maxillary dentures, a resin should also have a low density to ensure a light weight, and it should have good thermal conductivity to maintain the patient's ability to detect temperature changes.

MANIPULATION PROPERTIES

The resin should not produce toxic fumes or dust during handling and manipulation. It should be easy to mix, insert, shape, and cure, and it must have a relatively short **setting** time and be insensitive to variations in these handling procedures. Clinical complications—such as oxygen inhibition, saliva contamination, and blood contamination—should have little or no effect on the outcome of any handling procedure. In addition, the final product should be easy to polish; in case of breakage, it should be possible to repair the resin easily and efficiently.

ESTHETIC PROPERTIES

The material should exhibit sufficient translucency or transparency so that it can be made to match the appearance of the oral tissues it replaces. The resin should be colorless and capable of being tinted or pigmented, and there should be no change in color or appearance of the material subsequent to its fabrication.

CHEMICAL STABILITY

Conditions in the mouth are highly demanding, and only the most chemically stable and inert materials can withstand such conditions without deterioration.

BIOLOGICAL COMPATIBILITY

Polymers and resins should be tasteless, odorless, nontoxic, nonirritating, and otherwise not harmful to the oral tissues. To fulfill these requirements, a resin should be completely insoluble in saliva or in any other fluids taken into the mouth, T_g and it should be impermeable to oral fluids to the extent that the resin does not become unsanitary or disagreeable in taste or odor. If the resin is used as a filling or cementing material, it should set fairly rapidly and bond to tooth structure to prevent microbial ingrowth along the tooth-restoration interface. A more comprehensive overview of the biocompatibility of dental materials is presented in Chapter 7.

ECONOMIC CONSIDERATIONS

The cost of the resin and its processing method should be relatively low, and processing should not require complex and expensive equipment.

MECHANICAL AND PHYSICAL PROPERTIES OF POLYMERS

As illustrated in Figure 6-1, the combination of polymer composition, chain length, branching, crosslinking, and molecular orientation can produce a variety of properties. To meet the needs of various dental applications, these features are manipulated to produce a balance that approaches the ideal performance properties as closely as practical. These properties can be grouped into four interrelated categories: mechanical, rheological (flow), dissolution, and thermal.

MECHANICAL PROPERTIES—DEFORMATION AND RECOVERY

Applied forces produce stresses within polymers that cause materials to deform (i.e., undergo strain) via either elastic strain, plastic strain, or a combination of elastic plus plastic strain.

- *Plastic* strain is irreversible deformation that cannot be recovered and results in a new, permanent shape as the result of slippage (flow) among polymer chains.

- *Elastic* strain is reversible deformation and will be quickly and completely recovered when the stress is eliminated, as the result of polymer chains uncoiling and then recoiling.
- ***Viscoelastic*** strain is a combination of both elastic and plastic deformation, but only the elastic portion is recovered when the stress is reduced, as described in Chapter 3. Also, recovery is not instantaneous and occurs over time because the **elastic recovery** process is impeded by the viscous flow resistance among chains. The amount of deformation that is not recovered at the moment the stress is eliminated is known as *plastic deformation*.

In the absence of crosslinking, only relatively weak interpolymer-chain bonds (van der Waals and hydrogen bonds) are available to hold the polymer chains together in a solid state. Chain slippage decreases as chain length increases because the bonds between chains, together with chain entanglements, resist dislodgment of the individual chains. At a certain chain length the resistance provided by interchain bonds and entanglements becomes strong enough to exceed the covalent bond strength of the carbon-carbon bonds along the backbone chains. At this critical chain length, an applied force can rupture chains rather than dislodge them and cause one chain to slide past another. This balance between the strength of the interchain bonds and the covalent bonds along the backbone chains explains why the physical and mechanical properties of polymers increase with increased molecular weight up to a certain point. Subsequently, increased molecular weight becomes less important, as shown in Figure 6-1.

Although dependent on its type, a resin generally develops mechanical strength only when its degree of polymerization is relatively high, in the range of approximately 150 to 200 recurring mer units. Above this molecular weight, there is very little increase in strength with further polymerization. Likewise the molecular-weight distribution of the polymer plays an important role in determining physical properties. In general, a narrow distribution of molecular weight yields the most useful balance among required properties.

Long side chains extending from the main backbone chain (i.e., chain branching) generally produce a weaker resin with a lower softening temperature in comparison with linear-chain (nonbranched) polymers. This weakening occurs because the side chains act to separate the main chains, thus reducing the chain-to-chain attractive forces. This is the *plasticizing* effect discussed further in the following section on solvation. However, if the side chains can react with adjacent chains to form a crosslinked polymer, the strength of the polymer is increased.

CRITICAL QUESTIONS

What is the difference between elastomers and plastics? What causes some polymers to respond elastically to stresses and others to act viscoelastically?

RHEOMETRIC PROPERTIES

The rheometry, or *flow* behavior, of solid polymers involves a combination of elastic and plastic deformation followed by elastic recovery after the stresses are eliminated. This combination of elastic and plastic changes is termed *viscoelasticity*. The chain length, number of crosslinks, temperature, and rate of force application (fast impact versus slow extrusion) determine which type of behavior dominates (see also Chapter 3).

- ***Plastic flow***: Irreversible strain behavior that occurs when polymer chains slide over one another and become relocated within the material, resulting in permanent deformation. Branching and crosslinking impede plastic flow.
- *Elastic recovery*: Reversible strain behavior that occurs in the amorphous regions of polymers when the randomly coiled chains straighten and then recoil, like springs that return to their original locations without sliding past one another when the applied force is removed (Figure 6-5). Plastic and elastic properties are used to describe ideal materials. In fact, most polymeric materials can sustain a combination of elastic plus plastic strain during loading. Thus, elastomers do not always recover fully. Therefore, they retain a small degree of plastic deformation. Plastics exhibit a high level of plastic deformation but also have at least some small degree of elastic recovery. This phenomenon is called *viscoelastic recovery* (Figure 6-6).

CRITICAL QUESTION

Which effects are likely if a plasticizer is leached out of a polymer?

SOLVATION AND DISSOLUTION PROPERTIES

Polymers are usually slow to dissolve, and are seldom clearly either soluble or insoluble in any particular liquid. Also, their solvation characteristics are very sensitive to $\overline{M}_w$, $\overline{M}_w/\overline{M}_n$ (polydispersity), crosslinking, crystallinity, and chain

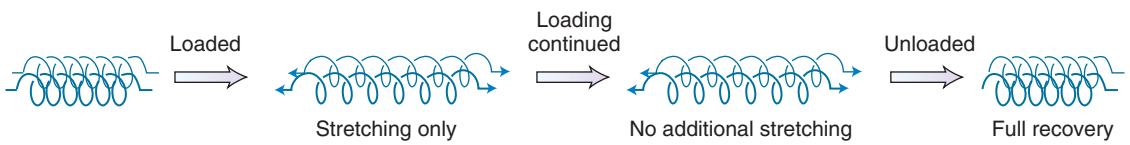


FIGURE 6-5 Elastic recovery: springlike behavior (rapid and reversible). Chains uncoil, but they do not slip past one another because of crystalline regions, entanglements, or crosslinks. Thus, they recoil completely when unloaded.

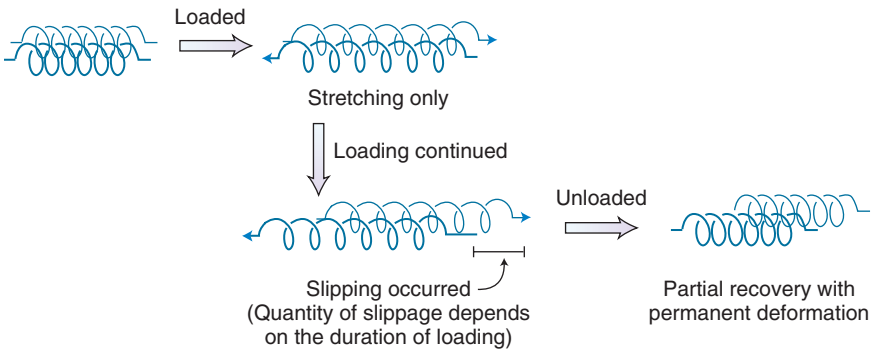


FIGURE 6-6 Viscoelastic recovery: chains stretch and uncoil and also slip past one another, producing plastic, irreversible, permanent distortion and partial recovery when unloaded.

branching. The following are polymer solvation characteristics relevant to dental use:

- The longer the chains (the higher the molecular weight), the more slowly a polymer dissolves.
- Polymers tend to absorb a solvent, swell, and soften rather than dissolve. Any dissolution occurs from the swollen state.
- Crosslinking prevents complete chain separation and retards dissolution; thus, highly crosslinked polymers cannot be dissolved.
- Elastomers swell more easily and to a greater extent than do plastics.
- Absorbed molecules (e.g., water) spread polymer chains apart and facilitate slippage between chains. This lubricating effect is called *plasticization*.
- Swelling of dental polymeric devices can adversely affect fit—as, for example, with full and partial dentures.

Crosslinking provides a sufficient number of bridges between linear macromolecules to form a three-dimensional network that decreases water sorption, decreases solubility, and increases the strength and rigidity of the resin. For example, crosslinking has been used widely in the manufacture of acrylic teeth to increase their resistance to degradation by alcohol and other solvents and the surface stresses produced by solvents. Crystalline regions act as physical crosslinks, reducing swelling and solubility.

Plasticizing compounds, known as *plasticizers*, are often added to resins to reduce their softening or melting/fusion temperatures. It is possible to make a resin that is normally hard and stiff at room temperature, flexible and soft by adding a plasticizer. For example, plastic water pipe made from polyvinylchloride (PVC) is hard and rigid and contains very little plasticizer, whereas PVC water-line tubing is soft and elastic and contains a very high level of plasticizer. In recent years certain plasticizers, particularly phthalates, have received public attention as a potential ingestion hazard in soft plastics used in infants' and children's toys.

A plasticizer acts to partially neutralize secondary bonds or intermolecular attractions that normally prevent the resin chains from slipping past one another (i.e., undergoing plastic flow) when the material is stressed. In some cases, this action is analogous to that of a solvent, with the plasticizing agent penetrating between the macromolecules and increasing the intermolecular spacing. This type of plasticizer is referred to as an external plasticizer because it is not a part of the polymer's structure. Its molecular attraction to the polymer should be extremely high so that it does not volatilize or leach out during the fabrication or subsequent use of the resin. Such a condition is seldom realized in practice, so this type of plasticizer is used sparingly in dental resins.

Plasticizing can also be accomplished by copolymerization with a suitable comonomer. In this case, the plasticizing agent becomes part of the polymer and acts as an internal plasticizer. For example, when butyl methacrylate is added to methylmethacrylate before polymerization, the polymerized resin is plasticized internally by the bulky butyl methacrylate segments (see Figure 6-14). The pendant butyl methacrylate groups occupy extra space between chains and increase intermolecular spacing, which enhances plastic flow. Plasticizers usually reduce the strength, hardness, and softening temperature of the resin. For example, both internal and external plasticizers are utilized to help form soft, cushioning liners for dentures.

? CRITICAL QUESTIONS

What is the difference between thermoplastic and thermosetting polymers? Which involves a reversible physical change and which involves an irreversible change?

THERMAL PROPERTIES

The physical properties of a polymer are influenced by changes in temperature and environment and by the composition, structure, and molecular weight of the polymer. In general, the higher the temperature, the softer and weaker the polymers become.

Polymers can be formed into many desired shapes, using processes that depend on whether the polymeric material is a "thermoset" or a "thermoplastic" type.

Thermoplastic resins:

- Soften on heating, and harden on cooling
- Can be reprocessed by heating and cooling

- Undergo a reversible reorganization among the molecular chains upon heating, as in denture-base resins

Thermoplastic polymers are made of linear and/or branched chains. They soften when heated above the *glass transition* (T_g)—the temperature at which molecular motion begins to force the chains apart. The resin can then be shaped and molded and, upon cooling, it will harden reversibly in this form. Upon reheating, such polymers soften again and can be reshaped, if required, before again being hardened by decreasing the temperature. This cycle can be repeated almost indefinitely. The setting reaction is reversible because of the relatively weak bonds among the molecular chains. Thus, in contrast to thermosetting resins, thermoplastic resins can melt and are usually soluble in organic solvents.Thermosetting resins (1) undergo a chemical change during the setting reaction; (2) are not softened by heat; (3) char; (4) decompose rather than melt; and (5) are crosslinked and as insoluble as resin-based composites.

Thermosetting polymers undergo a chemical change and become permanently hard when heated above the temperature at which they begin to polymerize; they do not soften again on reheating to the same temperature. They are usually crosslinked in this state, and thus, they are insoluble and will not melt. Instead, they decompose if heated to a high enough temperature. Thermosetting polymers generally have superior abrasion resistance and dimensional stability compared with thermoplastic polymers, which have better flexural and impact properties.

Without crosslinking, only the relatively weak bonds (described in the discussion of mechanical properties, above) hold the polymer chains together as a solid. When such a polymer is heated to its T_g or above, these break and the polymer chains then move more freely relative to each other. The increased chain mobility reduces strength and modulus of elasticity (see Figure 6-1) and it increases thermal expansion.

If two otherwise similar linear polymers are compared, the one with the higher molecular weight will also have a higher T_g. This is because as the length of the linear-polymer chain is increased, the number of bond sites increases along that chain. In addition, the longer length of the chain increases the chance for chain entanglements. Thus, the increased number of bond sites along each chain and the increased chances for chain entanglements explain why polymers with a higher molecular weight are stronger and also require more thermal energy to reach their T_g, as shown in Figure 6-1.

The number average molecular weight ($\overline{M}_n$) is indicative of both T_g and the strength of the polymer. As mentioned previously, the value for the number average molecular weight is lowered markedly by the presence of relatively few very low molecular weight polymer chains or unreacted monomers, which lower T_g and also considerably weaken the resin.

As the temperature increases, thermally induced rotations and vibrations among polymer segments increase. This molecular motion forces chains apart, breaks bonds, increases thermal expansion, and facilitates chain disentanglement. These factors, in turn, induce chain slippage and explain the thermoplastic behavior of a resin when the temperature exceeds T_g. As the degree of crosslinking increases, slippage is progressively reduced and the material becomes progressively more resistant to thermal softening.

CRITICAL QUESTION

What are the benefits and drawbacks of a heavily crosslinked polymer?

If a crosslinked resin is heated to its glass transition temperature T_g, it will resist plastic flow and a permanent change in shape. Instead, the polymer becomes rubbery in consistency. An elastomeric dental impression material can be described as a lightly crosslinked polymeric structure with a T_g lower than room temperature. The low T_g indicates that the chain segments are thermally activated at room temperature and can easily rotate, twist, and vibrate. In this manner the chains are rendered more flexible and yet the crosslinks prevent chain slippage and transfer all stresses to chain uncoiling rather than slipping past one another, thereby ensuring reversible recovery from distortion. Such crosslinking must occur only occasionally between the chains (lightly crosslinked). If a high degree of crosslinking is present, a network configuration prevails and the resin becomes rigid, brittle, and useless as an impression material. The situation is analogous to that described in Chapter 8 for the formation of calcium alginate in alginate gels. Such crosslinked bonds cause the polymer to return to its original shape after the load is released, as in the case of the alginate impression materials.

CHEMISTRY OF POLYMERIZATION

Monomers may be joined together by means of either addition or condensation reactions. In addition polymerization, monomers are activated one at a time and added together in sequence to form a growing chain. In condensation polymerization (also known as step-growth polymerization), the components are difunctional and all are or become reactive simultaneously. Chains then grow by the stepwise linking of bifunctional monomers that usually, but not always, produce a low-molecular-weight by-product, such as water or an alcohol, to be "condensed out"—hence the term *condensation polymerization*.

ADDITION POLYMERIZATION

Most dental resins are polymerized by a mechanism in which monomers add sequentially to the end of a growing chain. Addition polymerization starts from an active center, adding one monomer at a time to rapidly form a chain. In theory, the chain can grow indefinitely until the entire monomer is exhausted. The process is simple, but it is not easy to control. Two basic types of addition polymerization monomers are found in current dental products. One is based on opening of carbon-carbon double bonds and joining to form single

bonds, and the other is based on ring-opening reactions in which a three-atom ring is broken open and it then joins with another broken ring to form single bonds. Carbon-carbon double-bond units (–C=C–) are known as *vinyl* groups, and are most often exemplified in dentistry by methacrylate monomers (–C=C(CH_3)–COOR). Ring-opening monomers are represented by imine-containing compounds that contain two carbons plus one nitrogen ring, such as found in polyether impression materials (Chapter 8) and by epoxy compounds with rings containing two carbons and one oxygen, as found in silorane adhesives and restorative resins (Chapter 13). In this chapter vinyl- and methacrylate-based chemistry is used to illustrate the main features of addition polymerization.

Compared with step-growth polymerization (discussed later in this chapter), addition polymerization can produce giant molecules of almost unlimited size. There is no change in composition during addition polymerization. That is, the macromolecules are formed from monomers without change in composition because the monomer and the polymer have the same empirical formulas, in which the monomer structure is repeated many times in the polymer.

? CRITICAL QUESTIONS

What are the stages of activation and free radical initiation and curing? Which three activation processes are used for dental polymers?

STAGES IN THE ADDITION POLYMERIZATION OF VINYL MONOMERS

There are four stages in the addition polymerization chain reaction: **induction**, **propagation**, **chain transfer**, and **termination**.

Induction

Two processes control the induction stage—activation and initiation. For an addition polymerization process to begin, a source of free radicals, R•, is required. Free radicals can be generated by the activation of radical-producing molecules using a second chemical, heat, visible light, ultraviolet light, or energy transfer from another compound that acts as a free radical (Figure 6-7). Of these, chemical agents, heat, and visible light are most often used in dentistry.

$$R—R + \text{external energy} \rightarrow 2\ R\bullet \quad (1)$$

One of the requisites of an addition-polymerizable compound is the presence of an unsaturated group—that is, a double bond—as well as a source of **free radicals**. Theoretically, R• can be almost any free radical. A free radical is an atom or group of atoms possessing an unpaired electron (•). The unpaired electron confers an electron-withdrawal ability to the free radical. When the free radical and its unpaired electron approach a monomer with its high-electron-density double bond, an electron is extracted, and it pairs with the R• electron to form a bond between the radical and the monomer molecule, leaving the other electron of the double bond unpaired. Thus, the original free radical bonds to one side of the monomer molecule and forms a new free radical site at the other end. The reaction is now initiated.

Ethylene, $H_2C=CH_2$, the simplest monomer capable of addition polymerization, can be used for illustration:

$$R\bullet + H_2C=CH_2 \rightarrow RH_2C—CH_2\bullet \quad (2)$$

Initiation of the important dental resin methylmethacrylate is shown in Figure 6-8.

The free radical–forming chemical used to start the polymerization is not a catalyst (although it is often incorrectly described as such) because it enters into the chemical reaction and becomes part of the final chemical compound. It is more accurately called an initiator because it is used to start the reaction. A number of substances capable of generating free radicals are potent initiators for the polymerization of PMMA and other methacrylate-type resins used extensively in dentistry (Figure 6-8, Chapters 13 and 20). The most commonly employed initiator is benzoyl peroxide, which is activated rapidly between 50 °C and 100 °C to release two free radicals per benzoyl peroxide molecule (reaction 1 and Figure 6-7). Induction is the period during which initiator molecules become energized and break down into free radicals, followed by these radicals reacting with monomer molecules to initiate chain growth (reactions 2 and 3 and Figure 6-8). This period is greatly influenced by the purity of the monomer. Any impurities present that are able to react with activated groups can increase the length of this period by consuming the activated initiator molecules. However, the higher the temperature, the more rapid the formation of free radicals and consequently the shorter the induction period.

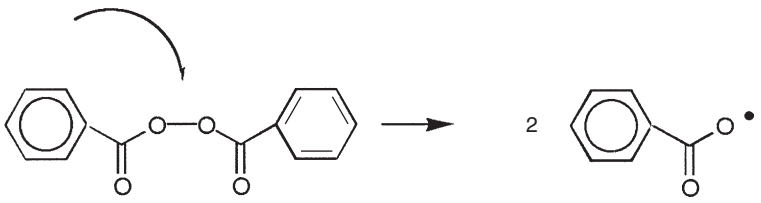


FIGURE 6-7 Activation (heat or chemical) of benzoyl peroxide (BPO). During activation, the bond between the two oxygen atoms (–O–O– or O:O) is broken and the electron pair is split between the two fragments. The dot adjacent to the oxygen atom (O•) symbolizes the unpaired electron of the free radical.

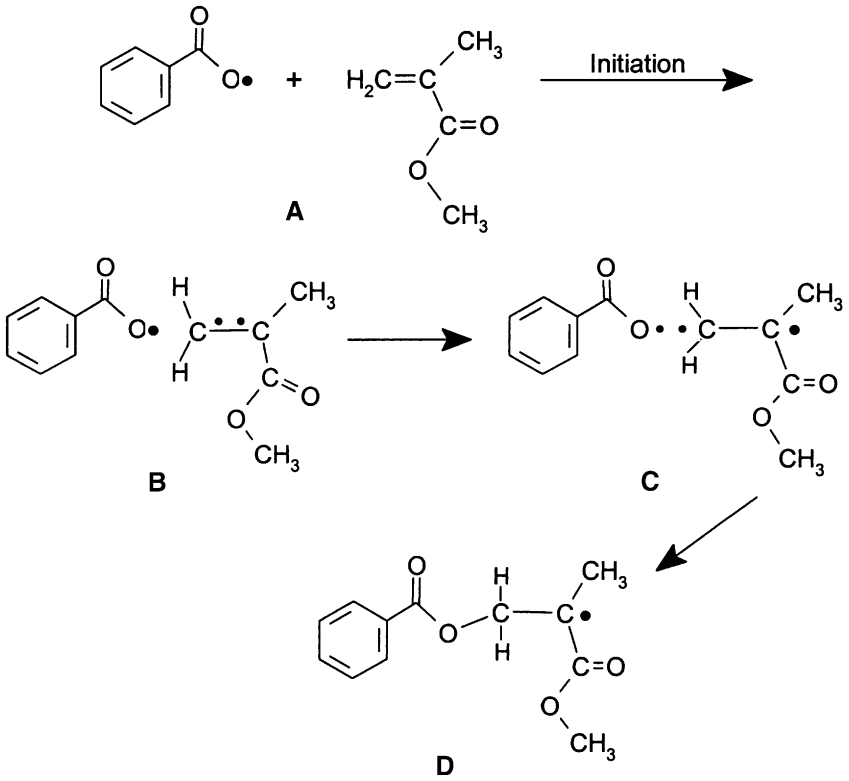


FIGURE 6-8 Initiation of a methylmethacrylate molecule. As the unpaired electron of the free radical approaches the methylmethacrylate molecule (**A** and **B**), one of the electrons in the double bond is attracted to the free radical to form an electron pair and a covalent bond between the free radical and the monomer molecule (**C** and **D**). When this occurs, the remaining unpaired electron makes the new molecule a free radical (**D**).

The polymerization processes useful for dental resins are commonly activated by one of three energy sources: heat, chemicals, and light. Most denture base resins are polymerized by heat activation, as explained previously, producing two free radicals, which then initiate and propagate the polymerization of methylmethacrylate monomer, as shown in reactions 1 through 4.

A second type of induction system is chemically activated at ambient oral temperature. Such a system consists of at least two reactants that, when mixed together, undergo a chemical reaction that generates free radicals. During storage, these components must be separated from each other; hence chemically induced systems always consist of two or more parts. An example of such a system is the tertiary amine (the activator) and benzoyl peroxide (the initiator), which are mixed together to initiate the polymerization of "self-cured" dental resins at room temperature. This process, in fact, is a special case of heat activation, because the presence of the amine reduces the thermal energy required to break the initiator into free radicals at ambient temperature (i.e., room temperature or mouth temperature). The amine forms a complex with benzoyl peroxide, which reduces the thermal energy and, thus, the temperature needed to split it into two free radicals.

A third type of induction system is light-activated. In this system, photons from a light source activate the initiator to generate free radicals that, in turn, can initiate the polymerization process. When this system was first introduced to dentistry, ultraviolet light was used. However, because of concerns about the effect of ultraviolet light on the retina and unpigmented oral tissues, its limited penetration depth, and the loss in intensity of the ultraviolet light source over time, initiator systems activated by visible light were subsequently developed. In the visible light–cured dental restoratives, camphorquinone and an organic amine (e.g., dimethylaminoethylmethacrylate) generate free radicals when irradiated by light in the blue-to-violet region. Light with a wavelength of about 470 nm is needed to trigger this reaction. Because no appreciable polymerization takes place at ambient temperature in the dark, such compositions can be one-part systems provided that they are stored where they are not exposed to light. However, factors such as light intensity, angle of illumination, and distance of resin from the light source can significantly affect the number of free radicals formed, thereby making this system highly technique sensitive.

Propagation

The resulting free radical-monomer complex then acts as a new free radical center when it approaches another monomer to form a dimer, which also becomes a free radical. This reactive species, in turn, can add successively to a large number of ethylene molecules so that the polymerization process continues through the propagation of the reactive center.

$$RH_2C{-}CH_2\bullet + H_2C{=}CH_2 \rightarrow RH_2C{-}CH_2{-}H_2C{-}CH_2\bullet \quad (3)$$

$$RH_2C{-}CH_2{-}H_2C{-}CH_2\bullet + H_2C{=}CH_2 \rightarrow RH_2C{-}(CH_2{-}H_2C)_2{-}CH_2\bullet \ldots \text{etc.} \quad (4)$$

Propagation reactions are further illustrated in Figure 6-9. Because little energy is required once chain growth begins, the process continues with evolution of heat and leads to large polymer molecules within seconds. Theoretically, the chain

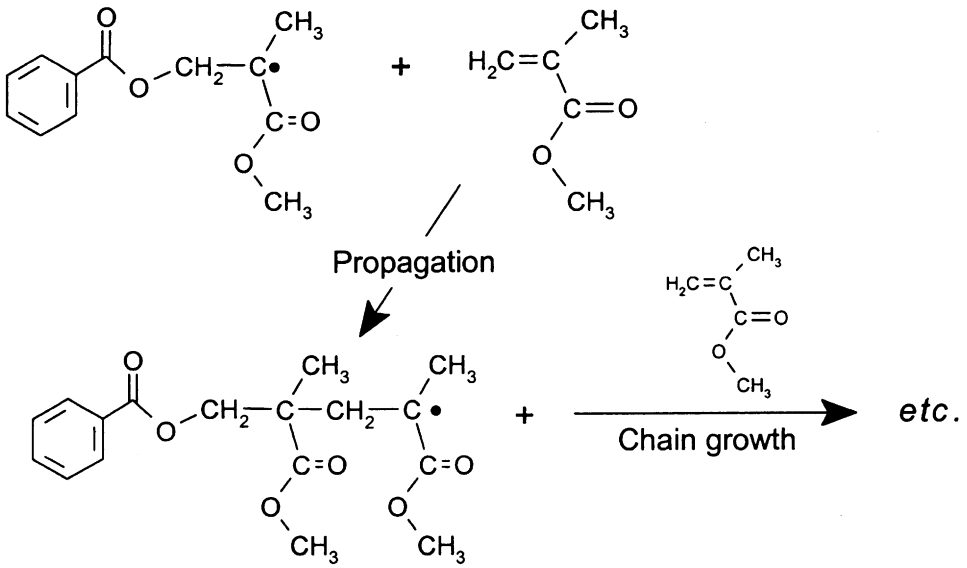


FIGURE 6-9 Propagation and chain growth. As the initiated molecule approaches other methylmethacrylate molecules, the free electron interacts with the double bond of the methylmethacrylate molecule and a new, longer free radical is formed.

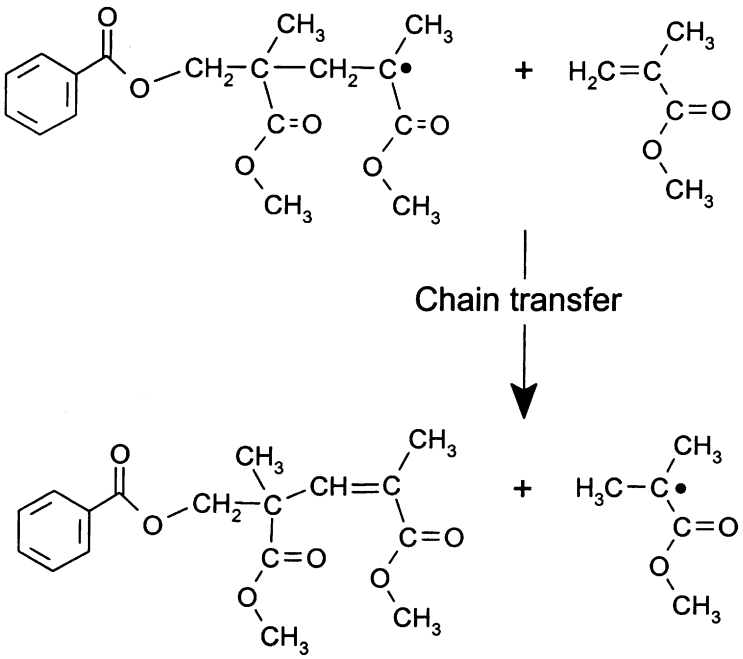


FIGURE 6-10 Chain transfer occurs when a free radical approaches a methylmethacrylate molecule and donates a hydrogen atom to the methylmethacrylate molecule. This causes the free radical rearrangement to form a double bond and become unreactive and the methylmethacrylate monomer to form a free radical that can participate in a chain-propagation reaction.

reactions should continue until all of the monomer has been converted to a polymer between the **initial set** and the **final set**. The process continues to complete the formation of the desired polymer. However, the polymerization reaction is never quite completed.

The growth of the polymer chain ceases when the reactive center is destroyed by one of a number of possible termination reactions (as discussed later). The entire addition polymerization process can be pictured as a series of chain reactions. The process occurs rapidly, almost instantaneously, with the release of exothermal energy, and considerable heat evolves.

Chain Transfer

In this process the active free radical of a growing chain is transferred to another molecule (e.g., a monomer or inactivated polymer chain) and a new free radical for further growth is created. For example, a monomer molecule may be activated by a growing macromolecule in such a manner that termination occurs in the latter (Figure 6-10). Thus, a new

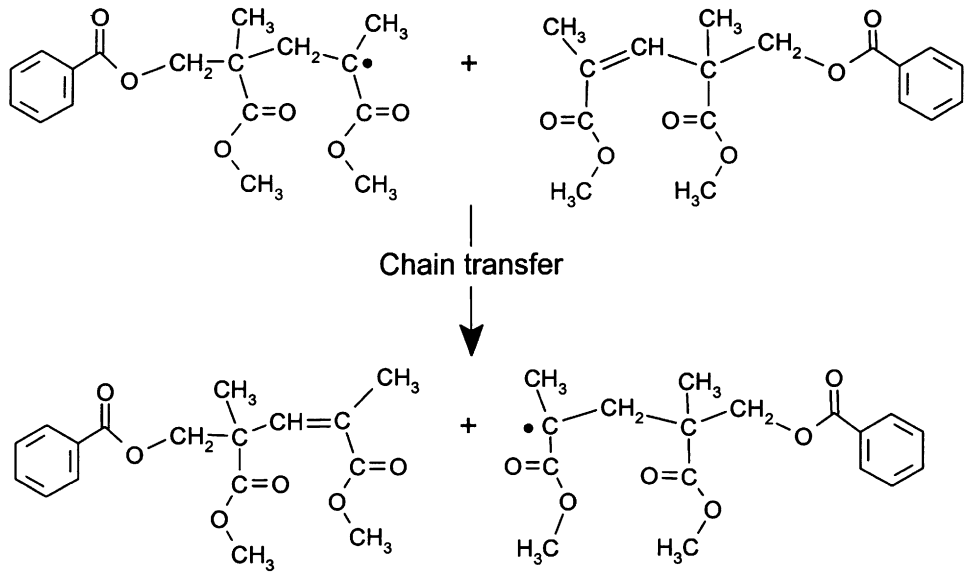


FIGURE 6-11 Another type of chain transfer can occur when a propagating chain interacts with the passivated segment that was formed in Figure 6-10. During this interaction, the passive segment becomes active while the active segment becomes passive.

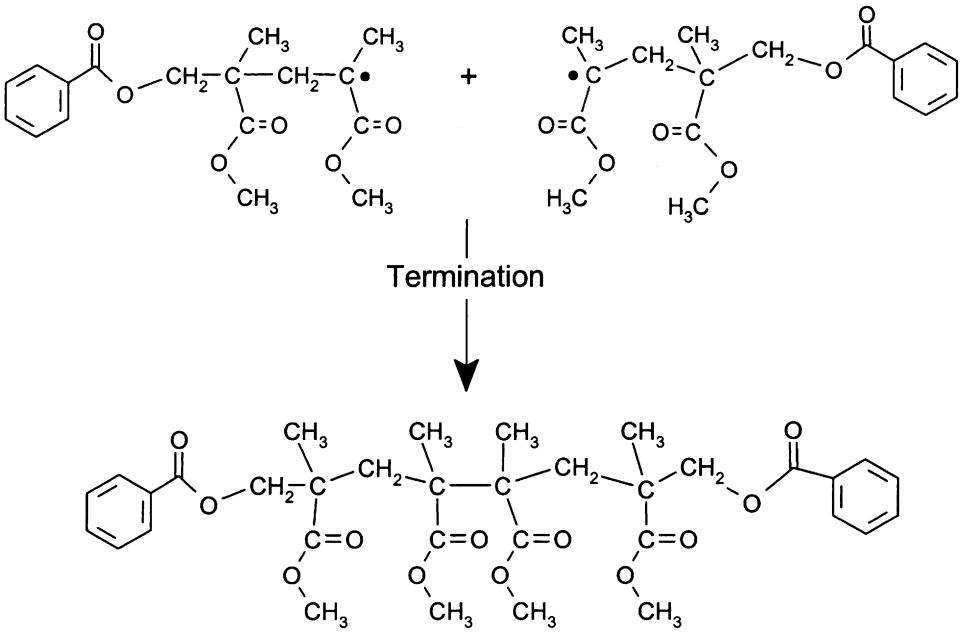


FIGURE 6-12 Termination occurs when two free radicals interact and form a covalent bond.

nucleus for growth results. In the same manner, an already terminated chain might be reactivated by chain transfer, and it will continue to grow (Figure 6-11). These processes differ from the termination reactions described below.

Termination

Although chain termination can result from chain transfer, addition polymerization reactions are most often terminated either by direct coupling of two free radical chain ends or by the exchange of a hydrogen atom from one growing chain to another.

Termination by direct coupling can be illustrated by the ethylene addition reaction. Continui ng from the propagation reaction (reaction 4), if a growing chain with "m" monomer units encounters another growing chain with "n" units, then:

$$\begin{aligned} &RH_2C{-}(CH_2{-}H_2C)_m{-}CH_2\bullet + \bullet H_2C{-}(CH_2{-}H_2C)_n{-}CH_2R \rightarrow \\ &RH_2C{-}(CH_2{-}H_2C)_m{-}CH_2{-}H_2C{-}(CH_2{-}H_2C)_n{-}CH_2R \end{aligned} \quad (5)$$

Both molecules combine and become deactivated by formation of a covalent bond (Figure 6-12).

Another means by which such an energy exchange can occur is the transfer of a hydrogen atom from one growing chain to another. As shown on the bottom-left side of Figure 6-13, this causes a double bond to be formed when the hydrogen atom is transferred.

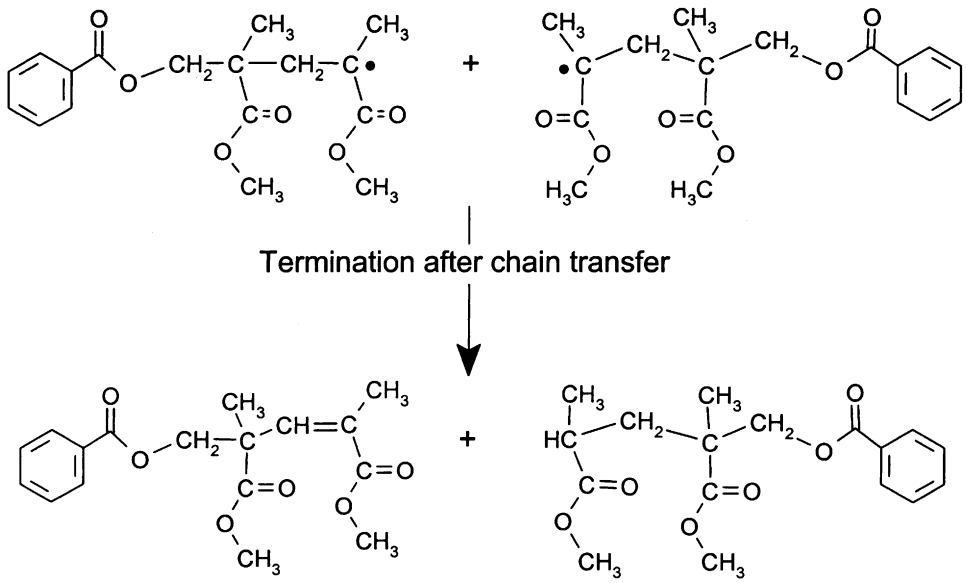


FIGURE 6-13 When two free radicals approach each other, a new double bond may be formed on the molecule that donates a hydrogen atom to the other free radical.

CRITICAL QUESTIONS

What mechanisms are responsible for the inhibition of polymerization? What are the benefits of inhibitors in dental resins? What role does O_2 play as an inhibitor?

INHIBITION OF ADDITION POLYMERIZATION

As noted in the previous section, the polymerization reactions are not likely to result in complete exhaustion of the monomer, nor do they always form polymers of high molecular weight. Impurities in the monomer often inhibit such reactions.

Any impurity in the monomer that can react with free radicals inhibits or retards the polymerization reaction. An impurity can react with the activated initiator or with an activated growing chain to prevent further growth. The presence of such inhibitors markedly influences the length of the induction period as well as the degree of polymerization.

For example, the addition of a small amount of a common inhibitor, such as hydroquinone, to the monomer inhibits spontaneous polymerization if no initiator is present and retards the polymerization in the presence of an initiator. Thus, inhibitors affect both the storage stability and the working time of a dental resin. For this reason, commercial dental resins commonly contain a small amount (approximately 0.006% or less) of an inhibitor such as the methyl ether of hydroquinone to aid in the prevention of polymerization during storage and, in the case of two-part (self-cure) systems, to provide adequate time for mixing and placement.

Oxygen reacts rapidly with free radicals, and its presence retards the polymerization reaction. It has been shown, for example, that the reaction velocity and the degree of polymerization are decreased if polymerization is conducted in open air in comparison with the higher values obtained when the reaction is carried out in an oxygen-deficient environment. The influence of oxygen on polymerization is governed by many factors such as concentration, temperature, and light intensity. It is important to be aware of the inhibiting effect of oxygen on the polymerization process. Thus, the clinical practice of "air thinning" of bonding resins should be avoided in order to optimize curing in important regions of a restoration. A common clinical practice is to cover and shape resins with a "matrix" strip, which helps to shape the resin and acts as a barrier to prevent contact with oxygen during curing. Such a matrix strip prevents a sticky, air-inhibited layer from forming on the surface.

RING-OPENING ADDITION POLYMERIZATION

The ring-opening reaction is the second type of addition polymerization used with current dental products. This typically involves monomers with one or more three-atom end-group rings, which open and then join with other broken rings to form single bonds, similar to the way carbon-carbon double bonds open and link up to form single bonds. In one sense, the –C=C– group can be considered to be a two-atom ring. Ring-opening monomers containing more than three atoms in the ring are known but as yet have no application as dental materials. Two types of three-atom ring monomers have found significant usage in dentistry: imines, with two carbons and a nitrogen, and epoxies, with two carbons and an oxygen. The imines are used in polyether impression materials and are discussed in Chapter 8. The epoxy monomers are used in the recently introduced silorane restorative and bonding resins and are discussed in Chapter 13.

STEP-GROWTH/CONDENSATION POLYMERIZATION

The reactions that produce step-growth polymerization can progress by any of the chemical reaction mechanisms that join two or more molecules to produce a simple nonmacromolecular structure. The primary compounds

react, often with the formation of by-products such as water, alcohols, halogen acids, and ammonia. The formation of these by-products is the reason step-growth polymerization often is called condensation polymerization. The structure of the monomers is such that the process can repeat itself and build macromolecules. This mechanism is also the one used in biological tissues to produce proteins, carbohydrates, deoxyribonucleic acid, and ribonucleic acid, which are exclusively formed via step-growth polymerization reactions.

In step-growth polymerization, a linear chain of repeating mer units is obtained by the stepwise intermolecular condensation or addition of the reactive groups in which bifunctional or trifunctional monomers are all simultaneously activated, as opposed to the activation of one monomer at a time in chain-growth addition polymerization. For example:

$$\begin{aligned}&\text{HO–(silicone)–OH} + n\ \text{HO–(silicone)–OH} \rightarrow \\ &\text{HO–(silicone)–(O–silicone)}_n\text{–OH} + n\ \text{H}_2\text{O}\uparrow\end{aligned} \quad (6)$$

This type of reaction is also illustrated in Chapter 8 on impression materials. In one reaction, water is removed in the process of joining trimercaptans to form a polysulfide rubber (see Figure 8-3); in the other case, ethanol is removed in the process of joining siloxane molecules to form silicone rubber (see Figure 8-4). At each step in the reaction a new bi- or trifunctional higher-molecular-weight compound is formed. As the reaction proceeds, progressively longer chains form until ultimately the reaction contains a mixture of polymer chains of large molar masses. In the case of the trifunctional reaction for a polysulfide impression material, a structure forms that is both branched and crosslinked (Figure 8-3).

As polymer science has progressed, the classification of condensation-polymerized resins has broadened. Because the goal is to minimize classification uncertainties, the term *step-growth polymerization* (rather than *condensation polymerization*) is preferred. Step-growth polymerized resins are those in which polymerization is accompanied by repeated step-wise elimination of small molecules. The formation of polymers by step growth is comparatively slow because the reaction proceeds in a stepwise fashion from monomer to dimer to trimer, and so forth, until large polymer molecules containing many monomer molecules are eventually formed. Such a polymerization process tends to stop before the chains have reached a truly large size because they become less mobile and less numerous as their chains grow.

? CRITICAL QUESTION

What are the practical benefits of using copolymer resins for dental applications?

COPOLYMERIZATION

In many of the polymerization reactions described above, the macromolecule is formed by the polymerization of a single type of structural unit. However, two or more chemically different monomers, each with some desirable property, can be combined to yield specific physical properties of a polymer. As defined earlier, the polymer formed is a copolymer, and the process of formation is known as copolymerization (Figure 6-14). In a copolymer, the relative number and position of the different type of repeating units may vary among the individual macromolecules, as in random, block, and branched copolymers (Figure 6-2).

Copolymerization is most easily illustrated with two monomers, although it is possible to incorporate more than two monomers. For example, two monomers ($H_2C{=}CHR^1$ and $H_2C{=}CHR^2$) consisting of ethylene derivatives can be incorporated, with either R^1 or R^2 substituted for one of the H-atoms, as shown below:

$$n\ H_2C{=}CHR^1 + m\ H_2C{=}CHR_2 \rightarrow (H_2C{-}CHR^1{-}H_2C{-}CHR^2)_{n+m} \quad (7)$$

This copolymer structure is highly idealized because the occurrence of alternately placed radicals in the chain would seldom occur. It is more probable that the positions of the radicals are random—a matter of probability. The composition of the copolymer depends on the relative reactivities of the two (or more) different monomers as well as the relative reactivity of like monomers among themselves. For example, if the tendency of $H_2C{=}CHR^1$ to homopolymerize (polymerization with itself) is so great that it polymerizes independently of $H_2C{=}CHR^2$, no copolymerization will occur, and the resulting resin will consist of a mixture of two polymers:

$$n\ H_2C{=}CHR^1 + m\ H_2C{=}CHR^2 \rightarrow (H_2C{-}CHR^1)_n + (H_2C{-}CHR^2)_m \quad (8)$$

Such an extreme condition seldom, if ever, occurs. In most instances, the cured polymer consists of a mixture of polymers and copolymers, with varying degrees of polymerization or copolymerization. Furthermore, as explained above, copolymers can vary in the molecular sequence and arrangement among the repeating random block and graft units. Copolymerization can have a very strong influence on the physical and mechanical properties of the resulting resin, changing them considerably from those of the respective homopolymers.

Many useful resins are manufactured by copolymerization. Methylmethacrylate, acrylic esters, and methacrylic esters all copolymerize readily, with little inhibition between monomer pairs. For example, small amounts of ethylacrylate may be copolymerized with methylmethacrylate to alter the flexibility and fracture resistance of a denture.

Grafting of various polymer segments onto a linear chain provides an important mechanism for modifying or tailor-making macromolecules to obtain required properties for specific uses. For example, block and graft polymers often show improved impact strength. In small quantities, these polymers can modify the adhesive properties of resins as well as their surface characteristics.

ACRYLIC DENTAL RESINS

As previously mentioned, for a **synthetic resin** to be useful in dentistry, it must exhibit exceptional qualities regarding its

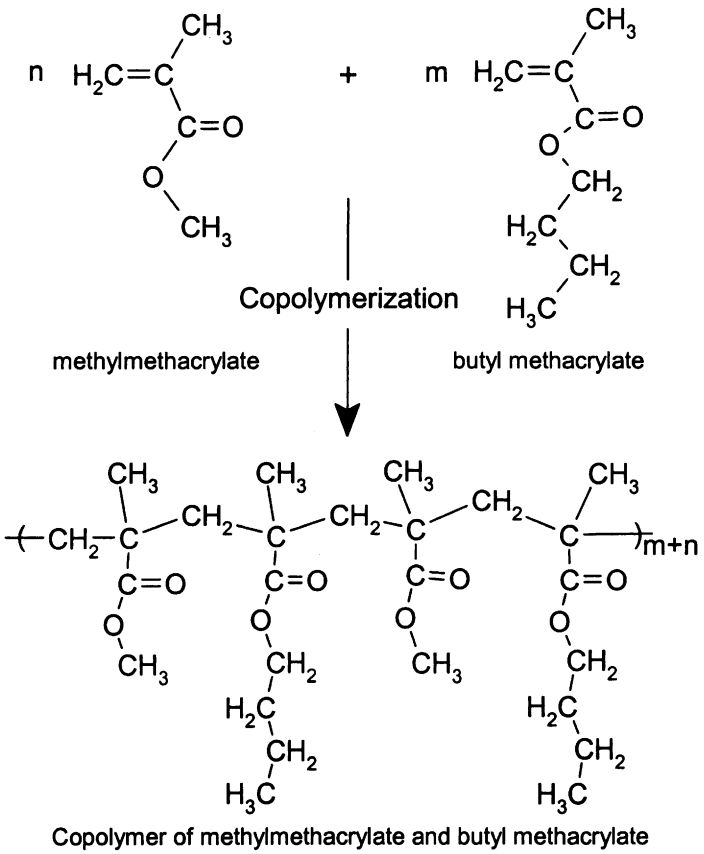


FIGURE 6-14 Copolymerization is exemplified here by the reaction between butyl methacrylate and methylmethacrylate. Because the butyl methacrylate molecules increase the equilibrium distance between polymer chains the intermolecular interactions decrease, which causes the glass transition temperature to decrease.

chemical and dimensional stability, yet it must also possess properties that render it relatively easy to process. It must be strong and hard but not brittle. The acrylate monomers (CH_2=CR^1COOR^2) have these qualities and consequently are widely used as dental materials. A few of these are discussed in the following sections.

ACRYLIC RESINS

The acrylic resins are derivatives of ethylene and contain a vinyl (–C=C–) group in their structural formula:

$$H_2C{=}CHR \qquad (9)$$

There are at least two acrylic resin series of dental interest. One series is derived from acrylic acid, CH_2=CHCOOH, and the other from methacrylic acid, CH_2=$C(CH_3)$COOH. Both polymerize by addition. Although the polyacids are hard and transparent, their polarity, related to the carboxyl group, causes them to imbibe water. Water tends to separate the chains and cause a general softening and loss of strength, making them generally unsuitable for dental use. The esters of these polyacids, however, are widely used for a variety of dental applications. For example, if R represents any ester radical, the polymerization reaction for poly(methacrylate) is:

$$CH_2{=}C(CH_3) \rightarrow —CH_2—C(CH_3)—CH_2—C(CH_3)—$$
$$\qquad\quad | \qquad\qquad\quad | \quad\ | \qquad (10)$$
$$\quad COOR \qquad\quad COOR \quad COOR$$

Because R can be almost any organic or inorganic radical, it is evident that thousands of different acrylic resins are capable of formation. This does not include the possibilities of copolymerization, which are even greater.

The effect of esterification on the softening point of a few of the poly(methacrylate) compounds is shown in Table 6-1.

For short chain lengths, increasing the length of the side chain lowers the softening point or glass transition temperature. For example, poly(methylmethacrylate) (PMMA) is the hardest resin of the series with the highest softening temperature. Poly(ethyl methacrylate) possesses a lower softening point and surface hardness, and poly(n-propyl methacrylate) has an even lower softening point and hardness.

METHYLMETHACRYLATE

PMMA by itself is not used in dentistry to a great extent in molding procedures. Rather, the liquid monomer methylmethacrylate (Figure 6-15) is mixed with the polymer, which

TABLE 6-1 Glass-Transition/Softening Temperatures of Polymethacrylate Esters

Poly(methacrylate)	T_g (°C)
Methyl	125
Ethyl	65
n-Propyl	38
Isopropyl	95
n-Butyl	33
Isobutyl	70
sec-Butyl	62
tert-Amyl	76
Phenyl	120

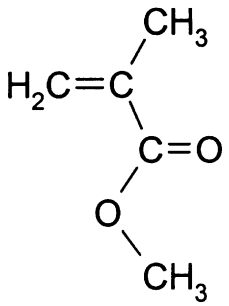


FIGURE 6-15 Methylmethacrylate molecule.

is supplied in the powdered form. The monomer partially dissolves the polymer to form a plastic doughlike material. In making dentures and various removable appliances this dough is packed into a mold, and the monomer is polymerized by one of the methods discussed previously. Consequently the monomer methylmethacrylate is of considerable importance in dentistry.

Methylmethacrylate is a transparent liquid at room temperature, with the following physical properties:

- Molecular weight = 100
- Melting point = 48 °C
- Boiling point (bp) = 100.8 °C (note how close this is to the bp of water)
- Density = 0.945 g/mL at 20 °C
- Heat of polymerization = 12.9 kcal/mol

Methylmethacrylate exhibits a high vapor pressure and is an excellent organic solvent. Although the polymerization of methylmethacrylate can be initiated by visible light, ultraviolet light, or heat, most dental products are initiated chemically.

The methacrylate monomers are not very technique-sensitive and can be polymerized under a variety of conditions, which is particularly useful in dentistry. For example, many resin systems do not polymerize at room temperature in the presence of air, whereas conditions for the polymerizing methylmethacrylate are not critical as long as the reaction is not carried out too rapidly, which generates excessive heat. The degree of polymerization varies with conditions of polymerization such as temperature, method of activation, type of initiator, initiator concentration, and purity. A volumetric shrinkage of approximately 21% occurs during the polymerization of pure methylmethacrylate, which can be a problem for accuracy of fit.

POLY(METHYLMETHACRYLATE) (PMMA)

As shown in Figure 6-15, PMMA is a transparent resin of water-like clarity that is transparent to light in the visible and ultraviolet range down to a wavelength of 250 nm. It is a hard resin with a Knoop hardness number of 18 to 20 KHN. It has a tensile strength approximately 60 MPa, a density of 1.19 g/cm^3, and a modulus of elasticity of approximately 2.4 GPa. It is also extremely stable: it does not discolor in ultraviolet light and it exhibits remarkable aging properties. It is chemically stable to heat below 125 °C, softens at 125 °C, and can be molded as a thermoplastic material. However, above 125 °C, PMMA begins to *depolymerize* and forms methylmethacrylate monomer, MMA, and at approximately 450 °C, 90% of the polymer will have depolymerized. PMMA of high molecular weight degrades to a lower molecular weight polymer at the same time that it is converted to monomers. Overall, PMMA is easy to handle, tough, wear-resistant, able to be pigmented to a lifelike appearance, able to be sterilized, easily cleaned, biologically safe, and very durable.

Like all acrylic resins, PMMA exhibits a tendency to absorb water by imbibition. Its noncrystalline structure possesses a high internal energy. Thus, molecular diffusion can occur in the resin because less activation energy is required. Furthermore, the carboxyl group, even though esterified, can form a hydrogen bridge to a limited extent with water. Because PMMA is a linear polymer, it is soluble in a number of organic solvents that may be found in a dental laboratory or operatory, such as chloroform and acetone.

MULTIFUNCTIONAL METHACRYLATE AND ACRYLATE RESINS

The backbone of the molecules formed in this system can have any shape, but methacrylate groups are always found at the ends of the chain and at the ends of branching chains. Bis-GMA, also known as Bowen's resin, is one of the first multifunctional methacrylates introduced in dentistry (Figure 6-16). Bis-GMA resin is an aromatic ester of a dimethacrylate, synthesized from an epoxy resin (ethylene glycol of bis-phenol A) and methylmethacrylate. Because bis-GMA has two –OH groups that form hydrogen bonds between the monomers, it is extremely viscous. A low-viscosity dimethacrylate, such as triethyleneglycol dimethacrylate (TEGDMA) (Figure 6-17), must be blended with it in order to reduce viscosity and provide good consistency and useful manipulation properties.

The rigid central core of two aromatic groups reduces the ability of bis-GMA molecules to rotate during polymerization and thereby to participate efficiently in the polymerization

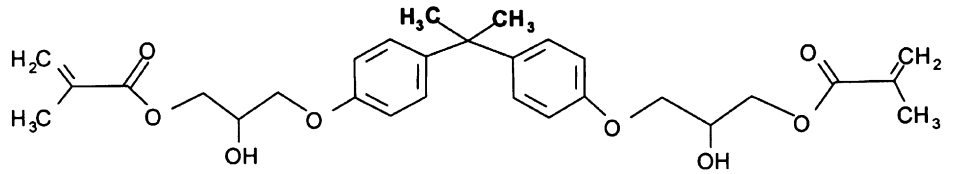


FIGURE 6-16 Bis-GMA molecule (bisphenol-A glycidylmethacrylate). The central part of the molecule is particularly stiff because of its restricted rotational ability due to steric hindrance between the two rings, with flexible propyl methacrylate end groups. Hydrogen bonding between the hydroxyl (–OH) groups on adjacent bis-GMA molecules restricts flow among the monomers and imparts a very high viscosity, similar to that of thick honey.

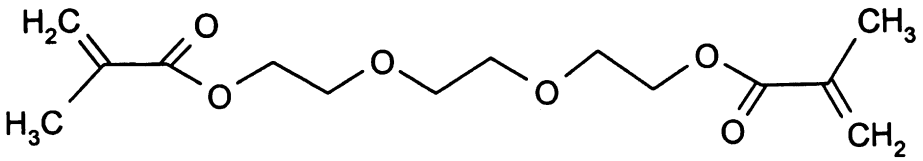


FIGURE 6-17 TEGDMA molecule. The polyether backbone structure ($–C_2H_5–O–$) is highly flexible. This facilitates molecular interaction during polymerization and increases the degree of conversion.

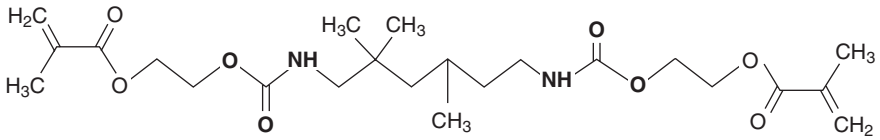


FIGURE 6-18 UDMA molecule. Urethane dimethacrylate is similar to bis-GMA but with two urethane groups (–NH–CO–O–) in a flexible central segment between ethyl dimethacrylate end groups.

process. Therefore, one of the methacrylate groups reacts more frequently than the other. This results in a bis-GMA molecule that forms a branch, or pendant group, along the polymer chain. Some of these branches crosslink with adjacent chains and some do not. The efficiency of polymerization and crosslinking is expressed by the percentage of reacted (converted) methacrylate groups after polymerization and is known as the degree of conversion.

Various dimethacrylate resin combinations have been explored through the years in attempts to reduce viscosity and to increase the degree of conversion. The urethane dimethacrylates (UDMA) have shown particular promise. UDMA resins comprise any monomer containing one or more urethane groups (–NH–CO–O–) and two methacrylate end groups (Figure 6-18). Several innovative dental products based on urethane dimethacrylate structures have recently been introduced (Chapter 13, Figures 13-24 and 13-25).

In addition to dimethacrylates, trifunctional and higher multifunctional monomers have also been utilized to enhance crosslinking and other properties. For example, dipentaerythiol penta-acrylate monophosphate (PENTA-P) is used in some dentin bonding agents. As shown in Figure 6-19, the PENTA-P structure contains as many as five acrylate groups per monomer molecule.

Polyacrylic acid (PAA) is an extensively used multifunctional resin to which hydroxyethylmethacrylate (HEMA) has been grafted (Figure 6-20). Such a modified PAA is used in light-curable glass ionomer cements (Chapter 14). Light exposure initiates free radical polymerization, causing the methacrylate groups to react. The reaction that crosslinks the PAA molecules constitutes the initial setting reaction. As

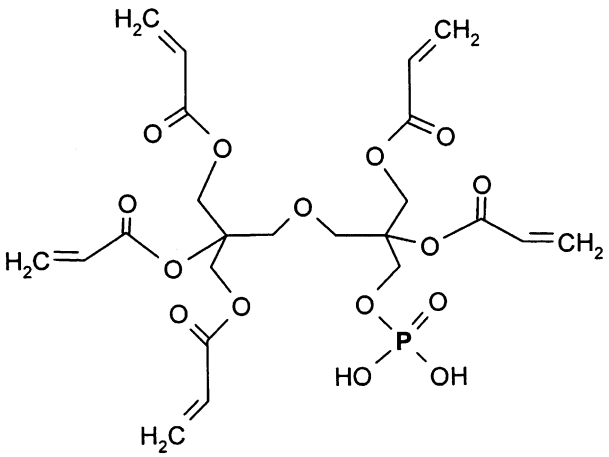


FIGURE 6-19 PENTA-P molecule. This multifunctional monomer contains a phosphate group ($–O–PO–[OH]_2$) and five polymerizable acrylate ($CH_2=CH–COO–$) groups. The phosphate group can etch enamel and dentin surfaces and promote adhesion, whereas the five acrylate groups increase polymerization reactivity and crosslinking ability.

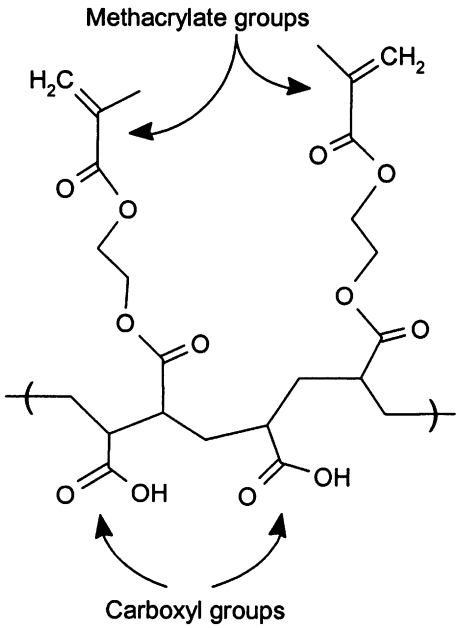


FIGURE 6-20 Polyacrylic acid with grafted ethyl methacrylate groups. The carboxyl groups (–COOH) can etch dentin and enamel by giving up their hydrogen ions. When this occurs, the molecule becomes negatively charged and forms bonds with positive ions present at the tooth surface, such as calcium. This ionic bond formation can also occur between polyacrylic acid chains, causing the material to set and harden. Another setting mechanism that can be used is addition polymerization. This polymerization reaction can be initiated by light, which causes the methacrylate groups (CH_2=C(CH_3)COO–) to react.

explained in detail in Chapter 14, following this reaction, the carboxylate groups continue to react with the glass particles through an acid-base reaction. During this reaction, the PAA releases the hydrogen ions and the PAA chains become negatively charged.

These negative charges, however, are balanced by cations leached from the glass. These cations, such as Ca^{2+} and Al^{3+}, form ionic bonds between the chains that now also become ionically crosslinked. In addition, the negatively charged PAA chains also form bonds to tooth tissues containing cations such as Ca^{2+}.

In this modified PAA molecule (Figure 6-20), it can be seen that as the number of methacrylate groups increases, the number of carboxylate groups decreases. This is important because fewer carboxylate groups reduce the extent of the acid-base reaction and weaken the enamel-dentin interaction. Thus, a light-cured glass ionomer consists of a combination of both addition polymerization and acid-base reactivity, yielding a so-called hybrid material. Further development using acidic monomers instead of HEMA-modified PAA has led to a type of resin known as a compomer, which displays physical properties similar to those of composite materials as well as the ability to release fluoride in a manner similar to that of glass ionomer cements.

ACKNOWLEDGEMENT

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http://www.pslc.ws/mactest/level3.htm
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http://www.lib.umich.edu/node/21860

CHAPTER 7

Biocompatibility

OUTLINE

Historical Perspective

Adverse Effects from Exposure to Dental Materials

Adverse Effects Data from National Registries

Allergic Reactions

Occupational Hazards for Dental Personnel

Hydrofluoric Acid

Biocompatibility Tests

Clinical Guidelines for Selecting Biocompatible Materials

KEY TERMS

Acute toxicity—Adverse response to a substance that causes ill effects relatively soon after a single exposure or after multiple exposures over a relatively short time (usually less than 2 weeks).

Adverse reaction—Any unintended, unexpected, and harmful response of an individual to a dental treatment or biomaterial.

Allergy—(1) A hypersensitivity reaction initiated by specific immunological mechanisms (Johansson et al., 2004); (2) abnormal antigen–antibody reaction to a substance that is harmless to most individuals; (3) antigen-inducing an allergic reaction.

Biocompatibility—(1) General definition: The ability of a biomaterial to perform its desired function with respect to a medical (or dental) therapy, without eliciting any undesirable local or systemic effects in the recipient or beneficiary of that therapy, but generating the most appropriate beneficial cellular or tissue response in that specific situation, and optimizing the clinically relevant performance of that therapy (Williams, 2008); (2) Long-term implantable device: Ability of the device to perform its intended function, with the desired degree of incorporation in the host, without eliciting an undesirable local or systemic effect in that host (Willliams, 2008); (3) Scaffold material for tissue engineering product: Ability to perform as a substrate that will support the appropriate cellular activity, including the facilitation of molecular and mechanical signaling systems, in order to optimize tissue regeneration, without eliciting any undesirable local or systemic responses in the eventual host (Williams, 2008).

Biointegration—The process of forming an interface between bone or other living tissue and an implanted material with no intervening space.

Chronic exposure—The contact with a substance that occurs over a long time (more than 1 year) (U.S. Agency for Toxic Substances and Disease Registry).

Estrogenicity—The potential of a chemical to act in the body in a manner similar to that of estrogen, the female sex hormone.

Hypersensitivity—(1) The objectively reproducible symptoms or signs initiated by an exposure to a defined stimulus at a dose tolerated by normal persons (Johansson et al., 2004); (2) abnormal clinical reaction or exaggerated immune response to a foreign substance that is manifested by one or more signs and symptoms, such as breathing difficulty, erythema, itching, sneezing, swelling, and vesicles.

Intermediate-duration exposure—The contact with a substance that occurs for more than 14 days and less than 1 year (compare with acute toxicity and chronic exposure) (U.S. Agency for Toxic Substances and Disease Registry).

Lethal dose fifty (LD_{50})—The calculated dose of a substance that is expected to cause the death of 50% of the entire population of specific experimental animals (U.S. National Institute of Occupational Safety and Health).

Lowest-observed-adverse-effect level (LOAEL)—The lowest tested dose of a substance that has been reported to cause harmful (adverse) health effects in people or animals (U.S. Agency for Toxic Substances and Disease Registry).

No-observed-adverse-effect level (NOAEL)—The highest tested dose of a substance that has been reported to have no harmful (adverse) health effects on people or animals (U.S. Agency for Toxic Substances and Disease Registry).

Osseointegration—The process of forming a direct structural and functional interface between live bone and an artificial implant surface without any intervening fibrous connective tissue.

Reference dose (RfD)—An Environmental Protection Agency (EPA) estimate, with uncertainty or safety factors built in, of the daily lifetime dose of a substance that is unlikely to cause harm in humans (U.S. Agency for Toxic Substances and Disease Registry). Note: The mission of the U.S. EPA is to protect human health and the environment. This mission includes aspects pertaining to dentistry such as fluorosis caused by excess levels of fluoride in drinking water.

Risk—The combined probability of a harmful effect and the severity of the effect.

Safety—The absence (freedom) from unacceptable risks. (Schmalz and Arenhold-Bindslev, 2009, Springer-Verlag, Berlin-Heidlburg).

Sensitization—The process by which an allergy antibody is produced, which reacts specifically to the causative foreign substance.

Toxic—Capable of causing injury or death, typically by a chemical agent.

Toxicity—The relative ability (dose-related effect) of a material to cause injury to biological tissues, ranging from improper biochemical function, organ damage, and cell destruction, to death.

Toxic dose low (TD_{Lo})—The lowest dose of a substance introduced by any route except inhalation over any given period that has been reported to produce any toxic effect in humans or carcinogenic, neoplastigenic, or teratogenic effects in animals or humans (U.S. National Institute of Occupational Safety and Health).

Xenoestrogen—A chemical that is not indigenous to the body but which acts in a manner similar to that of estrogen.

This chapter describes the conceptual aspects of **biocompatibility** with specific emphasis on the solid and liquid materials of greatest relevance to dentistry. Details on test methods for biocompatibility and the monitoring of inorganic and organic species are not included because these tests are not the responsibility of practicing dentists. Many excellent textbooks and reference sources are available that describe these test methods in great detail.

Placement of a material in the body creates an interface that must exhibit both biological and structural stability during the lifetime of the implanted device. These interfaces are dynamic, and their transitional functionality is dependent on the quality of the junction and the biocompatibility of the material. The dynamics of the interfacial interaction affect the material's biocompatibility and its acceptance by the body, which depend on the shape, size, and location of the material, its physical properties, its composition, and the stresses that develop during function.

? CRITICAL QUESTION

There are many types of tests for biocompatibility. Which tests can provide conclusive evidence to identify the specific cause of an allergic or **toxic** response to a restorative material?

Three major factors are linked to the success of dental materials: (1) material properties, (2) the design of the dental device, and (3) the biocompatibility of component materials. The biocompatibility of dental restorative materials is evaluated using compositional analysis, surface degradation tests, cell culture tests, clinical testing in humans, and animal model tests. The biocompatibility of a material depends on several factors:

1. The chemical nature of its components
2. The physical nature of the components
3. The types and locations of patient tissues that will be exposed to the device
4. The duration of the exposure
5. The surface characteristics of the material
6. The amount and nature of substances eluted from the material

The primary purpose of biocompatibility tests is to protect dental patients who will be treated with the materials and the office staff and lab technicians who will be handling these materials. Since no dental biomaterial is absolutely free from the potential risk of **adverse reactions**, the testing of biocompatibility is related to risk assessment. Thus, the challenge for the users of dental biomaterials is to select those products for which the known benefits far outweigh the known risks. Specific tests have been developed to screen restorative and implant materials for their biocompatibility. For materials, models have been developed to analyze the uptake, distribution, biotransformation, and excretion of metal ions or metal complexes in the body.

? CRITICAL QUESTION

Which five adverse reactions are *not* types of allergic reactions?

A *critical adverse effect* is the first event that is observed at the lowest exposure level. The location of this effect is called the *critical tissue*, or *critical organ*, and the concentration of a substance that produces this effect is the *critical concentration*. A metal such as mercury can be exposed to tissues as a solid binary phase (Ag_2Hg_3), as dissolved ions in saliva, and

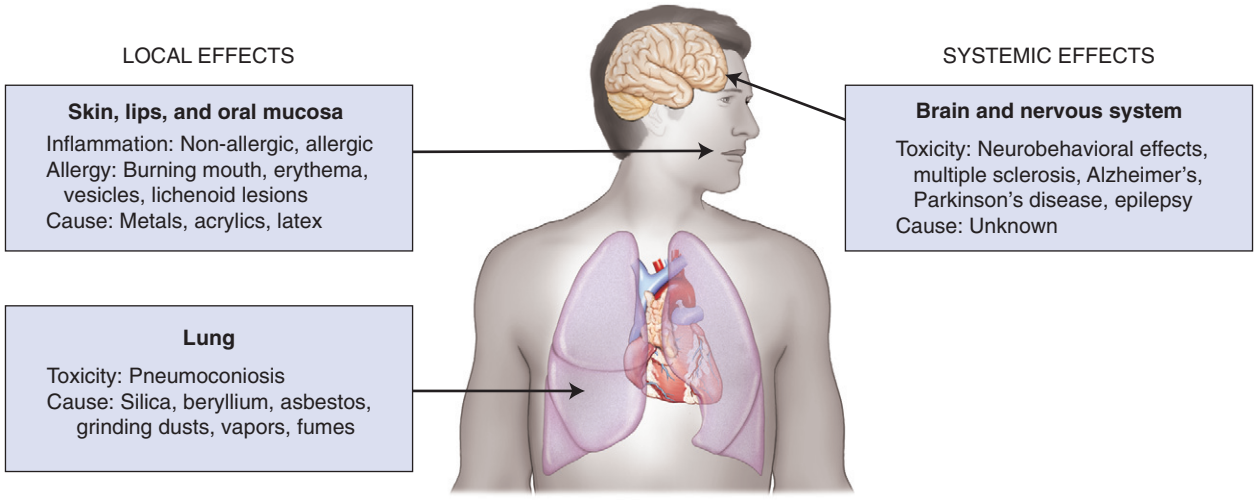


FIGURE 7-1 Schematic illustration of critical tissues and organs that may be susceptible to the adverse effects of dental materials.

as atoms in the vapor form. For this metal, one must be concerned about exposure levels, absorbed dose, body burden, and critical target-tissue concentrations. Shown schematically in Figure 7-1 are the critical tissue and organ sites that can be affected by exposure to dental restorative materials and auxiliary materials used to make impressions and models. Material components can be released during melting and casting of metals, fabrication of prostheses, grinding and polishing procedures, adhesive bonding, or cementing to prepared teeth. Exposure by deposition and possibly by local uptake occurs when any one of the four types of epithelial surfaces—oral tissue, gastrointestinal tract tissue, respiratory tract tissue, and skin—makes contact with one of these metal forms.

Determining the biocompatibility of dental materials is an extremely complex task that requires consideration of cell biology, patient risk factors, clinical experience, and materials science. This chapter discusses the relevant terminology, types of biological responses that materials may cause, types of tests used to characterize biocompatibility, and anatomical aspects of the oral cavity that influence biological responses to materials. Finally, recommendations are proposed on how clinical judgments should be made in assessing the biological safety of restorative materials.

Adverse reactions to dental restorative materials and auxiliary materials include one or more of the following effects: allergic reaction, chemical burn, pulp irritation, pulp damage, thermal injury, tissue irritation, and toxic reaction. The specific causes of these effects are difficult to diagnose because of the multifactorial nature of dental treatment and the subjective nature of patients' complaints or descriptions of their symptoms. Furthermore, there are no perfect tests for the confirmation or validation of diagnoses. For example, a visual sign of erythema in soft tissue adjacent to a new restoration may have resulted from mechanical trauma or an allergic reaction. However, an observational period may be required to determine if the effect is time limited, such as may have been caused by mechanical trauma or chemical irritation. If it is not time limited, one can assume that the erythema may have been caused by an allergic reaction. A patch test with dental test substances administered by an allergist may provide additional evidence of a potential **allergy** to one of the components of the material. Yet, the results of such testing are not 100% conclusive. There are no direct tests for the diagnosis of **toxicity** reactions. Specific tests such as urinary mercury concentration can help clinicians complement their differential diagnoses. Toxicity diagnoses are also based on the signs and symptoms presented by the patient and by a review of the history of possible exposures to a suspected toxin.

Traditionally, we have accepted the view that toxicity is dose dependent and allergy is dose independent. However, there is considerable uncertainty about which types of exposures lead to the **sensitization** of individuals to substances or ions released from dental restorative materials and auxiliary dental materials. Recent research suggests that dose effects for food allergies may be meaningful in describing the severity of allergic reactions. One of the common descriptors used is the dose corresponding to a 10% increase in an adverse effect relative to the control response. This is designated by ED_{10}. An analysis of a database for 450 subjects with peanut allergy indicated that the ED_{10} was 12.3 mg of whole peanut (average mass of 1000 mg per whole peanut) compared with a 5% increase (ED^{05}), corresponding to an ingested mass of 5.2 mg (Taylor et al., 2012). Thus, it is clear that sufficient data exist to establish a threshold level for a peanut allergy. However, there are no similar types of data for comparative evaluations of dose effects on the severity of allergic reactions to restorative materials. Instead, we must rely on the signs and symptoms expressed by our patients and the visual signs observed during clinical exams. In certain cases, allergy tests may have to be performed by an allergist or dermatologist (if appropriate) to assist in the diagnostic process. Specific dental test substances have been established for this purpose, and the treating dentist may have to make additional suggestions to

the allergist for tests of other dental substances that are of potential significance in each case (Gawkrodger, 2005; Khamaysi et al., 2006).

This chapter is not intended to offer a course on biocompatibility test methods or theory. It is an overview of biocompatibility concepts, terminology, outcome data from national registries of adverse effects, and principles of established test methods. This overview is designed to provide a brief review of established concepts to assist dentists and other health care professionals in the conservative selection and use of dental restoratives and auxiliary materials. It also provides the essential background information and statistics on adverse events that may be needed to draft evidence-based statements on the positive and negative aspects of biomaterials and to ensure that optimal informed consent procedures on material use are employed.

HISTORICAL PERSPECTIVE

? CRITICAL QUESTION

How do national and international governments protect dentists and their patients against the use of unsafe or bioincompatible dental products?

Since ancient times, a wide variety of relatively inert materials have been placed or implanted in humans to replace or repair missing, damaged, or defective body tissues. Bone, seashells, animal teeth, human teeth, metals, resin materials, inorganic compounds, and other tooth replacement materials have been used for replacement of missing teeth. For the restoration of damaged or decayed teeth, metals and nonmetals have also been used, with outcomes that have varied from short-term failure to limited success in certain individuals. Many of these treatments reflected situations in which the risks were far greater than the anticipated benefits. Some of these materials have caused immediate or delayed adverse reactions because of their allergenic or toxic potentials.

Tests for the safety of restorative dental materials must ensure that a candidate material is nontoxic and unlikely to cause adverse immunological effects. Evaluations of toxicity are designed to identify adverse health events caused by physical agents, chemical agents, or both. Paracelsus (1493–1541) correctly proposed that only the dose of a substance differentiates a toxic agent from a remedy (Siddiqui et al., 2003). No pharmacological agent is free of potential toxic effects, and no drug is free from the possibility of causing an adverse event in certain individuals. No test can produce results that can guarantee that a substance will not cause adverse effects in all individuals who are treated with the substance. The allowable percentage of adverse effects in a population is based on the risks to the health and life expectancy of the individuals who will be exposed to the product under the indicated conditions and the corresponding exposure doses for its components.

Biological testing of materials has evolved significantly over the past 50 years. Since the 1980s, testing has focused on primary tests for cytotoxicity, hemolysis, Styles' cell transformation, the Ames test, the dominant lethal response, oral **LD_{50}**, intraperitoneal (IP) LD_{50}, and the acute inhalation test. Secondary tests are also used. These include the mucous membrane irritation test (in hamsters' cheek pouches), dermal toxicity from repeated exposures, responses to subcutaneous implantation (e.g., in rats), and sensitization (of guinea pigs). Testing of dental materials also includes tests for pulp irritation responses, pulp capping effects, endodontic applications, and dental implant performance.

As cell-culture techniques evolve, research will continue to focus on mechanisms that control the biological responses to materials. Molecular biology and imaging techniques have recently been introduced. Biocompatibility testing in the future may lead to more reliable predictions of adverse effects, and this knowledge of biological properties may allow us to formulate materials that provide specific, desired biological responses.

INFLUENCE OF THE AMERICAN DENTAL ASSOCIATION

Methods and standards for testing the safety and effectiveness of dental materials have evolved slowly during the twentieth century. In 1930, the American Dental Association (ADA) formed a Council on Dental Therapeutics to oversee the evaluation of dental products. Also in 1930, the Council established the ADA's Seal of Acceptance program to promote the safety and effectiveness of dental products. However, in 2005, the ADA decided to phase out the Seal of Acceptance program for professional products. Instead, a decision was made to publish a product evaluation newsletter for ADA member dentists that focused on a specific category of professional products in each article. This newsletter, called the *Professional Product Review*, was initiated in July 2006 and the final phase-out of the ADA seal for professional products occurred on December 31, 2007. One of the major accomplishments of the ADA was the development and acceptance of ANSI/ADA Specification No. 41. Recommended Standard Practices for Biological Evaluation of Dental Materials. This specification represented great progress toward the establishment of biological tests for dental materials.

REQUIREMENTS OF THE U.S. FOOD AND DRUG ADMINISTRATION

The Dental Products Panel of the U.S. Food and Drug Administration (FDA) Medical Devices Advisory Committee reviews and evaluates data concerning the safety, effectiveness, and regulation of products for use in dentistry, and bone physiology relative to the oral–maxillofacial complex and makes appropriate recommendations to the FDA Commissioner.

In 1938, the U.S. Federal Food, Drug, and Cosmetic Act (FFDCA) authorized the FDA to oversee the safety of foods, drugs, and cosmetics. This act required evidence of drug safety before pharmaceutical products could be distributed to the public. More recently, in 1976, Medical Device

Amendments (MDA) to the FFDCA included regulation of medical devices, including dental devices, for the first time. The MDA of 1976 required that FDA classify all medical devices into one of three classes, according to risk, Class I, Class II, and Class III. Dental devices, which are not specifically exempted, are required to be cleared by FDA prior to distribution into interstate commerce. Currently, the Dental Devices Branch of the Center for Devices and Radiological Health regulates premarket clearance of dental devices.

Three regulatory classes (i.e., level of control, based on risk; necessity to provide reasonable assurance of safety and effectiveness of a device type):

1. **Class I:** Low risk—General Controls [generally exempt from 510(k)]
2. **Class II:** Moderate risk—General Controls & Special Controls [510(k) generally required]
3. **Class III:** High risk—General Controls & Premarket Approval (PMA) Application (PMA required; must demonstrate safety and effectiveness without relying on a predicate device)

A brief listing of FDA device classifications and applicant requirements are summarized below.

General Controls (Classes I, II, and III)

Registration of establishment and listing of devices to be marketed
Labeling and prohibition against misbranding and adulteration
Manufacturing in accordance with Good Manufacturing Practices (GMPs)
Premarket notification [510(k) requirements (if necessary)]
Adverse event reporting

Special Controls (Class II)

Performance standards (national or international consensus standards recognized by rule making)
Voluntary standards
Guidance documents
Postmarket surveillance
Patient registries and
Other actions the FDA decides are necessary to provide reasonable assurance of safety and effectiveness.

Premarket Approval: PMA (Class III)

Devices for which insufficient information exists to determine that general and special controls are sufficient to provide reasonable assurance of safety and effectiveness, and such devices that:
are life sustaining or life supporting;
are of substantial importance in preventing impairment of human health; or
present potential unreasonable risk of illness or injury.

510(k) Classification

The most common pathway to market for medical devices
A review to determine whether a new device demonstrates substantial equivalence (SE).
SE to a predicate device (pre-amendment or post-amendment) for which PMA is not required
FDA's determination of SE serves as the classification process for new devices
Most of the submissions to the Dental Branch are 510(k) types of submissions

Substantial Equivalence / Substantially Equivalent

A new device is deemed SE to a predicate device if:

1. It has the same intended use;
2. It has the same technological characteristics (includes chemistry, materials, design specifications, mechanical, or biological properties, etc.); or
3. It has different technological characteristics, but it does not raise new types of safety and effectiveness questions and is at least as safe and effective as the predicate device.

ADVERSE EFFECTS FROM EXPOSURE TO DENTAL MATERIALS

? CRITICAL QUESTIONS

Why might the local response and systemic response to a dental material differ? Which factors come into play to explain these differences?

LOCAL AND SYSTEMIC EFFECTS OF MATERIALS

Any biomaterial that is placed adjacent to a natural tissue in the body can induce local or systemic biological effects. These effects are controlled by the substances that are released from the material and the biological responses to those substances. The nature, severity, and location of these effects are determined by the distribution of released substances. For dental materials, local effects might occur in the pulp tissue, in the periodontium, at the root apex, or in nearby oral tissues such as the buccal mucosa or tongue (Figure 7-2). The arrows in this figure indicate the pathways that foreign substances from a restorative material, if present, take into the oral environment, the tissue space next to the periodontium (PD), the pulp chamber (P), or the periapical region (PA). The periodontal ligament is also an important tissue, since it is located in proximity to the pocket or attachment area, which is often a site for accumulation of biofilms and ions, atoms, or molecules of substances released from the cervical region of dental restorations that can extend into this area. Such accumulations can be metabolized, which could then change their biological properties. These local effects are a function of (1) the ability of substances to be distributed to these sites, (2) their concentrations, and (3) exposure times, which may range from seconds to years.

In a manner similar to local effects, systemic effects from dental materials are also a function of the distribution of substances released from dental materials. Their routes of entry into the body include the following sources: (1) ingestion and absorption; (2) inhalation of vapor; (3) leakage through the tooth apex; and (4) absorption through the oral

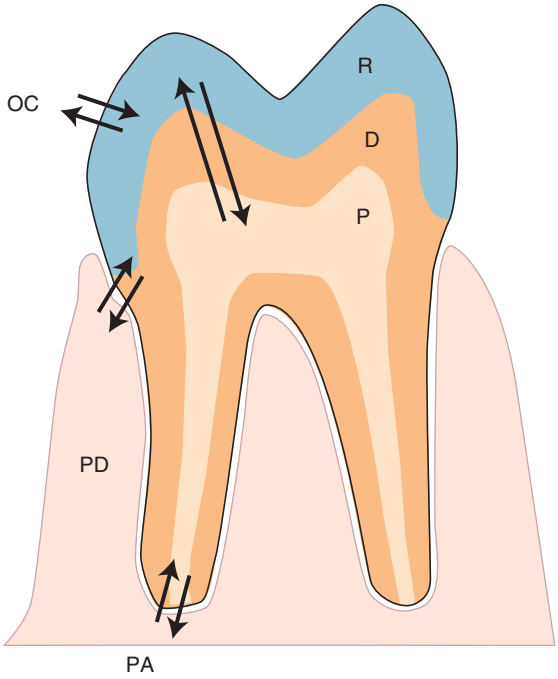


FIGURE 7-2 Schematic illustration of pathways that leached ions or substances may follow during in vivo degradation of a dental restoration (R) into the oral cavity (OC), dentin (D), the pulp chamber and the pulp tissue (P), the periodontium (PD), and periapical tissue and bone (PA).

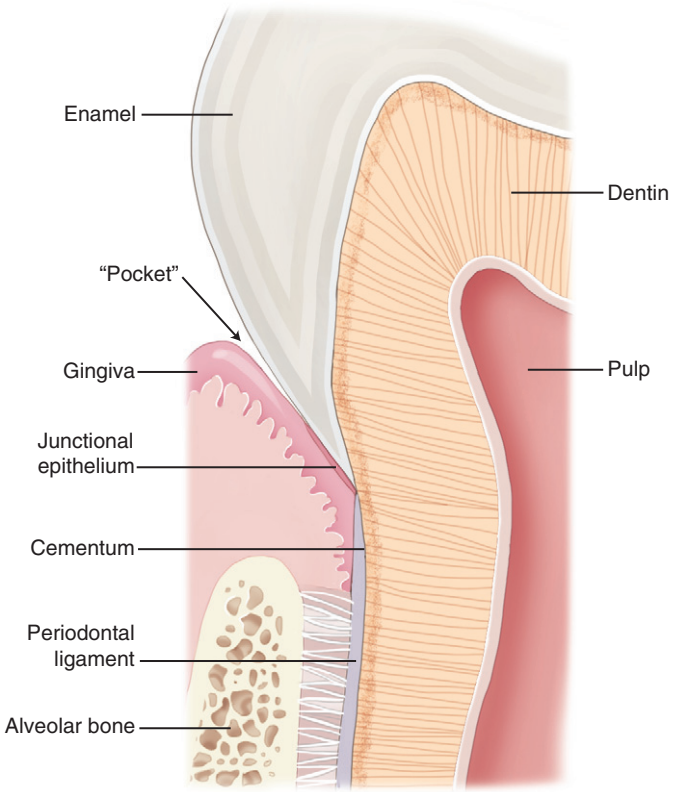


FIGURE 7-3 Schematic illustration of the periodontal attachment area. The gingiva is attached to the tooth's cementum surface just below the enamel with a specialized epithelium, which is called the *junctional epithelium*. The periodontal "pocket" is formed from the gingival tissue extension above the junctional epithelium. Cementum covers the dentin starting at the enamel–dentin junction. Below the gingiva, alveolar bone attaches to cementum through a tissue called the *periodontal ligament*. This ligament is not present when implants are osseointegrated with bone.

mucosa. Their migration to other sites can occur by diffusion through tissues or by flow through lymphatic channels or blood vessels. The ultimate systemic response depends on four key variables: (1) concentration of the substance; (2) time of exposure; (3) excretion rate of the substance; and (4) organ of importance or site at which exposure occurred. When substances are excreted slowly, their critical concentrations are reached more rapidly than are those concentrations of substances that are excreted quickly.

INFLAMMATORY AND ALLERGIC REACTIONS

Different types of biological responses to substances can occur in humans. These include inflammatory, allergic, toxic, and mutagenic reactions. However, not all of these have been documented for dental material exposures. The inflammatory response involves the activation of the host's immune system to ward off some challenge or threat. Inflammation may result from trauma (excessive force, laceration, and abrasion), allergy, or toxicity. Histologically, the inflammatory response is characterized by edema of the tissue caused initially by an infiltration of inflammatory cells such as neutrophils and, later in the chronic stage, to the action of monocytes and lymphocytic cells. The relationship of dental materials to inflammatory reactions is important because of chronic inflammatory responses such as pulp inflammation and periodontal disease. As indicated previously, teeth with cervical restoration margins can release ions or other substances into the gingival sulcus, and adverse reactions can affect the periodontal attachment and the periodontal ligament (Figure 7-3, with no restoration).

Allergies to substances, foods, and solid materials are well recognized by the public, but specific allergens are difficult for health care professionals to diagnose. An allergic reaction occurs when the body recognizes a substance, molecule, or ion as foreign, and the human immune system can react quickly, as during an anaphylactic reaction or slowly in delayed contact dermatitis. These reactions are insensitive to the amount of the allergen that is available or released.

An allergic reaction induces an inflammatory response that cannot easily be distinguished from reactions caused by a nonallergic inflammatory process or by low-grade toxicity. However, by observing the signs of the effect or the absence of the signs in other locations and by the process of elimination, some reasonably logical inferences may be drawn. In some cases, observation for 2 weeks or more, when possible, can lead to a resolution of the response because the effect was caused either by trauma, another noninflammatory process, or a self-limiting allergic condition. Examples of inflammatory reactions that may be caused by allergens leached as ions



FIGURE 7-4 Inflammatory response or possible allergic reaction adjacent to a class V resin-based composite. However, no patch test was performed to confirm this response. (Courtesy of Dr. Hyun-Ju Chung.)

from metals or other substances released by dental materials are shown in Figures 7-4 through 7-10. Figure 7-5 illustrates three potential sites for allergic reactions to nickel-containing metals: (1) a watchband buckle; (2) bilateral, fixed metal-ceramic prostheses with copings and framework made from nickel-alloy (crown on left and three-unit FDP on right); and (3) a severe reaction of lips to nickel-containing wire. Figure 7-5, *D*, illustrates positive responses to patch-test substances on a patient's back. In addition, bilateral lichenoid mucositis lesions which will be discussed later, are shown in Figure 7-11 on the buccal mucosa adjacent to gold alloy crowns.

Some materials, such as latex, can cause allergy directly by activating antibodies to the material. These are classified as Type I, II, or III reactions, according to the Gell and Coombs classification of immune responses (Gell and Coombs, 1963; Rajan, 2003). These reactions occur quickly and are modulated by antibody-producing eosinophils, mast cells, or B lymphocytes. In comparison, metal ions must first interact with a host molecule to produce a delayed Type IV **hypersensitivity** reaction, which is modulated by monocytes and T cells. This type is often associated with contact dermatitis.

A Type I reaction (mediated by IgE or IgG4) is an immediate atopic reaction (based on a genetic predisposition to the development of immediate hypersensitivity reactions to a common environmental antigen) or anaphylactic reaction when an antigen interacts with mast cells or basophils. *Atopy* refers to a personal tendency, familial tendency, or both occurring in childhood or adolescence whereby one becomes sensitized and produces immunoglobulin E (IgE) antibodies in response to normal exposures to allergens, usually proteins. As a result, these individuals develop symptoms such as asthma, rhinoconjunctivitis, or eczema.

A Type II response is a cytotoxic hypersensitivity reaction, Type III is an immune complex hypersensitivity reaction, Type IV is a delayed or cell-mediated hypersensitivity, and Type V is a stimulating-antibody reaction, which is rare and sometimes classified as a subcategory of Type II (Rajan, 2002).

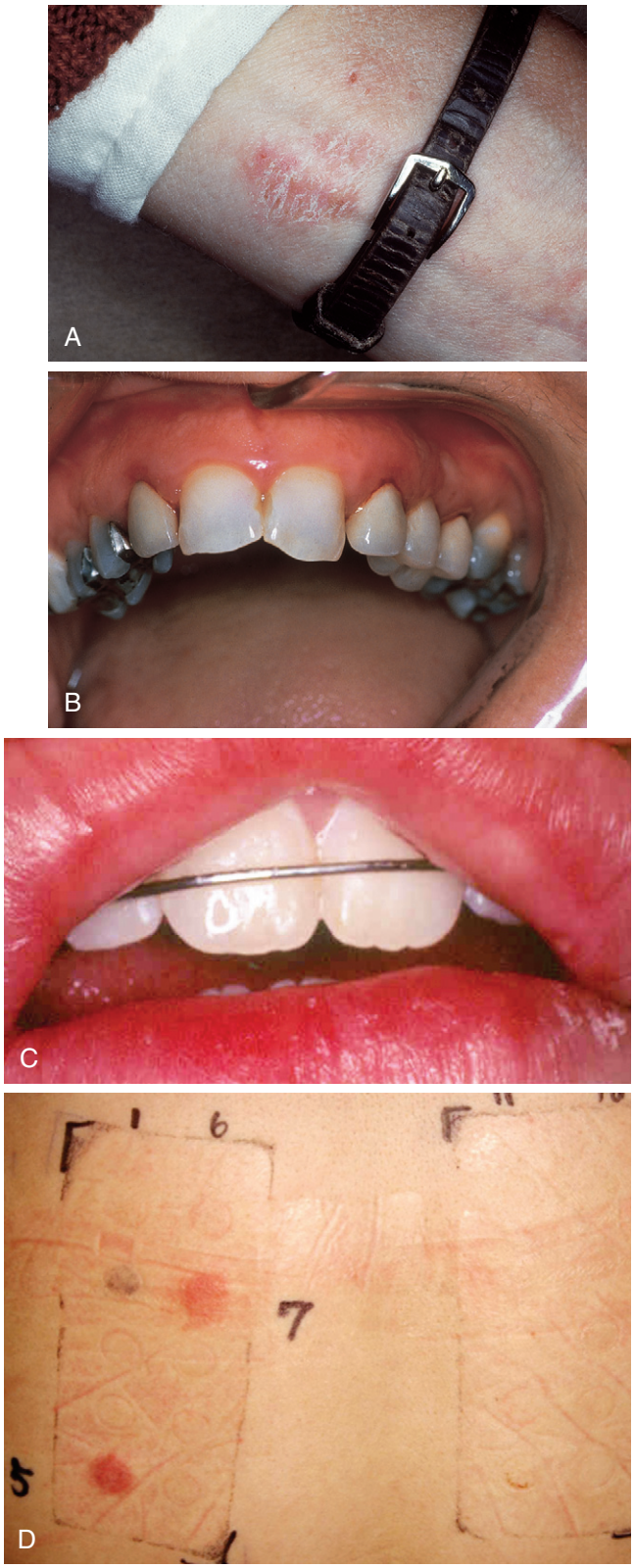


FIGURE 7-5 **A,** Possible allergic reaction to nickel alloy in watchband buckle. **B,** Bilateral erythema in a female patient that may have been associated with allergic reactions to nickel in a recently cemented metal-ceramic crown (*left side of photo*) and in two metal-ceramic crowns (*right side of photo*) of a three-unit fixed dental prosthesis. **C,** Severe allergic reaction in the lips of a patient who was exposed to a nickel-containing orthodontic wire. **D,** Positive responses to patch tests on a patient's back. (**C,** Courtesy of Dr. Donald Cohen; **D,** Courtesy of Dr. Young Ho Won.)

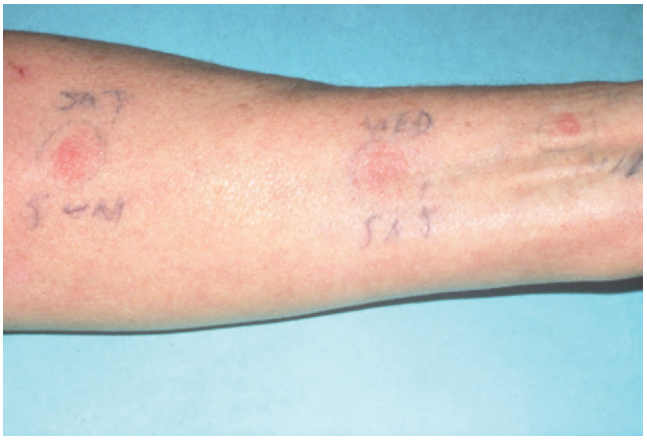


FIGURE 7-6 Photo of a patient's arm after she tested herself with metal discs made of a nickel–chromium (Ni-Cr) alloy. Note that the patient has noted the period during which the discs were taped to her arm prior to examination of the sites in a dental clinic. This type of test is not standardized, and the test results should not be used to confirm or reject the diagnosis of a suspected allergy to nickel or any of the other alloy components.



FIGURE 7-8 Inflammatory response adjacent to a crown (*lower right*) made from a metal coping. No definitive diagnosis can be made of a potential allergy to one of the component metals without testing the individual to a battery of dental patch test substances. Thorough dental and medical histories are also required for the evaluation of this condition. (Courtesy of Dr. Hyun-Ju Chung.)



FIGURE 7-7 Large blue-colored areas, typically referred to as an amalgam tattoo, which is a benign area of discolored membrane in the mouth. These examples are not associated with allergic reactions to mercury or any other metallic elements in the amalgam fillings. The discoloration is caused by small amalgam granules that have fallen into open wounds created during the condensation and carving of amalgam fillings in prepared teeth **(A and B)** or retrograde fillings in root apices **(C)**. (Upper two photos courtesy of Dr. Hyun-Ju Chung.)



FIGURE 7-9 Inflammation adjacent to the metal margin of a metal-ceramic crown. A potential allergy to one of the metal components should be explored, since such tissue responses to leached metal ions is one of the most prevalent adverse effects reported by national adverse effect registries. Furthermore, gingival reactions to metal oxides that were produced during the firing process for metal-ceramic crowns have also been proposed (Schmalz, Langer, and Schweikl. J Dent Res 77:1772-1778, 1998; Schmalz and Garhammer, Dent Mater 18:396-406, 2002). (Courtesy of Dr. Hyun-Ju Chung.)

CRITICAL QUESTION

How does the corrosion of metals contribute to their biocompatibility?

PRECURSORS TO ADVERSE EFFECTS OF DENTAL MATERIALS

Each biomaterial can degrade and release components under certain environmental and physical conditions. Metals can degrade by wear, dissolution, or corrosion. The difference between dissolution and corrosion is primarily related to the difference between chemical concentration gradients and electrical current gradients. A metal restoration can release metal ions as a result of chemical reactions, electrochemical forces, or mechanical forces (such as during abrasion). For some materials, such as ceramics and resin-based composites, cyclical stresses contribute to the breakdown of the material and release of components. Thus, the biocompatibility of the material is controlled by the degradation process. The biological response to a corrosion process depends on the composition of the material, the amount of the offending species released over time, the shape of the prosthesis, and its location on or within tissues.

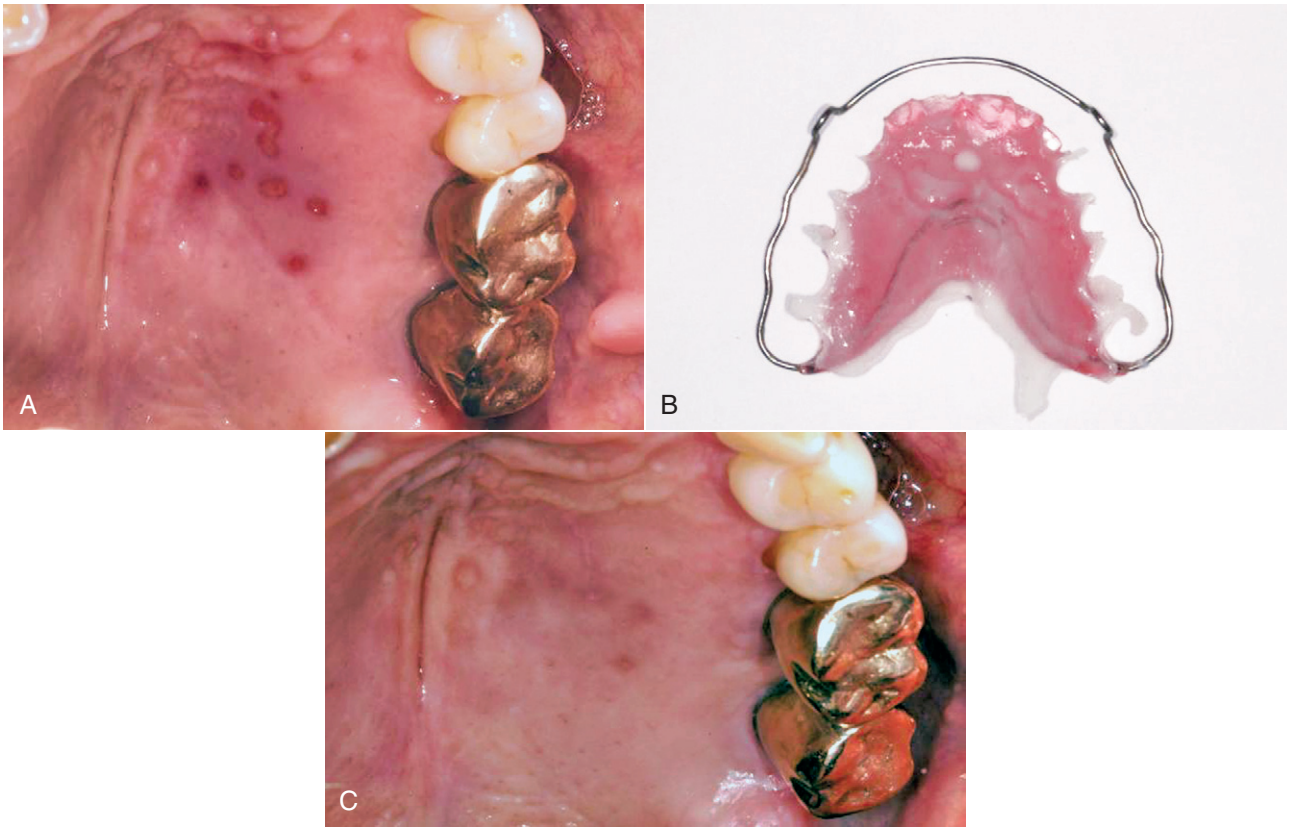


FIGURE 7-10 Erythematous reaction sites. Patch testing was not performed to confirm a suspected allergic response. **A,** Palatal area that was exposed to an acrylic palatal appliance . **B,** Acrylic appliance with embedded wire. **C,** Initial healing of palatal tissue shown in *A* within 2 to 3 days after removal of the palatal appliance. (Courtesy of Dr. Byung-Gook Kim.)

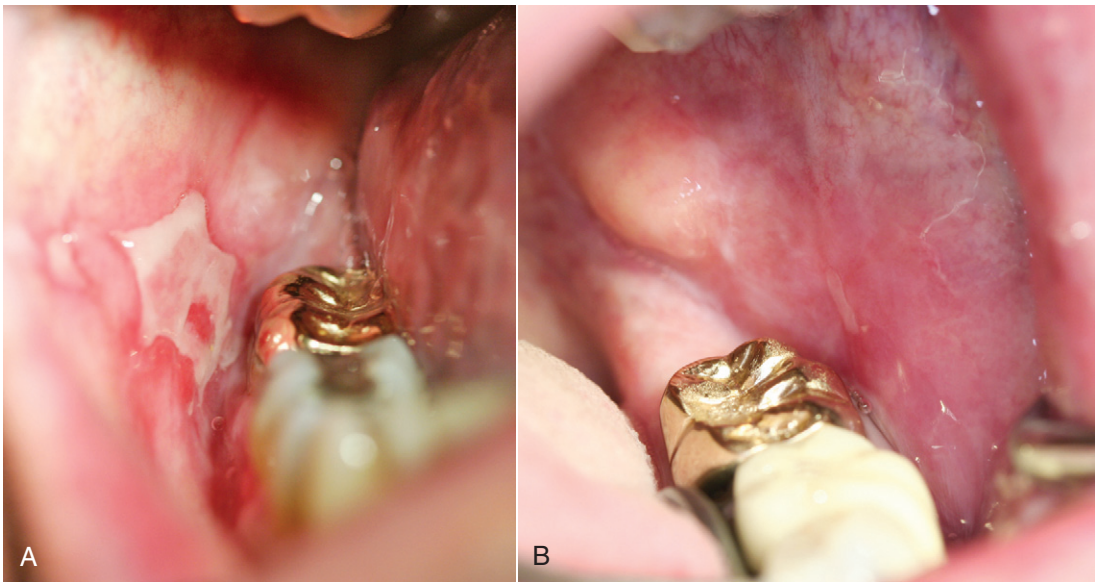


FIGURE 7-11 Bilateral lichenoid lesions that are associated with gold alloy crowns. **A,** Lichenoid mucositis lesion (*white area*) in tissue adjacent to a gold alloy crown. **B,** Lichenoid mucositis lesion in vestibular tissue next to gold alloy crown on opposite side of the arch. Patch testing of the patient was not performed. (Courtesy of Dr. Donald Cohen.)

Corrosion is not determined only by a metal's composition but also by the environment in contact with the metal. For example, acidic substances such as citrus juices or regurgitated hydrochloric acid alter the surfaces of ceramics. High pH environments may also increase the dissolution of some glass-phase ceramics. The environment–metal interface creates the conditions for corrosion. This interface is active and dynamic, the material breakdown products affect the body, and the body's environment affects the material's surface structure.

In addition to the degradation process, the biocompatibility of a material is also affected by its surface characteristics. Material surfaces are often different in composition from those of the interior structures of metals and resin-composites. Cast metals solidify first at the investment mold surface, and subsequently, the hottest area solidifies last. This transitional cooling process creates a composition gradient, which may lead to dissolution or corrosion behavior that is quite unpredictable.

Another factor that increases the potential for the release of potential allergens, mutagens, or toxins is the surface roughness of a restoration or prosthesis. For metals, a rough surface promotes corrosion, which increases the release of ions that may lead to adverse effects. Several types of beverages have caused degradation of two types of dental ceramics. Plaque accumulation also increases on roughened surfaces, and this may contribute to periodontal disease or caries.

Unfinished surfaces of resin-based composites and pit-and-fissure sealants have an oxygen-inhibited outer layer that may be more susceptible to leaching impurities such as bisphenol A. Some studies indicate that leaching of bisphenol A decreases over a relatively short period, and the results suggest that the toxicity risk is extremely low. However, the concentration of bisphenol A is dependent on the quality standards that the manufacturer follows relative to allowable impurity levels.

? CRITICAL QUESTION

Is it possible for a material to have no obvious biological effects by itself but still alter body functions?

Products that pass the primary tests, such as the toxicity test, then progress to secondary and usage tests (Figure 7-12). Today, the choice of the test method is based on risk assessment, which is also divided into separate stages of analysis. Details on such testing are provided in relevant ISO standards such as ISO 14971. This risk assessment is the basis for deciding whether new tests are necessary or not, or whether data from the scientific literature are sufficient. If they are necessary, cell culture tests are regarded as the first choice combined with animal tests for sensitization. Subsequently, risk assessment continues and decisions are made on whether or not further tests (e.g., animal tests or human clinical tests) are needed. Clinical tests in some countries are mandatory for materials that are considered to be of high risk. The final decision for market clearance is then made by an interchange between manufacturers and a third party such as a governmental agency or a private organization to which this authority has been granted by a government agency. Our profession seems to be overly complacent in its acceptance of new materials without demanding proof of their safety and efficacy. When a new product is introduced on the dental market, the advertisements tend to promote the clinical performance but rarely summarize the biocompatibility tests and results of these tests compared with results from control materials.

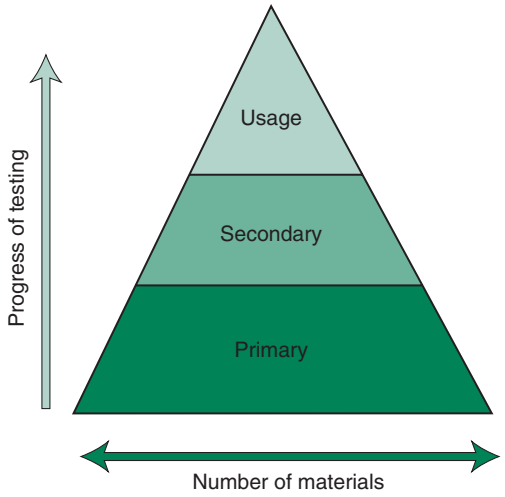


FIGURE 7-12 Classical progression of biocompatibility tests for evaluating a group of new dental materials. All of the products are screened initially using primary tests. Those that have favorable test results are then subjected to secondary tests. Finally, the best materials of the initial group are subjected to clinically relevant usage tests prior to decisions on whether or not they will be used for clinical trials in humans. (Courtesy of J. Wataha)

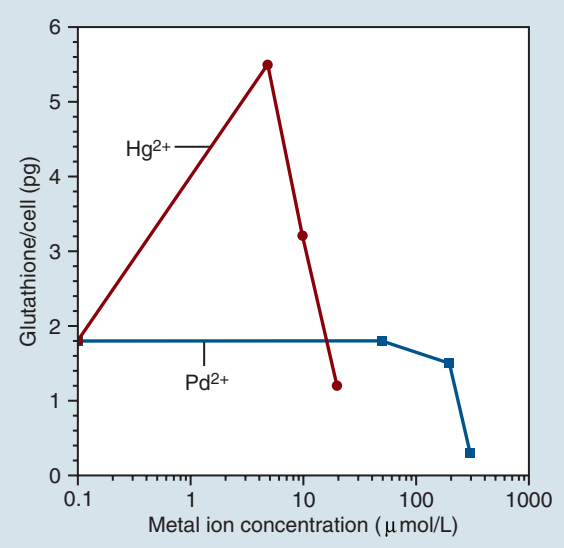


FIGURE 7-13 Response of monocytes in a cell culture after a 24-hour exposure to mercury ions (Hg^{2+}) or palladium ions (Pd^{2+}). Mercury ions produced a spike in glutathione at an ion concentration of about 8 μmol/L and a subsequent decrease as mercury became toxic to the cells. In contrast, during exposure to palladium ions, the glutathione content did not decrease significantly until the palladium ion concentration increased to between 200 and 300 μmol/L, which is far below the ion concentrations required to induce toxicity in these cells. Because both types of metal ions alter the chemical defense (glutathione production) against oxidative stress at subtoxic ion levels, these processes are believed to affect the immunotoxicity of these metals. (Courtesy of J. Wataha)

When such products are released to the profession, dentists, dental staff, and patients must assume that sufficient safety testing has been performed to minimize potential risks. However, even with the enormous number of peer-reviewed publications that have resulted from investigations of alleged toxic and immunological reactions to mercury in dental amalgam, the evidence, thus far, has been regarded by some groups as inconclusive. However, this scenario raises a most important question: How much evidence is sufficient to demonstrate that a product is sufficiently safe for general clinical use? Dentists must rely on the appropriate test methods that are required in standards and in legal regulations and assume that sufficient evidence of safety has been established for dental devices once they have been cleared for market use.

Since toxicity is dose dependent, it is obvious that materials that release too much of a substance can cause overt toxicity. The terms and definitions given previously indicate that there are different dose thresholds for various levels and probabilities of risk. Figure 7-13 shows a plot of cellular glutathione from monocytes that were exposed to mercury or palladium ions in a cell culture. Mercury ions are shown to increase the glutathione content of the monocytes in the cell culture, while palladium ions cause the glutathione content to decrease. Since glutathione is essential for maintaining the redox balance in the cells, exposure to these metallic ions can change the cellular function of the monocytes.

IMMUNOTOXICITY

Our understanding of the differences between toxicity, inflammation, allergy, and mutagenicity has become clearer as we learn more about the interactions between biomaterials and cells. The principal concept of immunotoxicity is that substances leached from materials can alter immune system cells, resulting in enormous biological consequences because of the amplifying nature of immune cells. These cellular alterations can occur initially because of the toxic effect of a leached substance. Monocytes control chronic inflammatory and immune responses, and they also secrete many substances that alter the actions of other cells. Thus, if substances leached from a biomaterial change the monocyte's ability to secrete these substances, the biological response can be greatly influenced and this may greatly impair cellular defense mechanisms against bacteria (Schmalz et al., 2011).

As stated earlier, cell function can either increase or decrease as a result of immunotoxic effects. As shown in Figure 7-13, mercury ions are known to increase the glutathione content of human monocytes in cell culture, whereas palladium ions decrease the cells' glutathione content. Glutathione is important in maintaining oxidative stress in cells, and any change in its concentration can alter cell function. Higher concentrations of mercury can also decrease glutathione as the ion concentration becomes more toxic.

Figure 7-14 shows a graph of the amount of tumor necrosis factor alpha (TNF-α) secreted by monocytes after exposure to hydroxyethyl methacrylate (HEMA) in different concentrations. The +LPS line represents the effect of cell stimulation by lipopolysaccharide while the –LPS line indicates that the monocytes were not stimulated

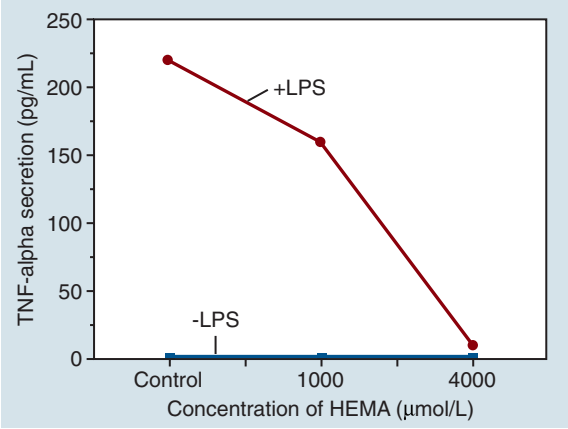


FIGURE 7-14 Reduction in secretion of tumor necrosis factor alpha (TNF-α) by monocytes after exposure to different concentrations of hydroxyethylmethacrylate (HEMA). The TNF-α secretion shown on the y-axis is plotted against HEMA concentration on the x-axis for cells that were either stimulated by lipopolysaccharide (+LPS) or not stimulated by lipopolysaccharide (–LPS). (Courtesy of J. Wataha)

by lipopolysaccharide. The significance of this effect is that relatively small amounts of HEMA released from bonding adhesives or resin-based composites can alter the normal functions of monocytes, thereby contributing to the potential immunotoxicity of some resin-based products.

PULPAL AND PERIODONTAL EFFECTS

The postoperative discomfort or pain caused by treatment with dental materials may result from any of several factors, including thermal trauma, chemical injury, microleakage, and allergy. The hydrodynamic theory of pulp pain is related to the movement of dentinal fluid and its influence on the odontoblastic processes. It is well known that dentin permeability increases substantially in areas closer to the pulp chamber. Thus, the damaging effect of a material, if such an effect occurs, is strongly influenced by the remaining thickness of dentin between the material and the pulp chamber. This outward fluid pressure from the pulp chamber toward the enamel is not sufficient to eliminate the inward diffusion of bacteria, bacterial products, or material components into the pulp. A major problem in the diagnosis or potential pulp damage caused by a material or substance is the fact that there is virtually no correlation between the histologically documented damage to the pulp and clinical symptoms. This is considered as a major drawback of clinical studies in this area.

Because the cervical margins of many dental restorations are near the periodontal attachment area (see Figure 7-3), the biocompatibility of these materials may influence the body's ability to defend against bacteria that cause periodontal disease. Further, the periodontal pocket, or gingival sulcus, may accumulate significant concentrations of leached substances that do not accumulate to these levels in other areas. In addition to the accumulation of leached or dissolved substances in subgingival areas, substances that are leached from root canal filling materials may accumulate next to the apical foramen. Substances that accumulate in these areas can lead to inflammatory reactions, allergic reactions, periodontal pathology, and periapical lesions.

CRITICAL QUESTION

How can microleakage influence the biological response to a material?

INTERFACES WITH DENTAL MATERIALS

Tooth-supported dental restorations consist of one or more prepared teeth, a monolayer or multilayer restorative material, and auxiliary dental biomaterials such as dental adhesives, cements, and sealing agents. Although several interfaces may be present in these restorations, the dentin–cement or dentin–resin interfaces are the most important in transition areas for transfer of leached substances into dentinal fluid. Dental cements such as zinc phosphate, glass ionomer, zinc polycarboxylate, and zinc oxide-eugenol do not require etching of dentin to be used as luting agents. In contrast, adhesive-bonded, resin-based cements may require acid etching of dentin to remove the smear layer and to expose the collagen mesh that allows infiltration of the bonding resin. This resin layer acts as a partial barrier to the transport of elements, ions, or substances that are released from a variety of restorative materials.

If the resin material does not penetrate the collagenous network or debonds from it as the resin shrinks during polymerization, a microscopic gap will form between the resin and dentin. This shrinkage may also occur with enamel. Although this gap is only a few microns wide, it is wide enough to permit bacteria to penetrate this interfacial space, since the average size of a *Streptococcus* bacterium is only about 1 µm in diameter. The dentin–resin interface occurs when the clinician attempts to bond resin-based restorative materials to dentin. The interface actually forms between the resin and the collagen network. Thus, the integrity of the resin–collagen interface will control the potential pulp-damaging effect of these restorations.

As shown in Figure 7-15, incomplete bonding or resin penetration into the collagen mesh of acid-etched dentin can lead to fluid ingress along gaps wider than 1 µm, which is referred to as *microleakage*. The microscopic gap for the so-called microleakage process may lead to several undesirable events. The bacteria that migrate to the pulp may initiate an infection of pulp tissue. The gap also promotes material breakdown along the unsupported margin. This breakdown increases the gap width, which allows larger particles and molecules to progress toward the pulp chamber. It also causes marginal staining and compromised esthetics that may lead to premature replacement. One in vitro study revealed less leakage for amalgam restorations compared with resin-bonded composites (Őzer et al., 2002).

If the resin penetrates the collagen network of dentin but does not penetrate it completely, then a much smaller gap (less than 0.1 µm in most cases) will exist between the mineralized matrix of dentin and the collagen–resin hybrid layer

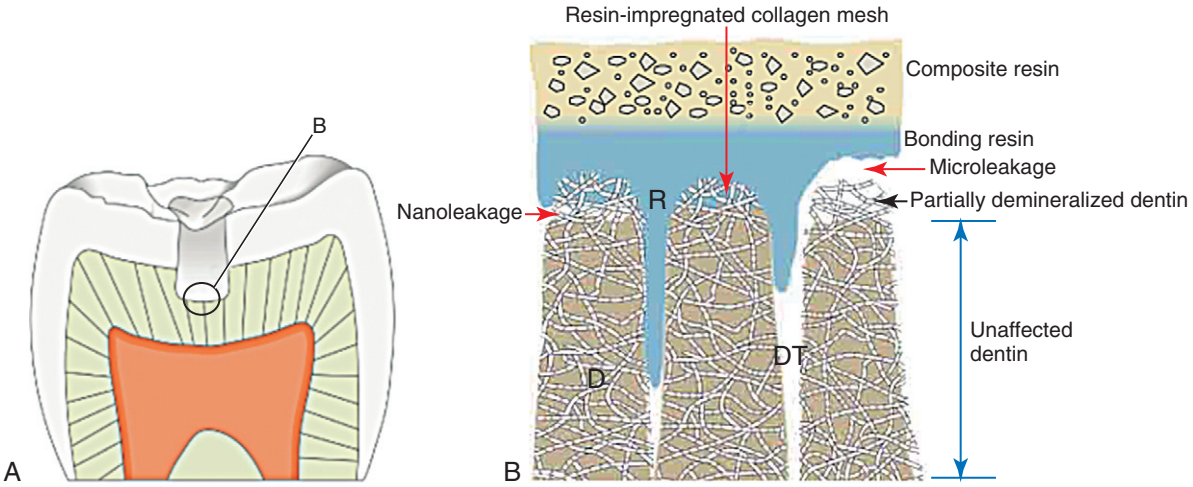


FIGURE 7-15 **A.** Cross-section of Class I composite restoration. **B.** Diagram illustrating the concepts of microleakage (right) and nanoleakage (letf) when bonding dental resins (R) to dentin (D). The dentin has been acid-etched in preparation for the application of the resin, which leaves the collagenous matrix of the dentin exposed (unshaded crosshatched area in upper right side). If the resin does not completely penetrate the collagen network (left) then a samll sapce of communication exists between the dentinal tubules (DT) and the external part of the tooth (arrow, left). This situation is called nanoleakage. On the other hand, if the resin fails to penetrate the collagen network at all, or debonds from it, then the space is much larger (arrow, right). This situation is called microleakage. In the ideal situation (center), the resin penetrates the collagen network all the way to the mineralized dentin. Nanoleakage and microleakage are both important factors in the biocompatibility of dental resin materials.

(see Figure 7-15). This much smaller gap has been claimed to allow nanoleakage, which probably does not allow bacteria or bacterial products to penetrate the marginal gaps of the restoration and the pulp. However, fluid exchange most likely occurs, and this may degrade the resin or the collagen network that is incompletely embedded with the resin, thereby reducing the longevity of the dentin–resin bond.

Nanoleakage is not known to occur between restorations and enamel because enamel contains virtually no organic mass and therefore has no collagenous matrix into which a resin may penetrate. Although it is unclear whether leakage toward or into the dental pulp chamber is a major factor in the biological response to dental materials, one must be aware of potential immune responses in the pulp and periapical tissues that may occur independently of leakage phenomena.

? CRITICAL QUESTION

What is the difference between **osseointegration** and **biointegration**?

INFLUENCE OF BIOCOMPATIBILITY ON THE OSSEOINTEGRATION OF IMPLANTS

The success of endosseous dental implants is based on the biocompatibility of the implant surface and the ingrowth of new bone into the surface through the process of **osseointegration**. Very few implant materials or implant coatings promote osseointegration. The most common implant materials include (1) CP Ti; (2) titanium-aluminum-vanadium alloy; (3) tantalum; and (4) some types of ceramics. Materials that allow osseointegration have very low degradation rates, and they tend to form surface oxides that enhance bony approximation. Some materials such as bioglass ceramics promote a perfect osseointegration of the bone. The general process of **biointegration** involves the adaptation of bone or other tissue to the implanted material without any intervening space along the tissue-material interface (see Chapter 20).

MERCURY AND AMALGAM

The controversy over the biocompatibility of amalgam has waxed and waned several times in the 170-plus year history of its dental use in the United States. Most of the controversy stems from the known toxicity of mercury and the question of whether mercury from amalgam restorations has toxic effects. Mercury occurs in four forms: as the metal (Hg^0), as an inorganic ion (Hg^{2+}), as a component of the silver-mercury phase, or in one of several organic forms such as methyl or ethyl mercury. Metallic mercury gains access to the body via the skin or as a vapor through the lungs. Ingested metallic mercury is poorly absorbed from the gut (0.01%), so the primary portal into the body is through inhalation of mercury vapor.

Absorption of specific metals through the oral mucosa, gastrointestinal tract, or respiratory tract can vary considerably for different chemical forms of a metal. Excretion may occur through exhaled vapor or through urine, feces, or skin. For example, mercury vapor is readily absorbed after inhalation. Dissolved mercury can be transported through blood and distributed to the brain and other organs and excreted by exhalation and in urine. Elemental mercury is transported to

blood cells and tissues, where it is oxidized rapidly to mercuric mercury (Hg^{2+}).

The most common forms of mercury that occur naturally in the environment are metallic mercury, inorganic salts, mercuric sulfide (HgS), mercuric chloride ($HgCl_2$), and methyl mercury (Ch_3Hg^+). Mercury forms numerous compounds, assuming +1 valence in mercurous compounds and +2 valence in mercuric compounds. The transformative ability of mercury can be either helpful or harmful. Microorganisms and various natural processes can convert metallic mercury to inorganic mercury compounds, inorganic mercury compounds to organic mercury compounds, and organic to inorganic compounds. Methyl mercury is the most common form that is transformed by natural processes; it is a more toxic form than ethyl mercury ($C_2H_5Hg^+$) or elemental mercury. Methyl mercury is a major safety concern because it bioaccumulates through the food chain; its pharmacokinetic half-life is longer (1.5 to 3 months) than that of ethyl mercury (less than 1 week). Moreover, it is accumulated in the body rather than being excreted in the gut, as occurs with ethyl mercury. In air, the concentrations of mercury range from about 0.01 to 0.02 $\mu g/m^3$.

Mercury accumulates in the kidneys. In the brain, metallic mercury can be converted to an inorganic form that is retained in the brain. Elemental mercury and mercury vapor have a half-life of 1 to 3 months. Mercury leaves the body by excretion through urine and feces.

Exposure to high levels of mercury can injure the brain, kidneys, and the developing fetus. The nervous system is sensitive to all forms of mercury, although the brain is most sensitive to metallic mercury and methyl mercury. Chronic mercury toxicity may be manifested as tremors; memory loss; and changes in personality, vision, and hearing. Children and fetuses are most sensitive to the effects of mercury on the nervous system. Selenium, an essential element, is claimed to be protective against the toxic effects of mercury.

Mercury is not regulated under the Clean Air Act (U.S. Code, Title 42, Chapter 85, signed by President Richard Nixon on December 31, 1970). The Clean Air Act is the law that defines the responsibilities of the U.S. Environmental Protection Agency for protecting and improving air quality and the ozone layer. The Clean Air Act Amendments were enacted by Congress in 1990 and legislation has made several minor changes since 1990. For air in the workplace, the Occupational Safety and Health Administration has set a permissible exposure limit (PEL) for mercury vapor in air of 0.1 mg/m^3.

The United Nations Environment Programme (UNEP) has organized global meetings through the UNEP Global Mercury Partnership to protect human health and the global environment from the release of mercury and its compounds by minimizing and, where feasible, ultimately eliminating global, anthropogenic mercury releases to air, water and land. Since 2001 the Governing Council/Global Ministerial Environment Forum of UNEP has discussed the need to protect human health and the environment from the releases of mercury and its compounds. By the end of 2011, three sessions of the Intergovernmental Negotiating Committee (INC) organized by UNEP had been held to prepare a Global Legally Binding Instrument on Mercury: INC1 (June 7-11, 2010, Stockholm, Sweden), INC2 (January 24-28, 2011, Chiba. Japan), and INC3 (October 31-November 4, 2011, Nairobi, Kenya). Although no globally-binding document on controlling mercury in dental amalgam and other mercury-containing products had been approved, a proposal for a "phase-down" of dental amalgam was supported combined with a need for research on more durable alternatives to dental amalgam and a renewed emphasis on prevention of caries and the associated need to reduce the need for restorations throughout the world.

Biological monitoring of the metal species and content in urine, whole blood, plasma, or serum is recommended for specific metal species depending on the level of biological risk and the critical target tissues that are involved. Sampling of metals in hair, nails, feces, bone, and teeth is also advocated in certain cases.

Several studies have shown that amalgams release sufficient vapor to cause absorption of between 1 and 3 μg/day of mercury, depending on the number and size of amalgam restorations present (Langworth et al., 1988; Berglund, 1990; Mackert and Berglund, 1997; Ekstrand et al., 1998). The inhaled mercury gains access to the bloodstream via the alveoli of the lungs. From the blood, mercury is distributed throughout the body, with a preference for fat and nerve tissues. Mercury is also ingested as particles produced by wear, and about 45 μg/day of mercury may reach the gut either as the amalgam form or as dissolved and released Hg^{2+} ions. The absorption of ionic mercury is also poor (approximately 1% to 7%). Mercury trapped in amalgam particles is also poorly resorbed. Methyl mercury is not produced from amalgams but is generally a product of bacteria or other biological systems acting on metallic mercury. Methyl mercury is the most toxic form of mercury and is also very efficiently absorbed from the gut (90% to 95%). Methyl mercury is absorbed mainly from the diet, particularly from fish (especially shark, swordfish, and tuna), which contribute a significant portion.

Concerns about mercury stem from its toxicity and its relatively long half-life in the body. The toxicity of mercury is well known; the symptoms depend somewhat on the form. Acute symptoms are neurologically based or kidney based, ranging from paresthesia (at 500 μg/kg or above) to ataxia (at 1000 μg/kg or above), joint pain (at 2000 μg/kg or above), and death (at 4000 μg/kg or above). The lowest known level for any observable toxic effect is 3 μg/kg. This level translates to about 30 μg of mercury per gram of creatinine clearance in the urine. At chronic exposure levels, the symptoms are more subtle and include weakness, fatigue, anorexia, weight loss, insomnia, irritability, shyness, dizziness, and tremors in the extremities or the eyelids. Although amalgams do not release anywhere near toxic levels of mercury, the long half-life of mercury in the body raises concerns among some individuals. The half-life ranges from 20 to 90 days, depending on the form, with methyl mercury exhibiting the longest half-life and inorganic forms the shortest. Numerous tests for

the body burden of mercury have been developed, including those based on the analysis of blood, urine, and hair. Of these test parameters, measurement of mercury in the urine after 24 hours may be the best long-term indicator of the total metallic mercury body burden, normalized to grams of creatinine clearance from the kidneys.

Humans are exposed to mercury from a variety of sources in addition to dental amalgams. There are extremely sensitive methods for detecting mercury in parts per trillion; these methods have made it possible to analyze the sources of mercury exposure for humans. Estimates of intake levels from air (in micrograms per day) are 0.12 for Hg^0, 0.04 for Hg^{2+}, and 0.03 for methyl mercury. Water probably contributes about 0.05 µg/day and food about 20.0 µg/day in the form of Hg^{2+}. Depending on one's diet, the consumption of fish contributes about 0.9 µg/day of Hg^0 and 3.8 µg/day of methyl mercury. These values place the 1 to 3 µg/day of absorbed Hg^0 vapor from amalgams in perspective. Thus, the intake of mercury is a complex issue with many sources and forms of exposure. Furthermore, there is considerable variability from individual to individual depending on diet, environment, and dental status. Despite the confirmed exposure of humans to these low levels of mercury, the biological effects of these levels are insignificant.

Numerous studies have attempted to determine whether mercury exposure from dental restorations or other sources contributes to any documentable health problem. Several studies have estimated the number of amalgam surfaces needed to expose an individual to mercury concentrations with a minimum observable effect (slightly impaired psychomotor performance, detectable tremor, and impaired nerve conduction velocity). Estimates are that several hundred amalgam surfaces would be necessary to achieve these levels. Even if all 32 teeth were restored on all surfaces with amalgam, the total number of surfaces (counting incisal edges) would be only 160. Other studies have measured renal function in patients in whom all of the amalgam was removed at the same time (the worst possible case). Despite markedly elevated blood, plasma, and urine levels of mercury, no renal impairment was noted. Still other studies have attempted to look at blood cell types and cell numbers in dentists, who are presumably exposed to higher levels of mercury because of their daily occupational exposure. No effects of mercury have been noted. Other studies for neurological symptoms in children populations occupationally exposed have shown no effects (Bellinger et al., 2006, 2007; DeRouen et al., 2002, 2006). In summary, there are simply no data to show that mercury released from dental amalgam is harmful to the general population.

METHACRYLATES AND RESIN-BASED COMPOSITES

The best screening substance for methacrylate allergy caused by dental material products is HEMA. This result confirms previous findings (Goon et al., 2006), which revealed that HEMA alone picked up 96.7% of the patients with methacrylate allergy and 100% of the dental personnel with methacrylate allergy.

The frequency of positive responses to the common allergen test substances were reported as follows: gold sodium thiosulfate, 14.0%; nickel sulfate, 13.2%; mercury, 9.9%; palladium chloride, 7.4%; cobalt chloride, 5.0%; and HEMA 5.8% (Goon et al., 2006).

ESTROGENICITY

In 1996, a research group claimed that dental sealants released estrogenic substances in sufficient quantities to warrant concern (Olea et al., 1996). Since then, the **estrogenicity** of dental composites has also been questioned, particularly for use in children. Estrogenicity is the ability of a chemical to act as the hormone estrogen does in the body. If these chemicals are not indigenous to the body, the substance is called a **xenoestrogen**. The occurrence of xenoestrogens in the environment has been a concern for many years. Environmentalists fear that these substances will alter reproductive cycles and developmental processes in wildlife, and there is evidence to support these concerns with regard to humans. The concern about estrogens in dentistry centers around a chemical called *bisphenol A* (*BPA*), which is a synthetic starting point for bis-GMA (bisphenol-A-glycidyldimethacrylate) composites in dentistry as well as many other plastics. The fear is that the release of these substances might alter normal cellular development or cell maintenance if BPA has estrogenic effects, even at the impurity levels that may be encountered in practice. It is generally accepted that BPA is released from bis-DMA, which is also used in dental products. However, if bis-DMA is used, the amount released after placement of a restorative filling is too small to be of concern. However, to overcome any concerns, products free of bis-DMA can be used.

There is fairly convincing evidence that BPA and BPA dimethacrylate may act on the estrogenic receptors in cells. Thus, these chemicals are probably xenoestrogens. This evidence is derived from molecular modeling studies and studies of estrogen receptor-BPA binding in vitro. However, these studies have also shown that BPA is probably 1000-fold less potent as an estrogen than the native estrogen hormone.

One test commonly used to assess xenoestrogenic activity is the *E-screen assay*. This in vitro test relies on the growth response of breast cancer cells, which are sensitive to potential estrogenic compounds. Typically, the compound in question is applied to the cells and cell growth is measured over a 24- to 72-hour period. A compound is deemed to be estrogenic if the growth rate of cells exceeds that of control compounds without the xenoestrogen. The E-screen test has several problems that make its accuracy suspect. First, the test does not confirm that the chemical acts on the estrogenic receptor, a requirement for true estrogenicity. Second, the test uses cell growth to define estrogenicity, and many factors can cause such growth in addition to the estrogenic potential of the agent or substance. Finally, there are several other problems such as the reliability and sensitivity of the cell lines used and the difficulty of controlling the variables. These factors cast doubt on the reliability of the E-screen assay as a predictor of estrogenicity.

Although the estrogenicity of BPA has been confirmed, there is little evidence that dental composites have estrogenic effects in vitro or in vivo. The original report of estrogenic effects in 1996 appear to have been overstated because several errors in the method and interpretation have subsequently been reported in the literature. Studies have shown only trace amounts of BPA in dental composites, and attempts at eluting BPA from polymerized composites have yielded either low or undetectable amounts. Coupled with the relative insensitivity of BPA as an estrogen and the likely dilution of any released BPA, the risks of estrogenic effects in vivo appear low. No studies have convincingly shown evidence of these effects from dental resin–containing materials.

OTHER BIOLOGICAL CONSIDERATIONS FOR RESINS

The explosion in the use of resin-based composites for restorative work has raised questions about the biological safety of these materials. The primary risk of these materials appears to be allergy related, and the risk is highest for dental personnel because of frequent exposure to nonpolymerized materials. Allergy to other types of dental materials such as latex gloves and monomeric substances also represents the greatest risks of an adverse biological effect for dental office staff. The allergenicity of methylmethacrylate is well documented, and the use of gloves is not effective in preventing contact because most resin monomers pass easily through gloves. Also, allergic reactions to other methacrylates have been reported. The allergic reactions occur primarily as contact dermatitis, with the resins acting as haptens via delayed hypersensitivity (Type IV) mechanisms. In rare cases, anaphylactic responses have been reported, and dermatitis may be so severe as to be disabling. In the most severe cases, individuals may need to change work activities or change to a different profession.

Resins also have significant toxic effects, which are clearly demonstrated through the use of in vitro tests. The results of these tests are often comparable with, and sometimes worse than, the effects resulting from the use of metals. There is ample evidence that resins release nonpolymerized components into biological environments, although the release in vivo of specific substances is not well documented for either resins or metals. Resin components have also been shown to traverse dentin, and newer techniques that advocate direct pulp capping with resins expose pulp directly to these materials. The long-term, low-dose effects of resin components that are released are not well understood, and detecting adverse effects in vivo is difficult. Limited clinical evidence has linked the use of resins to oral inflammation. There is also limited in vivo evidence to show that resins may allow the growth of some bacterial species. Other studies have advocated the use of special resins as antimicrobial agents to be incorporated into dental restorative materials.

TITANIUM AND TITANIUM ALLOYS

In vitro evaluation of titanium biocompatibility, percentage attachment efficiency, and proliferation of human fetal fibroblasts and human gingival fibroblasts reveals that a surface layer of titanium oxide (Ti_2O_3) has the ability to coexist with living tissues and organisms. Based on these studies one can conclude that titanium is relatively nontoxic, noninjurious, and not physiologically reactive. Titanium has a light weight, high strength, and excellent durability when exposed to chemical agents. However, it is susceptible to attack by acidic fluoride products.

BASE METAL AND NOBLE METAL ALLOYS

Predominantly base metal alloys are classified by the ADA as those containing less than 25% by weight of noble metals (gold, platinum, palladium, rhodium, ruthenium, iridium, and osmium). Noble alloys are classified as those that contain between 25% and 60% of these noble metal elements. High noble metal alloys are classified by the ADA as those containing at least 40% gold and 60% of noble metal elements. Stainless steel (Fe-C-Ni-Cr), cobalt–chromium (Co-Cr), nickel–chromium (Ni-Cr), and cobalt–nickel–chromium (Co-Ni-Cr), classified as base metal alloys, and commercially pure titanium (CP Ti) are used most often for removable fixed restorations and orthodontic appliances. Some evidence suggests that metal appliances can lead to gingivitis or periodontitis. The severity of these adverse effects varies as a function of atomic or molecular characteristics (Schmalz and Garhammer, 2002). Metallic components and microparticles from cast metal restorations have been found in contiguous plaque and gingival tissues. Although high-gold-content noble alloys are more resistant to corrosion than other alloys, most local adverse effects seem to occur when noble and base alloys are used together.

Metal ions can be leached from cast metal restorations or wrought appliances into the oral cavity. Since high-noble (HN) and noble (N) alloys are corrosion resistant, one might expect a negligible level of leaching. However, allegations of adverse effects caused by leaching of palladium have raised concerns on the biocompatibility of these alloys (Wataha and Hanks, 1996). Biocompatibility studies of a high-gold alloy (Iropal W), two low-gold alloys (Argenco 9 and Gold EWL-G), a high-palladium alloy (Argipal), two palladium–silver (Pd-Ag) alloys (Argenco 23 and EWL-G), one Ni-Cr alloy (Wiron-88), two Co-Cr alloys (Wironium and Wirocast), and a 22k gold alloy revealed that the strongest responses were derived from the Ni-Cr alloy and the weakest response was from the 22k gold alloy. These analyses were based on use of the subcutaneous implantation (histopathological) method. Cast metal discs were implanted for 15, 30, or 60 days in rats. The high-gold alloy and the high-palladium group showed reactions similar to those of the 22k gold alloy. However, the low-gold alloy and the Pd-Ag alloys ranked between the base metal alloy and the precious metal alloys.

Metallic ions released through corrosion processes are responsible for much of the metal–protein or metal–cell interaction behavior of dental metals and alloys. However, the surface structure of the metal, its composition, and its electrochemical properties also contribute to local interactions. Increased plaque accumulation can cause adverse inflammatory reactions in the adjacent soft tissues. Ions released from the superficial layers of cast alloys may be quite cytotoxic.

No correlation has been found between the noble metal content of alloys and the severity of corrosion. However, some base metals, such as nickel-chromium-beryllium (Ni-Cr-Be) alloys, exhibit increased corrosion in low-pH environments. Also, microscopic particles can be abraded from metallic restorations during wear processes. In sufficient quantities, metal ions such as copper, nickel, and beryllium can be released and subsequently induce inflammation of the adjacent periodontal tissues and the oral mucosa.

No evidence exists to prove that dental metallic materials are mutagenic, genotoxic, or carcinogenic. Although in vitro evidence suggests that the immune response can be altered by various metal ions, their role in oral inflammatory diseases such as gingivitis and periodontitis is unknown. Allergic reactions to metallic dental restorations have been described above. Nickel is known to be highly allergenic, especially in females. It has been reported that 34% to 65% of patients who are allergic to nickel are also allergic to palladium. Further, palladium allergy seems to occur when individuals have been sensitized to nickel.

Few studies have measured the release rate of metal ions via in vivo corrosion. The amount and nature of released cations varies depending on the type of alloy, the environment, and the corrosion mechanism, including the concentration cell type, crevice corrosion, galvanic cell corrosion, stress corrosion, and pitting corrosion. The chemical composition of the corrosive solution, the pH, ion composition, artificial saliva characteristics, cell culture medium, and serum are significant variables as well. Some evidence indicates that multiphase alloys tend to release metal ions in proportion to their ion compositions.

NICKEL AND BERYLLIUM

Of many metals used in dentistry, nickel is a common chemical element in many base metal dental alloys, such as those used for crowns, fixed dental prostheses, removable partial dentures, and some orthodontic appliances. Nickel is also used in many types of endodontic files, although the duration of exposure through the use of files is far shorter. The use of nickel-based alloys for fixed prosthodontics in the United States has increased dramatically over the past 30 years and its use currently represents somewhere between 30% and 50% of the market. The use of nickel in dental alloys has been controversial for many years because of the allergenic potential of nickel ions and nickel compounds.

Nickel is the most allergenic metal known, with an incidence of allergic reactions between 10% and 20%. Reactions to nickel are more common among women, presumably because of the chronic exposure to nickel through jewelry, although the incidence among men is increasing. Reactions to nickel-containing dental alloys are well documented, and these can be quite severe in sensitized individuals. These reactions are probably under-reported because they are often subtle and can resemble periodontal inflammation (see Figure 7-5, *A, B*) or the erythema that results from excessive pressure on the palatal mucosa by metal frameworks. These reactions may also occur only outside the mouth.

Not all individuals with nickel allergy will react to intraoral nickel, and it is currently not possible to predict which individuals will react. Because the frequency of nickel allergy is high, it is possible that individuals will become sensitized to nickel after placement of nickel-containing alloys in the mouth.

Some studies in guinea pigs have suggested that oral exposure to nickel induces immunological tolerance. As stated previously, there is a possible cross-reactivity between nickel and palladium allergy. Almost all patients who are allergic to palladium will be allergic to nickel, whereas only about 33% of those allergic to nickel will be allergic to palladium. The mechanisms of the high allergy frequency to nickel are not known, but there is probably a genetic component. In addition, the tendency of nickel-containing alloys to release relatively large amounts of nickel ions probably contributes to their allergenicity. This release is particularly high in acidic conditions, especially for Ni-Cr alloys with less than 20% by weight of chromium.

Nickel has other adverse biological effects in addition to allergy. Nickel ions (Ni^{2+}) are a documented mutagen in humans, but there is no evidence that nickel ions cause any carcinogenic response intraorally. Nickel ions, along with cobalt and mercury, have also been shown to be nonspecific inducers of inflammatory reactions. Specifically, nickel ions appear to induce intercellular adhesion molecules in the endothelium, and they induce the release of cytokines from monocytes and other cells. It is not known to what extent these mechanisms contribute to any intraoral inflammation around nickel-containing crowns.

It is well known that nickel-based alloys can exhibit significant corrosion and release of nickel ions in a low-pH environment. Beryllium-free Ni-Cr alloys are more corrosion-resistant than beryllium-containing alloys. Base metal alloys containing both beryllium and nickel exhibit high beryllium release rates, which may pose a health risk.

In vitro environments do not necessarily simulate in vivo conditions. Many biological factors—including the biofilm characteristics, organic acid composition, and types of enzymes produced by oral microorganisms or those present in food—may contribute to alloy corrosion in vivo. Interactions between metallic restorations and patient factors such as consumption frequency of acidic foods and beverages and composition of saliva, can significantly affect intraoral corrosion. Corrosion may also be accelerated by phagocytotic cells such as human neutrophils (Yang et al., 1992). This has been demonstrated in clinical observations of removable partial denture frameworks made of titanium.

Wear can also accelerate the corrosion processes in vivo because of the local breakdown of the passivation layer (Khan et al., 1999). The dual action of corrosion and wear may accelerate breakdown in the oral environment.

In one study (Reuling et al., 1990), the corrosion rates of two Ni-Cr alloys with nearly identical compositions were significantly different. These results confirm that the release of metal ions from the alloys is not necessarily proportional to the nominal alloy composition (Wataha et al., 1991). On

the basis of these studies, it is clear that the release of metal ions cannot be predicted from the nobility or the overall composition of cast alloys. Each product must be evaluated individually for its corrosion behavior and the release of metal ions in specific corrosive environments.

Although no general correlation has been demonstrated between alloy composition and cytocompatibility, severely cytotoxic alloys generally have contained higher amounts of nickel than biocompatible products.

Although beryllium is known to be highly toxic, it is used in some Ni-Cr alloys in concentrations of 1% to 2% by weight (approximately 5.5% to 11% atomic content) to increase the castability of these alloys and lower their melting range. It also tends to form thin adherent oxides that are required to promote atomic bonding of porcelain. The use of beryllium in dental alloys is controversial because of its biological effects. First, beryllium is a documented carcinogen in either the metallic (Be^0) or ionic (Be^{2+}) state, although there are no studies showing that dental alloys containing beryllium cause cancer in humans. Any reaction is most probably mediated by beryllium released from the alloys, and although such release has been documented intraorally and in vitro, it is not as prominent as for nickel. Acidic environments enhance beryllium release from Ni-Cr alloys.

Furthermore, beryllium-containing particles that are inhaled and reach the alveoli of the lungs may cause a chronic inflammatory condition called berylliosis. In this condition, the alveoli of the lung are engorged with lymphocytes and macrophages. T cells in susceptible individuals proliferate locally in the lung tissue, presumably in a delayed hypersensitivity reaction to the beryllium metal. Berylliosis occurs only in individuals with a hypersensitivity to beryllium and may occur from inhalation of beryllium dusts (from grinding or polishing alloys), salts, or fumes such as those encountered in casting beryllium-containing alloys. Thus, dental lab technicians would presumably be at the highest risk of adverse effects from exposure to beryllium dusts and vapors.

CYTOTOXICITY OF METALS AND DENTAL CASTING ALLOYS

Cytotoxicity is often reported by an IC_{50} value, which is the inhibitory concentration (IC) that causes a 50% reduction in cell growth. A study of 43 metal salts, using the colony formation method and two types of cells (fibroblasts and osteoblast-like cells), revealed that IC_{50} depends on the types of metallic elements, their chemical states, and their elemental concentrations (Yamamoto et al., 1998). The IC_{50} for the salts with the highest toxicity (greater than 10^{-5} mol/L) were $CdCl_2$, VCl_3, $AgNO_3$, $HgCl_2$, $SbCl_3$, $BeSO_4$, and $InCl_3$. Their IC_{50}s differed by four orders of magnitude from the IC_{50} of the lowest-toxicity salt. The relatively high-toxicity salts—HgCl, $Ti(NO_3)_3$, $TINO_3$, $GaCl_3$, $CuCl_2$, $MnCl_2$, $CoCl_2$, $ZnCl_2$, $NiCl_2$, $SnCl_2$, $IrCl_4$, CuCl, $RhCl_3$, $Pb(NO_3)_2$, $Cr(NO_3)_3$, and $Bi(NO_3)_3$—had IC_{50}s below 10^{-4} mol/L for each cell line (Arvidson et al., 1987).

Another study reported the metabolic as well as the morphological response of cultured human gingival fibroblasts to salt solutions of beryllium (Be^{2+}), chromium (Cr^{6+} and Cr^{3+}), nickel (Ni^{2+}), and molybdenum (Mo^{6+}) ions that may be released from dental alloys (Messer et al., 1999). The evaluation parameters included viability, lysosomal activity, oxygen consumption, membrane integrity, DNA synthesis, ribonucleic acid (RNA) synthesis, protein synthesis, intracellular adenosine triphosphate (ATP) levels, and glucose-6-phosphate dehydrogenase activity. Whereas Ni^{2+} ion solutions altered metabolic functions at concentrations of 3 to 30 parts per million (ppm) compared with Cr^{3+} and Mo^{6+} at concentrations of 10 and 100 ppm, Cr^{6+} and Be^{2+} were the most toxic ions, which caused cellular alterations at concentrations of 0.04 to 12 ppm. Heavy metal ions such as Ni^{2+} and Co^{2+}, released from an implanted alloy by corrosion, can be distributed systemically by proteins, such as albumin. Cast CP Ti has been found to be highly biocompatible (Berstein et al., 1992; Wang and Li, 1998). Further, it was observed that the corrosion resistance of a noble or base metal alloy does not permit one to draw conclusions as to its biocompatibility. It was also found that solid specimens of gold-based solders combined with a substrate alloy were very often less cytotoxic than the solders alone. Only three solder-substrate alloy combinations revealed more pronounced toxic reactions than the single solders (Wataha et al., 1995).

Various studies have shown that copper is more toxic than gold, palladium, and titanium. However, this result may be misleading since copper is more susceptible to corrosion. Thus, analyses of cytotoxicity test results should also consider the relative corrosion rates of specific elements in various solutions including artificial saliva.

A shortcoming of conventional cell-culture studies is that the results do not usually reflect the long-term in vivo behavior of cast dental alloys. Thus, some alloys are tested both immediately after being polished and up to a year after being conditioned in a biological medium. Some alloys that were cytocompatible at baseline were also not cytotoxic after 10 months, and highly cytotoxic alloys were significantly less cytotoxic after 10 months. Thus, one could assume that restorations that have been in place for a year or more may present a reduced risk of cytotoxic effects.

In addition to the nature and quantity of released cations, surface topography of a cast metallic structure may be an important factor for biocompatibility. Thus, released metal ions as well as surface topography may contribute to local adverse effects in the gingiva and periodontium adjacent to cast restorations.

DENTAL CERAMICS

Dental materials are exposed to a wide range of solids and liquids with a range of pH values and temperatures in the oral environment. Therefore, excellent chemical durability is an important prerequisite in selecting ceramics as well as other restorative dental materials. Overall, the risk of surface degradation is low, and feldspathic ceramics have been used as clinical veneers for many years without significant biocompatibility issues.

Ceramic materials are known for their high levels of biocompatibility. Metal oxides such as Al_2O_3, BaO, CaO, K_2O, Li_2O, Na_2O, ZnO, and ZrO_2 are components of either dental core ceramics or dental veneering (layering) ceramics, and silicon dioxide (SiO_2) is the principal matrix phase component of all veneering ceramics. These oxides and related compounds in dental ceramics exhibit minimal dissolution in normal oral fluids and beverages. However, highly acidic environments can increase the release rates of certain metal and silicon ions. For example, acidulated phosphate fluoride (APF) is known to corrode the surfaces of veneering porcelains as well as glaze and stain ceramics. This is an extreme case, which suggests that APF should not be used in patients who have ceramic or metal–ceramic restorations.

ZIRCONIA BIOCOMPATIBILITY

Yttria-stabilized zirconia (Y-TZP) has a material density of greater than 6.0 g/cm^3 and a maximum operating temperature of 2000 °C. This material has the highest flexural strength (900 MPa) of the zirconia materials. Its flexural strength can increase to 1400 MPa when it is processed by hot isostatic pressing (HIP). The hardness of Y-TZP is 13 to 13.5 GPa. Its fracture toughness is 8 MPa·m$^{1/2}$, and its coefficient of thermal expansion (CTE) is relatively low (10.2×10^{-6}/K). The excellent mechanical properties of this material are a result of a very small grain size, extremely low porosity, and transformation toughening.

The biocompatibility of zirconia has been evaluated extensively. No local or systemic cytotoxic effects or adverse reactions have been traced to zirconia. The bone response of zirconia in vivo and the inflammation adjacent to zirconia have been shown to be satisfactory. Furthermore, bacteria and pathogen seem to adhere to zirconia to the same extent as to other materials.

SENSITIZATION TO AND IRRITATION BY CERAMICS

Several investigators have demonstrated that, unlike other dental materials, most dental ceramics do not induce an adverse effect when they contact the oral mucous membrane. Others have shown that glazed ceramics, which have been used in implant trials, caused very mild inflammatory reactions. These glazed ceramics were less irritating than resin-based composite or gold.

Thus, compared with other dental materials, ceramic has no or very limited potential to induce irritation or sensitizing reactions. Since this evidence shows that ceramic materials do not cause direct irritation to cells of the mucous membrane, one can conclude that minor observed irritations may be attributed to mechanical irritation, e.g., from roughened surfaces.

RADIOACTIVITY

Naturally occurring radioactivity has been detected in certain dental ceramics. Veronese et al. (2006) reported that the dose rates from natural radionuclides in feldspathic porcelains and glass ceramics were about 10 times higher than the background value, whereas resin-based composites and alumina-based ceramics exhibited negligible beta dose rates, which were similar to those from natural teeth. The high beta dose levels emitted from feldspathic porcelains and glass ceramics were mainly ascribable to potassium 40 (K^{40}). Concentration activities determined from gamma-spectrometry ranged from 2.01 to 2.9 becquerel per gram (Bq/g). However, these activities are below the threshold limit of 10 Bq/g for K^{40}. No adverse effects that are caused by exposure to radiation from dental ceramics have been documented in the literature. A further contribution to the beta dose rate from rubidium 87 (Rb^{87}) was possibly associated with rubidium added as a fluorescence activator, or to improve mechanical properties. These levels exceed the maximum level of 1 Bq/g permitted by ISO standard 6872. The specific activities of uranium and thorium were significantly lower than the levels reported in earlier periods when the addition of uranium to dental porcelain materials was used to enhance fluorescence. The dosimetry results of zirconia samples suggest the presence of segregated clusters of radionuclides. These results confirmed that patients with veneering ceramics and certain glass ceramics are subjected to higher dose levels (although well within safety limits) compared with the general population.

LATEX

Both patients and office staff are exposed to latex from many sources, including toy balloons, condoms, swim goggles, dishwashing gloves, hairnet elastics, clothing elastics, footwear, cervical diaphragms, and hot water bottles. Of particular interest in dentistry is the use of latex gloves and latex rubber dams, which expose both patients and dental personnel to this potential allergen. In the early 1980s, when HIV infection became a major safety issue, dental personnel began to routinely wear gloves to reduce the risk of transmission. Since that time, the incidence of latex hypersensitivity reactions has increased enormously. In 1991, the FDA estimated that about 6% to 7% of surgical personnel may be allergic to latex. Surveys of dental professionals have shown that 42% have adverse reactions to occupational materials, most of which were related to dermatoses of the hands and fingers. Adverse reactions to latex gloves have been reported in 3.7% of adult patients and 5.7% of pediatric patients.

Natural latex products are made from a white milky sap harvested from a tree growing in tropical regions. Ammonia is added to the sap to preserve it, but at the same time, the ammonia hydrolyzes and degrades the sap proteins to produce allergens. Vulcanization is the process by which liquid latex is hardened into rubber through the use of sulfur compounds and heat. These chemicals may be allergenic themselves and are often present to some degree in the final product. The manufacturing process leaches the allergens by soaking the rubber products in hot water. The leaching water is changed repeatedly to decrease the concentration of the allergens, but leaching brings other allergens to the surface and unfortunately places the highest concentrations near the skin of the wearer. Thus, the allergenicity of a given batch of latex will be dependent on how the latex was collected, preserved, and

processed. Synthetic latex is also available, but it produces the same problems except that naturally occurring proteins and their degradation products are not present.

CRITICAL QUESTION

What evidence or documentation can you provide to dental patients to assure them that amalgam is a safe material for dental restorations?

ADVERSE EFFECTS DATA FROM NATIONAL REGISTRIES

Reporting systems for monitoring intraoral reactions to dental materials complement traditional biocompatibility evaluations of dental materials products. Because of the overwhelming number of dental biomaterials that have been developed in recent years, it is essential that such reporting systems be established to assist dental practitioners in their optimal selection and use. In addition to revealing information regarding the frequency and nature of adverse effects, monitoring of these registry databases may reveal changes in the profiles of adverse reactions that facilitate the postmarketing surveillance of dental materials.

From 1993 to 2011, three countries had established registries for spontaneous reporting of adverse effects that result from the use of dental materials. In 1993, a national reporting system was established in Norway, funded by the Ministry of Health and Social Affairs. It was coordinated by the Dental Biomaterials Adverse Reaction Unit at the University of Bergen. This unit was established as an adverse reaction registry and to serve as a clinical evaluation resource for patients with suspected adverse reactions—that is, undesirable side effects allegedly associated with a dental material. Similar reporting registries were established in Sweden in 1996 and in the United Kingdom in 1999.

Although some countries have established systems for submitting adverse effects reports, only a few of these are sufficiently comprehensive to encourage periodic reviews of the data and publication of the results. Reports from these programs are described below. Although the forms for reporting adverse effects in individual countries have been refined over the past two decades, limited guidance is available to alert dentists and office staff members to the most relevant signs and symptoms of adverse effects that should be considered in the treatment of their dental patients.

Some Scandinavian studies (Jacobsen and Hensten-Pettersen, 1989, 1993; Kallus and Mjör, 1991) revealed that adverse effects on personnel associated with exposure to dental materials were extremely rare. In spite of the weekly exposure of dentists and their staff members to topical anesthetics, resin sealants, adhesives, resin composites, temporary acrylic resins, cements, impression materials, metals, latex gloves and rubber dams, oral rinses, and auxiliary materials, the percentage of adverse effects is negligibly low. The incidence of these reactions ranges from 0.038% (1 in 2600) to 0.143% (1 in 700).

One study (Vamnes et al., 2004) investigated the relationship between patient complaints and objective clinical findings based on 899 adverse effects reports that had been submitted between 1993 and 1999 to the Dental Biomaterials Adverse Reaction Unit (DBARU) at the University of Bergen in Norway. The reports submitted by dentists and physicians were based on subjective symptoms, objective findings, or both. Reported reactions were compared with clinical findings obtained after dental and medical examinations at the DBARU. These examinations involved patients who had reported reactions primarily to amalgam fillings (84%) and metals in fixed dental prostheses (11%). Reactions to resins, cements, removable denture materials, and endodontic materials were also reported but at a much lower frequency (2% to 4%). In 80 of the patients, the examinations revealed edema, lichenoid reactions, ulcers, vesicles, erythema, and atrophy. For 35 of these patients, the intraoral findings from examinations at the DBARU were similar to those in the dentists' reports. For another 45 patients, objective intraoral signs of reactions that had not been reported were found upon examination. Patients with suspected adverse reactions have reported anxiety, burning sensation, concentration difficulty, depression, dry mouth, disturbance of taste, pain in muscles and joints, dizziness, fatigue, headache, memory problems, and restlessness. Many patients reported subjective symptoms without any observed objective signs of adverse effects or reactions.

Another DBARU report was based on 296 patients, 70% of whom were women between 40 and 49 years of age, who were referred primarily for effects attributed to dental amalgam (85%) and metals in crowns and bridges (11%). Nearly all of the patients (96%) reported general subjective symptoms of muscle and joint pain, fatigue, and memory problems. Complaints involving the orofacial tissues (lips, face, and temporomandibular joint) and intraoral symptoms were also reported. The investigators could not identify a specific cause-and-effect relationship between the dental biomaterials in question and the patients' general symptoms. Twenty patients were advised to replace their filling materials because of contact lesions. Another 20 patients were advised to replace the involved restorative materials because of allergy verified by positive patch test results. The use of resin-based composites has increased in Norway, and the use of amalgam has virtually been eliminated there. Despite this trend, far fewer patients were referred to the DBARU for resin and cement reactions. Some investigators suggest that these reactions may be less frequent and more short-term in nature so that only longstanding reactions were referred for clinical examination. Furthermore, they hypothesized that the low percentage of intraoral findings in patients with reactions claimed to be related to amalgam might be associated with the patients' subjective longstanding symptoms. For adverse reaction reports associated with metals in fixed prostheses, most of the reactions seemed to be local reactions.

A study of a preliminary survey (Scott et al., 2004) by the U.K. Adverse Reactions Reporting Project (ARRP) was designed to measure the severity of adverse reactions to

dental materials in the United Kingdom. The reporting forms distributed to dental professionals were modified versions of the forms used by adverse reaction units in Bergen, Norway, and Umeå, Sweden. The ARRP received 1075 complete reports of adverse reactions observed or experienced by dental staff and patients. Most of the patient-related adverse reactions (16.3%) were associated with metals (n = 175). These metal-exposure effects were mainly lichenoid reactions associated with amalgam restorations (n = 124, or 70.9%). Dental technicians reported acrylic resin as the cause of hand dermatitis in 61.1% (44 out of a total 72) of the reported cases. Dental surgery staff reported gloves as the cause of hand dermatitis in 75.0% of cases (398 out of a total 531). These results indicate that dental staff members are at risk mostly from an adverse reaction to latex gloves, whereas most patients are at risk for reactions associated with metals. For dental technicians, the greatest danger of an adverse reaction was from acrylic resins. The authors of this report emphasized the need to inform dental professionals of the adverse reaction registries and the need to respond to their surveys to minimize the potential for underreporting adverse effects.

The Swedish National Register of Side Effects (SNRSE) was established in 1996. It was set up in collaboration with Medical Odontological faculty of the University of Umeå, Sweden. This reporting registry is similar to the one that has been in use since 1993 at the University of Bergen, Norway, and the Swedish unit has collaborated with the Norwegian unit.

One study revealed the types and duration of side effects to resin-based dental materials based on 618 reports (456 on patients and 162 on dental practitioners) from 1996 to 1999 that had been submitted to the SNRSE (Tillberg et al., 2009). The link between the material and the reaction was assessed as *probable*, *possible*, *uncertain*, or *unclassifiable*, depending on the probability of the relationship and the quality of information submitted by the observer. The inclusion criteria for the patients to be accepted into the study were (1) reactions thought to be caused by direct resin-based restorations; (2) reactions that the expert group of the SNRSE had assessed to be *probable* or *possible*; and (3) reactions occurring during the years 1996 to 1999. Fifteen percent of the patients made complaints related to treatment with composite and bonding materials. The majority of complaints were based on intraoral effects or a combination of intraoral and extraoral effects that occurred within 24 hours after treatment. The most common adverse effects were related to skin, oral ulcers, and burning mouth complaints. These effects disappeared in 50% of the patients in less than a week. The investigators concluded that immediate reactions to resin-based materials were more common than delayed allergic reactions and the mechanism responsible for the immediate reactions was probably nonallergic in most cases.

Dental materials are among the most widely used synthetic biomaterials to be placed in the human body. They are classified as medical devices according to the European Medical Devices Directive (EMDD). According to the EMDD, reports of serious or life-threatening reactions should be sent to the manufacturers of the products and not necessarily to a neutral oversight organization.

In the U.S., the 1976 Medical Device Amendments, which became effective in 1984, require device manufacturers to report deaths, serious injuries and malfunctions to the U.S. FDA. A device malfunction represents the failure to perform as intended, or failure to meet design specifications when the failure has caused or contributed to serious injury or death. In 1990, the Safe Medical Devices Act extended reporting requirements to user facilities including hospitals, ambulatory surgical facilities, nursing homes, and outpatient treatment and diagnostic facilities (excluding employee health or school-based clinics, or the offices of health care professionals).

The FDA receives adverse event reports on devices as either individual reports or summary reports. Individual reports include voluntary reports submitted by health care providers and consumers through MedWatch (http://www.fda.gov/Safety/MedWatch/default.htm), the safety information and adverse event reporting program of the FDA. Mandatory reports are submitted by manufacturers and user facilities. Fuller and Parmentier (2001) reported that 28,555 reports on dental devices were submitted to the FDA over a 35-month period between 1996 and 1999. Injuries represented 64.4% of the reports, 90% of which were associated with endosseous implants. Malfunction of dental devices accounted for 34.8% of these reports. Only two deaths were reported (0.007%) during this period.

ALLERGIC REACTIONS

The previous reviews of reports from three national registries of adverse events reveal that most of the effects were associated with metals. Furthermore, patch tests for potential allergies to dental materials also suggest that the most likely allergens were components of cast dental alloys (Ditrichova et al., 2007). In this study, patch tests were performed on 25 subjects with lichenoid lesions located on the buccal mucosa, tongue and lips. Two sets of allergens, the "European Standard" and "Dental Screening" (Chemotechnique Diagnostics, Sweden) were used, supplemented with pulverized amalgam, iridium, indium, menthol, sorbic acid and platinum.

Tests were performed in accordance with ICDRG guidelines (International Contact Dermatitis Research Group). A total of 15 patients (60% overall) exhibited sensitization to one or more allergens, with a total of 31 positive reactions. The greatest frequency of positives were associated with dental metals (27 positive reactions). The order of tested metals according to frequency of positive reactions was mercury (24%), amalgam (24%), nickel (16%), palladium (16%), cobalt (12%), gold (8%), chromium (4%), and indium (4%). The correspondence of the material's presence in the mouth to the positive test result was 44%. However, susceptibility to allergic reactions varies considerably from one metal to another. Some estimates indicate that 15% of the population is sensitized to nickel, whereas only 4.2% (Valentine-Thon et al., 2006) of the population is sensitized to titanium.

No standard patch test for Ti has so far been adopted, and positive reactions to Ti have only rarely been demonstrated with skin testing. Patch testing in general has been validated only for the epidermal antigen contact test, which may itself induce sensitization of naive T lymphocytes, and is relevant primarily for detecting dermal effects of hypersensitivity (contact dermatitis). *In vitro* testing with the lymphocyte transformation test (LTT) on the other hand, can detect both dermally and non-dermally sensitizing allergens (e.g. beryllium). A version of LTT called memory lymphocyte immunostimulation assay (MELISA®) was selected for investigating hypersensitivity to Ti. Müller and Valentine-Thon (2006) demonstrated that titanium can induce clinically-relevant hypersensitivity in a subgroup of patients chronically exposed via dental or endoprosthetic implants.

Palladium-based alloys have been associated with stomatitis and oral lichenoid reactions, and palladium allergy seems to occur mainly in patients who have been sensitized to nickel. Except for titanium, many casting metal elements, including nickel, palladium, cobalt, gold, and chromium, have the potential to induce adverse reactions in hypersensitive patients. Individuals who are allergic to a metal are likely to exhibit allergic contact dermatitis as well as lichenoid lesions. Based on one study of 25 patients with lichenoid lesions, positive responses to standard patch tests were found for amalgam (25%), nickel (16%), palladium (16%), cobalt (1%), gold (8%), chromium (4%), and indium (4%). In another study of patients who exhibited patch test reactions to mercury compounds, partial or complete replacement of amalgam fillings led to a significant improvement in nearly all patients (Laeijendecker et al., 2004).

In 1996, the Finnish Contact Dermatitis Group patch tested more than 4000 patients (2300 to 2600 of the patients for most allergens) with a dental screening series (Kanerva et al., 1996, 2001). The irritant reactions were scored as "irritant" or "doubtful," and allergic responses were scored as +, ++, or +++, respectively. A reaction index was calculated, on the irritancy of the patch test substances. The most frequent allergic patch test reactions were induced by nickel (14.6%), ammoniated mercury (13%), mercury (10.3%), gold (7.7%), benzoic acid (4.3%), palladium (4.2%), cobalt (4.1%), and 2-hydroxyethylmethacrylate (HEMA) (2.8%).

Co-reactivity between palladium and nickel has been suggested, especially in females. Finnish adolescents 14 to 18 years of age who had received orthodontic treatment with metallic appliances were patch tested with palladium chloride and nickel sulfate. A total of 700 subjects (77% of those invited)—417 (60%) girls and 283 (40%) boys—participated. The majority of the girls (91%) had pierced ears. Orthodontic treatment was equally common (67% to 70%) in both the boys and the girls. The girls had a much higher frequency of allergic patch test reactions to both nickel sulfate and palladium chloride. Of the 700 adolescents tested, 48 (7%) had a positive patch test reaction to palladium chloride. Of the 417 girls, 44 (11%) were positive for palladium chloride, whereas only 4 of the 283 boys tested (1%) had a positive patch test reaction to palladium chloride. Three patients reacted to palladium chloride only, whereas all other patients with allergic patch test reactions to palladium chloride also had positive test reaction to nickel sulfate. The results support the concept of cross-reactivity between nickel sulfate and palladium chloride.

Nickel is one of the metals most likely to initiate such reactions. Individuals who wear jewelry are also more susceptible because of the common addition of nickel as an alloying element. Men who have body piercings and metallic decorations are susceptible to metal allergies (Ehrlich et al., 2001). This study supported the theory of co-reactivity of nickel and cobalt but not for nickel and palladium.

Other high-risk situations for metal allergies are exposures to soil, saltwater, cement, leather, antiperspirants, belt buckles, metal denture frameworks, pins, bra strap attachments, and zippers. However, one investigator (Hensten-Pettersen, 1992) concluded that even though base metal alloys were alleged to be a major concern to the dental profession, relatively few case reports have substantiated this concern. In fact, allergy to gold-based dental restorations has been more commonly reported. He hypothesized that tolerance induction may be a possible benefit of the use of intraorally placed alloys. In nonsensitized individuals, oral antigenic contacts to nickel and chromium may induce tolerance rather than sensitization.

Few studies have classified the clinical manifestations of contact allergic dermatitis from exposure to specific allergens in the dental series for contact dermatitis. The results from one study (Khamaysi et al., 2006) indicate that the most frequent oral manifestations were cheilitis and perioral dermatitis (25.6%), burning mouth (15.7%), lichenoid lesions (14.0%), and orofacial granulomatosis (10.7%). A total of 14.9% of the patients were dental personnel, each of whom suffered from hand dermatitis. The most common allergens were gold sodium thiosulfate (14.0%), nickel sulfate (13.2%), mercury (9.9%), palladium chloride (7.4%), cobalt chloride (5.0%), and HEMA (5.8%). Positive reactions to metals were frequent in all the clinical variants, and no specific association between a specific clinical presentation and a particular allergen was found. An allergy to mercury does not seem to contribute to the pathogenesis of oral lichenoid reactions. One should note that oral lichen planus lesions are more generalized and that oral lichen-planus-like (lichenoid) lesions occur primarily/only at the contact area with the causative material, although such a reaction can also be caused by chronic mechanical trauma.

A 2009 study (Raap et al., 2009) explored the relationship between positive patch test reactions to metal alloys used in dentistry or their salts and clinical symptoms. This study comprised 206 patients who underwent patch testing with dental metals because of suspected contact allergy. Twenty-eight patients (13.5%) had positive patch test reactions to dental metals. The majority of positive patch test reactions occurred for gold sodium thiosulfate, palladium chloride, and nickel sulfate, followed by amalgam, ammoniated mercury, and cobalt chloride and amalgam metals (copper, tin, and zinc), and ammonium tetrachloroplatinate ($n = 1$).

Only 7% of the patients had a clinically relevant contact allergy on the oral mucosa (3.5% with lichen planus and 3.5% with stomatitis). The conclusions of the study were that contact allergies to dental metals are infrequent and that the most frequent contact allergens were gold sodium thiosulfate and palladium chloride.

Hosoki et al. (2009) revealed that allergies to metals in some patients were manifested not only as lichen planus and contact dermatitis responses but also as psoriasis-like reactions (pustulosis palmaris et plantaris), which may occur on hands, feet, or the entire body. Patch testing of 78.8% females and 21.2% males indicated that 68.8% of the patients had one or more positive patch test reactions. The most common allergens were nickel (25.0%), palladium (24.4%), chromium (16.7%), cobalt (15.9%), and tin (12.5%). Pustulosis palmaris et plantaris reactions are considered a subcategory of psoriasis and affect the palms of the hands and the soles of the feet. These effects can be very painful and may make it difficult to perform manual tasks or to walk. Thus, treatment of these patients is critically important to relieve their suffering.

If a patient is allergic to a metal or other material, an allergic response to it on first contact and allergy symptoms will appear within 10 days. After sensitization to the particular substance, even brief contact with that allergen may cause the allergic contact dermatitis to reappear within 24 to 48 hours (Website, Asthma and Allergy Foundation of America: http://www.aafa.org/display.cfm?id=9&sub=23&cont=329). One of the most common signs is a change in the color of the skin, which usually appears on the spot that was in contact with the metal. Other areas can exhibit signs after the initial reaction has occurred. The general signs of contact allergies include (1) reddish, itchy, swollen skin; (2) vesicles; (3) scaly areas; (4) darkening of affected tissue; (5) leathery skin; and (6) cracked skin. The best "cures" for these reactions are avoidance of the suspected metals, use of nonmetallic jewelry, use of hypoallergenic jewelry such as that containing titanium, or a high gold content (e.g., 18 karat or more).

A study of 139 published cases of allergic reactions to dental metallic restorations showed that these patients suffered from local irritations primarily in the form of gingivitis and stomatitis (Hildebrand et al., 1989). Only 23.7% of 139 persons revealed general reactions. When the restorations were removed, 82.7% of the patients recovered from the allergic reactions. Analysis of these data demonstrates that local allergic reactions to metals may often be underdiagnosed as inflammatory reactions.

In other studies, lichenoid reactions, swelling, and pain in oral soft tissues and lips have been observed. In several patients, gold ions caused an allergic contact gingivostomatitis, which was similar in appearance to erosive lichen planus (Izumi, 1982; Laeijendecker and van Joost, 1994). Many of these patients had a history of reactions to gold jewelry.

Observations in another study, Vamnes et al. (2004) revealed that patch testing with substances in dental materials produced 23% positive responses to gold sodium thiosulfate, 28% to nickel sulfate, 14% to cobalt chloride, 9% to palladium chloride, 6% to mercury, and 8% to components of resin-based materials (18 substances).

From a dermatological perspective, dental patients are exposed to a wide range of potential allergens, but adverse events seem to be rare. However, if one considers a frequency of adverse events per year in only 0.1% (1/1000) of this population, 312,800 individuals in the U.S.A. will have been affected in 2012. Exposure of patients to dental materials and other products can elicit signs or symptoms such as burning, tingling, cheilitis, oral lichenoid lesions, and swelling of the face, lips, tongue, palate, and buccal mucosa. It has been suggested that patients who exhibit an immediate- or delayed-type hypersensitivity reaction be evaluated using patch tests of skin and allergen-specific IgE tests of blood. However, most of these allergic reactions were caused by contact allergy to metals, cosmetics, food additives, flavors, and acrylates. The main cause of immediate-type allergic reactions was latex. Adverse reactions following the use of local anesthetics occurred in less than 5% of cases, and immediate-type allergic reactions to these agents were rare.

Marcusson et al. (1998) evaluated the relationship between the test results of metal allergies for 397 patients who claimed to have experienced a variety of subjective symptoms related to dental restorative materials and the corresponding allergies of eczematous patients. The difference between the frequency of metal allergy in the dental group was statistically significant or close to significance for nickel sulfate, potassium dichromate, cobalt chloride, palladium chloride, and gold sodium thiosulfate. These findings suggest that the dental patient group represents a subgroup with a high frequency of metal allergies.

The relationship between oral complaints or symptoms to cast dental alloys from 86 patients (65 females, 21 males) in Eastern Bavaria and the results of patch testing of potential metal allergens has been investigated (Garhammer et al., 2001). Positive skin reactions were demonstrated as follows: (1) 15.1% ($n = 13$) to 5% nickel sulfate; (2) 8.1% ($n = 7$) to 1% palladium chloride; (3) 5.8% ($n = 5$) to (1 and 2) combined; (4) 5.8% ($n = 5$) to 0.5% gold sodium thiosulfate; (5) 3.5% ($n = 3$) to 1% cobalt chloride; and (6) 1.2% ($n = 1$) to 0.25% ammonium tetrachloroplatinate. The nickel response had no relevance, since none of the patients' restorations contained nickel. However, 5 of the 13 patients (38.5%) who tested positive for nickel exhibited a positive reaction to 1% palladium chloride. The authors of this study concluded that allergy is a rare cause of adverse effects and that the subjective complaints of patients regarding their metal restorations were similar to those reported for other restorative materials such as dental amalgam and acrylic resin.

Based on a retrospective study of patch tests (Finn Chambers on Scanpor tape applied to the upper back) from a medical center in Israel from 2000 to 2004, the extent and severity of adverse reactions to dental materials were evaluated to determine the frequency of allergens of the dental series associated with contact dermatitis and to identify the relationship between the allergens of dental relevance and clinical manifestations (Khamaysi et al., 2006). Between 2000

and 2004, 121 patients aged 20 to 80 years were patch-tested and evaluated. Examinations revealed that the most frequent oral manifestations were cheilitis and perioral dermatitis (25.6%), burning mouth (15.7%), lichenoid reaction (14.0%), and orofacial granulomatosis (10.7%). Dental personnel, representing 18 (14.9%) of the 121 patients, all suffered from hand dermatitis.

It has been observed that patients with a previous history of positive skin reactions to nickel did not develop local or systemic adverse effects in response to a nickel-containing alloy. No association between patients' orofacial complaints and patch test results was found (Yontchev et al., 1986).

The components of dental allergy tests have included both noble metal and base metal elements. One group has proposed an allergy test for metal ions released from dental restorations, including the following elements/ions: Au^{3+}, Pd^{2+}, Zn^{2+}, Mo^{6+}, Sn^{2+}, Ga^{3+}, Co^{2+}, Cr^{3+}, Cr^{6+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, and Si^{4+} (van Loon et al., 1986).

A study of 60 persons documented that nickel has the highest allergenic potency, followed by chromium, cobalt, silver, copper, palladium, platinum, and gold (Kansu and Aydin, 1996). Allergic reactions to 49 selected casting alloys, commercially pure titanium (CP Ti), and amalgam were investigated in an epidemiological study population of 763 patients. Most frequently, nickel, cobalt, and silver caused allergic irritations. In addition, a surprisingly high incidence of positive dermal reactions to titanium (4.2%) has been reported (Valentine-Thon et al., 2006). This result indicates that titanium should also be considered in the diagnosis of allergic reactions to metallic dental restorations.

Metals of the platinum group exhibit a considerable allergenic potency. In particular, allergic reactions to palladium—including contact dermatitis, intraoral contact mucositis, and lichenoid reactions—have been reported. However, Wataha and Hanks (1996) concluded that palladium does not pose an increased risk to the health of patients because of the limited dissolution rate of palladium from these alloys. However, one should note that palladium in cast metals may react differently in single-phase compared with multiphase dental alloys that tend to be less corrosion resistant. The corrosion products of these multiphase alloys may affect the allergenicity as well as the cytotoxicity of palladium-based alloys differently compared with single-phase alloys. The presence of gold alloy restorations significantly increases the prevalence of gold sensitivity. A total of 136 asymptomatic patients were patch-tested for gold sensitivity. Of 136 patients tested, 33.8% of those with gold restorations had positive skin reactions, whereas only 10.8% of the patients without gold restorations exhibited positive reactions (Schaffron et al., 1999).

? CRITICAL QUESTION

When a dentist decides to place an implant or to restore a tooth, which potential adverse effects can be caused solely by the material used?

TOXICITY

Toxicologists are trained to analyze the biochemical and molecular mechanisms that produce adverse effects through foreign substances such as restorative materials and auxiliary dental products. Paracelsus (1493–1541), who is sometimes referred to as the first modern medical scientist[15] or as the father of toxicology, stated in German, "Alle Ding' sind Gift, und nichts ohn' Gift; allein die Dosis macht, daß ein Ding kein Gift ist." This is translated as, "All things are poison, and nothing is without poison; only the dose permits something not to be poisonous." Alternative translations of the latter phrase are: "The right dose differentiates a poison from a remedy," and "The dose makes the poison."

TOXICITY TESTS

These tests are designed with the following elements: (1) a test organism such as cells and selected strains of bacteria through higher-order plants and animals, (2) a specific response or biological endpoint; (3) an exposure or test period, and (4) a dose or a dose curve. The test design should be a good human model—that is, an objective response that can be reproduced with comparable results—and the test time should be of reasonable length.

DOSE–RESPONSE RELATIONSHIPS

Toxicity tests exhibit a dose–response relationship when there is a consistent mathematical relationship between the proportion of individuals responding and a given dose for a given exposure period. For example, the number of mortalities increases with an increase in the dose of chemicals given to a group of organisms. Since toxicity is dose dependent, the effect of a specific dose of a therapeutic substance may be toxic, nontoxic, or beneficial. The quantity of a substance (in milligrams) ingested by test animals is often expressed as a ratio of milligrams per kilogram of body weight (mg/kg).

The species of test organisms differ in how they respond to specific chemicals. The same species of an organism may show variations in response to a given dose. Typically, this intraspecies variation follows a normal distribution when one plots the number of responding organisms against the response for a given dose. A dose can be described either as a lethal dose (LD) in a test when the response is death or an effective dose (ED), for which the response is another observable outcome. A dose–response plot allows us to identify the doses that affect a percentage of the exposed population. For example, LD_{50} is the dose that kills 50% of the test organisms.

SIGNIFICANCE OF DOSE–RESPONSE RELATIONSHIPS

By comparing the LD_{50} of chemicals in animals we can rate the relative **acute toxicity** of each chemical. For example, DDT (LD_{50} for rats = 113 mg/kg), an insecticide, is considered more toxic than ethyl alcohol (LD_{50} for rats = 1400 mg/kg). By multiplying this LD_{50} dose (mg/kg) by 70 kg (the average weight of a human) and assuming that humans are as sensitive as the species that were exposed to the test substance, we can estimate the LD_{50} for humans of average size.

However, the LD_{50} serves only as a rough estimate of one aspect of the toxic potential of a substance.

SHORTCOMINGS OF DOSE-RESPONSE DATA

Before using the LD_{50} dose–response data to assess the overall toxicity of a compound, one should note that an LD_{50} dose is a single value on a plotted graph and does not identify the time-dependency of the dose–effect relationship. Second, the LD_{50} is a measure of acute toxicity, not chronic effects. A complete battery of toxicity tests includes analyses of subacute toxicity, chronic toxicity, carcinogenicity, and reproductive toxicity. Thus, the LD_{50} dose should be used with extreme caution.

EXPOSURE PATHWAYS FOR TOXINS IN HUMANS

The three main pathways through which harmful substances are likely to enter the body are (1) absorption through skin and eye contact, (2) inhalation, and (3) ingestion. Skin acts as a barrier against the entry of foreign substances into the body. If this protective barrier is broken by abrasions or lacerations, toxic chemicals can penetrate the barrier and migrate into the body. In addition, exposure to some organic solvents can increase the permeability of skin to substances that would ordinarily be able to penetrate the surface. Furthermore, skin has a large surface area, which facilitates contact by toxic substances.

The fastest way for toxic substances to enter the body is through inhalation (see Figure 7-1). Inhaled vapors or particulate matter can make immediate contact with respiratory tissues and soon thereafter with the bloodstream. Once a substance has entered the bloodstream, it is transported rapidly throughout the body.

Based on the patch testing of dental personnel who were referred as patients to the Department of Occupational and Environmental Dermatology, Stockholm, hand eczema was diagnosed in 63% of 174 cases, 67% being classified as irritant contact dermatitis and 33% as allergy-induced contact dermatitis (Wrangsjo et al., 2001). Further diagnoses included other eczemas, urticaria, rosacea, psoriasis, tinea pedis, bullous pemphigoid, and no skin disease. A total of 59% of the participants had positive reactions to substances in the standard series and 40% to substances exclusive of the dental series. Of the 22% patients who had positive reactions to methacrylates, the majority reacted to several test preparations. Reactions to HEMA, EGDMA (ethyleneglycol dimethacrylate) and MMA (methylmethacrylate) were most frequent, and 37% were positive only to methacrylates; the remaining 15 also had reactions to allergens in the standard series; 95% of these had hand eczema and 5% had facial eczema. The most frequent allergens besides methacrylates were nickel, cobalt, palladium, fragrance mix, colophonium, and thiuram mix. Allergy to natural rubber latex was diagnosed in 14 of 137 (10%) subjects. In summary, irritant hand dermatitis was the dominant diagnosis. Contact allergy to methacrylate was seen in 22% of the patch-tested patients.

Ingestion of potentially harmful substances by lab technicians and dental staff is not as great a concern as is exposure through skin and lungs. Compared with penetration of skin, ingestion opportunities are limited because there are very few dental substances that can be swallowed.

REACTIONS TO TOXIC AGENTS

There are several adverse reactions that can be caused by exposure to biomaterial substances and processes. These include reactions to the following:

1. Systemic toxins such as chemical agents, which can act on target organs or organ systems
2. Asphyxiants, which deprive the tissues of oxygen (anoxia)
3. Irritants, which cause inflammation of tissues by direct contact
4. Allergic sensitizers, which activate the production of antibodies—which, in turn, react with the antigen to make it a latent complex (when the body becomes exposed one or more times to the sensitized agent, the concentration of antibodies increases until an antigen–antibody reaction, or allergic reaction, results in one or more symptoms)
5. Carcinogens, which are substances known to cause cancer in an organism
6. Reproductive toxins, such as mutagens or teratogens

Toxic chemicals, such as those that may be handled by dentists and lab technicians, can cause a localized or systemic reaction by contacting the skin or tissue directly by ingestion in liquid or solid form or by inhalation as dusts, particles, mists, fumes, or other types of vapors. In addition to reacting to chemical carcinogens, patients may also be affected by physical carcinogens, such as ionizing radiation. Further discussion of the nature of carcinogens or reproductive system toxins is beyond the scope of this book.

GENOTOXICITY, MUTAGENICITY, AND CARCINOGENICITY

Genotoxicity refers to any adverse effect on the DNA of an organism. If the adverse effect is transferred to the next (heritable) generation of cells, the effect is called mutagenicity. Mutagenic reactions occur when a physical or chemical agent changes the genetic material of an organism, usually deoxyribonucleic acid (DNA) permanently, thereby increasing the frequency of mutations above the normal background level. Mutations may be caused directly, through interactions between a substance and DNA, or indirectly, by altering cellular processes that control DNA integrity. Mutations are common occurrences in the DNA of all humans and they may result from many factors such as radiation, chemicals, and genetic errors in the DNA replication process. Several metal ions from dental materials—such as beryllium, copper, and nickel—are known mutagens, and some components of other materials such as root canal sealers have also been shown to be mutagenic. Resin-based materials have also been identified as having some mutagenic potential. However, it must be emphasized that mutagenicity does not have the same consequences as carcinogenicity, or the ability to form tumors. In fact, many mutations are repaired and others are irrelevant or insignificant. Equally important is the fact that

the material and nature of an exposure can control the mutagenic or carcinogenic response. No dental material has ever been shown to be carcinogenic in dental patients.

Much effort has been devoted to validating the potential of certain metals, monomers, and other dental substances to impair the local and systemic immune responses of dental patients with cast metallic restorations. Why is our interest in immunological effects so high? The adverse effects of dental material substances generally are limited to local tissue reactions, and toxic effects from typical concentrations of metal ions, monomers, and other substances have not been proven. However, if any impairment of the autoimmune system was traced to an interaction with dental materials, the impact on the practice of dentistry and on the quality of life of our patients could be enormous. Gender may play a significant role in this scenario. Both the innate and adaptive immune responses of females are somewhat more robust than those of males. Females are somewhat more susceptible to autoimmune disorders such as systemic lupus erythematosus, rheumatoid arthritis, and multiple sclerosis.

Since these gender differences are largely attributed to estrogen levels, any interaction of the body with biomaterial substances that affect the production of estrogen or its associated enzymes or that attack native cells as if they were foreign bodies may play a major role in causing these severe systemic diseases. Thus, research must continue to screen material components for their ability to induce autoimmune disturbances. Such research may focus on cytokines (the molecules that carry signals between the immune system cells), apoptosis (a measure of the relative ability of the immune system to eliminate cells that die normally), and B cells (which are unique white blood cells that are important for fighting off bacteria). Too little or excessive estrogen production may lead to insufficient B cells or the inability to support their survival longer than is desirable.

The induction of immune mediators by metallic materials has been investigated using lymphocyte cell lines. Expressions of the inflammatory mediator interleukin 2 (IL-2) and the immune effector IgG by T and B cells were found after incubation with three copper-based casting alloys. The production of these immune mediators was altered by released cations (Bumgardner et al., 1993). Lipopolysaccharide (LPS)–stimulated osteoblast-like cells increased IL-1a and TNF-α after the cells were incubated with cobalt, chromium, and titanium. This study showed that metal ions disrupted cytokine release, osteoblast function, and the synthesis of type I collagen.

Cytokines can be released from unstimulated and stimulated peripheral blood mononuclear cells after incubation with chromium ions. In addition, chromium cations can reduce cell viability, DNA synthesis, secretion of IL-6, and expression of soluble IL-2 receptor. These results suggest that chromium may suppress the immune system (Donati et al., 1998).

Several metal ions (Ag, Au, Cu, Hg, Ni, Pd, Pt, and Zn) have induced the secretion of proteins from macrophages (Wataha et al., 1995). Subtoxic concentrations of a nickel solution also induced an increase of IL-1a and TNF-α secretion from unstimulated and LPS-stimulated THP-1 monocytes (macrophages) (Wataha and Hanks, 1996). In most cases, carcinogenic metal ions are not mutagenic in bacterial test assays. Alteration of DNA repair processes and carcinogenic effects have been reported for Cd^{2+}, Ni^{2+}, and Co^{2+} (Hartwig, 1995). Nickel has exhibited a relatively weak mutagenic activity.

There is evidence that metallic components derived from cast dental prostheses can modulate the expression of various immunological factors. An increased expression of cytokines after LPS stimulation by various cell types indicates that bacterial toxins and cations released by corrosion may collectively cause inflammatory effects related to oral mucositis, gingivitis, periodontitis, and alveolar bone resorption.

Genotoxic effects have been reported for beryllium and gallium salts (Kuroda et al., 1991). Occupational data indicate that beryllium may increase the risk of lung cancer and other tumors in humans (Aller, 1990; Ashby et al., 1990; Hayes, 1997). No genotoxic effects were found for orthodontic appliances (wires, brackets, extension screws) fabricated with base metal alloys and CP Ti (Assad, et al., 1998; Tomakidi, 2000; Wever et al., 1997). No genotoxic effects were found for several titanium-containing alloys, CP Ti, and one Ni-Cr–based alloy (Wang and Li, 1998). There is some evidence, which suggests that nickel, cobalt, chromium, and beryllium tend to increase cancer risk in humans. However, there is no validated evidence to prove that dental casting alloys are genotoxic or carcinogenic.

CRITICAL QUESTIONS

Which risks are associated with handling of base metal alloys? Which dental personnel are most likely to exhibit adverse effects to dental materials?

OCCUPATIONAL HAZARDS FOR DENTAL PERSONNEL

Dental technicians seem to have an increased risk for occupational diseases during the fabrication of dental metallic restorations. Technicians are exposed to significantly more platinum, palladium, and gold than do road construction workers or high school graduates. This confirms that laboratory technicians work in areas of high occupational metal exposure. Inhalation and aspiration of various dust and toxic vapors, which are generated during the heating and melting of certain alloys, may irritate the respiratory and gastrointestinal systems of these technicians.

Pneumoconiosis is a severe fibrotic lung disease that can be caused by **chronic exposure** to inorganic dust. The fabrication of base metal prostheses can significantly increase the incidence of pneumoconiosis among dental technicians working in laboratories with insufficient dust-handling facilities. A clinical screening of dental technicians in Crete revealed a 9.8% prevalence of pneumoconiosis. Previous epidemiological studies have documented a prevalence of this lung disease in approximately 15.4% of technicians after

20 years or more of exposure. The prevalence in the general population is less than 1%.

Exposure to dust from Co-Cr, Co-Cr-Mo, and Ni-Cr-Be alloys was identified as a possible reason for pneumoconiosis in dental technicians. The risks of benign pneumoconiosis induced by hard metals are well documented. Malignant pneumoconiosis is caused by dust from crystalline silica, asbestos, or beryllium. Silicosis is the most common occupational disease among dental technicians, whereas the risk for berylliosis is not well documented. Isolated particles from abrasives like silica and silicon carbide, which are also generated during the finishing of base metal frameworks, further the individuals' risk of developing an occupational lung disease.

Allergic reactions to nickel and beryllium increases the IgE concentration or alters various other blood parameters that are indicative of allergic reactions has been reported for these individuals. These observations confirm that the processing of base metal alloys containing nickel, chromium, or cobalt does not increase the risk of allergy to these metals. There is no evidence proving that metallic restorations threaten the health of dental personnel other than technicians. Because of the increased risk for pneumoconiosis, the installation dust exhaust collectors in dental laboratories is highly recommended.

There is no evidence to suggest that metallic dental restorations increase mutagenic and carcinogenic risks in humans. Except for laboratory technicians, there is also no indication that metallic dental materials are an occupational hazard for dental personnel. The laboratory technicians have a higher risk for fibrotic lung diseases caused by dust from metals and abrasives, but only if there is insufficient exhaust ventilation in dental laboratories. Taken together, the knowledge about the mechanisms of biological interactions between metallic dental restorations and oral or systemic tissues is still very limited. One might speculate that metal ions induce local allergic reactions that may be misdiagnosed as inflammatory reactions.

Adverse occupational reactions are common and dental staff exhibited various forms of hand or facial dermatitis as well as respiratory disease. Contact-type reactions seem to occurred most often because of exposure to acrylates, formaldehyde, fragrances, latex, and rubber additives. Latex allergies are well recognized because dental office staff seem to be most susceptible to this type of allergen.

Irritation problems are more likely to cause hand dermatitis in dental personnel compared with dermatitis caused by contact allergy. Patch testing of patients is recommended for those who exhibit contact-type allergy and blood tests for those who have experienced immediate-type allergic reactions possibly related to dental treatments or materials. Testing of dental personnel is also indicated for individuals who exhibit hand or facial dermatitis or respiratory distress as a result of their exposure to work materials (restorative materials and auxiliary materials) and their work environment (dusts, fumes, and vapors). Such individuals should be referred to medical specialists for proper testing, diagnosis, and treatment (if indicated).

HYDROFLUORIC ACID

Etching of glass-phase ceramics and glass ceramics by hydrofluoric acid (HF) has been performed occasionally to promote bonding of these ceramics to resin-based composites. This etching process has been performed both in the lab and in the mouth. Since HF is an extremely corrosive acid, it is significantly more hazardous than many of the other acids used in dental labs and offices. Technicians and dentists should be well informed on the risks of exposure to HF and methods that are effective in dealing with accidental HF exposures.

EXPOSURE OF SKIN, MUCOSA, AND EYES TO HYDROFLUORIC ACID

HF is corrosive and readily destroys tissue. Exposure of the eyes to HF may result in blindness or permanent eye damage. HF readily penetrates human skin, allowing it to destroy soft tissues and to decalcify bone. Chemical burns from HF are typically very painful and slow to heal. Skin exposure to high concentrations of HF (≥50%) immediately causes significant and painful destruction of tissue. In addition to the chemical burns induced by exposure to skin or other tissues, systemic fluoride poisoning can also occur. A significant concern over the use and possible exposure of tissue to relatively low concentrations of HF is that the pain or burning sensations may not be experienced until several hours after exposure. Because of this delayed effect of HF to produce severe tissue damage possibly without pain, all tissues that have been exposed to HF should receive immediate first-aid care, medical evaluation, and follow-up evaluations even if the injury appears insignificant and no pain is experienced.

INHALATION OF HYDROFLUORIC ACID VAPOR

Inhaled HF vapor can damage the lungs. Delayed effects may not be apparent for hours after the initial exposure. The U.S. Occupational Safety and Health Administration (a division of the U.S. Department of Labor) has set a limit for exposure to individuals for airborne concentrations to an average of 3 ppm HF over an 8-hour workday. Long-term or chronic exposure to HF can result in *fluorosis*, a syndrome characterized by weight loss, bone embrittlement, anemia, and general ill health.

VENTILATION DURING USE OF HYDROFLUORIC ACID

To minimize inhalation of HF vapor, gels and liquids should be used with adequate ventilation. Concentrations greater than 5% should be handled inside a chemical fume hood.

EYE AND SKIN EXPOSURE TO HYDROFLUORIC ACID

When eyes have been exposed to HF, they should immediately be irrigated at an eyewash station for at least 15 minutes with large volumes of water while the eyelids are held apart and away from the eyeballs. Calcium gluconate gel must not be applied to the eyes. In all cases of where the eyes have been exposed to acids, immediate medical attention should be sought.

SKIN EXPOSURE TO HYDROFLUORIC ACID

If small areas of the hand or forearm have been contaminated, these areas must immediately be washed in a sink. If calcium gluconate gel is readily available, rinsing should be limited to 5 minutes so that application of the gel can be quickly initiated so as to limit the migration of fluoride ions. The calcium gluconate gel should be reapplied to the affected areas every 15 minutes. If calcium gluconate gel is not available, the affected areas should be rinsed for at least 15 minutes. Contaminated clothing must be removed and placed in a hood or plastic bag. Prompt medical attention should be sought in all instances of skin exposure to HF.

NEUTRALIZATION OF HYDROFLUORIC ACID BY CALCIUM GLUCONATE GEL

Available as a commercial product, this gel is a topical antidote for HF residue on exposed skin. It combines with HF to form insoluble calcium fluoride, thereby preventing the extraction of calcium from tissues and bones. Calcium gluconate has a limited shelf life and should be refrigerated and replaced with a fresh supply after its expiration. Disposable gloves should be used in applying calcium gluconate gel to the skin.

HAZARDS ASSOCIATED WITH OTHER FLUORINE COMPOUNDS

Other chemicals containing fluorine—such as ammonium fluoride, ammonium bifluoride, and sodium fluoride—may react with acid or water to produce HF. One should review the Material Safety Data Sheets (MSDSs) of all fluoride compounds to learn the safety precautions that are recommended to reduce the risk of HF exposure.

BIOCOMPATIBILITY TESTS

? CRITICAL QUESTION

Which factors influence the conditions for a biocompatibility test?

TEST REQUIREMENTS

The specific use of a material in the body has a direct bearing on the biological response it produces. There are some major requirements of any test for biocompatibility. Three of the most significant ones are that: (1) the test should be performed under conditions that simulate the actual use of the material in the body; (2) the test conditions should reflect the effects of the material's time in the body on the biological response; and (3) the stresses induced in the material under its intended function should be considered in the interpretation of the biological response.

The test conditions should reflect whether or not the material will (1) contact soft tissue or mineralized tissue; (2) be external to the oral epithelium; (3) serve as an endosseous implant; (4) be exposed directly to bone, tissue fluid, blood, and saliva; and (5) be separated by some barrier such as dentin between the material and living cells. Special attention must be paid to materials that communicate through the epithelium or lie completely beneath the epithelium.

Short-term exposures such as those of impression materials or temporary cements are used only for a few minutes to a few weeks in the mouth. Their biological responses are likely to differ from those that occur after 10 years of exposure. The short-term responses are likely to be allergic reactions, but they are unlikely to be toxic or mutagenic effects. In general, the most demanding tests are designed to evaluate materials that are expected to remain present for the longest times.

The induced stresses may be physical, chemical, or thermal in nature. Thus biomaterials that flex, deform plastically, leak, or fracture easily in the oral environment may cause adverse effects, including discomfort, sensitivity, restoration failure, postoperative pain, and pulp trauma related to filling removal, tooth preparation, and replacement of the restorative material.

? CRITICAL QUESTION

Is there one best test to measure biocompatibility?

ADVANTAGES AND DISADVANTAGES OF BIOCOMPATIBILITY TESTS

Three types of tests are used to analyze the biocompatibility of dental materials: (1) an in vitro test, (2) an animal test, and (3) a usage test performed clinically in animals or humans. Each of these tests has advantages and disadvantages, and each type is used to evaluate a material before it can be sold to dental practitioners. No single test can accurately estimate the biological response to a material. In addition, there is no clear consensus on the optimal combinations of tests that must be performed for each type of material.

For in vitro tests, the candidate material or an extract of the material is placed in direct or indirect contact with some biological system outside of an organism. Direct contact exposes a material or an extract of a material directly to the biological environment, whereas indirect contact involves a barrier such as agar, a membrane filter, or dentin. In vitro tests can be conducted in cell culture dishes, test tubes, or other containers. Biological systems may consist of mammalian cells, cellular organelles, tissues, bacteria, or certain enzymes. These tests can be used to measure cell growth, cellular function, and the integrity of a cell's genetic material.

In vitro tests are relatively fast and inexpensive and they can be standardized relatively easily. Also, in vitro tests can be controlled very well to provide highly reliable data and reproducible measurements. Perhaps the greatest disadvantage of in vitro tests is their limited relevance to clinical practice. For example, a test that measures cytotoxicity using osteoblast cell cultures may be somewhat irrelevant if the material never contacts osteoblasts in vivo. The in vitro tests lack the ability to simulate complex interactions that exist in an organism between and among the immune, inflammatory, and circulatory systems. In vitro tests can be used to check if a substance eluted from the test material has the general

potential to be harmful to cells. In vitro tests can also be used to elucidate the cellular mechanism of a toxic reaction, e.g., if a substance from a test material disturbs the redox balance of cells.

Animal tests involve the placement of a material in an organism. Test animals include baboons, cats, dogs, ferrets, guinea pigs, hamsters, mice, monkeys, pigs, rats, and sheep. Animal tests differ from vitro tests in that an intact animal is used rather than cells or tissues from an animal. In some animal tests, the test materials are not applied as in the patient, e.g., when restorative materials are implanted subcutaneously in rats. In this case a more nonspecific toxic response is evaluated. In other animal tests, the materials are ground and fed to the animals (e.g., rats) in so-called acute or chronic toxicity tests; this process simulates the oral uptake of the materials, although oral ingestion in such quantities is not realistic. Therefore, these tests are becoming discontinued. In other animal tests, e.g., those involving guinea pigs, the ability of a substance from a material to sensitize and then elicit an allergic reaction is evaluated. These test methods have provided reliable data that can be extrapolated to humans. Many other animal-based test methods are described in the literature for testing certain material properties, e.g., mutagenicity or carcinogenicity, but they are seldom used for testing dental materials. In contrast, tests are applied in the test animal as they are in the patient, e.g., a restorative material in Class V cavity preparations is placed in monkey teeth. However, such usage tests can also be performed in humans, e.g., in teeth that are scheduled for extraction because of orthodontic reasons.

Thus, the advantage of animal tests lies in their ability to permit an intact biological system to respond to or interact with a candidate material. The material can thereby interact with many complex biological systems to obtain a biological response. The disadvantages of animal tests are their high cost, control difficulty, and the length of time that may be required to obtain a measurable response. These tests are criticized by animal rights activists and other individuals because of concerns regarding the ethical treatment of test animals. Finally, the relevance of animal tests in simulating human responses is often challenged. In spite of these disadvantages, animal tests are essential for evaluating new materials prior to their clinical use.

Usage tests are the most clinically relevant tests. They are performed either in animals or humans. Such a test requires that the material be placed in a clinically relevant environment similar to that to which the material would be exposed in clinical practice. When a usage test is performed in humans, it is called a *clinical trial*. The choice of animals for a usage test is more limited than that for other animal tests because of the size or anatomy of a given animal species. Consequently, usage tests tend to involve larger animals with anatomy similar to that of humans. The ultimate relevance of a usage test depends on the extent to which the test simulates the clinical use of the product.

It is tempting to consider a usage test involving humans as the best test method. However, even human clinical trials have some limitations. Very often no histology is performed, and from clinical symptoms alone, no evaluation of the real damage, e.g., of the pulp after placement of a restorative material, is possible. Furthermore, teeth that are scheduled for extraction because of orthodontic reasons are normally obtained form young patients. These teeth have open apices, which may react differently from teeth of older patients with narrow apical openings and with potentially previous damage from caries.

Usage tests have several disadvantages, including their design complexity, difficulty to control experimentally, and interpretation challenges. These tests are also extremely costly. If humans are used in a clinical trial, approval for the proposed usage tests must be obtained from an institutional review board. A test for the long-term performance of a material may take 5 years or more, which adds considerably to the typically high cost of using human subjects. Finally, human usage tests may involve legal and confidentiality issues that do not occur for animal and in vitro tests.

? CRITICAL QUESTION

If you were presented with a new material, never before used in a human being, how would you decide if it was safe as a dental restorative material?

HOW TESTS ARE USED COLLECTIVELY TO MEASURE BIOCOMPATIBILITY

Advertisements for new restorative materials rarely provide comprehensive information on the biocompatibility tests that were performed to judge the safety of the products. This situation exists for several reasons. First, the dental profession has not observed many severe toxic reactions or anaphylactic reactions that are of life-threatening proportions. Second, dentists are often more concerned with potential clinical performance and simplicity of technique than with poorly defined side effects. Third, the profession is well aware that there is no single simple test that unequivocally establishes biocompatibility of products on a quantitative basis. Finally, the profession seems to operate on the assumption that most if not all of the potential adverse effects can be corrected simply by removing the suspected material.

Dental health professionals are well aware of the fact that no single test is sufficient to evaluate the biocompatibility of a new material. Rather, in vitro, animal, and usage tests can collectively classify a material's general safety for clinical use. However, the role of each of these basic tests in the overall evaluation process is unclear. Three test phases have been distinguished in the testing of a new biomaterial: primary, secondary, and usage tests (see Figure 7-12). Primary tests are performed initially for screening a new material; these tests are usually in vitro in nature and may include cytotoxicity and mutagenicity tests. Primary tests can also include animal tests to measure systemic toxicity. Secondary tests are usually conducted in animals to observe outcomes such as the immune response, dermal irritation, chronic toxicity, or response upon implantation.

The test of a new material represents a relatively linear progression from primary to secondary to usage tests (see Figure 7-12). Initially, primary tests are performed, and materials that pass these tests then undergo secondary tests. Similarly, materials that pass the secondary tests are subjected to usage tests.

In the late 1970s and early 1980s, research was performed to compare in vitro animal tests, and usage tests for materials employed clinically in dentistry for many years. These studies revealed that in vitro and animal tests do not necessarily predict the results of usage tests or successful clinical experience with the material. So how is a dental practitioner to decide whether a material is sufficiently safe or not? The manufacturer must perform the required tests, which ensure that its products are safe, i.e., free from unacceptable risks of the probability and severity of harmful effects. Thus, the primary responsibility falls on the producer although the dentist must be familiar with the potential adverse effects of restorative materials.

One of the criteria for selecting a material is the time the product has been used in service without any reports of adverse events. Where are adverse events recorded and how can these reports be accessed? The answer to this question was given in an earlier section on adverse event registries in several countries. A search of the websites in Norway, Sweden, and the United Kingdom would allow a clinician to review reports on existing materials to determine the types of adverse effects that were most likely for specific types of materials. Next, a search of the PubMed or Web of Science literature with key words or MeSH terms, which can be identified by librarians, if necessary, should be performed to identify if any reports of the specific product have been recorded. Finally, a request should be made to national agencies in the dentist's home country to determine whether any adverse events reports have been made. As one might expect, unless catastrophic failures have occurred soon after the product's introduction, the shorter the time that the product has been in existence, the smaller is the number of adverse effects reports that will be found.

A major concern on regarding in vitro test data used to select a material is the relatively poor correlation among these tests. However, when tests are performed under simulated clinical conditions, more reasonable correlations are found.

ADVANTAGES AND DISADVANTAGES OF BIOCOMPATIBILITY STANDARDS

The first biocompatibility test standard, Document No. 41 for Recommended Standard Practices for Biological Evaluation of Dental Materials, was approved in 1972 by the ADA Council on Dental Materials, Instruments, and Equipment (later called the Council on Scientific Affairs) on behalf of the American National Standards Institute. This document was produced, in part, in response to a requirement of the U.S. Congress for the biological testing of all medical devices. This requirement was formalized by the passage of the Medical Device Bill in 1976. The FDA classifies dental materials as *devices*. This classification requires less stringent testing than is required for drugs, which must pass performance tests for safety and efficacy. Dental devices need to meet only safety test requirements.

An update to ADA Document No. 41 for the biological testing of dental materials was published in 1982 to include tests for mutagenicity. The initial tests require in vitro assays for cytotoxicity, red blood cell membrane lysis, mutagenesis, carcinogenesis, and animal tests for systemic toxicity (by oral ingestion). Secondary evaluations include animal tests for inflammatory or immune responses, and usage tests include tests for pulp and bone response. Based on a thorough risk assessment according to relevant ISO standards and an evaluation of the existing literature, the manufacturers have the responsibility of selecting the appropriate and necessary biological tests for their products. Finally, the manufacturer is fully responsible legally for any adverse effects arising from the use of the products, which may have been prevented by performing state-of-the-art tests.

ISO STANDARD 10993

To evaluate the biocompatibility of a medical device (which includes dental materials) prior to testing in a clinical study, a series of standards were developed. Unlike ADA/ANSI Document No. 41, ISO 10993 is not restricted to dental materials. In 2010, ISO Standard 10993 consisted of 20 parts, each addressing a different area of biological testing. For example, Part 3 specifies tests for genotoxicity, carcinogenicity, and reproductive toxicity, whereas Part 4 describes tests for materials that interact with blood and Part 20 specifies the principles and methods for immunotoxicology testing of medical devices. The standard identifies initial tests for cytotoxicity, sensitization, systemic toxicity, and supplementary tests for chronic toxicity, carcinogenicity, and biodegradation. The initial tests may be either in vitro or animal tests, whereas the supplementary tests are performed on animals or humans. The document provides suggestions for test selection based on how long the material will be present; whether it will contact the body surface, blood, or bone; and if it will communicate externally once it is placed internally. For dentistry, ISO 7405 is also relevant. It describes the the tests that are specific for dental materials or for which ample experience exists for the materials. For example, all usage tests are described in ISO 7405 as well as cell culture tests that are specially designed for restorative materials such as the dentin barrier test.

Because of the multifactorial nature of biocompatibility, standardization is essential for the unbiased comparison of results from different studies, but they have some significant disadvantages. Many standards cannot keep pace with the development of new scientific technology. In addition, standards are developed based on agreements and compromises among manufacturers, academicians, and the lay public. Thus, they tend to be developed quite slowly. Standards are also arbitrary in nature because proposed thresholds for acceptability and criteria for determining unacceptable performance are rarely accepted universally. However, in spite of these limitations, standards for biological testing are

necessary to ensure the biological safety of medical and dental products.

MATERIAL SAFETY DATA SHEETS

Each dental product is supplied with a *Material Safety Data Sheet* (*MSDS*), also known as a *Product Safety Data Sheet* (*PSDS*), or a COSHH data sheet in the United Kingdom. This is a report on the properties of a particular substance, for example, melting point, boiling point, and flash point. This report is intended for occupational settings and is essential for workers and emergency personnel because it describes procedures for handling or working with the material safely. In addition to physical data, it identifies toxicity risks, health effects, first-aid procedures, reactivity, storage and disposal conditions, and, where applicable, procedures for firefighting, the types of protective equipment that should be used and procedures that must be followed for accidental releases and handling of spills.

Potentially harmful substances must be properly labeled to minimize the risk of injuries to personnel and others who may come in contact with the material or substance, risks to the health of individuals, and risks of environmental exposure. Labels may include hazard symbols, for example, the European Union label, e.g., with a black diagonal cross on an orange background.

NFPA 704 is a standard managed by the U.S.-based National Fire Protection Association. It defines the "fire diamond" symbol intended for emergency personnel to quickly and easily identify the risks posed by hazardous materials. This is necessary to help determine what, if any, special equipment should be used, procedures followed, or precautions taken during the first moments of an emergency response.

Labeling on packages or delivery devices that contain potentially hazardous substances exhibits symbols indicating the types of hazards that may be encountered. The color-coded markings fall into one of four categories: (1) *blue* for the level of health hazard, (2) *red* for flammability, (3) *yellow* for (chemical) reactivity, and (4) *white* for unique hazards. Each of the health, flammability, and reactivity categories is rated on a scale from 0 (no hazard or normal substance) to 4 (severe risk). An example of such a label is shown in Figure 7-16.



FIGURE 7-16 Labeling on a liquid dispenser that indicates the color-coded hazard levels in each of four categories. (From Sorrentino SA, Remmert LN: *Mosby's Textbook for Nursing Assistants*, 8th ed. St. Louis, 2012, Mosby.)

CLINICAL GUIDELINES FOR SELECTING BIOCOMPATIBLE MATERIALS

? CRITICAL QUESTION

What information is required to judge the safety of metallic, resin composite, and ceramic products?

It is clear from past experience that clinicians will continue to be confronted with choices of new materials and claims of their clinical performance. Unconditional biocompatibility may be claimed by some manufacturers. It is difficult for clinicians to evaluate the biological safety of new materials and manufacturers' claims. However, with knowledge of biocompatibility issues and some common sense, clinicians can make rational judgments about biological safety. Several critical steps will ensure an informed decision. These steps are described below.

DEFINE THE INTENDED USE AND INDICATIONS FOR RESTORATIVE MATERIALS

An important consideration in evaluating biological safety is how the materials will be used. As discussed previously, the use of a material plays a crucial role in its biocompatibility. For example, if a ceramic material has been successful as an anterior restorative material, it may not always be as successful as a posterior material. Clinicians should determine if the material's proposed use is new and if it has been tested in the proposed use. If the material is used in a new way or new environment, more caution is advised. Furthermore, the manufacturer's website may list the indications for use. To minimize the risk of litigation resulting from unexpected adverse events, the lab technician and dentist must adhere to the specified indications for use.

IDENTIFY THE MAIN COMPONENTS OF THE MATERIAL

A second consideration is the composition of the material. The principal components may be listed in the MSDS, as discussed previously. However, elemental concentrations of potential allergens may not be listed on the MSDS. Studies have shown repeatedly that very small changes in composition or processing of a material can alter its biocompatibility. Clinicians should ask the research director of the manufacturing company for specific compositions, and they should ask lab technicians if the material's composition or processes are different or have changed from those associated with previous materials. If so, caution is advised in applying previous biological data and processing principles to the new situation.

CRITICAL QUESTION

A sales representative introduces a new restorative material in your office or at a trade show. What do you need to know from him or her about the material's biocompatibility tests?

HOW SHOULD CLINICIANS EVALUATE THE SAFETY AND PERFORMANCE OF DENTAL MATERIALS?

In previous sections emphasis has been placed on the difficulties of relating in vitro or animal tests to clinical applications. There are some instances when clinicians will not have sufficient data from clinical trials to make an informed decision. In these cases, they must rely on in vitro or animal tests. The first consideration is to identify which tests have been used. Clinicians should not simply accept at face value nondescript statements such as "The material has been subjected to biocompatibility tests and no adverse effects were observed." If clinical trial results are available, it is important to make sure that the conditions and duration of the test are relevant for the practice.

The quality and relevance of usage test data depend on the fidelity of reproducing the clinical use. If animal or in vitro test results are the only ones available, then clinicians should question the design of these tests and the methods employed, making sure that testing conditions were as relevant as possible including multiple types of tests performed under different clinically relevant conditions. A well-controlled comparison with existing similar types of materials is always preferable to an isolated test on one material. The known and potential adverse effects of dental materials such as those summarized in Table 7-1 should be investigated periodically to ensure that patients will be presented with accurate information related to the benefits and risks of proposed treatments. Manufacturers may be reluctant to fully divulge biocompatibility test information, especially when the results for their products are not as favorable as those for other products in a test series. In some cases, a representative may simply refer a potential purchaser to the MSDS for a product.

RISKS VERSUS BENEFITS OF DENTAL MATERIALS

Numerous in vitro studies have documented that each metallic dental restoration releases cations as a result of corrosion. These ions may be distributed both in the oral cavity and may enter the systemic circulatory system. Nickel-based alloys in particular exhibit increased corrosion at low pH but their lower stable cost and their higher elastic modulus tend to offset partially the greater benefits of high-noble-content alloys. Beryllium-containing nickel-based alloys have been found to be significantly more susceptible to corrosion than were beryllium-free alloys, but beryllium is known to improve castability and promote the formation of a stable oxide to optimize atomic bonding to porcelain. Generally, however, cation release cannot be predicted on the basis of the overall composition or the nobility of an alloy. Furthermore, it is not well known whether these in vitro data represent in vivo conditions accurately.

TABLE 7-1 Adverse Effects and Drawbacks of Dental Restorative Materials

Restorative Material	Potential Adverse Effects
Dental amalgam	Contact dermatitis or sensitization to metal elements
	Lichenoid lesion
	Adverse pulpal response or postoperative sensitivity
	Thermal sensitivity of pulp
	Symptoms of acute mercury toxicity
	Symptoms of chronic mercury toxicity
Resin-based composite	Contact dermatitis or sensitization to methacrylates
	Lichenoid lesion
	Estrogenic effects of bisphenol A
	Cytotoxicity or systemic effects
	Systemic effects of other free monomers or leached substances
	Postoperative sensitivity from polymerization stresses and marginal gaps
Cast metal and condensed foil	Contact dermatitis or sensitization to metals, especially nickel, copper, and beryllium
	Lichenoid lesion
	Thermal sensitivity of pulp
	Systemic effects of leached metal ions
Ceramic	Respiratory effects from silica dust excessive wear of antagonist tooth structure
	Susceptibility to chipping fracture of veneering ceramic

The in vivo effects of substances eluted from dental materials on the immune system are as yet unknown. However, although nickel is known to elicit allergic reactions and to enhance corrosion, it is used successfully in orthodontics. The risk of allergic reactions can be minimized by questioning the patient, parent, or care giver about existing allergies. In this way, the evaluation of benefit versus risk generally can favor the use of certain metals and alloys.

Local and systemic allergic reactions to many metals have been observed, with nickel being the most frequent allergenic element. Additionally, various other factors can contribute to biological interactions of metallic restorations, such as physicochemical surface parameters (atomic ratio of noble to nonnoble metals etc.), phase formation, wear, and the quality of the manufacturing process itself. The importance of these factors remains unclear, since very little information from in vivo studies is available.

There is no evidence to suggest that metallic dental restorations increase the mutagenic and carcinogenic risks in humans. Except for laboratory technicians, there is also no indication that metallic dental materials are an occupational hazard for dental personnel. However, laboratory technicians

have a higher risk of developing fibrotic lung diseases caused by the inhalation of dust from metals and abrasives, especially when there is insufficient exhaust ventilation or no dust or vapor handling procedures are required in dental laboratories.

The comparison of benefits versus risks for resin-based materials such as sealants and composites is more straightforward. One of potential adverse effects is the release of bisphenol A (BPA) from dental resin materials such as from bis-DMA containing sealants or from bis-GMA sealants (only if included as an impurity). However, the amounts of BPA are extremely small and sealing of pits and fissures in enamel surfaces is a highly effective means for preventing caries lesions or lesion progression in these sites. Thus, the analysis of benefits versus risks clearly favors the use of resin-based sealants.

? CRITICAL QUESTION

In the final analysis, who is responsible for deciding which materials are biologically safe for use in dentistry. The in vivo effect of substances eluted from dental materials on the immune system—the patient, the dentist, or the manufacturer?

Although the manufacturer is responsible for ensuring that its products are safe when used under recommended conditions, the health care individuals should confirm that required testing has been performed. Dental health professionals should recognize that no material is absolutely free of potential adverse effects. On the basis of previous descriptions of test results and the data from adverse effect registries, it is clear that the multifactorial nature of biocompatibility phenomena requires a practitioner to use several sources of information to select restorative materials that are safe and effective for each patient. Since the national registry data reveal the relatively high percentage of complaints from patients about metallic restorations, one should be extremely cautious in using metals in patients who claim to have allergies to metals. Recently, increasing numbers of allergic reactions have also been reported for resinous materials and the dentist should routinely ask the patient about all existing allergies before any material is used for preventive or restorative treatment.

It should be obvious that dental practitioners cannot simply follow a "cookbook" approach to select restorative materials for their patients. Instead, they must use their best clinical judgment—based on scientific evidence, personal experience in dentistry, and statements from patients, their physicians, and previous dentists, when applicable—to ensure that all possible risks are minimized. Once the practitioner makes a treatment decision, the patient should be informed of the benefits and risks of the proposed treatment and of any alternative treatments. Then, for medical and legal requirements to be satisfied, the patient must give his or her consent for the proposed treatment.

It is well known that there is considerable variability in the treatment planning process. The benefits and risks stated to patients by their practitioners are also likely to vary significantly from practice to practice. Obviously, some of the decisions will be based on accepting greater risks for the predicted benefits, whereas others will be based on a very conservative philosophy, which suggests that the risks of adverse effects should be exceptionally low. In some of these cases, when considerable risks exist, no treatment may be the best choice. For example, if some patients claim that they are allergic to several types of potential allergens, including metals, cosmetics, and food substances, extreme caution is indicated to minimize the probability of an adverse reaction. However, if restorative treatment is essential to restore occlusion and function, these risks may be accepted, although informed consent procedures must still be satisfied before treatment is begun.

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PART 2

AUXILIARY DENTAL MATERIALS

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CHAPTER 8

Impression Materials

OUTLINE

Classification of Impression Materials

Elastomeric Impression Materials

Making Impresssions with Elastomeric Materials

Properties of Elastomeric Impression Materials

Hydrocolloids

Inelastic Impression Materials

KEY TERMS

Accelerator—A compound that speeds up the reaction; also refers to the catalyst in the reaction of impression materials.

Addition reaction—A polymerization reaction in which each polymer chain grows to a maximal length in sequence.

Base paste (base putty)—The component that forms the main three-dimensional structure of a final impression.

Cast—A dimensionally accurate reproduction of a part of the oral cavity or extraoral facial structures that is produced in a durable hard material.

Catalyst paste (catalyst putty)—A component of a polymerization reaction that decreases the energy required for the reaction and usually does not become part of the final product; however, the term *catalyst* has been used for the structural component of dental materials that initiates the polymerization reaction.

Colloid—A solid, liquid, or gaseous substance made up of large molecules or masses of smaller molecules that remain in suspension in a surrounding continuous medium of different matter.

Condensation reaction—A polymerization process in which bifunctional or multifunctional monomers react to form first dimers first, then trimers, and eventually long-chain polymers; the reactions may or may not yield by-products; the preferred term is *step-growth polymerization*. All condensation impression materials yield by-products.

Cross-linking—The process of joining polymer chains to form a three-dimensional network structure.

Elastomer—Any of various polymers having the elastic properties of natural rubber.

Fusion temperature—The temperature below which a definite reduction in plasticity occurs during cooling of an impression compound.

Gel—A network of fibrils forming a weak, slightly elastic brush-heap structure of hydrocolloid; also the solid network structure of a cross-linked polymer.

Gelation—The process of transforming a hydrocolloid from a sol to a gel.

Imbibition—The displacement of one fluid by another immiscible fluid in a hydrocolloid. In the context of impression materials, it is the uptake by agar or alginate when immersed in water.

Inelastic—Incapable of sustaining significant elastic deformation without fracturing under stress.

Initiator—The component that starts a polymerization reaction; types include photoinitiators, chemical initiators, and heat initiators.

Micelle—An aggregate of surfactant molecules or ions in solution.

Model—A positive full-scale replica of teeth, soft tissues, and restored structures used as a diagnostic aid for the construction of orthodontic and prosthetic appliances; a facsimile used for display purposes.

Polymerization—A chemical reaction that transforms small molecules into large polymer chains.

Pseudoplasticity—The tendency of a material to become less viscous as the shear rate increases and to recover viscosity immediately upon the elimination of shear stress.

Rheology—Pertaining to the science that describes the fluid or flow characteristic of materials.

Set—The state of being sufficiently rigid or elastic to permit removal from the mouth without plastic deformation.

Setting time—The time from the start of mixing to the point where the material loses its flow potential or plasticity.

Shear thinning—The tendency for viscosity to decrease as the shearing rate increases (see *pseudoplasticity* and *thixotropy*).

Static mixing—A technique of transforming two fluid (or paste-like) materials into a homogeneous mixture without mechanical stirring; it requires a device that forces two streams of material into a mixer cylinder, such that as the streams move through the mixer, while the stationary elements in the mixer continuously blend the materials.

Syneresis—The expression of fluid onto the surface of gel structures.

Thixotropy—The property of certain gels or fluids to become less viscous when sufficient energy in the form of impact force or vibration is applied to overcome its yield stress; at rest they require a specific time to return to the previous viscous state. Both pseudoplasticity and thixotropy are shear-thinning processes; the difference is that changes in pseudoplastic viscosity do not exhibit the time dependency characteristic of thixotropy.

Undercuts—The recessed areas on dental structures, including teeth, edentulous ridges, prostheses, and restorations.

Viscoelasticity—The ability of a material to strain instantaneously like an elastic solid during rapid stretching or to resist shear flow and to strain linearly over time (like honey) when a stress is applied slowly.

Construction of a **model** or **cast** is an important step in numerous dental procedures. Various types of casts and models can be made from gypsum products using an impression mold or negative likeness of a dental structure (Figure 8-1). The dentist designs and constructs both removable and fixed prostheses on a gypsum cast. Thus, the cast must be an accurate representation of oral structures, which requires an accurate impression.

CRITICAL QUESTIONS

Which of the seven criteria that ensure accurate impression making are related to the time the impression material is in the mouth? Which one is related primarily to the properties of a **set** impression?

To produce accurate replicas of intra- and extraoral tissues, the impression materials should be (1) sufficiently fluid to adapt to the oral tissues, (2) viscous enough to be contained in a tray, (3) able to transform (set) into a rubbery or rigid solid in the mouth in a reasonable time (less than 7 min), (4) resistant to distortion or tearing when removed from the mouth, (5) dimensionally stable long enough to allow one or more casts to be poured, (6) biocompatible, and (7) cost-effective in terms of time as well as the expense of the associated processing equipment.

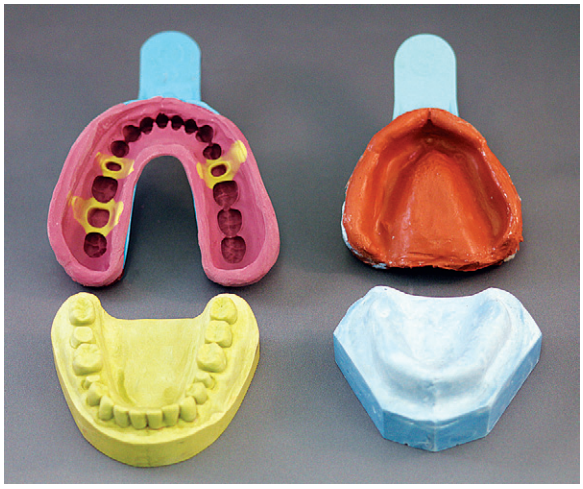


FIGURE 8-1 Impressions of dentate (*left*) and edentulous arches (*right*) with the resulting respective gypsum casts.

Environmental conditions and the type of tissue dictate the choice of materials, quality of the impression, and quality of the cast. This chapter discusses the unique properties of currently used impression materials and describes how these characteristics affect the quality of an impression and of the cast or model made from the impression.

CRITICAL QUESTION

How are dental impression materials classified?

CLASSIFICATION OF IMPRESSION MATERIALS

Impression materials that are used today can be classified according to their composition, mechanism of setting, mechanical properties, and applications. Table 8-1 shows the classification based on the setting mechanism and mechanical characteristics. The composition of the materials is discussed later.

SETTING MECHANISM

There are two basic setting mechanisms: reversible and irreversible. *Irreversible* implies that chemical reactions have occurred and that the material cannot revert to a previous state in the dental office. For example, alginate, zinc oxide–eugenol (ZOE) impression paste, impression plaster, and elastomeric impression materials, which set by chemical reactions, are irreversible. On the other hand, reversible materials, such as agar and impression compound, soften upon heating and solidify slightly above body temperature with no chemical change taking place.

TABLE 8-1 Classification of Dental Impression Materials

	MECHANICAL CHARACTERISTICS	
Setting Mechanism	**Inelastic**	**Elastic**
Chemical reaction (irreversible)	Plaster of Paris Zinc oxide–eugenol	Alginate Polysulfide Polyether Condensation silicone Addition silicone
Thermally induced physical reaction (reversible)	Impression compound	Agar

MECHANICAL PROPERTIES

The set impression materials can be rigid (**inelastic**) or elastic. A set rigid material is highly resistant to flexure, and it fractures suddenly when stressed, in a manner similar to that of chalk. Material is not flexible and will fracture when deformed, like chalk. ZOE impression paste, impression plaster, and impression compound are inelastic impression materials. The term *elastic* means that the material is flexible and can be deformed and still return to its original form when unstressed. Examples include agar, alginate, and **elastomers**.

CLINICAL APPLICATION OF IMPRESSION MATERIALS

Elastic impression materials can be stretched or compressed slightly, and they then rebound when the impression tray is removed from the mouth. They are capable of accurately reproducing both the hard and soft structures of the mouth, including the **undercuts** and interproximal spaces. The extent of the rebound determines the accuracy of the material.

Inelastic impression materials, such as ZOE paste and plaster, are ideal for making impressions of edentulous jaw structures or soft tissue because, in the proper consistency, they do not compress the tissue during seating of the impression tray. Impression compound is often used to make trays for the construction of full dentures.

ELASTOMERIC IMPRESSION MATERIALS

Elastomers comprise a group of synthetic polymer-based impression materials that are chemically cross-linked when set and that can be stretched and yet rapidly recover to their original dimensions, like vulcanized natural rubber when the applied stress is released. Chemically, there are three elastomers based on the backbone of polymer chains: polysulfide, silicone (condensation and addition), and polyether. Representative products are shown in Figure 8-2. In this chapter, they are called elastomeric impression materials.

They are supplied in two components, a **base paste** and a **catalyst paste** (or liquid) that are mixed before making impressions. They are often formulated in several consistencies, including extra low, low, medium, heavy, and putty, in increasing order of filler content. Extra-low and putty forms



FIGURE 8-2 Representative commercially available elastomeric impression materials.

are available only for condensation and addition silicones. Polysulfide is provided only in light-body and heavy-body consistencies. There is no heavy-body product for condensation silicone. Pigments are added to give each material a distinct color.

Hydrocolloids, which are discussed in later sections, are elastic impression materials but they are not categorized as elastomers.

POLYSULFIDE

The base paste, is a polysulfide polymer that contains a multifunctional mercaptan (-SH) called a polysulfide polymer, a suitable filler (such as lithopone or titanium dioxide) to provide the required strength, a plasticizer (such as dibutyl phthalate) to confer the appropriate viscosity to the paste, and a small quantity of sulfur, approximately 0.5%, as an accelerator. The catalyst (or accelerator) paste contains lead dioxide, filler, and plasticizer as in the base paste, and oleic or stearic acid as a retarder to control the rate of the setting reaction. Lead dioxide is the component that gives polysulfide impression material its characteristic brown color. The terms *catalyst* and *accelerator* used here and with other impression materials are actually misnomers. *Reactor* is a more appropriate term for the reactions associated with polysulfide and other types of impression materials.

Each paste is supplied in a dispensing tube with appropriately sized bore diameters at the tip so that equal lengths of each paste are extruded from each tube to provide the correct ratio of polymer to **cross-linking** agent. Since the composition of the material in the tube is balanced with that of the accelerator, the matched tubes supplied by the manufacturer should always be used.

The reaction starts at the beginning of mixing and reaches its maximum rate soon after spatulation is complete (Figure 8-3). At this stage, a resilient network has started to form. During the final set, a material of adequate elasticity and strength is formed that can be removed past undercuts quite readily. Moisture and temperature have a significant effect on the course of the reaction. In particular, hot and humid conditions will accelerate the setting of polysulfide impression material. The reaction yields water as a by-product. Loss of this small molecule from the set material has a significant effect on the dimensional stability of the impression.

CONDENSATION SILICONE

The materials are supplied as a base paste and a low-viscosity liquid catalyst (or paste catalyst), a two-paste system, or a two-putty system. The putty can be used as the tray material in conjunction with a low-viscosity silicone, that is referred to as the putty-wash technique.

The base paste consists of α-ω-hydroxyl-terminated polydimethyl siloxane (Figure 8-4). The curing of this material involves a reaction of tri- and tetra-functional alkyl silicates in the presence of stannous octoate as a catalyst. The material sets by cross-linking between terminal groups of the silicone polymers and the alkyl silicate to form a three-dimensional network (Figure 8-4). Ethyl alcohol is a by-product of the condensation setting reaction. Its subsequent evaporation accounts for much of the contraction that takes place in the setting impression.

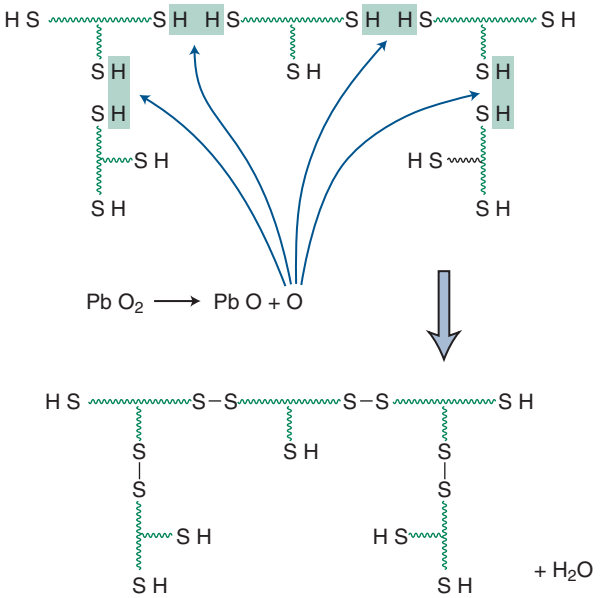


FIGURE 8-3 Polymerization of polysulfide impression material. SH groups interact with oxygen released from lead dioxide (*left*). Completion of the condensation reaction results in water as a by-product (*right*). Pendant –SH is for cross-linking and terminal –SH is for chain lengthening of the polymer.

ADDITION SILICONE

This material is often called a polyvinyl siloxane (PVS) or vinyl polysiloxane (VPS) impression material. In contrast to the condensation silicone, the addition silicone is based on addition **polymerization** between divinylpolysiloxane and polymethylhydrosiloxane with a platinum salt as the catalyst (Figure 8-5). The base paste contains polymethylhydrosiloxane, as well as divinylpolysiloxane. The catalyst (or accelerator) paste contains divinylpolysiloxane and a platinum salt. The platinum salt and polymethylhydrosiloxane are separated before mixing. Both pastes contain fillers.

No reaction by-products are formed as long as the correct proportions of divinylpolysiloxane and polymethylhydrosiloxane are used and there are no impurities. However, the residual polymethylhydrosiloxane in the material can lead to a secondary reaction with each other or with moisture, to produce hydrogen gas. Technically, hydrogen gas is a reaction by-product that does not affect the dimensional stability of the impression. Nonetheless, the hydrogen gas evolved can result in pinpoint voids in the gypsum casts poured soon after removal of the impression from the mouth. Manufacturers may add a noble metal, such as palladium, as a scavenger for the released hydrogen gas. The impression should be left overnight if epoxy will be used for pouring models.

One of the disadvantages of the silicone impression materials (including condensation silicones) is their inherent hydrophobic nature. A nonionic surfactant can be added to the paste in the manufacturing process to render a degree of hydrophilicity to the surface of the material. This surfactant migrates toward the surface of the impression material and has its hydrophilic segment oriented toward the surface—a phenomenon that makes the surface more wettable by water. These impression materials still require a dry field for impression making. Pouring the set impression with a gypsum-forming mixture is facilitated because the wet stone has a

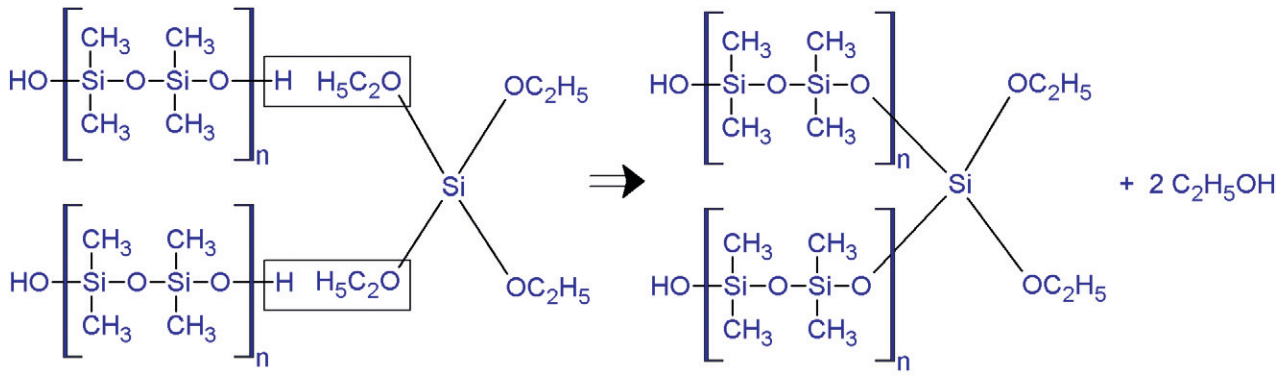


FIGURE 8-4 Condensation polymerization of α-ω-hydroxy-terminated poly (dimethyl siloxane) with tetraethyl orthosilicate in the presence of stannous octoate (catalyst). The reaction results in the release of ethanol molecules.

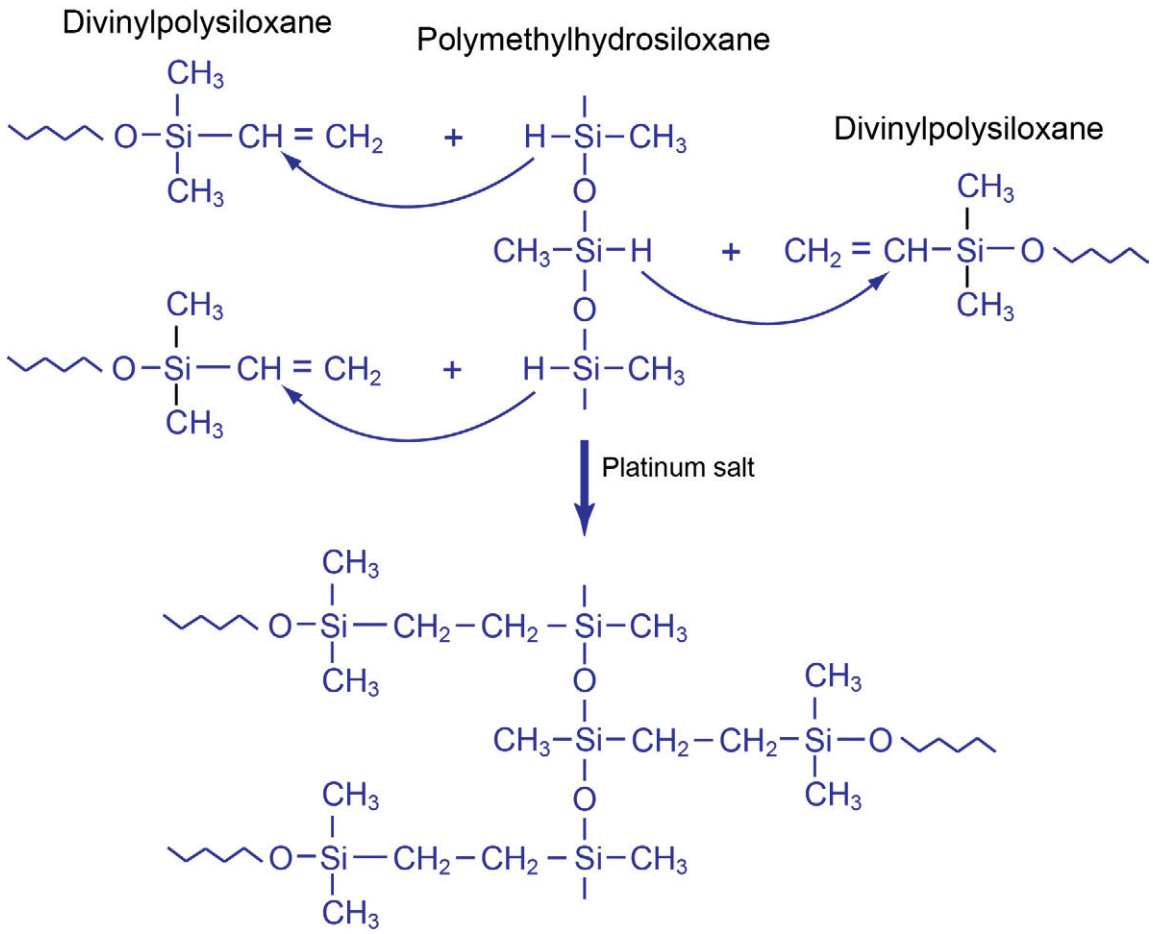


FIGURE 8-5 Polymerization of addition silicone. Hydrogen atoms along the backbone structure of the vinyl silicone chain move to the vinyl groups during addition polymerization (*top*). Final structure after the platinum salt has initiated the addition polymerization reaction (*bottom*). The zigzag line at the other end of divinylpolysiloxane represents repeating units of dimethylsiloxane with a vinyl terminal.

greater affinity for the hydrophilic surface. The clinical significance of hydrophilic additives is discussed in subsequent sections.

Sulfur contamination from natural latex gloves inhibits the setting of addition silicone. Some vinyl gloves may have the same effect because of the sulfur-containing stabilizer used in the manufacturing process. The contamination is so pervasive that touching the tooth with latex gloves before seating the impression can inhibit the setting of the critical surface next to the tooth.

Medium-body addition silicone has also been formulated for making impressions for diagnostic purposes, as a substitute for alginate impression material (discussed later). The advantage of these so-called alginate substitutes is the ability to make multiple, accurate diagnostic casts from one impression. Laboratory studies have reported that they exhibited better detail reproduction and less variability in linear dimensional change than irreversible hydrocolloid.

POLYETHER

There are two types of polyether impression materials. The first is based on the ring-opening polymerization of aziridine rings, which are at the end of branched polyether molecules (Figure 8-6, *left*). The main chain is probably a copolymer of ethylene oxide and tetrahydrofuran. Cross-linking and setting are promoted by an **initiator** and an aromatic sulfonate ester (Figure 8-6, *top*), where R is an alkyl group. This produces cross-linking by cationic polymerization via the imine end groups (Figure 8-6). The material is supplied as two pastes. The base paste contains the polyether polymer, colloidal silica as filler, and a plasticizer such as glycol ether or phthalate. The accelerator paste contains an alkyl-aromatic sulfonate in addition to the filler and plasticizer. The ether-dominated polymer backbones make this group of materials the most hydrophilic of all elastomeric impression materials.

The second type is based on an acid-catalyzed condensation polymerization of polyether prepolymer with alkoxysilane terminal groups. The mechanism is similar to that observed in condensation silicones having low-molecular-weight alcohols as by-products. This material is often called a hybrid. Since the ether-linkages constitute the main component of the polymer chains, these materials behave very much like the first type of polyether impression material.

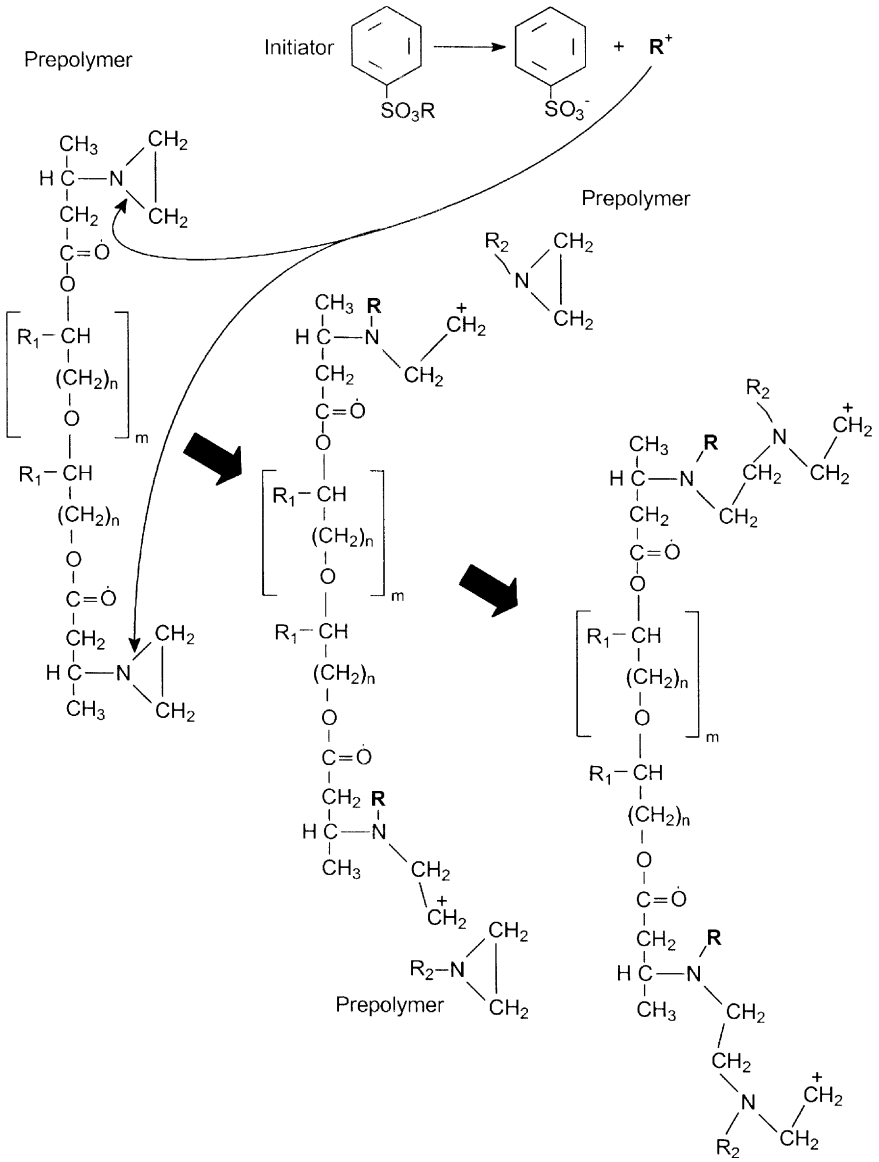


FIGURE 8-6 The initiator, aromatic sulfonate ester, dissociates and forms alkyl cations that bind the nitrogen atoms of the aziridine ring terminals of the prepolymer (*top, left*). The arrows indicate binding between the cations (R^+) with the nitrogen atoms. This action opens up the ring, and the reacted prepolymer (*center*) now has two charged ethylene imine terminals (–NR–CH_2–C^+H_2), which can react with the nitrogen atoms of adjacent unreacted prepolymers, shown as the R_2-aziridine ring. This chain-propagation polymerization reaction yields a larger molecule (*right*), which continues growing by binding with aziridine rings of additional unreacted prepolymers. The polymerization reaction terminates when the growing chain combines with a counterion.

CRITICAL QUESTION

What are the steps needed to produce casts and dies for prosthetic procedures?

MAKING IMPRESSSIONS WITH ELASTOMERIC MATERIALS

The use of elastomeric impression material to fabricate gypsum models, casts, and dies involves six major steps: (1) preparing a tray, (2) managing tissue, (3) preparing the material, (4) making an impression, (5) removing the impression, and (6) preparing stone casts and dies.

IMPRESSION TRAYS

The use of a custom tray (Figure 8-7, *A*) is recommended to reduce the quantity of material required to make impressions; thus, any dimensional changes attributed to the materials are minimized. A custom tray allows a uniform distribution of impression material between the tray and the object, which also improves accuracy. This is especially true for polysulfide impression material. The use of custom trays for polyether and addition silicone impressions is not critical, since these materials are stiffer and have less polymerization shrinkage than the polysulfide material. In addition, disposable stock trays (Figure 8-7, *B*) work satisfactorily. Note that the use of less material in a custom tray reduces the compressibility of the impression, which can make removal of the impression tray more difficult. When severe undercuts are present, the use of a custom tray should be avoided. The stock tray should be rigid, thereby minimizing flexure of the tray during impression making. Disposable stock trays are also used to support the putty when the putty-wash technique is used for making impressions. Prior to making an impression, a uniform thickness of tray adhesive is applied on the tray surface, extending over its edge, and it is allowed to dry (through evaporation of solvent). A slightly roughened



FIGURE 8-7 Impression trays. Custom tray (*left*) and stock tray (*right*).

surface on the tray will increase adhesion. Tray adhesives are not interchangeable among different types of materials.

When the material is used correctly, either custom or stock trays yield clinically acceptable impressions.

TISSUE MANAGEMENT

The margins of tooth preparations for fixed prostheses often extend to or below the free margin of the gingiva. To ensure access for the tooth preparation and for making the impression, it is necessary to displace the gingival tissues, control gingival hemorrhage, and control sulcular fluids. Among the most popular methods of gingival displacement is the use of gingival retraction cord. An electrosurgical unit or a soft tissue laser can also be used.

The objective of placing a retraction cord is to displace the gingival tissue laterally away from the margin of the preparation. One or two gingival retraction cords are placed under the margin around the tooth for at least 5 min before making impressions. The double-cord technique is used when the margin is very close to the gingival attachment. A fine cord is placed at the base of the crevice to facilitate moisture control, with a larger cord placed on top of the first and near the coronal extent to displace the gingiva laterally. The latter, outermost cord is removed, leaving the fine cord within the crevice while the impression is made. A single cord is sufficient to deflect the soft tissue around the margin when the preparation margin is at or slightly above the gingival crest.

Retraction cords may be impregnated with a hemostatic agent by dipping the cord in a hemostatic solution prior to placement. These agents can have unintended side effects and should be used with caution. For example, epinephrine, which is used widely, is of particular concern in patients with cardiovascular disease. In addition, agents with a low pH can remove the smear layer and superficial dentin apical to the margins of the preparation, possibly leading to postoperative sensitivity of some teeth.

? CRITICAL QUESTION

How does **static mixing** achieve a uniform mixture? What is the main difference between static mixing and dynamic mixing?

MANIPULATION OF IMPRESSION MATERIALS

Currently, elastomeric impression materials are supplied for three modes of mixing: hand mixing, static mixing, and dynamic mechanical mixing (Figure 8-8).

Hand Mixing

The user should dispense the same lengths of materials onto a mixing pad or glass slab (Figure 8-8, *A*). The catalyst paste is first collected on a stainless steel spatula and then spread over the base paste. The mixture is then spread over the mixing pad. The mass is then scraped up with the spatula blade and spread uniformly back and forth on the mixing pad. This process is continued until the mixed paste is uniform in color, with no streaks of the base or catalyst appearing in the mixture. If one of the components is in liquid form, such as the catalyst for condensation silicones, a length of the base is dispensed from the tube onto a graduated mixing pad and drops of the liquid catalyst corresponding to the length of the base are added. These materials are somewhat difficult to mix because of the difference in the viscosity of the two components.

The two-putty systems available for condensation and addition silicone are dispensed by volume using an equal number of scoops of each material. The best mixing technique is to knead the material with one's fingers until a uniform color is obtained. When the catalyst is a liquid, as in the case of condensation silicones, this kneading procedure with the fingers is applicable.

Static Mixing

This technique transforms two fluid (or paste-like) materials into a homogeneous mixture without mechanical mixing. The device used to accomplish this mixing is a gun for compressing materials in a two-cylinder cartridge, which contains the base and catalyst separately, as well as a mixing tip (Figure 8-8, *B*). The mixing tip is made of helical mixer elements in a cylindrical housing (Figure 8-9). The mixer elements are a series of alternating right- and left-turn 180° helixes positioned so that the leading edge of one element is perpendicular to the trailing edge of the next (Figure 8-9, *B*). The length of each element is about the same as the inner diameter of the cylindrical housing.

The base and catalyst are pressed from the cartridge into the mixing tip as one stream of a two-layer material. The leading edge of the first element splits the material entering the mixer into two streams. The streams that flow in either side of the helix will make a 180° turn (Figure 8-9, *A*) when they reach the second element. Both streams are split by the leading edge of the second element, and two substreams (one from each original stream) combine into two new streams entering the second element. This process is known as flow division. Assuming that there is no intermixing between the two substreams as they merge, the new stream will have a two-layer structure. After flowing through "n" elements, the number of layers in the stream of material increases to 2^n. The most common mixing tips for impression material mixing have 11 or 12 elements. The stream of material that exits the



FIGURE 8-8 Mixing systems. **A**, Hand mixing. Two equal lengths of the material are dispensed on the mixing pad with the mixing spatula. **B,** Static mixing. When the trigger is pulled, the plunger is driven forward (to the left), so that the base and catalyst pastes are forced from the cartridge into the mixing tip (*extreme left*). The pastes pass through the bore and exit the nozzle as a uniform mixed paste. Four different sizes of mixing tips are shown; the more viscous the material, the larger is the mixing tip that should be used. Syringe tips can be fit to the nozzle to deliver the mixed paste directly to the prepared teeth. **C**, Static mixing syringe. These syringes fit the cartridge, as the mixing tips shown in **B**. The base and catalyst are first injected into the respective barrel. A plunger then forces the material through a smaller static mixing tip. It can deliver the light body material directly onto the abutment(s). **D,** Dynamic mechanical mixing. The motor-driving mechanism forces the material into the mixing tip and makes the impeller (*insert*) inside the tip rotate. The function of the impeller is only to mix the material.

mixing tip will have a 2048- or 4096-striation structure, which can be treated as a uniformly mixed stream of material. In addition, as the materials make turns along the helix, the rotational circulation causes a radial mixing of the materials. Thus, mixing between substreams occurs before the next flow division that further increases the uniformity of the mixture. Since there is no mechanical mixing, porosity caused by mixing with air is avoided. The mixing tips vary in their diameter, length (number of helical mixer elements), and the size of openings for a specific consistency.

The mixed impression material is injected directly into the adhesive-coated tray or, if the "syringe tip" is in place, onto the prepared teeth. Static mixing provides greater uniformity in proportioning and mixing, yields fewer voids in the mix, and reduces the mixing time. In addition, there are fewer possibilities for contamination of the material. One precaution that should be taken in using these automixing devices is to make sure that the openings of the tubes that dispense the pastes remain unclogged. Problems can be avoided if one expresses a small amount of material from the cartridge before attaching the mixing tip. This type of device has also been adapted to mix and dispense temporary crown and bridge acrylic materials and cements that are used for luting and for producing restorations (Chapter 14).

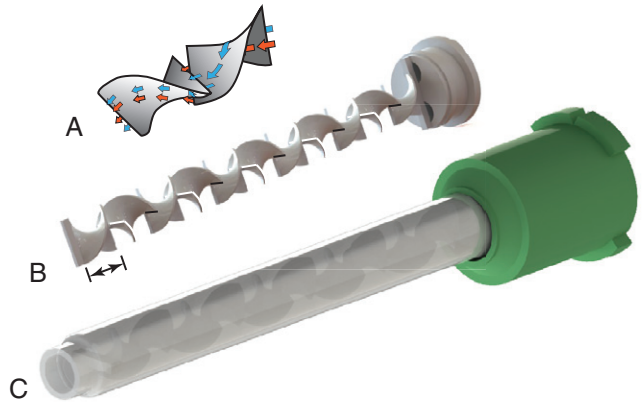


FIGURE 8-9 Design of a static mixing tip. **A**, Mechanism of mixing in a two-element model. The two-element model shows that the materials injected into a left-turn helix are immediately split into two streams. Both streams make a 180° counterclockwise turn when they reach the leading edge of the next element, a right-turn helix. Each stream is split as it enters the new element. Two new streams, made of combining two substreams, one from each original stream, now make a 180° clockwise turn when they reach the trailing edge of the element. When there is a third element present, each substream will be split again and the total of substreams will be eight (2^3). **B,** Mixer elements with 11 helixes. The double-headed arrow delineates the size of one element. The appearance of size difference between neighboring elements is caused by the orientation. **C,** Mixing tip with encased mixer elements. (Courtesy of K-J. Söderholm.)

Dynamic Mechanical Mixing

The device shown in Figure 8-8, *C*, uses a motor to drive parallel plungers, forcing the materials into a mixing tip and out into an impression tray or syringe; meanwhile, the motor-driven impeller, which is inside the mixing tip, mixes the materials as they are extruded through the tip. The function of the impeller is only to mix the materials as they are passing through; it does not propel the material. The materials are supplied in collapsible plastic bags housed in a cartridge. The amount of material retained in the mixing tip is slightly greater than that used in static mixing. In using this device, thorough mixing of higher-viscosity materials can be achieved with little effort. Both polyether and addition silicone impression materials of various viscosities are available with this dispensing system.

? CRITICAL QUESTION

How does each impression-making technique take advantage of the unique properties of the impression materials?

MAKING AN IMPRESSION

Elastomeric impression materials are typically supplied in several viscosities to accommodate different techniques for impression making. Three techniques for making impressions are discussed in this section.

Multiple-Mix Technique

A syringe material (light body) and a tray material (heavy body) are used in this technique. Usually, the two groups of materials are mixed simultaneously, each by a different person. With the mechanical devices described earlier, the materials now can be mixed as needed by one individual. The lighter material is injected from the filled syringe or directly from a static mixing gun within and around the tooth preparation. The filled tray is then inserted in the mouth and seated over the syringe material, which has been extruded on hard and/or soft tissue. The tray material will force the syringe material to adapt to the prepared tissues. The two materials should bond together upon setting. If either material has progressed past its working time when the two materials are brought together, the bond between them will be compromised. If a partially set material is seated, it will be compressed elastically. Once removed from the mouth, the impression will "spring back" or relax, and the dies from this impression will be too narrow and too short, as illustrated in Figure 8-10.

In rare cases a clinician may attempt to repair an impression that has small defects or that lacks sufficient detail. This is usually performed by cutting away the interproximal and gingival areas of the impression. Even with proper relief of the initial impression, it will be difficult to reseat the tray precisely. Entrapment of a minute fragment of impression material or debris will eliminate any chance of a successful repair. The impression material's surface must be roughened to ensure that the new material bonds to the set impression. The safest method is to make a new impression when bubbles or similar defects are detected in critical areas.

Monophase Technique

Medium-body polyether and addition silicone are often used for the monophase or single-viscosity technique. The procedure is similar to that of the multiple-mix technique except that only one mixture is made, and part of the material is placed in the tray, and another portion is placed in the syringe for injection in the cavity preparation, prepared teeth, or soft tissue. The success of this technique depends on the pseudoplastic (**shear thinning**) properties of the materials. When a medium-viscosity material is forced through the syringe tip, the viscosity is reduced to allow the material to adapt well to the preparation. Meanwhile, the material in the tray retains its medium viscosity, and, when seated, it can force the syringe material to flow past critical areas of the tooth preparation. Table 8-2 shows the effect of shear rate and elapsed time on some monophase addition silicones.

? CRITICAL QUESTION

What are the consequences of placing an impression material in the mouth after the working time has expired?

Putty-Wash Technique

This method was originally developed for condensation silicone to minimize the effect of associated dimensional changes. The thick putty material is placed in a stock tray and a preliminary impression is made. This procedure results in what is essentially an intraoral custom-made tray formed by the

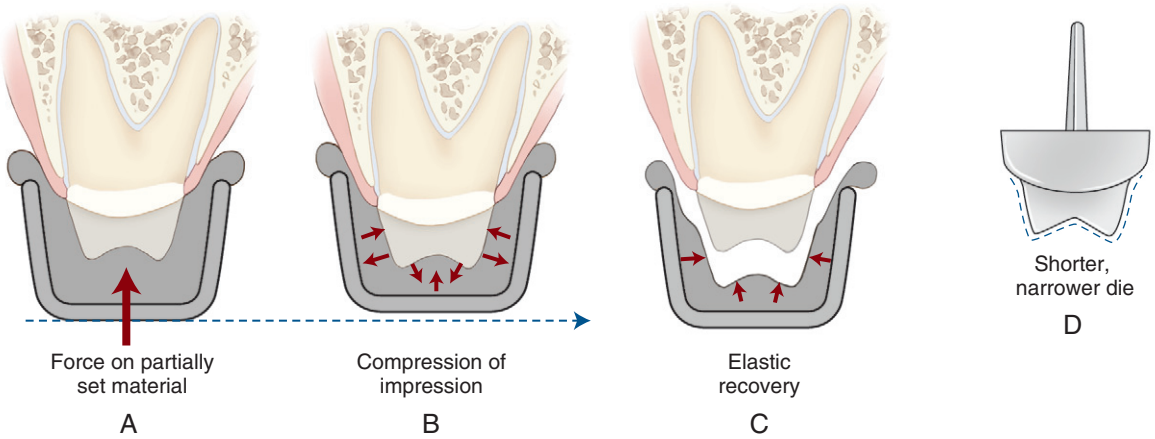


FIGURE 8-10 Effect of seating tray material that has passed its working time and developed some elasticity. **A,** Impression tray containing elastomeric impression material is seated too late as elasticity starts to develop. **B,** Increased seating pressure is applied to overcome the stiffness of impression material. **C,** Distortion develops during recovery of excessive elastic deformation (spring back). **D,** The die produced in the inaccurate impression is too narrow and too short.

TABLE 8-2 Viscosity ($\times 10^4$ cp) of Single-Phase Vinyl Polysiloxanes at 37 °C

	VISCOSITY AT 1 MIN		VISCOSITY AT 1.5 MIN	
Material	**0.5 rpm**	**2.5 rpm**	**0.5 rpm**	**2.5 rpm**
Baysilex (Miles)	122.1 (2.8)*	68.9 (2.5)	211.2 (14.7)	148.8 (1.2)
Green-Mouse (Parkell)	133.7 (8.9)	56.7 (2.9)	247.9 (14.9)	78.0 (2.8)
Hydrosil (Caulk)	194.2 (8.5)	129.4 (4.1)	398.1 (7.8)	153.5†
Imprint (3M)	106.5 (12.2)	79.7 (2.2)	245.1 (8.9)	146.2 (5.9)
Omnisil (Coe)	156.8 (11.5)	102.5 (1.9)	347.1 (5.2)	153.5‡

From Kim K-N, Craig RG, Koran A: Viscosity of monophase addition silicones as a function of shear rate. *J Prosthet Dent* 67:794, 1992.
*Numbers within parentheses represent the standard deviation of the mean.
†Value at 75 s after mixing.
‡Value at 77 s after mixing.

putty. Space for the light-body "wash" material is provided either by cutting away some of the "tray" putty or by using a thin polyethylene sheet as a spacer between the putty and the prepared teeth during preliminary impression making. One can also generate the space by vacuum forming a blank plastic sheet on a cast and then make the impression with the putty material. A mixture of the thin-consistency wash material is placed into the putty impression and on the preparation; then the tray is reseated in the mouth to make the final impression.

An alternative approach is to inject the wash material around the preparation and then immediately seat the tray with freshly mixed putty over the wash material. However, this approach risks displacing too much wash material by the putty, so that a critical area of the preparation is reproduced in the putty without the required detail. Occlusal stops should be used in the tray to avoid having the teeth penetrate through the wash or syringe material when the plastic putty mass is being seated.

When the latter technique is used, distortion or incomplete details can result because of excessive pressure applied to the setting putty. After being removed from the mouth, the pressure in the impression is released and the putty recovers its "elastic deformation." The distortion produced by the stiff, compressible putty results in a short, narrow die (Figure 8-10). In addition to excessive pressure, some of the distortion in putty-wash impressions may be attributable to inadequate space for the wash material.

REMOVAL OF THE IMPRESSION

Under no circumstances should the impression be removed until the curing has progressed sufficiently to provide adequate elasticity, so that distortion will not occur. One method for determining the time of removal is to inject some of the syringe material onto a space that is not in the field of operation before inserting the impression tray. This material can be probed with a blunt instrument from time to time; when it is firm and returns completely to its original contour, the impression is sufficiently elastic to be removed. When a multiple mix technique is used, it is advisable to test both the syringe and the tray materials in this manner. Typically, the impression should be ready for removal within at least 10 minutes from the time of mixing, allowing 6 to 8 minutes for

the impression to remain in the mouth. Manufacturers usually provide the optimal time for removal after mixing.

The mechanics of removing the impression involves separation at the impression/tissue interface and stretching of the impression. The first step is to break the physical adhesion between the tissue and the impression; therefore, an impression material, such as polyether, that wets the tissue well will require extra effort to break the seal for the removal. The second step stretches the impression enough to pass under the height of contour of the hard tissue to remove the impression; therefore, using a material of higher rigidity will require a greater force to stretch the impression to facilitate removal. Polysulfide has the lowest viscosity and ranks as one of the least stiff of the elastomeric impression materials of a similar consistency. This flexibility allows the set material to be easily removed from undercut areas and from the mouth with a minimum of stress.

In addition, all elastomeric impression materials are viscoelastic, and it is necessary to use a quick snap to minimize plastic deformation of the impression during the final step of the removal process. The phenomenon of viscoelastic behavior is discussed in subsequent sections.

PREPARATION OF STONE CASTS AND DIES

The hydrophobic characteristics of silicone impression materials make them suitable for pouring of epoxy resin to produce dies. However, this hydrophobicity makes pouring with gypsum products challenging, as it increases the potential of forming voids in gypsum dies and casts. There are a number of surfactant sprays, also known as debubblizers, that can improve the surface wettability of the silicone impression material for the stone slurry. Only a thin layer of surfactant should be applied to the impression surface. A dilute solution of soap is also an effective surfactant. An alternative to the use of a surfactant is to select a hydrophilized addition silicone (discussed later). Pouring of a stone cast in a polyether or polysulfide impression does not require the aid of a surfactant.

The excellent dimensional stability of addition silicone and polyether impression materials makes it possible to construct two or three casts or dies from these materials. It is also possible to construct successive stone dies or casts from polysulfide impressions when duplicate stone dies are needed. However, each successive die will be less accurate than the first die constructed from the material. The time interval between impression pours should not be greater than 30 minutes. To minimize tearing and gross distortion after the first pour, the clinician should remove the excess gypsum-forming mass from undercut areas along the periphery of the tray. Be aware that the stiffness of the impression material makes it difficult to remove the stone cast from the impression. A weak stone cast may fracture during removal.

PROPERTIES OF ELASTOMERIC IMPRESSION MATERIALS

The goal of impression making is to produce an accurate impression that can yield a cast or die that reproduces the surface details and precise shape of the original tissue as closely as possible. Meanwhile, the dimensions of the impression should remain stable during the production of dies or casts. In this section, the properties relevant to impression making with elastomers are described.

CRITICAL QUESTION

Why is it not advisable to alter the base/catalyst (accelerator) ratio as a means of controlling working or **setting time**?

WORKING AND SETTING TIMES

Table 8-3 lists working and setting times for the various kinds of elastomeric materials as measured by an oscillating rheometer. The working time, which begins at the start of mixing and ends just before the elastic properties have developed, must be greater than the time required for mixing, filling the syringe and/or tray, injecting the material on tooth preparations, and seating the tray. The setting time is the time that has elapsed from the beginning of mixing until the curing process has advanced sufficiently that the impression can be removed from the mouth with no distortion. Remember, however, that polymerization may continue for a considerable time after setting. An increase in temperature accelerates the rate of polymerization of all elastomeric impression materials; therefore, the effect of temperature on working and setting time should be taken into consideration.

Working time and setting time decrease as the filler content in the materials increases. Altering the base/catalyst ratio will change the curing rate of these impression materials. Normally, having more base materials in the mixture tends to increase the working and setting times. One should be aware that this is not economical, as a portion of the paste is not used. Moreover, since the accelerator paste contains a retarder as well as a reactor, increasing the base/accelerator ratio may not produce a predictable change in the polymerization rate.

REPRODUCTION OF ORAL STRUCTURE DETAIL

A surface reproduction test is a requirement of national standards for elastomeric impression materials. There is little

TABLE 8-3 Working and Setting Times of Elastomeric Impression Materials

	MEAN WORKING TIME (MIN)		MEAN SETTING TIME (MIN)	
Impression Material	**23 °C**	**37 °C**	**23 °C**	**37 °C**
Polysulfide	6.0	4.3	16.0	12.5
Condensation silicone	3.3	2.5	11.0	8.9
Addition silicone	3.1	1.8	8.9	5.9
Polyether	3.3	2.3	9.0	8.3

From Harcourt JK: A review of modern impression materials. *Aust Dent J* 23:178, 1978.

doubt that these elastomers can record detail to the finest degree. When dental stone is poured on the surface of such test impressions, the finest detail is not always reproduced. The reason for this situation is that the elastomeric impression materials are capable of reproducing detail more accurately than can be transferred from the stone die or cast, which may not be capable of such accuracy.

The clinical significance of the surface reproduction tests is not entirely evident. It is possible that the detail obtained from the elastomeric impression materials under in vitro test conditions might be greater than that obtained in the mouth because of the hydrophobicity exhibited by some of these materials.

? CRITICAL QUESTION

Why is rapid seating of an impression tray not advisable for a pseudoplastic impression material?

RHEOLOGICAL PROPERTIES

Impression materials are introduced into the mouth as viscous pastes with precisely adjusted flow properties. The viscosity and flow behavior of the unmixed components are also important in regard to the ease of mixing, air entrapment during mixing, and the tendency for the trapped air to escape before the impression is made.

Ideally, the impression material should flow freely and wet the tissue as it is being injected to achieve adaptation, and then resist flow away from the intended surface areas. The same procedure will facilitate spreading of heavy-body material on the impression tray and retain it in the tray. This phenomenon is called shear thinning (Chapter 3). Essentially, a stress-thinning material becomes less viscous when stressed as during injection and then recovers its viscosity when it rests on the tissue or or in the tray. All elastomeric impression materials exhibit shear-thinning characteristics before setting.

There are two categories of shear-thinning phenomena, **pseudoplasticity** and **thixotropy**, depending on how the material responds to the applied stress and how it behaves at rest. A pseudoplastic material displays decreasing viscosity with increasing shear stress, and recovers its viscosity immediately upon a decrease in shear stress. A thixotropic material does not flow until sufficient energy in the form of an impact force or a vibration force is applied to overcome the yield stress of the material. At rest it takes a specific time to regain its previous viscous state. Drip or run-off tests, which record the quantity of impression material that flows away from the preparation, have been used to demonstrate the phenomenon of thixotropy. Essentially the tests determine whether or not the impression material at rest continues to flow under the influence of gravity. Manufacturers that emphasize their materials being thixotropic also note that the materials exhibit no slump when injected on a vertical surface. They usually do not mention the duration of time delay. In this context, the phenomenon should be termed extreme shear thinning as the material retains an immobile state at rest, but flows freely flowing under stress.

The benefit of thixotropy in impression making has been disputed, since the time duration needed for the impression material to recover the necessary viscosity may be unacceptable. Other reports suggest that a thixotropic material should facilitate handling and make better impressions. However, the latter does not address the effect of time lag on the impression-making process.

Earlier generations of addition silicone impression materials did not have thixotropic properties, while recent formulations exhibit various degrees of thixotropy. It is not clear if this effect resulted from a change in formulation or the measurement technique. One should be aware that these studies are often conducted with unmixed base and catalyst pastes. From the point of impression making, the viscosity of uniformly mixed impression also increases with polymerization regardless of the effect of thixotropy; therefore, the impact of thixotropy during impression making may not be critical. In addition, confirming the thixotropic nature of a material without reporting the time lag required before regaining the intrinsic viscosity is not meaningful. Nonetheless the phenomena of thixotropy still needs to be investigated further.

Finally, it is important to note that the shear-thinning property of addition silicone and polyether impression materials enable the clinician to use a monophase impression-making technique to capture the details needed for fixed prostheses to produce an impression that is more stable and resistant to distortion than a light-viscosity material.

? CRITICAL QUESTION

How does the viscoelastic property of impression materials dictate the manner in which an impression must be removed from a patient's mouth?

ELASTICITY AND VISCOELASTICITY

An impression material sustains some deformation as it is removed from the mouth but it must rebound to its pre-removal dimensions. An impression with a sufficiently high elastic limit should not sustain permanent deformation. The elastic properties of these elastomeric impression materials improve with an increase in curing time in the mouth, since the setting time stated by the manufacturer is not always adequate for the development of sufficient elasticity to prevent permanent deformation upon removal of the impression. An extra time of 1 or 2 min before removal may be beneficial.

The relative amount of permanent deformation in compression following strain induced during removal increases in the following order for impression materials: addition silicone, condensation silicone, polyether, and polysulfide. Recovery of elastic deformation following strain is less rapid for the polysulfide material than for the other three types of impression materials.

To understand why impression material may exhibit permanent deformation after being subjected to a compressive force during removal and why recovery of elastic deformation occurs when an impression material rests on a benchtop over time, one must recognize that all elastomeric impression materials are viscoelastic materials. The characteristics of a viscoelastic solid are intermediate between those of an elastic solid and a viscous liquid. An elastic solid can be viewed as a spring (S1 and S2 in Figure 8-11), which deforms instantly to a certain extent when one applies a specific force. The deformation will be reversed completely when the force is removed. On the other hand, a viscous liquid behaves in a manner similar to that of an oil dashpot (D1 and D2 in Figure 8-11), which does not respond instantly to any sudden external force but deforms as the load is applied constantly over time. The dashpot continues to deform at a rate proportional to the duration of force application. Compared with the reversible behavior of an elastic solid, the deformation exhibited by the dashpot is permanent. Only a force applied from the opposite direction can restore the dashpot to its original form. The simplest model that demonstrates the viscoelastic behavior is a Maxwell-Voigt model (Figure 8-11, *A*), which consists of a spring (S1) and a dashpot (D1) in series and a second set (S2 and D2) in parallel.

When a compressive force is applied, S1 responds instantaneously with a definite amount of strain (deformation). At this instant, neither D1 nor D2 responds to the force applied. Meanwhile, S2 cannot respond because the inertia of D2 is preventing S2 from responding (Figure 8-11, *B*). When the force is maintained on the model, D1 and D2 will begin to move and stop when the force is removed. During this period, S2 moves as much as D2 (Figure 8-11, *C*). Meanwhile, spring S1 maintains the same magnitude of strain and the amount of movement by D2 is proportional to the duration of force application. When the load is removed, the deformation by spring S1 recovers while the rest remains unchanged (Figure 8-11, *D*). As time passes, spring S2 slowly overcomes the inertia of dashpot D2 and recovers along with D2 (Figure 8-11, *E*). This process usually takes time, and the deformation may not recover completely. The deformation of dashpot D1 never recovers.

According to the model, the amount of deformation exhibited by D2 is the permanent deformation observed after removal of the impression. The effort of S2 to recover to its original dimension is equivalent to the elastic recovery of the impression over time. It is apparent from the model that keeping the time of applied force on the impression to a minimum will result in the least amount of permanent deformation. This explains why removal of the impression should be done in a snap, if possible, and a teasing or rocking method should be avoided. However, a slight teasing action will first be required to break the seal between the impression material and the hard and soft tissues.

The polyvinyl siloxane impression materials exhibit the most elastic recovery of the currently available materials. Distortion on removal from undercuts is virtually nonexistent because these materials exhibit the lowest permanent distortion after excessive strain in compression. However, the excellent elastic properties present a problem in that the heavy-body putty material begins to acquire elastic properties while it is still in the working-time stage. If the material is at an advanced stage of elasticity and is compressed excessively during the seating of the impression, distortion can occur when the material elastically rebounds (Figure 8-10).

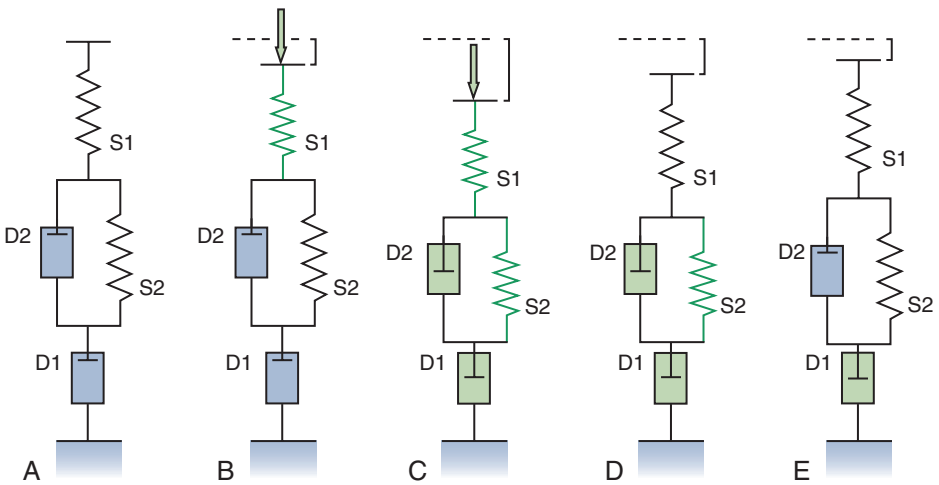


FIGURE 8-11 A mechanical model showing the response of a viscoelastic material to external loading and unloading. **A,** Maxwell-Voigt viscoelastic model in a stress-free state. **B,** During loading, only spring S1 contracts in response to the load. **C,** When the loading continues, the pistons in dashpot D1 and D2 move proportionally to the duration of loading. Spring S2 contracts along with dashpot D2. No change is expected for spring S1. **D,** The moment the load is released, spring S1 recovers instantly, whereas the rest of the elements remain unchanged. Spring S2 should also recover instantly but is retarded by the sluggishness of dashpot D2. **E,** As time passes, spring S2 recovers and extends dashpot D2 slowly to near its original position. Dashpot D1 remains unchanged. The right-hand bracket on the top of each model denotes the degree of deformation.

The stiffness (elastic modulus) of earlier generations of impression materials of similar viscosity was reported to increase in the following order: polysulfide, condensation silicone, addition silicone, and polyether. The difficulty of removing earlier generations of polyether impressions from undercut areas was attributed to their high modulus of elasticity. These materials were so stiff that making impressions of severely periodontally involved teeth with polyether carried the risk of tooth extraction. The new generations of polyether impression materials with a stiffness lower than that of hydrophilic PVS were formulated specifically to address concerns about the stiffness of the early materials. Although the new polyether materials are significantly more flexible than that of PVS at the time of removal, their adhesion, which results from the inherent hydrophilicity, can still make the impression removal difficult. It has been hypothesized that increasing the portion of ether prepolymer in the final formulation will increase the initial hydrophilicity of the material and maximize precision of the impression. It is important to note that increased precision also implies greater adhesion between the impression and the tissue, and increased difficulty of removing the impression. Because of the reduced rigidity, these new generations of polyether impression material may not be the material of choice for the "triple-tray" technique, where the impression material's stiffness during removal compensates for the flexibility of the tray. Although these new materials are flexible during removal, they have been shown to increase their elastic moduli for some time after removal. As the formulation of impression materials continues to evolve to accommodate specific needs, grouping the stiffness of impression materials based on the backbone of polymer chains is becoming less meaningful.

? CRITICAL QUESTIONS

What is the difference between tear strength and tear energy? Why is tear energy more meaningful for impression making?

TEAR STRENGTH

Low-viscosity impression materials are used in interproximal and subgingival areas during impression making. The subgingival regions of the impression are often very thin and can tear during impression removal, leaving a portion embedded within the gingival sulcus (Figure 8-12). The amount of force needed to tear a specified test specimen divided by the thickness of the specimen is called the tear strength. There is no standard method for testing the tear strength of impression materials, since ISO 4823 (Dentistry—Elastomeric impression materials) does not address such a test method. Figure 8-13 shows two configurations described in a non-dental standard (ISO 34-1; Rubber, vulcanized or thermoplastic—Determination of tear strength—Part 1: Trouser, angle and crescent test pieces) that have been used by the dental community for testing impression materials.

A tear-strength test measures the resistance of an elastomeric material to fracture when subjected to a tensile force acting perpendicular to a surface flaw. The ranking of tear strength from the lowest to highest of the impression materials is as follows: silicones (addition and condensation), polyether, and polysulfide. However, the literature has shown that some polyethers or silicones have a higher tear strength than certain polysulfides.

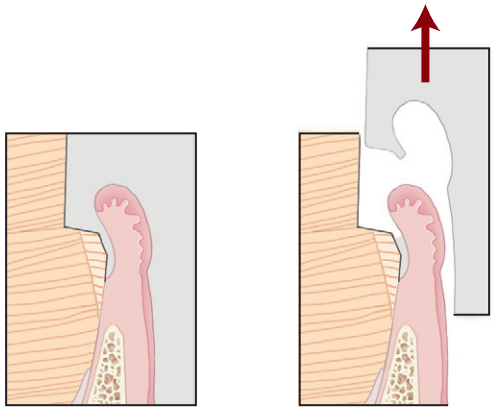


FIGURE 8-12 **A,** A properly retracted soft tissue will leave a narrow space to be filled by the light-viscosity impression material. **B,** The impression material has torn during removal.

Tear strength is influenced by consistency and the manner of removing the materials. An increased consistency usually increases the tear strength of the material. The addition of a thinning agent to the mixture reduces tear strength slightly but increases flexibility substantially. A quick snap in removing the impression usually increases the tear strength, as the action increases the resistance of the material to deformation (strain).

The definition of tear strength assumes no dimensional change for the test specimen. Regardless of the magnitude of its tear strength, an impression material undergoes a certain amount of strain during removal. For the same tooth preparation, a material that can be stretched a great deal elastically before fracture will likely remain intact more than a material that fractures at a much lower tensile strain. Thus, the use of tear strength to distinguish the resistance of an impression material to tearing is not very meaningful. The new value, which is called the tear energy, tear energy is calculated by dividing the force (F) needed to keep the crack propagating divided by $t/(1+\lambda)$, where t is the thickness of the specimen and λ is the extension ratio (Figure 8-13). The calculated value also has the unit of N/m, which can be converted to $N{\cdot}m/m^2$ and then J/m^2, a unit of energy per unit area. The extension ratio equals the extended portion of the length (Δl) at the end of the test divided by the original length of the specimen (l).

Polysulfide materials have the highest resistance to tearing. Therefore, thin sections of polysulfide impression material are less likely to tear than polyether or silicone impression materials of a similar thickness. However, because of their susceptibility to permanent distortion, polysulfide impressions may distort rather than tear. This presents a problem, since tearing can be seen immediately by carefully checking

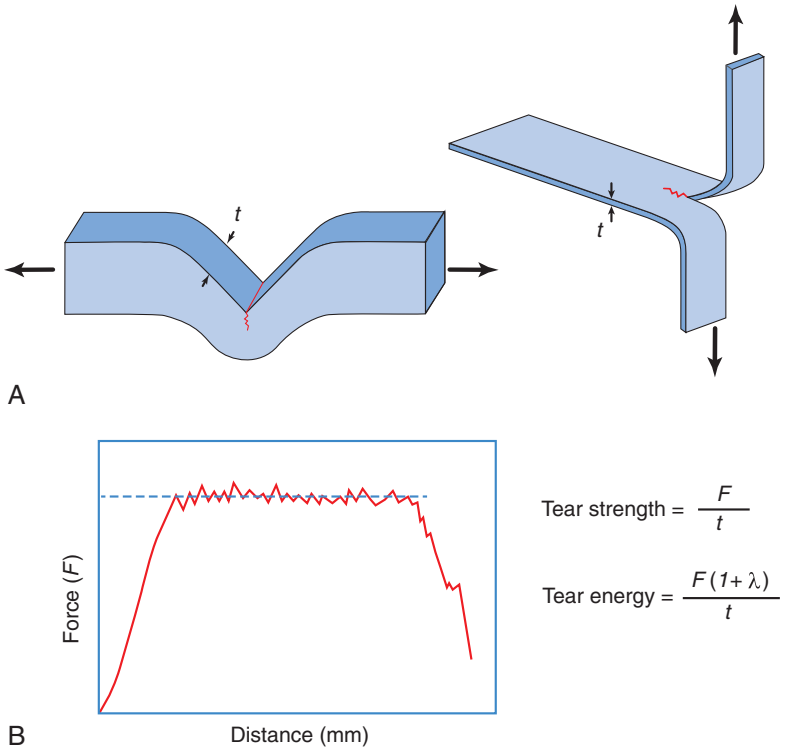


FIGURE 8-13 **A**, Two configurations of tear-strength test specimens: Die C or right-angle design such as described in the ASTM D624 Plastic Test Standard (*left*) and trouser design configuration (*right*). **B**, Force-distance curve of a typical tear test and calculation of tear strength and tear energy. The plateau of the curve (*dotted line*) indicates the force (*F*) needed for initiation and propagation of the crack. The thickness of the specimen is *t* and the extension ratio is λ, which equals the extended portion of the specimen length at the end of the test divided by the original length of the specimen.

the impression, whereas distortion cannot be detected by visual inspection. Thus, distortion can result in a metal or ceramic crown that does not seat completely. Because the strain rate influences tear resistance and permanent deformation, the impression should be strained rapidly for as short a time as possible to minimize adverse effects.

CRITICAL QUESTION

What are the six main causes of impression inaccuracy?

DIMENSIONAL STABILITY

It is important to distinguish between dimensional accuracy and dimensional stability. The former refers to the lack of dimensional change during curing and shortly after removal from the mouth. The latter refers to the lack of dimensional changes over time. Accuracy is the more important property when impressions are poured up immediately with a die material. This distinction is important because the two do not go hand in hand; materials may be accurate but not stable or inaccurate but stable.

There are six major sources of dimensional change: (1) polymerization shrinkage, (2) loss of a **condensation reaction** by-product (water or alcohol), (3) thermal contraction from oral temperature to room temperature, (4) absorption of water or disinfectant over a period of time, (5) incomplete recovery of deformation because of viscoelastic behavior, and (6) incomplete recovery because of plastic deformation. Dimensional changes during curing have been measured directly and indirectly using confined and freestanding

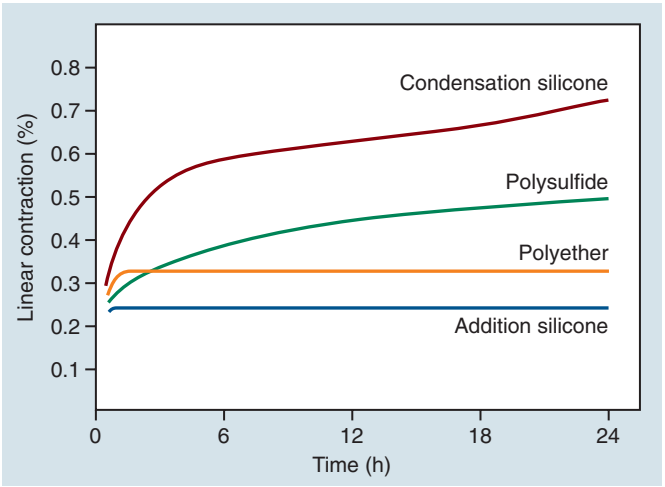


FIGURE 8-14 Representative linear contraction of four elastomeric impression materials.

specimens of the elastomers in various geometrical shapes. In ANSI/ADA Specification No. 19 (ISO 4823), a disk of the impression material is placed on a talc-covered glass plate. At the end of 24 hours, the contraction should not exceed 0.5% for type I and III materials, or 1.0% for a type II material. Thus, the measurement includes contraction associated with a thermal change (37 °C to 23 °C), polymerization shrinkage, and loss of volatile components.

Figure 8-14 shows the mean linear contraction for four elastomers using the method just described. It is evident that all materials change dimensionally over time. The change is

greater in magnitude for the polysulfide and condensation silicone materials than for the polyether and addition silicone elastomers. This result is expected because polysulfide and condensation silicone lose polymerization by-products, i.e., water, and alcohol, respectively.

If maximal accuracy is to be maintained with polysulfide and condensation silicone materials, the slurry mix for a stone die or cast should be poured immediately into the impression after it is removed from the mouth. *Immediately* is defined as within the first 30 minutes even when the putty-wash technique is used for silicone materials.

The stability of the addition silicone and polyether materials suggests that these impressions do not have to be poured with a gypsum product immediately. In fact, these impressions are often sent to the lab to be poured. It should be noted, however, that some later-generation polyethers are not as dimensionally stable as their predecessors; therefore, immediate pours may be needed. Research has shown that a cast produced from an addition silicone impression between 24 hours and 1 week was as accurate as a cast made in the first hour assuming that there was no effect associated with the formation of hydrogen bubbles. These materials exhibit the least amount of distortion from the loads imposed on the set material. Thus, multiple pouring of the impressions and removal of the casts will not alter the dimensional stability of the impression even though a substantial force is needed each time a cast is removed from the impression.

One variable that has a negative effect on the polyether impression is the absorption of water or fluids and the simultaneous leaching of the water-soluble plasticizer. Thus, the polyether impression should be stored in a dry (relative humidity below 50%), cool environment to maintain its accuracy and should never be left for protracted periods in disinfecting solutions.

? CRITICAL QUESTION

Why are hydrophilic materials potentially more susceptible to distortion during disinfection prior to being poured with a gypsum-forming product?

DISINFECTION

Condensation silicones, addition silicones, and polysulfides can be disinfected with all EPA-registered disinfectants without the loss of surface quality or accuracy if the disinfection time is short. The impressions should be immersed for the time specified for each disinfectant. After disinfection, the impression should be removed, rinsed, and poured with the gypsum product as soon as possible.

It is important to note that a long immersion time may cause the surfactant in the hydrophilic polyvinyl siloxane to leach out and render the impression less hydrophilic. The polyethers are also susceptible to dimensional change if immersed for a long time (more than 10 min) because of their pronounced hydrophilic nature, which tends to promote water absorption from the surroundings.

Table 8-4 shows a guide for selecting appropriate disinfection methods for all types of impressions that are transferred subsequently to a dental laboratory.

? CRITICAL QUESTION

How does the surfactant added to hydrophilize PVS affect the contact angle of water droplets during the setting and pouring of casts with gypsum?

WETTABILITY AND HYDROPHILIZATION

Contact angles of distilled water on set silicone impressions are approximately 100°, which makes this group of materials the most hydrophobic among all elastomeric impression

TABLE 8-4 Guide for the Selection of Appropriate Disinfection Methods for Impressions Transported to a Dental Laboratory

Material	Method	Recommended Disinfectant	Comments
Alginate	Immersion with caution Use only disinfectant for a short-term exposure time (<10 min for alginate)	Chlorine compounds or iodophors	Short-term glutaraldehyde has been shown to be acceptable, but time is inadequate for disinfection.
Agar			Do not immerse in alkaline glutaraldehyde!
Polysulfide and silicone	Immersion	Glutaraldehydes, chlorine compounds, iodophors, phenolics	Disinfectants requiring more than 30-min exposure times are not recommended.
Polyether	Immerse with caution Use disinfectant only for a short exposure time (<10 min)	Chlorine compounds or iodophors	ADA recommends any of the disinfectant classes; however, short-term exposures are essential to avoid distortion.
ZOE impression paste	Immersion preferred; spraying can be used for bite registrations	Glutaraldehydes or iodophors	Not compatible with chlorine compounds! Phenolic spray can be used.
Impression compound		Iodophors or chlorine compounds	Phenolic spray can be used.

materials. The use of a more hydrophobic impression material may lead to a high frequency of voids in the cast. It is possible to spray a surfactant on these hydrophobic impressions prior to pouring with gypsum mixtures. A nonionic surfactant such as the one based on a block copolymer of siloxane and ether groups may be added to the bulk of the material during the manufacturing process. The siloxane group is hydrophobic, and this property facilitates dispersion of the surfactant in the bulk of PVS. The ether group is hydrophilic and is oriented toward the surface when the surfactant migrates by diffusion to the surface region. This type of PVS is called a hydrophilized PVS.

In vitro studies of surface wettability of set impressions typically use distilled water as the probing liquid. The results confirm that there are significant reductions in contact angles of hydrophilized PVS relative their non-hydrophilized counterparts. Use of an aqueous solution saturated with $CaSO_4$ yields similar results. Examination of stone casts confirms that elastomers, which exhibit the least contact angle with water, also produce stone casts with fewer voids.

The use of optical tensiometry, which analyzes the shape of liquid drops on the surface using a video image, allows observation of contact angles of water droplets on freshly mixed impression materials in real time. Numerous studies have reported a decrease in water contact angles on silicones, hydrophilized PVS, and polyethers over the setting period. This decrease can be as much as 70° for hydrophilized PVS and less for polyether. Chemical analyses of water droplets show that they all acquire substances from their respective impression materials. For hydrophilized PVS, the water droplets may absorb a sufficient quantity of surfactant and become a liquid of lower surface tension. The lowering of surface tension makes water droplets spread wider on the surface of PVS, yielding lower contact angles. This observation leads to the hypothesis that hydrophilicity of the PVS has not changed, but the surface tension of the probing water has been reduced by the acquired surfactant. Some clinical observations seem to support this hypothesis, as there is no difference between non-hydrophilized and hydrophilized PVS with respect to the reproducibility of detail on wet surfaces. However, another clinical study reports that hydrophilized PVS yields a significantly higher proportion of void-free impressions than its non-hydrophilized counterpart. For polyethers, the substances acquired by the water droplets represent a low-molecular-weight compound associated with polyethers, and their effect on the surface tension of the water droplet is small. Thus, a smaller decrease in the contact angle is observed.

As soon as hydrophilized PVS encounters oral fluids during impression making, it begins to release surfactant to its surroundings. It is known that there is an adequate amount of surfactant trapped on the surface of set PVS impressions, thereby providing hydrophilicity for the pouring of gypsum dies. Whereas one might believe that the decrease of contact angle over the period of setting is equivalent to good wetting of the impression material on moist tooth surfaces, the clinical relevance remains unclear for two reasons. First, the decrease in contact angle may be attributed mainly to the lowering of surface tension of the water droplets by the surfactant, so that the actual improvement in the hydrophilicity of the impression may be much less significant than it appears. Second, there are conflicting clinical observations. This conflict is not surprising when one realizes that some materials contain very hydrophilic surfactants that are readily leached from the surface while others contain surfactants that are balanced in their hydrophilic-lipophilic properties, so that the lipophilic end remains buried near the surface while the hydrophilic chain is exposed on the surface. In the latter case very little leaching occurs and multiple pours are facilitated.

CRITICAL QUESTION

How can a torn impression material cause gingival inflammation?

BIOCOMPATIBILITY

The clinical relevance of tests for the assessment of the cytotoxicity of dental materials is widely recognized. Various types of tests are covered in ISO 10993-5, Biological Evaluation of Medical Devices: Tests for In Vitro Cytotoxicity. Comparing the cell cytotoxicity for different impression materials reveals that polysulfide materials result in the lowest cell death count and the set polyether impression material produces the highest cell cytotoxicity scores (Figure 8-15). Similar results are also observed in multiple exposure tests.

The most likely elastomer-induced biocompatibility problem occurs when a fragment of impression material is trapped in a patient's gingival sulcus. In fact, fragments of impression materials have been found in soft tissues, under the periosteum, in the spongy bone, and in the maxillary sinus. This can also occur in implant dentistry, particularly during second-stage implant surgery or during single-stage surgery. A foreign body of impression material is known to cause a severe gingival inflammation, which may be misdiagnosed as an adverse effect of the tooth preparation or cementation. If evidence of tearing is detected during careful visual inspection of the impression (Figure 8-12), it is important to examine the gingival sulcus immediately to remove any remnant of the impression or any other foreign body, such as a piece of retraction cord. The radiopacity of polysulfide materials is an advantage in these situations.

Some concerns exist about the hypersensitivity potential of the polyether catalyst system. Contact dermatitis from the polyether, especially as experienced by dental assistants, has been reported. In contrast, no cytotoxic effects have been reported clinically from exposure to polyether components, particularly the imine catalyst.

SHELF LIFE

Properly compounded impression material does not deteriorate appreciably in the tube or container before the expiration date when it is stored in a dry, cool environment. When one observes clear liquid being expressed along with the material, it is an indication of plasticizer segregation and is indicative

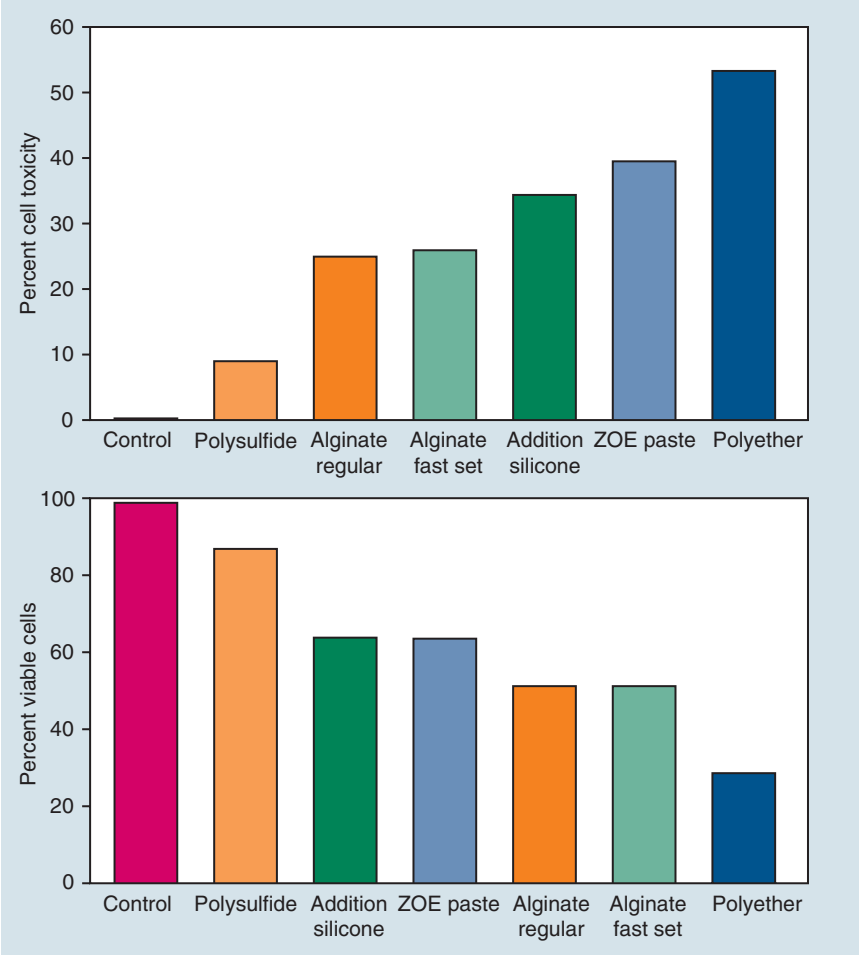


FIGURE 8-15 Results of a cytotoxicity test of impression materials. **A**, Graph of cell cytotoxicity shows that, after three days of incubation with Vero cells, all of the impression materials were cytotoxic to varying degrees. The relative cytotoxicity of each material is shown relative to the control. **B,** The graph of cell viability exhibits the relative percent of viable cells after being exposed to the impression materials. (Adapted from Sydiskis RK, Gerhardt DE: Cytotoxicity of impression materials. *J Prosthet Dent* 69:431, 1993.)

of manufacturing error or excessive temperature extremes during storage.

EFFECT OF MISHANDLING

The failure to produce an accurate epoxy or gypsum die or cast is more likely associated with an error in handling the impression material rather than a deficiency in the material properties. The common failures experienced with impression materials and their causes are summarized in Table 8-5. The comparative properties of elastomeric impression materials are listed in Table 8-6. A summary of the characteristics of the elastomeric impression materials is given in Table 8-7.

? CRITICAL QUESTION

What is the difference between a solution and a hydrocolloid?

HYDROCOLLOIDS

A **colloid** is a substance that is microscopically dispersed uniformly throughout another substance. This description appears to be similar to that of a solution. Contrary to the true solutions, which exist as a single phase, a colloidal system consists of two separate phases: the dispersed phase and the dispersion phase. If the dispersion phase of a colloidal system is water, it is called a hydrocolloid. The sizes of the colloid particles range from 1 to 200 nm. In this section the characteristics of the two hydrocolloids for impression making, agar and alginate, are described.

CHARACTERISTICS OF HYDROCOLLOIDS

During impression making, the material sets from a flowable state to a solid state. This change of state associated with hydrocolloids is called the sol-gel transformation. A sol is a colloidal dispersion of very small particles in a continuous liquid medium and a **gel** is a suspension that behaves like an elastic solid. If a hydrocolloid contains an adequate concentration of the dispersed phase, the sol, under certain conditions, may change to a gel. In the gel state, the dispersed phase forms agglomerates in the form of chains or fibrils, also called **micelles**. The fibrils may branch and intermesh to form a brush-heap structure, which can be envisioned as resembling the intermeshing of tree branches or twigs in a brush pile. The dispersion medium is held in the interstices between the fibrils by capillary attraction or adhesion.

AGAR (REVERSIBLE HYDROCOLLOID)

The physical change of agar from sol to gel is induced by lowering the temperature. The gel liquefies to a sol when it is heated to a temperature known as the liquefaction

TABLE 8-5 Common Failures Occurring with the Use of Elastomeric Impression Materials

Type of Failure	Causes
Rough or uneven impression surface	Incomplete polymerization caused by premature removal from the mouth, improper ratio or mixing of components, or presence of oil or other organic material, such as plaque, on the teeth
	For addition silicone, surface agents such as latex, that contaminate the material and inhibit polymerization
	Too rapid polymerization from high humidity or temperature
	Excessively high accelerator/base ratio with condensation silicone
Bubbles	Air incorporated during mixing
Irregularly shaped voids	Moisture or debris on surface of teeth
Rough or chalky stone cast	Inadequate cleaning of impression
	Excess water that is not blown off of the impression
	Excess wetting agent left on impression
	Premature removal of cast; improper powder/water ratio of stone
	Failure to delay pour of addition silicone that does not contain a palladium salt for at least 20 min
Distortion	Resin tray not aged sufficiently; still undergoing polymerization shrinkage
	Lack of adhesion of elastomer to the tray caused by not applying enough coats of adhesive, filling tray with material too soon after applying adhesive, or using incorrect adhesive
	Lack of mechanical retention to the impression tray
	Excessive bulk of material
	Insufficient relief for the reline material (if such technique is used)
	Development of elastic properties in the material before tray is fully seated
	Continued pressure against impression material that has developed elastic properties
	Movement of tray during polymerization
	Premature removal of impression from mouth
	Improper removal of impression from mouth
	Delayed pouring of the polysulfide or condensation silicone impression

TABLE 8-6 Comparative Properties of Elastomeric Impression Materials

Property	Polysulfide	Condensation Silicone	Addition Silicone	Polyether
Working time (min)	4–7	2.5–4	2–4	3
Setting time (min)	7–10	6–8	4–6.5	6
Tear strength (N/m)	2500–7000	2300–2600	1500–4300	1800–4800
Percent contraction (at 24 h)	0.40–0.45	0.38–0.60	0.14–0.17	0.19–0.24
Contact angle between set material and water (°)	82	98	98/53*	49
Hydrogen gas evolution (Y/N)**	N	N	Y†	N
Automatic mixing (Y/N)**	N	N	Y	Y
Custom tray (Y/N)**	Y	N	N	N
Unpleasant odor (Y/N)**	Y	N	N	N
Multiple casts (Y/N)**	N	N	Y	Y
Stiffness (value of 1 indicates greatest stiffness)‡	3	2 (1)	2 (1)	1 (2)
Distortion on removal (value of 1 indicates the greatest and 4 the least potential distortion)	1	2	4	3

*The lower contact angle resulted from testing of a hydrophilized PVS.
**(Y/N) stands for yes or no.
†A hydrogen absorber is often included to eliminate hydrogen gas evolution.
‡The numbers in the parentheses reflect the ranking when soft formulation of polyether impression material is considered.

TABLE 8-7 Characteristics of Elastomeric Impression Materials

Generic Type	Advantages	Disadvantages
Polysulfide	Long working time	Requires custom tray
	High tear resistance	Stretching leads to distortion
	Margins easily seen	Compatible with stone
	Moderate cost	Stains clothing
		Obnoxious odor
		Pour within 1 hour
Condensation silicone (putty wash)	Putty for custom tray	High polymerization shrinkage
	Clean and pleasant	Volatile by-product
	Good working time	Low tear strength
	Margins easily seen	Hydrophobic
		Pour immediately
Vinyl polysiloxane	One material	Hydrophobic
	Putty for custom tray	No flow if sulcus is moist
		Low tear strength
	Automix dispense	Putty displaces wash
	Clean and pleasant	Wash has low tear strength
	Margins easily seen	
	Ideally elastic	Putty too stiff
	Pour repeatedly	Putty and wash separate
	Stable: delay pour	Difficult to pour cast
Polyether	Fast-setting	Stiff, high modulus
	Clean	Bitter taste
	Automix dispense	Need to block undercuts
	Least hydrophobic of all elastomers	Absorbs water
		Leaches components
	Margins easily seen	High cost
	Good stability	
	Delay pour	
	Shelf life: 2 y	
Agar	Moist field OK	Requires special equipment
	Accurate and pleasant	Thermal discomfort
	Hydrophilic	Tears easily
	Low cost	Pour immediately
	Long shelf-life	Difficult to see margins and details
Alginate	Moist field OK	Not accurate/rough
	Clean and pleasant	Tears easily
	Hydrophilic	Pour immediately
	Low cost	Can retard setting of gypsum
	Long shelf-life	

temperature (70 °C to 100 °C). When the sol is cooled, it becomes a gel at a point known as the **gelation** temperature (between 37 °C and 50 °C). Thus, it is called a reversible hydrocolloid. The gelation temperature is critical for impression making. If it is too high, the heat from the sol may injure the oral tissues. Conversely, if the gelation temperature is too far below oral temperature, it will be impossible to make the impression because the sol will not covert to a gel.

TABLE 8-8 Composition of Commercial Reversible Hydrocolloid Impression Materials

Component	Function	Composition (%)
Agar	Brush-heap structure	13–17
Borate	Strength	0.2–0.5
Sulfate	Gypsum hardener	1.0–2.0
Wax, hard	Filler	0.5–1.0
Thixotropic materials	Thickener	0.3–0.5
Water	Reaction medium	Balance

Composition

Agar, a polysaccharide extracted from certain types of seaweed, is the main active ingredient in the material, while water is the major constituent in the agar impression material (Table 8-8). A small percentage of borax is added to strengthen the gel. Since borax is a potent retarder for the setting of gypsum, an accelerator such as potassium sulfate is added to counteract the effect of borax. Other fillers—such as diatomaceous earth, clay, silica, wax, rubber, and similar inert powders—are used to control strength, viscosity, and rigidity, as previously discussed for elastomeric impression materials. Thymol and glycerin may also be added as a bactericidal agent and plasticizer, respectively. Pigments and flavors are usually included as well. The hydrocolloid is usually supplied in two forms, syringe material and tray material.

? CRITICAL QUESTION

What is the purpose of having three water tanks set at three different temperatures in a conditioning unit for agar impression materials?

Making the Agar Impression

This process requires a three-compartment conditioning unit (Figure 8-16) for the agar tray material that allows liquefaction, storage, and tempering, while the agar syringe material is used only in the liquefaction and storage compartments.

The first step in impression making is to liquefy the hydrocolloid gel in the tube in boiling water at 100 °C for a minimum of 10 minutes. The tube is then placed in a storage bath at 65 °C to retain the sol condition until it is needed. For the immediate preparation step, the impression tray is filled with hydrocolloid sol from the tube taken from the storage bath, a gauze pad is placed over the top of the tray material, and the tray is placed in the water-filled tempering compartment (at about 45 °C) of the conditioning unit. The tempering time is 3 to 10 min, just sufficient to ensure that all the material has reached a lower temperature (55 °C or less). In any case, the loaded tray should never be left in this bath for more than 10 minutes as partial gelation can occur, thereby making the material unusable.

Just before tempering the tray material is completed, the syringe material is taken directly from the storage compartment and applied to the prepared teeth. The syringe material is never tempered since it must be maintained in a fluid state to enhance adaptation to the tissues. Normally, the temperature of the syringe material is cooled sufficiently, as it is extruded, so it is comfortable for the patient. The syringe material is first applied to the base of the preparation; then the remainder of the prepared tooth is covered. The tip of the syringe is held close to the tooth, and it remains embedded below the surface of the syringe material to prevent entrapment of air bubbles. The water-soaked outer layer of the hydrocolloid-loaded tray and the gauze covering the tray impression material are removed to ensure firm bonding to the syringe hydrocolloid. The tray is immediately brought into position, seated with light pressure, and held with a very light force. Too much pressure may displace the syringed agar sol from the tooth and distort the impression.

Gelation is accelerated by circulating cool water (approximately 18 °C to 21 °C) through the tray for 3 to 5 min. During the gelation process, the tray must be held in the mouth until gelation has proceeded to a point at which the gel strength is sufficient to resist deformation or fracture.

As discussed in the section on elastomeric impression materials above, hydrocolloid materials exhibit viscoelastic behavior; therefore, it is necessary to remove the impression with a snap and not to tease it out. Any twisting or flexure should be avoided. Properly done, the resulting impression will accurately reproduce the dimensions and details of hard and soft tissues.

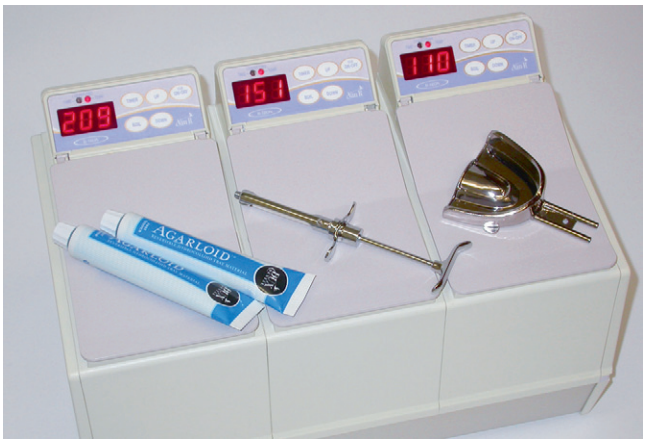


FIGURE 8-16 Conditioning unit for agar impression materials. The three compartments are used for liquefying the material (*left*), storing after boiling (*middle*), and tempering the tray hydrocolloid (*right*). The number on the display shows the temperature setting in °F. Also shown in the figure are the tray hydrocolloid, a syringe for injecting hydrocolloids, and an impression tray. Note the two tubes are extending out from the handle of the tray for water circulation.

Distortion during Gelation

Some contraction occurs because of the physical change in the hydrocolloid transformation from a sol to a gel. If the material is held rigidly in the tray, the impression material will shrink toward the center of its mass, thereby creating larger dies. Since the sol is a poor thermal conductor, rapid cooling may cause a concentration of stress near the tray where the gelation first takes place. Consequently, water at approximately 20 °C is more suitable for cooling the impression than is ice water.

ALGINATE (IRREVERSIBLE HYDROCOLLOID)

The setting of alginate hydrocolloid is a process of cross-linking alginic acids with calcium ions. The alginic acid, which is extracted from certain brown seaweed, is a linear copolymer of β-D-mannuronic acid and α-L-guluronic acid (Figure 8-17). Mannuronic and guluronic acids are epimers. It is known that the block structure within the alginic acid can vary significantly. Alginates with higher guluronic acid levels normally show a stronger interaction with calcium, and hence, yield greater gel strength. For impression-making purposes, the alginate is richer in mannuronic acid.

Composition

The chief active ingredient in the alginate impression materials is one of the soluble alginates, such as sodium, potassium, or triethanolamine alginate. Table 8-9 shows a formula for the powder component of an alginate impression material. The diatomaceous earth acts as a filler to increase the strength and stiffness of the alginate gel. It also produces a smooth texture and ensures the formation of a firm gel surface that is not

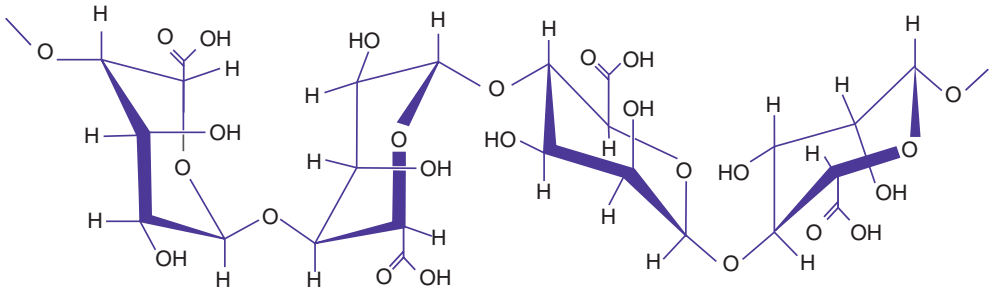


FIGURE 8-17 Structural formula of alginic acid. Alginic acid is a linear copolymer with homopolymeric blocks of β-D-mannuronic acid and its epimer α-L-guluronic acid covalently link together in different sequences or blocks.

$$K_{2n} - \text{Alginate} + n\ Ca\ SO_4 \longrightarrow n\ K_2SO_4 + Ca_n - (\text{Alginate})_2 \quad \text{(A)}$$

$$2\ Na_3PO_4 + 3\ CaSO_4 \longrightarrow Ca_3(PO_4)_2 + 3\ Na_2SO_4 \quad \text{(B)}$$

FIGURE 8-18 **A**, Setting reaction of alginate. **B**, Controlling setting time by limiting the availability of calcium ions.

TABLE 8-9 Powder Composition for an Alginate Impression Material

Component	Function	Weight Percentage
Potassium alginate	Soluble alginate	15
Calcium sulfate	Reactor	16
Zinc oxide	Filler particles	4
Potassium titanium fluoride	Gypsum hardener	3
Diatomaceous earth	Filler particles	60
Sodium phosphate	Retarder	2

tacky. Zinc oxide also acts as filler and has some influence on the physical properties and setting time of the gel. Calcium sulfate dihydrate is a reactor providing calcium ions that cross-link the alginate sol. A retarder is added to control the setting time. A fluoride, such as potassium titanium fluoride, is added as an accelerator for the setting of the stone to ensure a hard, dense cast surface when the stone is poured in the impression. This fluoride is also called a surface hardener.

When powder in the alginate can is fluffed to break loose the particles, the diatomaceous earth, which is made up of fine porous silica particles, will become airborne when the lid is removed. Long-term exposure through inhalation of these fine silica particles can cause silicosis and pulmonary hypersensitivity. In an effort to reduce the dust encountered after tumbling, manufacturers have introduced a "dustless" alginate in which they have incorporated polyethylene glycol or polypropylene glycol on the alginate powder to agglomerate the particles. This causes the powder to become denser and less able to become airborne. Color indicators have been added in some formulations to reveal the stage of the setting reaction. This is to assist the operator in deciding when to proceed to the next step of impression making.

Two-paste alginate impression materials are also available; these are known as modified alginates. One paste contains a sol of alginate, fillers, retarder, and other ingredients like glycols and dextrose. The other paste consists of gypsum dihydrate, fillers, retarder, glycerol or glycols, gypsum surface modifier, and some silicone oil.

? CRITICAL QUESTION

How does the retarder optimize the working time of alginate impression material?

Gelation Process

The typical sol-gel reaction can be described simply as a reaction of soluble alginate with calcium ions from calcium sulfate

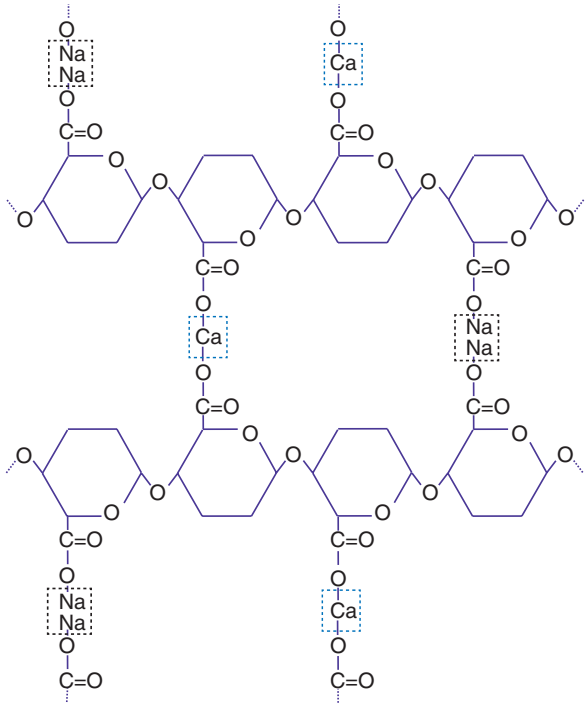


FIGURE 8-19 Schematic illustration of sodium alginate cross-linked with calcium ions. The base molecules represent the sodium salt of alginic acid, in which hydrogen atoms of carboxyl groups are replaced by sodium atoms. With the exception of polar groups, all side chains have been omitted for simplification.

and the formation of an insoluble calcium alginate (Figure 8-18, *A*). Structurally, calcium ions replace the sodium or potassium ions of two adjacent molecules to produce a cross-linked complex or polymer network (Figure 8-19). The production of the calcium alginate is so rapid that it does not allow sufficient working time. A water-soluble phosphate salt (e.g., trisodium phosphate) is added to the composition as a retarder to extend the working time. The strategy is that the calcium ions will react preferentially with the phosphate ions in the solution (Figure 8-18, *B*). Thus, the rapid reaction between calcium ions and the soluble alginate is deferred until phosphate ions from trisodium phosphate are exhausted. The amount of retarder is adjusted to provide the proper setting time. A similar gelation process is expected with the modified alginate product.

Controlling Setting Time

A slight modification in the W/P ratio or the mixing time can have marked effects on two important properties of the gel, tear strength, and elasticity; thus, the setting time is best regulated by the amount of retarder added during the manufacturing process. Usually, the manufacturers make

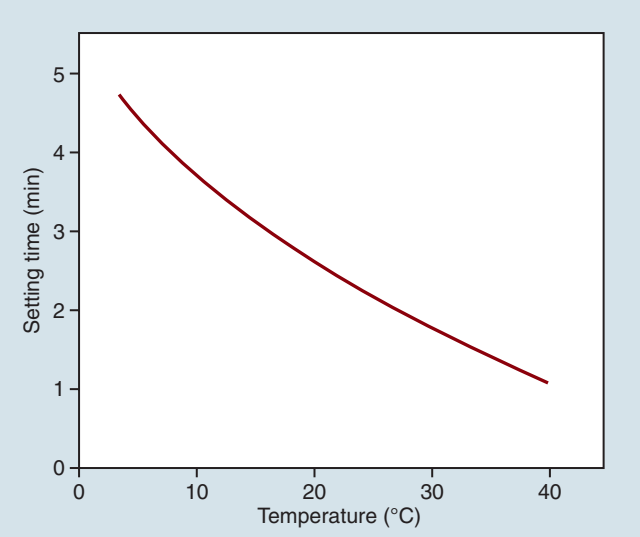


FIGURE 8-20 Effect of water temperature on the setting time of an alginate impression material.

both fast-setting alginate (1.5 to 3 min) and normal-setting alginate (3 to 4.5 min) to give clinicians a choice of the materials that best suit their working style.

Clinicians, however, can safely influence the setting time by altering the temperature of the water. It is evident from Figure 8-20 that the higher the temperature, the shorter is the setting time. The temperature of the mixing water should be controlled carefully within a degree or two of a standard temperature, usually 20 °C, so that a constant and reliable setting time can be obtained. In hot weather, special precautions should be taken to provide cool water for mixing so that premature gelation does not occur. It may even be necessary to precool the mixing bowl and spatula, especially when small amounts of impression material are to be mixed.

Tap water naturally contains certain levels of metallic ions, primarily calcium and magnesium. It has been shown that compared with distilled water for mixing of alginate impression material, the use of tap water with a high hardness may accelerate the setting of the alginate. If one observes that the setting time has decreased in a new office or clinic location, the effect of the hardness of the tap water on setting time should be considered as a possible cause.

? CRITICAL QUESTION

Why is it especially important to add water to the rubber mixing bowl before adding the powder when one is mixing a fast-setting alginate impression material?

Preparation of Alginate Impression Materials

A proper mixture of water and powder is essential. The measured powder is added slowly to the premeasured water that has already been poured into a clean rubber bowl. The powder is incorporated into the water by carefully mixing with a metal or plastic spatula that is sufficiently flexible to adapt well to the wall of the mixing bowl. If the powder is placed in the mixing bowl first, penetration of the water to the bottom of the bowl is inhibited and a longer mixing time may be required to ensure a homogeneous mix. Care should be taken to avoid incorporating excessive air into the mix. A vigorous figure-eight stropping motion is best, with the mix being wiped or stropped against the side of the rubber-mixing bowl to express air bubbles. All of the powder must be incorporated thoroughly in the water.

TABLE 8-10 Compressive Strength of an Alginate Gel as a Function of Gelation Time

Time from Gelation (min)	Compressive Strength (kPa)
0	330
4	770
8	810
12	710
16	740

The mixing time is particularly important; 45 s to 1 min is generally sufficient, depending on the brand and type of alginate (fast set or regular set). The instructions on the package should be followed precisely for the mixing time, working time, and setting time for the material one is using. The result should be a smooth, creamy mixture that does not readily drip off the spatula when it is raised from the bowl. Several mechanical mixing devices are available for the alginate materials. They include a rotating mixing bowl, a mechanical mixer with time-control unit, a vacuum mixer for powder/water mixing, and a dynamic mechanical mixer, similar to the one for elastomers (Figure 8-8, *D*) for two-paste alginate products. Their principal benefits are convenience, speed, and the reduction of human error.

Clean equipment is important because many of the problems and related failures are attributable to dirty or contaminated mixing or handling devices. Contaminants, such as small amounts of gypsum left in the bowl from a previous mix of plaster or stone, can accelerate the set. It is best to use separate bowls for mixing alginate and stone.

Ideally, the powder should be weighed and not measured volumetrically by means of a scoop. However, unless a grossly incorrect or inconsistent method is used for scooping the powder, the variations in individual mixes should have no measurable effect on the physical properties.

Making the Alginate Impression

It is imperative that the impression be retained on the tray so that it can be withdrawn from the perimeter of the teeth. Therefore, a perforated metal tray is preferred. If a plastic tray or a metal rim-lock tray is selected, a thin layer of alginate tray adhesive should be applied and allowed to dry completely before mixing and loading the alginate in the tray. Alginate is a weak material; therefore, a sufficient bulk of material is needed. The thickness of the alginate impression between the tray and the tissues should be at least 3 mm.

As shown in Table 8-10, the compressive strength of alginate doubles during the first 4 min after gelation, but it does

not increase appreciably thereafter. Most alginate materials improve in elasticity over time; this minimizes distortion of the material during impression removal, thus permitting superior reproduction of undercut areas. Data clearly indicate that the alginate impression should not be removed from the mouth for at least 3 min after gelation has occurred. It is possible to leave an alginate impression in the mouth too long. With certain alginates, it has been shown that if the impression is held for 6 to 7 min after gelation rather than 3 min, significant distortion may result.

Since alginate is a viscoelastic material, its tear strength is increased when the impression is removed along a vertical path with a snap. The speed of removal must be a compromise between a rapid movement and a slower rate that is more comfortable for the patient. Usually an alginate impression does not adhere to the oral tissues as well as some of the elastomers do, so it is easier to remove the alginate impression rapidly. However, it is always best to avoid torquing or twisting the impression in an effort to remove it quickly. Specifically, the handle should be used minimally during breaking of the air seal ("suction") or removal of the tray from the teeth.

Strength

Manufacturers' directions supplied with the product should be followed in all respects. Any deviation from the instructions can have adverse effects on the gel strength. For example, if too much or too little water is used in mixing, the final gel will be weakened, making it less elastic. Insufficient spatulation results in failure of the ingredients to dissolve sufficiently so that the chemical reactions can proceed uniformly throughout the mass. Overmixing breaks up the formation of the calcium alginate network and reduces its strength.

Shelf Life

Two major factors that affect the shelf life of alginate impression materials are storage temperature and moisture contamination from ambient air. The alginate impression powder can be purchased in individually sealed bags or in bulk form in a can. The individual bags are preferred since there is less chance for contamination during storage and the correct water/powder ratio is ensured. Nevertheless, the bulk form in a can is by far the most popular. If the bulk powder form of alginate is used, the lid should be firmly replaced on the container as soon as possible after dispensing the powder so that moisture contamination is minimized.

An expiration date under a stated condition of storage should be clearly identified by the manufacturer on each package. It is best not to stock more than a year's supply in the dental office. The material should be stored in a cool, dry environment.

PROPERTIES OF HYDROCOLLOID IMPRESSION MATERIALS

The quality of a stone cast depends on the properties of the hydrocolloid impressions before pouring and the potential interaction between gypsum and alginate during setting of the gypsum. In this section, details on dimensional stability, gypsum/hydrocolloid interaction, accuracy, disinfection, and effects of mishandling are described.

? CRITICAL QUESTION

How can distortion of a hydrocolloid impression be minimized during storage?

Dimensional Stability

Once the hydrocolloid impression is removed from the mouth and exposed to air at room temperature, some shrinkage associated with **syneresis** and evaporation will occur. Conversely, if the impression is immersed in water, swelling caused by **imbibition** can occur. Figure 8-21 shows that the material has shrunk in air and excessive expansion has occurred during subsequent imbibition.

The storage medium, such as 2% potassium sulfate solution, or 100% relative humidity in a storage chamber, is suggested to reduce the dimensional change of agar impressions. Results obtained for impressions made from one agar hydrocolloid product stored in several media are given in Figure 8-22. These results are typical; they indicate that 100% relative humidity is the best storage environment to preserve the normal water content of the impression.

Thermal changes also contribute to dimensional change. With alginates, impressions shrink slightly because of the

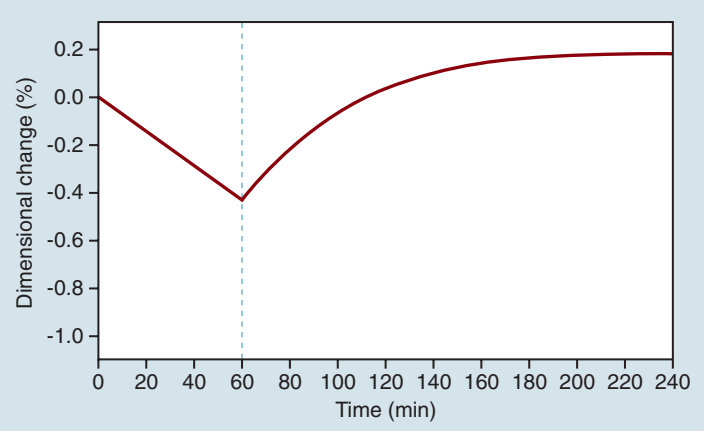


FIGURE 8-21 Linear contraction of a representative reversible hydrocolloid in air (31% to 42% relative humidity) within the initial and subsequent expansions in water. The dashed line indicates the start of water immersion.

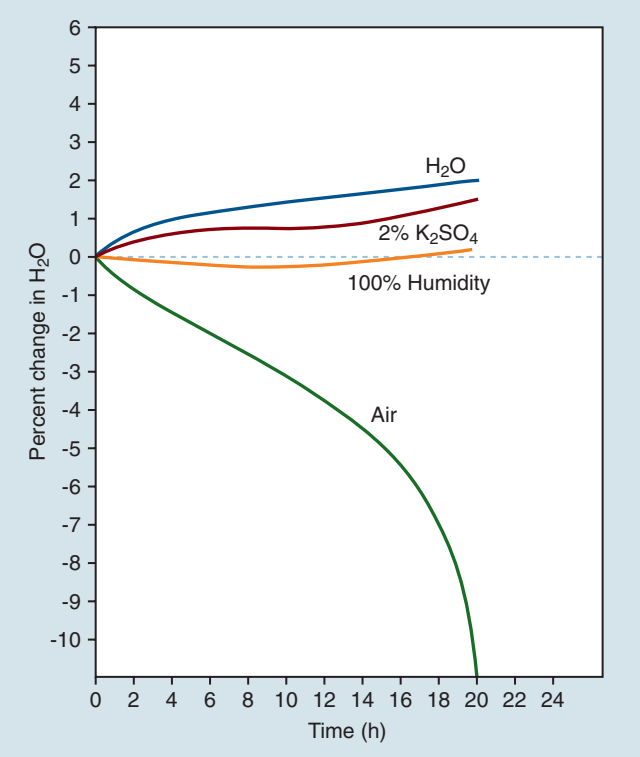


FIGURE 8-22 Percent change in water content according to weight of an agar impression material in various storage media. At 100% relative humidity, the percent change is minimal.

thermal differential between mouth temperature (37 °C) and room temperature (23 °C). The agar hydrocolloids experience a temperature shift in the opposite direction, from the chilled water-cooled tray (15 °C) to the warmer room temperature. Even this slight change can cause the impression to expand and become less accurate.

If pouring the impression must be delayed, it should be rinsed in tap water, disinfected, wrapped in a surgical paper towel, saturated with water, and placed in a sealed plastic bag or humidor.

CRITICAL QUESTION

Why do both agar and alginate include a gypsum hardener and how does it function?

Compatibility with Gypsum

Agar impression material contains borax, which is a known retarder for setting of gypsum products. The gelation process of alginate impressions produces not only insoluble calcium alginate but also sodium sulfate, which is a gypsum-setting accelerator at low concentration, but becomes a retarder at a higher concentration. In addition, polysaccharide also inhibits the setting of gypsum. Because of retardation, the surfaces of the gypsum models prepared from hydrocolloid may be too soft for use as dies or casts.

The deficiency of gypsum setting can be overcome in two ways: (1) by immersing the agar impression in a solution containing a gypsum accelerator, such as 2% potassium sulfate solution, prior to pouring the impression with the gypsum-forming product or (2) by incorporating a gypsum surface hardener in the material, such as the sulfate used in the formulation for agar hydrocolloid (Table 8-8) and the potassium titanium fluoride used in alginate (Table 8-9). The solubility of potassium titanium fluoride is about 1.3 g per 100 mL of water at 20 °C. The fluoride on the surface of alginate will form fine calcium fluoride precipitates with the calcium from the gypsum. Fine calcium fluoride particles become nuclei that accelerate the setting of gypsum.

A rough stone surface will result if excess rinsing water has collected on the surface of the impression at the time of pouring the stone mixture. A dried gel surface, on the other hand, will result in its adherence to the surface of the cast, which can result in tearing upon its removal. The surface of the impression should be shiny but with no visible water film or droplets at the time of pouring. After the impression has been filled with stone, somewhat superior stone surfaces may be obtained if the impression is placed in a humidor while the stone hardens.

The stone cast or die should be kept in contact with the impression for a minimum of 30 min, preferably for 60 min, before the impression is separated from the cast. A longer time may be needed for slow-setting gypsum. It is wise to separate the cast from the impression within a reasonable time so that desiccation of the hydrocolloid does not occur, thereby avoiding abrasion of the gypsum cast during its removal.

CRITICAL QUESTION

What is the optimal method for disinfecting an alginate hydrocolloid impression without causing significant distortion or degradation?

Disinfection

Since the hydrocolloid impression must be poured within a short time after removal from the mouth, the disinfection procedure should be relatively rapid to prevent a dimensional change. The current protocol for disinfecting hydrocolloid impressions recommended by the Centers for Disease Control and Prevention is to use household bleach (1-to-10 dilution), iodophors, or synthetic phenols as disinfectants. After the impression has been rinsed thoroughly, the disinfectant can be sprayed liberally on the exposed surface. The impression is then immediately wrapped in a disinfectant-soaked paper towel and placed in a sealed plastic bag for 10 minutes. Finally, the wrapped impression is removed from the bag, unwrapped, rinsed, and shaken to remove excess water. The impression is then poured with the stone of choice. An alternative disinfection method is by immersion, but this should not exceed 10 minutes (Table 8-4).

Accuracy

Agar is among the most accurate of impression materials. Most alginate impressions are not capable of reproducing the finer details observed in impressions with other elastomeric impression materials. Nevertheless, alginate materials are

sufficiently accurate that they can be used to make impressions for removable partial dentures.

Effects of Mishandling

Common causes of failures encountered with reversible and irreversible hydrocolloid impression materials are summarized in Table 8-11. See Table 8-7 for a summary of the characteristics of the hydrocolloids.

? CRITICAL QUESTION

What is the principle that makes the combined agar-alginate technique effective?

LAMINATE TECHNIQUE (ALGINATE-AGAR METHOD)

A modification of the traditional agar procedure is the combined agar-alginate technique. The agar in the tray is replaced with a mix of chilled alginate that bonds to the agar expressed from a syringe. The alginate gels by a chemical reaction, whereas the agar gels by means of contact with the cool alginate rather than with the water circulating through the tray. Since it is the agar, not the alginate, that contacts the prepared teeth, maximal detail is reproduced. Because only the syringe material needs to be heated, equipment cost is lower and less preparation time is required. The main disadvantages of this technique are as follows: (1) the bond between the agar and the alginate is not always sound; (2) the higher viscosity of the alginate material displaces the agar hydrocolloid during seating; and (3) the dimensional inaccuracy of the alginate hydrocolloid limits its use to single units. To address the bonding issue, ISO 13716 (Dentistry—Reversible-irreversible hydrocolloid impression material systems) requires that the bond between the two materials under tensile stress should be in excess of 50 kPa. Nevertheless, this laminate technique is the most cost-effective way of producing an impression with adequate detail.

DUPLICATING MATERIALS

Both types of hydrocolloids are used in the dental laboratory to duplicate dental casts or models for the construction of prosthetic appliances and orthodontic models. Agar hydrocolloid is more popular in the lab because it can be used many times. In addition, with intermittent stirring, agar hydrocolloid can be kept in a liquid form for 1 or 2 weeks at a constant pouring temperature. These factors make the cost of reversible impression materials quite reasonable.

The hydrocolloid-type duplicating materials have the same composition as the impression materials but their water content is higher. Consequently, the agar or alginate content is lower, which influences their compressive strength and percent permanent set. These property requirements are

TABLE 8-11 Common Causes of Failed Hydrocolloid Impressions

	CAUSES	
Effect	**Agar**	**Alginate**
Grainy material	Inadequate boiling	Improper mixing
	Storage temperature too low	Prolonged mixing
	Storage time too long	Excessive gelation
		Water/powder ratio too low
Separation of syringe materials	Water-soaked tray material surface not removed material	Not applicable
	Premature gelation of either material	
Tearing	Inadequate bulk	Inadequate bulk
	Premature removal from mouth	Moisture contamination
	Syringe material partially gelled when tray was seated	Premature removal from mouth
		Prolonged mixing
External bubbles	Gelation of syringe material, preventing flow	Undue gelation preventing flow
		Air incorporated during mixing
Irregularly shaped voids	Material too cold	Moisture or debris on tissue
Rough or chalky stone model	Inadequate cleansing of impression	Inadequate cleaning of impression
	Excess water or hardening solution left in the impression	Excess water left in impression
	Premature removal of die	Premature removal of the impression
	Improper manipulation of stone	Model left in impression too long
	Air drying of the impression before pouring	Improper manipulation of stone
Distortion	Impression not poured within 30 min	Impression not poured immediately
	Movement of tray during gelation	Movement of tray during gelation
	Premature removal from mouth	Premature removal from mouth
	Improper removal from mouth	Improper removal from mouth
	Use of ice water during initial stages of gelation	

identified in ANSI/ADA Specification No. 20 (ISO 14356; Dentistry—Duplicating material).

INELASTIC IMPRESSION MATERIALS

Inelastic impression materials exhibit an insignificant amount of elastic deformation when they are subjected to bending or tensile stresses. In addition, they fracture without exhibiting any plastic deformation if the stress from applied pressure exceeds their tensile, shear, or compressive strength values. These materials include impression plaster, impression compound, and ZOE impression paste. Because of their inability to sustain a substantial amount of elastic deformation without fracture, their use in dental impression making is limited.

CRITICAL QUESTION

Which properties of impression plaster make it attractive for making impressions associated with multiple-unit implants?

IMPRESSION PLASTER

Impression plaster is a β-calcium sulfate hemihydrate used at a water/powder ratio of approximately 0.5 to 0.6. Its fluidity makes it suitable for making impressions of soft tissues in the uncompressed state, a characteristic of mucostatic impression material. Because of its rigidity, the use of impression plaster has been suggested for making preliminary impressions or splinting transfer coping utilized to produce long-span implant-supported prostheses.

Composition

To make plaster a suitable impression material, the expansion and the setting times should be controlled by incorporating compounds designed to mediate the handling properties. Potassium sulfate is added as an anti-setting expansion agent to reduce the setting expansion and a retarder like borax is added to the powder to balance the setting acceleration caused by the potassium sulfate and to bring the setting time under control. A pigment, such as alizarin red, may be added to make a clear distinction between the impression and the model after casting of the model. As an alternative, an anti-expansion solution containing potassium sulfate, borax, and pigment may be used with a standard white plaster.

Manipulation

Because freshly mixed plaster is too fluid to be retained in a stock tray, a custom tray can be constructed using a 1- to 1.5-mm spacer with acrylic resin or shellac. Preliminary impressions can be made with dental compound, and impression plaster can be used as the wash material (discussed further on, with impression compounds). The technique for inserting the impression into the mouth involves "puddling" the impression into place. With the remaining plaster in the tray, the tray is seated in a single movement. Then the tray is gently moved from side to side and anteroposteriorly to take advantage of the fluidity of the material. The hemihydrate particles are capable of absorbing moisture from the surface of the oral soft tissues, allowing intimate contact between the impression material and the tissues. In view of the fluidity of the material, the resulting impression may be difficult to remove.

The plaster impression material is very brittle and fractures easily. When the impression involves an undercut area, it is necessary to fracture the impression to facilitate removal from the mouth. The fragments are then reconstructed to form the completed impression.

Long, narrow strips of wax can be adapted around the periphery of the impression. This is called beading. The impression is then coated with a thin layer of separating medium and cast in fresh plaster; otherwise, separation would be impossible. The beading provides a clear indication of where the impression ends, which prevents overtrimming and overextension. Disinfection of a plaster impression can be achieved with a 10-min soak in sodium hypochlorite solution, as described previously.

Impression making associated with implants requires the use of square direct or tapered indirect transfer copings for the transfer of implant positions before fabrication of the prosthesis. For multiple-unit impressions, the direct technique may use splinted or nonsplinted implant transfer copings. The materials used to splint copings can be resin composite, plaster, or acrylic resin with or without reinforcement. The results of published studies are inconclusive as to whether the impression copings should be splinted or not. One study reports that, in a case of no splinting, the use of impression plaster resulted in less expansion of the cast but more variance and less predictability relative to a polyether impression material.

IMPRESSION COMPOUND

Impression compound, also called modeling plastic, is a thermoplastic material supplied in the form of sheets and sticks. There are two types of impression compounds available. Type I is a lower-fusing material for making impressions in the oral cavity; it may be supplied in either sheet or stick form (Figure 8-23). Type II is a higher-fusing material, also called

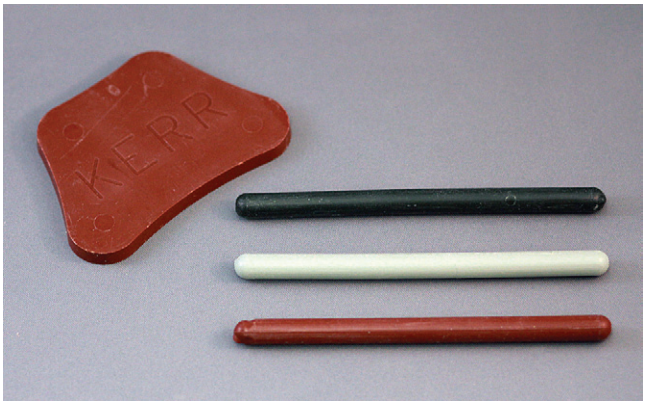


FIGURE 8-23 Typical type I cake-and-stick configurations of commercial impression compound. The melting temperatures are soft green, 50.0 °C to 51.1 °C; gray, 53.3 °C to 54.4 °C; and red, 54.4 °C to 55.6 °C.

tray compound, used for forming trays to be used in the oral cavity.

An impression of soft tissue is obtained with tray compound. This impression is referred to as the primary impression. It is then used as a tray to support a thin layer of a second impression material, which is to be placed against the tissues. This impression is known as the secondary impression. Secondary impressions may also be made with a ZOE wash paste, hydrocolloid, impression plaster, or elastomer. The other common application of compound is for border molding of an acrylic custom tray during fitting of the tray.

Composition

In general, compounds are composed of a mixture of waxes, thermoplastic resins, filler, and a coloring agent. Shellac, stearic acid, and gutta-percha are added to improve plasticity and workability. The waxes or resins in the impression compound are the principal ingredients of the matrix. Filler is added to increase the viscosity at temperatures above that of the mouth and to increase the rigidity of the compound at room temperature.

CRITICAL QUESTION

Why does impression compound material require a slow heating process to be converted to a plastic state?

Manipulation

Softening by heat is a prerequisite for the use of compounds. Their utilities are dictated by their responses to temperature changes in the surrounding environment. The **fusion temperature** of the compound corresponds to a definite reduction in plasticity of the material during cooling. Above this temperature, the material remains plastic while the impression is being made. Once the impression tray is seated, it should be held gently (passively) in position until the impression cools below the fusion temperature. Under no circumstances should the impression be disturbed or removed until it reaches oral temperature.

The thermal conductivity of these materials is very low, indicating the need to allow an extended time to achieve thorough cooling and heating of the compound. The material should be uniformly soft at the time it is placed in the tray and thoroughly cooled in the tray before the impression is withdrawn from the mouth. Cold water can be sprayed on the tray while it is in the mouth until the compound is thoroughly hardened prior to removal of the impression tray. Failure to attain a complete hardening of the material before withdrawing the impression can result in a significant distortion of the impression by relaxation.

A compound stick may be softened over a flame, but the sheet should be immersed in warm water to ensure uniform softening of the material. When a direct flame is used, the compound should not be allowed to boil or ignite so that the constituents are volatilized. Prolonged immersion or overheating in the water bath is not indicated; the compound may become brittle and grainy if some of the low-molecular-weight ingredients leach out of the material. Softening of the compound in a warm water bath is the method recommended for separating the cast from a compound impression after the stone sets.

Dimensional Stability

Relaxation of the impression compound can occur in a comparatively short time, especially with an increase in temperature. The result is warping or distortion of the impression. The safest method of minimizing such distortion is to allow thorough cooling of the impression before removal from the mouth and to construct the cast or die as soon as possible after the impression has been obtained—at least within the first hour.

Disinfection

The recommended disinfectant solution for the compound is 2% alkaline glutaraldehyde solution. The impressions should be immersed in this solution for the required time, rinsed, and poured immediately (Table 8-4).

CRITICAL QUESTION

Why does ZOE set faster in a humid environment?

ZINC OXIDE–EUGENOL (ZOE) IMPRESSION PASTE

The reaction between zinc oxide and eugenol yields a relatively hard mass that has been involved in a wide range of applications in dentistry, including use as an impression material for edentulous mouths, a surgical dressing, bite registration paste, temporary filling material, root canal filling material, cementing medium, and temporary relining material for dentures.

Composition and Setting

ZOE impression pastes are dispensed as two separate pastes. A typical formula is shown in Table 8-12. One tube contains zinc oxide and vegetable or mineral oil; the other contains eugenol and rosin. The vegetable or mineral oil acts as a

TABLE 8-12 Composition of a Zinc Oxide–Eugenol Impression Paste

Components	Percentage
Tube No. 1 (base)	
Zinc oxide (French-processed or USP)	87
Fixed vegetable or mineral oil	13
Tube No. 2 (accelerator)	
Oil of cloves or eugenol	12
Gum or polymerized rosin	50
Filler (silica type)	20
Lanolin	3
Resinous balsam	10
Accelerator solution ($CaCl_2$) and color	5

plasticizer and aids in offsetting the action of the eugenol as an irritant.

Oil of cloves, which contains 70% to 85% eugenol, is sometimes used because it produces less of a burning sensation when it contacts the patient's soft tissues. The addition of rosin to the paste in the second tube facilitates the speed of the reaction and yields a smoother, more homogeneous product. Canada balsam and Peru balsam are often used to increase flow and improve mixing properties. If the mixed paste is too thin or lacks body before it sets, a filler (such as a wax) or inert powder (such as kaolin, talc, or diatomaceous earth) may be added to one or both of the original pastes.

The setting reaction is ionic in nature and requires an ionic medium in which it can proceed at any desired rate. It is well established that the first reaction is the hydrolysis of zinc oxide to its hydroxide (Figure 8-24). Some formulations do not contain water in the paste and the setting of the material is retarded until the mixed paste encounters moisture in the patient's mouth. Other anhydrous formulations contain acetic acid or zinc acetate to accelerate the reaction. In any case, water provides additional acceleration. When the two pastes are mixed, the phenol –OH of the eugenol acts as a weak acid and undergoes an acid-base reaction with zinc hydroxide to form a salt, zinc eugenolate (Figure 8-24). Two further coordinate bonds are formed by donation of pairs of electrons from the methoxy oxygen to zinc. One of the chief disadvantages of the ZOE pastes is the possible stinging or burning sensation caused by the eugenol as it leaches out and contacts soft tissues. Zinc oxide can react with various carboxylic acids and form ZOE-like materials. Orthoethoxybenzoic acid (EBA) is a valuable substitute for eugenol in this regard. Bactericidal agents and other medicaments can be incorporated without interfering with the reaction.

Manipulation

Mixing of the two pastes is accomplished on an oil-impervious paper or glass mixing slab. The proper proportion of the two pastes is generally obtained by squeezing two strips of paste of the same length, one from each tube, onto the mixing slab. A flexible stainless steel spatula is typically used for the mixing procedure. The two strips of contrasting colors are combined with the first stroke of the spatula, and the mixing is continued for approximately 1 min, or as directed by the manufacturer, until a uniform color is achieved.

These materials are classified as a hard paste (type I) or soft paste (type II). The final set should occur within 10 min for a type I paste (hard) and 15 min for a type II paste (soft). When the final set occurs, the impression can be withdrawn from the mouth. The actual time will be shorter when setting occurs in the mouth, since humidity and temperature can accelerate the setting reaction.

The clinician can shorten setting time by adding a small amount of zinc acetate or additional accelerator or a drop of water in the paste before mixing or by extending the mixing time. The use of a cool spatula and mixing slab is also effective in prolonging the setting time.

A paste of a thick consistency or high viscosity can compress the tissues, whereas a thin, fluid material results in an impression that captures a negative replica of the tissues in a relaxed condition with little or no compression. In any event, the impression paste should be homogeneous. Pastes of varying consistencies are commercially available. An advantage of a heavier consistency material is its increased strength.

Dimensional Stability

The dimensional stability of the impression pastes is quite satisfactory. A negligible shrinkage (less than 0.1%) may occur during hardening. No significant dimensional change subsequent to hardening should occur with high-quality commercial products. The impressions can be preserved indefinitely without the change in shape that can result from relaxation or other causes of warping. This condition can be satisfied only if the tray material is dimensionally stable.

Disinfection

The recommended disinfectant solution for ZOE impression paste is 2% alkaline glutaraldehyde solution. The impressions should be immersed in this solution for the required time, rinsed, and poured immediately (Table 8-4).

Other Applications of ZOE Pastes

After a gingivectomy (i.e., the surgical removal of diseased or redundant gingival tissues), a ZOE paste may be placed over the wound to aid in the retention of a medicament and to promote healing. These pastes are generally softer and slower

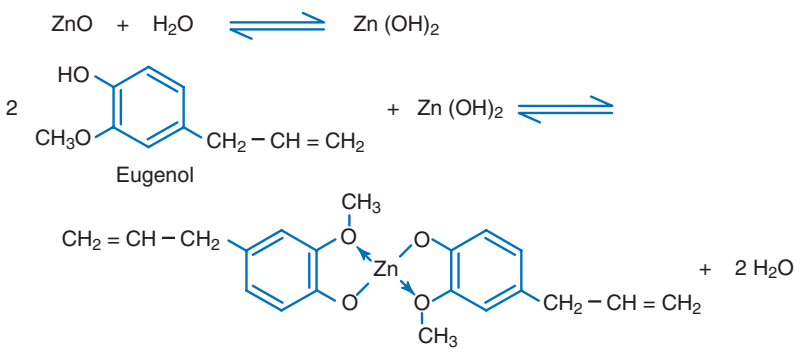


FIGURE 8-24 Setting reaction of zinc oxide–eugenol. Arrows between zinc and oxygen of methoxy groups indicate coordinate bonds.

in their setting reaction in comparison with impression pastes. The mixture should be capable of being formed into a rope that is packed into the gingival wounds and the interproximal spaces to provide retention of the dressing. The final product should be strong enough to resist displacement during mastication but not so brittle that it shears readily under localized stresses.

ZOE pastes are also used as bite registration pastes in the construction of complete dentures and fixed or removable dental prostheses. The ZOE impression paste offers almost no resistance to closing of the mandible, thus allowing a more accurate interocclusal relationship record to be formed. Furthermore, the ZOE interocclusal record is more stable than one made in wax.

ACKNOWLEDGMENTS

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CHAPTER
9

Gypsum Products

OUTLINE

Production of Gypsum Products

Setting of Gypsum Products

Setting Expansion

Strength of Set Gypsum Products

Types of Gypsum Products

Manipulation of Gypsum Products

KEY TERMS

Calcination—The process of heating a solid material to drive off volatile chemically combined components such as water and carbon dioxide.

Cast—A reproduction of the shape and surface of a structure made in an impression of the surface.

Dental plaster (plaster of Paris)—The beta form of calcium sulfate hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$).

Dental stone—The alpha form of calcium sulfate hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$).

Die—A reproduction of a prepared tooth made from a gypsum product, epoxy resin, a metal, or a refractory material.

Gypsum—Calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$).

Gypsum-based investment—A refractory material consisting of silica and gypsum as a binder used to produce a mold for the metal casting process.

Hygroscopic setting expansion—The expansion that occurs when gypsum or a gypsum-bonded investment sets while immersed in water (usually heated to approximately 38 °C [100 °F]).

Model—A positive likeness of an object.

Normal setting expansion—The expansion that occurs when gypsum or a gypsum-bonded investment sets in ambient air.

Gypsum ($CaSO_4 \cdot 2H_2O$; calcium sulfate dihydrate) is a mineral mined in various parts of the world, but it is also produced as a by-product of flue gas desulfurization in some coal-fired electric power plants. Various crystalline forms of gypsum, such as selenite and alabaster, exist in nature. **Gypsum** products are supplied as fine hemihydrate powders that are produced by heating ground gypsum particles. After mixing with water, the mixture reverts back to gypsum. This unique property of gypsum products has led to numerous applications through history. A mixture of plaster (a gypsum product), lime, and water was used in joining the stone blocks of ancient Egypt's pyramids. Gypsum and gypsum products are used today for many applications including building construction, soil conditioning, food additives, pharmaceuticals, medical devices, and dental applications.

The primary applications of gypsum products in dentistry include the production of study models for oral and maxillofacial structures and their use as auxiliary materials for dental laboratory operations involved in the production of dental prostheses. They are also used to form models and casts on which wax dental prostheses and restorations are constructed. When a gypsum product is mixed with refractory fillers, such as different crystalline forms of silica, it becomes more heat resistant, which makes it useful to form molds for the casting of molten metal in an anatomic form for dental restorations. This form of material is known as a **gypsum-based investment** and it is discussed in Chapter 10.

CRITICAL QUESTION

Calcination is a process of removing the water of crystallization from the dihydrate. What happens if hemihydrate powder is mixed with water?

PRODUCTION OF GYPSUM PRODUCTS

These materials are produced by calcining calcium sulfate dihydrate (gypsum). Commercially, the gypsum is ground and subjected to temperatures of 110 °C to 130 °C (230 °F to 266 °F) in open containers to drive off part of the water of crystallization. This corresponds to the first step in the reaction (Figure 9-1). The principal constituent of gypsum-based products is calcium sulfate hemihydrate [$(CaSO_4)_2 \cdot H_2O$ or $CaSO_4 \cdot \frac{1}{2} H_2O$]. The resulting particle is a fibrous aggregate of fine crystals with capillary pores (Figure 9-2, *A*) known as *plaster of Paris* or **dental plaster** in dentistry. As the temperature is further raised, it becomes an anhydrite. This process is known as *calcination*.

As shown in Figure 9-1, when gypsum is heated in a kettle, vat, or rotary kiln that maintains a wet environment; a crystalline hemihydrate called **dental stone** is produced in the form of rods or prisms (Figure 9-2, *B*). Because of differences in crystal size, surface area, and degree of lattice perfection, the resulting powders are often referred to as α-hemihydrate for dental stone and β-hemihydrate for plaster of Paris. The β-hemihydrate crystals are characterized by their "sponginess" and irregular shape. In contrast, the α-hemihydrate crystals are denser and have a prismatic shape.

When hemihydrate particles are mixed with water, the reaction in Figure 9-1 is reversed. The α-hemihydrate produces a much stronger and harder dihydrate structure than that resulting from β-hemihydrate. The chief reason for this difference is that the β-hemihydrate crystals are more irregular in shape and porous in character and require more water to wet the powder particles so that they can be stirred and poured. The amount of water required can also be reduced by grinding the hemihydrate particles to eliminate needlelike crystals and to provide better packing characteristics.

It is clear that various gypsum products require different amounts of water. These differences are accounted for principally by the shape and compactness of the crystals. These factors are regulated by the manufacturer and they are dependent on the type of process used, dehydration temperatures, particle size of the gypsum to be calcined, the calcination time, the grinding time for the final product, and addition of surface-active ingredients to the final product.

If the calcination process occurs under pressure in a 30% calcium chloride solution or in the presence of more than 1% of sodium succinate, the resulting hemihydrate crystals will be shorter and thicker than those produced in a closed container (Figure 9-2, *C*). Residual calcium chloride or sodium succinate is removed by washing the powder with hot water. This type of gypsum-producing product is called modified α-hemihydrate or **die** stone. These crystals require even less water for mixing.

CRITICAL QUESTION

Which unique property of hemihydrate and dihydrate makes the dissolution-precipitation theory of gypsum setting possible?

SETTING OF GYPSUM PRODUCTS

The reaction between gypsum products and water produces solid gypsum, and the heat evolved in the exothermic reaction is equivalent to the heat used originally for calcination. Set gypsum products probably never attain 100% conversion unless they are exposed to high humidity for a long time. Therefore, there are unreacted hemihydrates remaining in the set materials (Figure 9-3).

SETTING REACTIONS

There are three theories of gypsum setting. The colloidal theory proposes that, when mixed with water, hemihydrate enters into the colloidal state through a sol-gel mechanism. In the sol state, hemihydrate particles are hydrated to form dihydrate, thereby entering into an active state. As the measured amount of water is consumed, the mass converts to a solid gel. The hydration theory suggests that rehydrated plaster particles unite through hydrogen bonding with sulfate groups to form the set material. The most widely accepted mechanism is the dissolution-precipitation theory, which is based on dissolution of the hemihydrate particles in water followed by instant recrystallization to the dihydrate. This reaction has become possible because the solubility of hemihydrate in water is four times greater than that of the dihydrate near room temperature (Figure 9-4). Thus, the setting reactions occur as follows:

1. When the hemihydrate is mixed with water, a suspension is formed that is fluid and workable.
2. The hemihydrate dissolves until it forms a saturated solution of Ca^{2+} and $(SO_4)^{2-}$.
3. This saturated hemihydrate solution is supersaturated with respect to the solubility of the dihydrate; precipitation of dihydrate occurs.

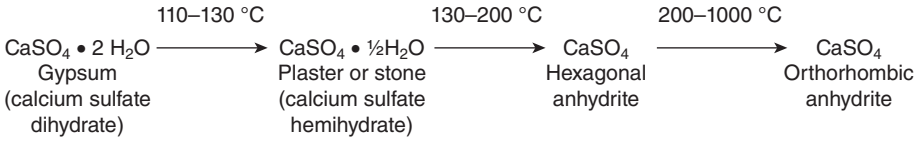


FIGURE 9-1 Calcination process for gypsum.

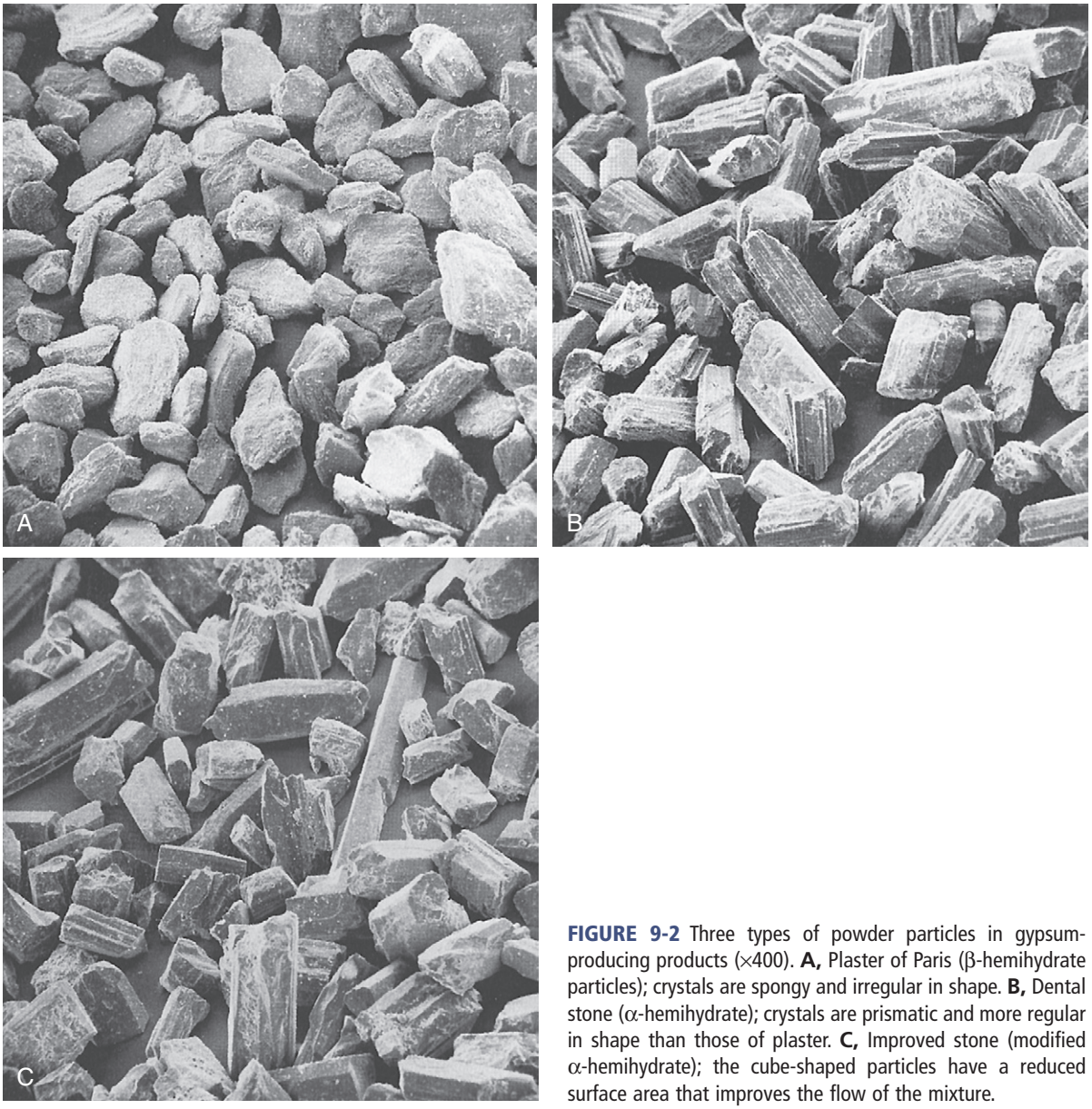


FIGURE 9-2 Three types of powder particles in gypsum-producing products (×400). **A,** Plaster of Paris (β-hemihydrate particles); crystals are spongy and irregular in shape. **B,** Dental stone (α-hemihydrate); crystals are prismatic and more regular in shape than those of plaster. **C,** Improved stone (modified α-hemihydrate); the cube-shaped particles have a reduced surface area that improves the flow of the mixture.

$$\underset{\text{Calcium sulfate hemihydrate}}{(CaSO_4)_2 \bullet H_2O} + 3H_2O \longrightarrow \underset{\text{Calcium sulfate dihydrate}}{2\,CaSO_4 \bullet 2\,H_2O} + \text{unreacted } (CaSO_4)_2 \bullet H_2O + \text{heat}$$

FIGURE 9-3 Reaction of gypsum-producing products with water.

4. As the dihydrate precipitates, the hemihydrate continues to dissolve. The process proceeds as either new crystals form or further growth occurs on the crystals already present until no further dihydrate can precipitate out of solution.

The setting reaction takes time to complete and changes in the mixture begin as soon as the hemihydrate and water are mixed together. X-ray diffraction data for set gypsum products indicate that there is less than 50% dihydrate present in Type IV and V stones, about 60% in Type II die materials, and over 90% in Type I plasters.

CRITICAL QUESTION

How can one determine if the hemihydrate and water mixture has set?

QUANTIFYING SETTING REACTIONS

The hemihydrate and water must be mixed uniformly to ensure a homogeneous reaction through the entire mixture. It must also maintain its workable state as long as possible to facilitate pouring of a **model** or the casting investment. One must also recognize the stage at which the

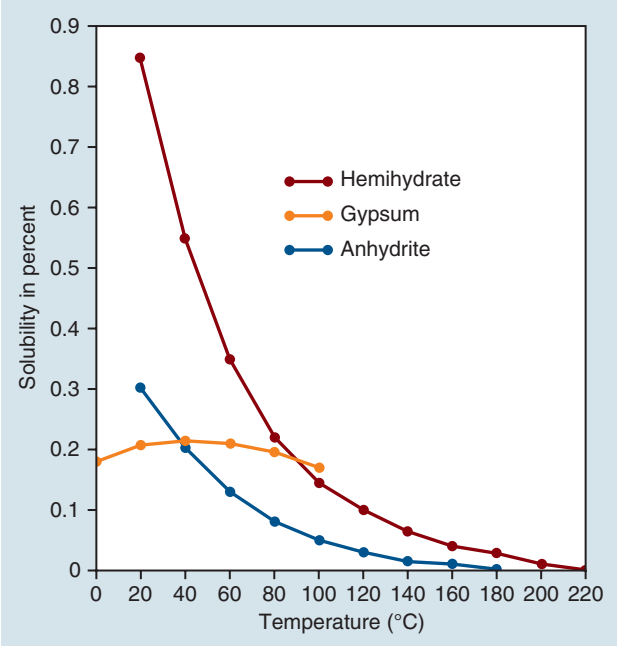


FIGURE 9-4 Temperature dependence of calcium sulfate solubility in water.

mixture has gained enough strength to resist fracture, which may be caused by the stress produced during removal of the model from the impression.

The time from addition of powder to the water until mixing is completed is called the *mixing time*. Mechanical mixing is usually completed in 20 to 30 seconds. Hand spatulation generally requires at least a minute to obtain a smooth mixture. The time from the start of mixing to the point where the consistency is no longer acceptable for the product's intended purpose is the *working time*. Generally, a 3-minute working time should allow sufficient time for mixing, pouring an impression and a spare impression, and cleaning the equipment before the gypsum becomes unworkable. As the reaction proceeds, the excess water on the surface is taken up in forming the dihydrate, so that the mix loses its surface gloss and gains strength. When the mix can resist penetration by a Gillmore needle, which has a tip 2.12 mm in diameter and weighs 113.4 g, the time elapsed is called the *initial setting time*. At this point, the mass still has no measurable compressive strength and the cast cannot be safely removed from the impression. The elapsed time at which a heavier Gillmore needle, weighing 453.6 g and with a tip 1.06 mm in diameter, leaves only a barely perceptible mark on the surface is called the *final setting time*.

The elapsed time for each stage varies from material to material. The manufacturers usually provide this information with the product.

? CRITICAL QUESTION

How can we control gypsum's setting rate?

CONTROL OF THE SETTING TIME

Depending on the use of the gypsum product, it is necessary to control its setting time for each specific application. Theoretically, there are at least three mechanisms that can achieve such control. These include:

1. Solubility of the hemihydrate—If the solubility of the hemihydrate is increased, supersaturation of the dihydrate is achieved faster, which accelerates the rate of dihydrate crystal deposition.
2. Number of nuclei of crystallization—Nucleation is the first step at which Ca^{2+} and SO_4^{2-} in solution start to assemble into clusters on the nanometer scale, becoming stable under the operating conditions. These stable clusters constitute the nuclei. The greater the number of nuclei of crystallization, the faster the dihydrate crystals will form and the sooner the mass will harden. Any preexisting fine dihydrate particles will also serve as nuclei.
3. Rate of crystal growth—Increasing or decreasing the rate of crystal growth will accelerate or retard the setting time.

In practice, these mechanisms have been incorporated in the formulation of the material by the manufacturer and by manipulation techniques performed by the operator. For example, fine gypsum particle residues from incomplete calcination or addition by the manufacturer will shorten the setting time because of the increase in the number of nuclei. Grinding of hemihydrate particles during manufacturing increases not only the rate of dissolution of the hemihydrate solution but also the number of nuclei. This increase in nuclei density results in a more rapid rate of crystallization.

The amounts of water and hemihydrate should be gauged accurately by weight. The weight (or volume) of the water divided by the weight of the hemihydrate powder is known as the water/powder ratio, which is abbreviated as W/P. For example, if 100 g of dental stone is mixed with 28 mL of water, the W/P ratio is 0.28. This ratio is an important factor in determining the physical and mechanical properties of the final gypsum product. The use of a higher W/P ratio decreases the number of nuclei per unit volume. Consequently, the setting time is prolonged (Table 9-1). An increase in the W/P ratio also causes a decrease in the strength and a decrease in the setting expansion of the set gypsum products, which will be discussed later.

Some gypsum crystals form immediately when the plaster or stone is brought in contact with the water. As the mixing starts, the formation of these crystals increases. At the same time, the crystals are broken up by the spatulation process, which results in more nuclei of crystallization. Therefore, within practical limits, the longer and the more rapidly the gypsum product is mixed, the shorter is the setting time.

Usually an increase in water temperature leads to an acceleration of a chemical setting reaction. This reaction is more complex for gypsum products. Figure 9-4 shows that the difference in solubility between hemihydrate and gypsum becomes smaller with increasing temperature, and this condition lowers the driving force for forming the dihydrate; it also results in a slower setting reaction. The decreased driving

force causes the effect of temperature on the setting time to be erratic and to vary from one material to another. Little change in setting time occurs between 0 °C and 50 °C. If the temperature of the plaster-water mixture exceeds 50 °C, a gradual retardation occurs. As the temperature approaches 100 °C, no reaction takes place. This is the reason why very hot water (near the boiling temperature) is used to wash impurities like calcium chloride and sodium succinate from improved stone powder.

CRITICAL QUESTION

What are the recommended methods to accelerate or retard the setting time for a given gypsum-forming product?

MODIFIERS FOR CONTROLLING SETTING TIME

Chemical modifiers have been used extensively to increase or decrease the setting time of gypsum products; they are called *retarders* and *accelerators*, respectively. The manufacturers use both types of compounds to formulate gypsum products with specific setting times.

The chemical that increases the rate of hemihydrate dissolution or precipitation of dihydrate accelerates the setting reaction. The most commonly used accelerator is potassium sulfate, which is particularly effective in concentrations greater than 2%. Slurry water flowing out from a model trimmer contains numerous fine gypsum particles that act as nuclei of crystallization and that can serve as an effective accelerator. It is important that the slurry water be agitated before use to disperse these fine gypsum particles. Increasing the time or the speed of mixing can create more nuclei by crushing the developing dihydrate crystals into smaller particles, thereby accelerating the setting of the mix. At a concentration of 2% of the hemihydrate, sodium chloride is an accelerator. Sodium sulfate has its maximum acceleration effect at approximately 3.4%. Several inorganic salts play dual roles in the setting kinetics of dihydrate, which are accelerators at low concentration and retarders at higher concentration. For example, borax, a known retarder for gypsum setting, has been shown also to promote the growth of dihydrate crystals, but only at a concentration lower than 0.2 mM (about 0.08 g/L).

One should recognize that significant acceleration of the reaction time could compromise the optimal flow characteristics of the material. The manufacturer has added accelerators, retarders, and other controlling agents, so it is not wise to add other ingredients that may counteract the effects of components that are already incorporated into the product. Therefore, one should select a product from the manufacturer's catalogue with the specific setting time that the operator needs.

TABLE 9-1 Effect of Water/Powder Ratio (W/P) and Mixing Time on the Setting Time of Plaster of Paris

W/P Ratio	Mixing Time (min)	Setting Time (min)
0.45	0.5	5.25
0.45	1.0	3.25
0.60	1.0	7.25
0.60	2.0	4.50
0.80	1.0	10.50
0.80	2.0	7.75
0.80	3.0	5.75

From Gibson CS, Johnson RN: Investigation of setting of plaster of Paris. *J Soc Chem Ind* 51:25-38, 1932.

CRITICAL QUESTION

When a mixture of hemihydrate and water sets, the resulting object is always porous. Why?

SETTING EXPANSION

Regardless of the type of gypsum product selected, an expansion of the mass can be detected during the change from the hemihydrate to the dihydrate. Depending on the composition of the gypsum product, this observed linear expansion may be as low as 0.06% or as high as 0.5%. This phenomenon is contrary to what is expected when hemihydrate reverts to the denser dihydrate form. If equivalent volumes of the hemihydrate, water, and the reaction product (dihydrate) are compared, the volume of the dihydrate formed will be 7.11% less than the equivalent combined volumes of the hemihydrate and water (Figure 9-5). This represents a 2.37% linear shrinkage of the gypsum object. The phenomenon of *setting expansion* can be explained on the basis of crystallization.

MECHANISM OF SETTING EXPANSION

The crystallization of dihydrates can be pictured as an outgrowth of crystals from nuclei of crystallization. Crystals growing from the nuclei can intermesh with and obstruct the growth of adjacent crystals. When the process repeats itself with thousands of the crystals during growth, an outward stress or thrust develops, producing an expansion of the entire mass. Thus, a setting expansion can take place even

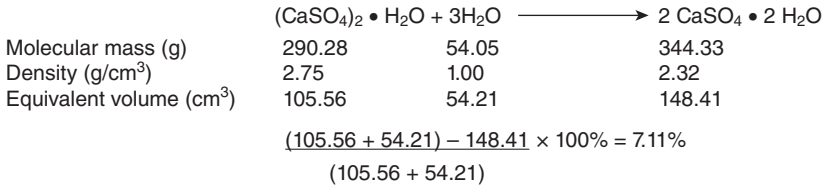


FIGURE 9-5 Volume changes from conversion of calcium sulfate hemihydrate to dihydrate.

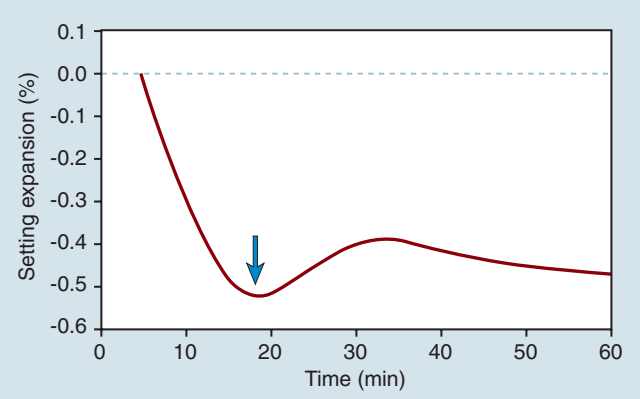


FIGURE 9-6 Dimensional changes that occur during the setting of a gypsum product. The arrow indicates the initial set at approximately the lowest point of the curve.

though the true volume of the crystals alone may be less than calculated. Therefore, the structure immediately after setting is composed of interlocking crystals between which are micropores and pores containing the excess water required for mixing. On drying, the excess water is lost, resulting in a porous structure.

Figure 9-6 shows the dimensional change during setting of a gypsum product. The mixture exhibits an initial contraction followed by an expansion and smaller contraction. If the mixture is spread on a glass surface, the distance between any two reference points on the surface of the mixture will not change appreciably during the induction period, the time until the onset of initial setting. It is the adhesion of the mixture to the glass that prevents the expected contraction. In fact, any contraction will appear in the reduction of the height of the mixture on the glass. Only when the crystalline framework is sufficiently rigid (after the initial set) will the force of expansion overcome the adhesion to produce a visible setting expansion.

Therefore, when the technician or dentist produces gypsum models in impression molds, only the setting expansion that occurs after the initial set is of interest. Any contraction that occurs during the induction period does not affect the dimension of the cast relative to the mold because the mixture is still fluid at this stage and the contraction occurs at the free surface, an area that is not in contact with the mold. When enough crystals have formed to produce the outward thrust by impingement, setting expansion follows. The onset of initial setting occurs at approximately the minimal point of the curve, the point at which expansion begins. Since the contraction prior to initial setting occurs at the free surface, the final dimension of the cast relative to that of the impression mold includes a setting expansion of approximately 0.12%, according to Figure 9-6. Naturally, the quantities of setting expansion vary among different gypsum products.

CONTROL OF SETTING EXPANSION

As can be noted from the results presented in Table 9-2, a lower W/P ratio and a longer mixing time will increase the setting expansion. Each of these factors increases the nuclei density. The effect of the W/P ratio on the setting expansion is to be expected on theoretical grounds. At higher W/P ratios, fewer nuclei of crystallization per unit volume are present compared with the greater density of nuclei in thicker mixes. Because it can be assumed that the space between the nuclei is greater in such a case, it follows that there is less growth interaction of the dihydrate crystals and less outward thrust. However, the most effective method by which to control setting expansion is through the addition of chemicals by the manufacturer.

TABLE 9-2 **Effect of Water/Powder Ratio (W/P) and Mixing Time on Setting Expansion of Plaster of Paris**

W/P Ratio	Mixing Time (min)	Setting Expansion (%)
0.45	0.6	0.41
0.45	1.0	0.51
0.60	1.0	0.29
0.60	2.0	0.41
0.80	1.0	0.24

From Gibson CS, Johnson RN: *J Soc Chem Ind* 51:25T, 1932.

? CRITICAL QUESTION

Thus far, the setting of plaster or stone has occurred in air. What would happen if the hemihydrate and water mixture were allowed to set under water? Keep in mind that the solubilities of hemihydrate and dihydrate are very low in water, and one should not be concerned that the mixture will dissolve without vigorous stirring.

HYGROSCOPIC SETTING EXPANSION

Imagine that the initial mix is represented in the top row of Figure 9-7 (stage I) by the three round particles of hemihydrate surrounded by water. Under normal setting conditions, the crystals of the dihydrate begin to form on the nuclei. The water around the particles is reduced by hydration and these particles are drawn more closely together because surface tension of the water keeps the water surface area at a minimum (stage II). As the crystals of dihydrate grow, they contact each other and the water around the particles again decreases (stage III). Further dihydrate growth consumes more water and should draw the crystals together as before, but the outward thrust of the growing crystals opposes this contraction (stage IV). Eventually, the crystals become intermeshed and entangled (stage V).

Stage I of the middle row (hygroscopic setting conditions) of Figure 9-7 shows an identical mixture of hemihydrate (the area delineated by the dashed circle) under water (the area outside of the dashed circle). The hydration of hemihydrate particles here would proceed as usual. Since they are under water, the water consumed by hydration will be immediately replenished by the immersion water and the distance between the particles would remain the same (stage II). The surface

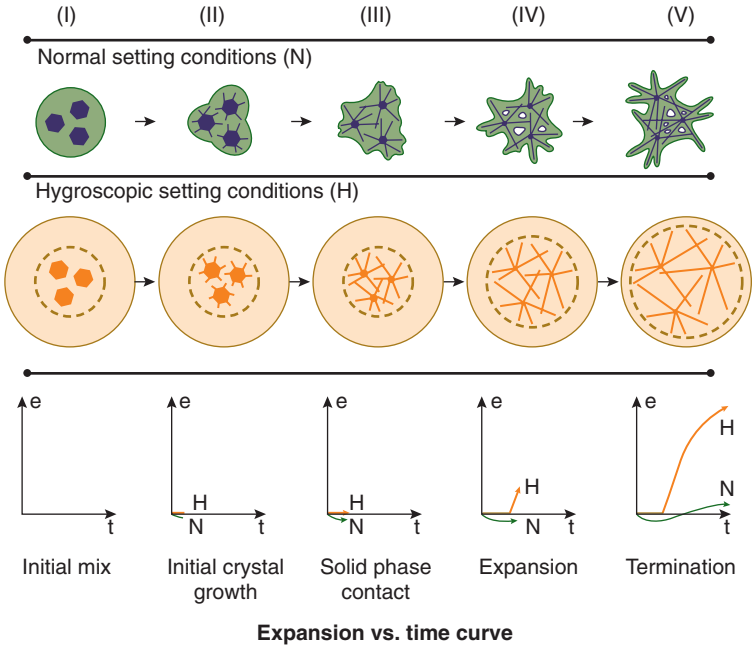


FIGURE 9-7 Diagrammatic representation of the setting expansion of gypsum products. In the top row, the crystal growth is inhibited by the surface tension of water surrounding the growing crystals. In the middle row, the gypsum mixture (*the area surrounded by the dashed circle*) is immersed in water during setting (*represented by the larger solid circle*); the immersion water provides more room for longer crystal growth. The bottom row shows the expansion (e) over time (t) for hygroscopic setting expansion (H) and normal setting expansion (N). (Adapted from Mahler DB, Ady AB: An explanation for the hygroscopic setting expansion of dental gypsum products. *J Dent Res* 39:378-379, 1960.)

tension of the water will still keep the surface area of the water at a minimum, except that in this case it would be the surface area of the immersion water, which will have no impact on the distance between growing dihydrates. As the dihydrate crystals continue to grow and contact each other, no reduction in the distance between crystals is expected (stage III). This means that the crystals will grow much more freely during the early stages (stage IV), before the intermeshing finally prevents further expansion (stage V). Consequently, the observed setting expansion that occurs when the gypsum product sets under water is greater than that which occurs during setting in air.

To distinguish between the two setting conditions, the setting expansion without water immersion is usually called *normal setting expansion* (N in the bottom row of Figure 9-7), whereas the expansion that occurs under water is known as *hygroscopic setting expansion* (H in the bottom row of Figure 9-7). The **hygroscopic setting expansion** is a physical phenomenon and is not caused by a chemical reaction any more than is the **normal setting expansion**. Therefore, the variables that can cause an increase or decrease in the normal setting expansion will have the same effect on the hygroscopic setting expansion. For example, a reduction in the W/P ratio and increased spatulation will result in a higher hygroscopic expansion.

The hygroscopic expansion obtained during the setting of dental stone or plaster is about twice that of the normal setting expansion. The greater hygroscopic setting expansion of gypsum-bonded casting investments is used in the fabrication of cast gold alloy restorations. Other investment materials that do not use gypsum as binder have also exhibited similar expansion when they set under water. Since warm water (approximately 38 °C) is often used as the immersion water for hygroscopic expansion, one theory of hygroscopic expansion suggests that at this higher temperature the wax pattern expands during the setting of the investment material. More discussion on hygroscopic expansion of investment materials is presented in Chapter 10.

Note that *hygroscopy* means the ability of a substance to attract water molecules from the surrounding environment through either absorption or adsorption. The hygroscopic setting expansion described here is not the result of absorption or adsorption. Therefore, the term *hygroscopic setting expansion* of gypsum products is technically incorrect. Nonetheless, this term will be retained in explanations of the setting expansion of gypsum.

? CRITICAL QUESTION

How does the presence of water in the pores of set gypsum affect the strength of the gypsum object?

STRENGTH OF SET GYPSUM PRODUCTS

The strength of set gypsum products is generally expressed in terms of compressive strength, although diametral tensile strength (Chapter 4) should also be considered to determine the overall strength characteristics.

EFFECT OF WATER CONTENT

As expected from the theory of setting, the strength of plaster or stone increases rapidly as the material hardens after the initial setting time. However, the free water content of the set product definitely affects its strength. For this reason, two strength properties of gypsum are reported: the *wet strength* (also known as *green strength*), and the *dry strength*. The wet strength is the strength that is determined when water in excess of that required for hydration of the hemihydrate remains in the test specimen. When such excess water is removed by drying, the strength obtained is the dry strength.

TABLE 9-3 Effect of Drying on the Strength of Plaster of Paris

Drying Period (h)	Compressive Strength (MPa)	Weight Loss (%)
2	9.6	5.1
4	11.7	11.9
8	11.7	17.4
16	13.0	– –
24	23.3	18.0
48	23.3	18.0
72	23.3	– –

From Gibson CS, Johnson RN: *J Soc Chem Ind* 25-38, 1932.

TABLE 9-4 Effect of the Water/Powder (W/P) Ratio and Mixing Time on the Strength of Plaster of Paris

W/P Ratio	Mixing Time (min)	Compressive Strength (MPa)
0.45	0.5	23.4
0.45	1.0	26.2
0.60	1.0	17.9
0.60	2.0	13.8
0.80	1.0	11.0

From Gibson CS, Johnson RN: *J Soc Chem Ind* 51:25T, 1932.

The dry strength may be two or more times as high as the wet strength. Consequently, the distinction between the two is of considerable importance.

The effect of drying on the compressive strength of set plaster is shown in Table 9-3. Note the relatively slight gain in strength that occurred after 16 hours. Between an 8-hour and a 24-hour drying period, only 0.6% of the excess water was lost yet the strength doubled. A similar change in surface hardness takes place during the drying process. An explanation of this phenomenon is that as the last trace of water is lost, fine crystals of gypsum precipitate serve as anchors between the larger crystals. Thus, if excess water is reconstituted by immersion or absorption, these small crystals are the first to dissolve and the reinforcing anchors are lost.

Microwave irradiation has been used to speed up the drying of gypsum casts. For example, one study showed that irradiation for 1 minute can result in a strength equivalent to that obtained after drying in air for 24 hours. Some studies suggest that there is a strengthening effect after casts are dried by microwave irradiation, whereas other studies have shown a slight decrease in strength compared with casts dried in ambient air. In general, microwave irradiation, a timesaving procedure, may be associated with some dimensional changes. The time needed varies with the microwave oven setting and type of cast being dried.

EFFECT OF W/P RATIO

As previously noted, the set plaster or stone is porous, and the greater the W/P ratio, the greater the porosity. As might be expected on such a basis, the greater is the W/P ratio, the less is the dry strength of the set material, as shown by the data in Table 9-4, because fewer dihydrate crystals are available per unit volume. Material that is mixed at a high W/P ratio has a diametral tensile strength as high as 25% of the corresponding compressive strength. When materials are mixed at low W/P ratios, the diametral tensile strength is less than 10% of the corresponding compressive strength.

Figure 9-8 is a plot of the strength as a function of the W/P ratio for the five different types of gypsum products used in dentistry (discussed later). The figure includes data from

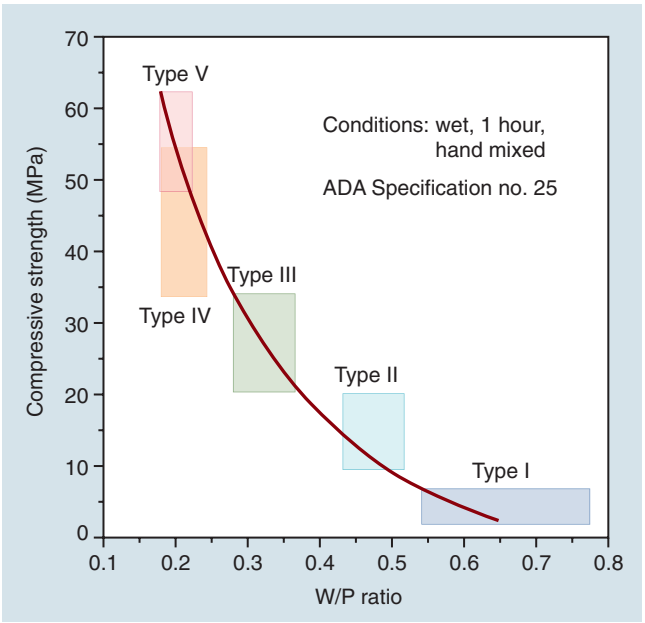


FIGURE 9-8 Compressive strength as a function of W/P ratio for five types of gypsum products.

many of the products on the market that meet American National Standards Institute/American Dental Association (ANSI/ADA) Specification No. 25 for dental gypsum products; the strength ranges represent the wet strength at 1 hour. The strength increases as the specimens dry and it can double in a week. Although the W/P ratio varies for the particular brand of plaster or stone, the typical recommended ranges of W/P ratios are shown in Table 9-5 for the five types of gypsum products.

EFFECT OF MANIPULATION AND ADDITIVES

As shown in Table 9-4, the spatulation time also affects the strength of the plaster. In general, an increase in mixing time increases the strength to a limit that is approximately equivalent to that of hand mixing for 1 minute. If the mixture is overmixed, the gypsum crystals will be broken up and the final product will hold less crystalline interlocking structure.

The addition of an accelerator or retarder lowers both the wet strength and the dry strength of the gypsum product.

TABLE 9-5 Properties of Five Types of Gypsum Products*

Type	W/P Ratio	Setting Time (min)	Two-hour Setting Expansion (%)		One-Hour Compressive Strength[§] (MPa)
			Min	Max	
I. Plaster, impression	0.50–0.75	4 ± 1	0.00	0.15	4.0
II. Plaster, model	0.45–0.50	12 ± 4	0.00	0.30	9.0
III. Dental stone	0.28–0.30	12 ± 4	0.00	0.20	20.7
IV. Dental stone, high strength	0.22–0.24	12 ± 4	0.00	0.10	34.5
V. Dental stone, high strength, high expansion	0.18–0.22	12 ± 4	0.10	0.30	48.3

*Properties required of five gypsum products covered by American Dental Association Specification No. 25.
[§]Minimum values.

Such a decrease in strength can be partially attributed to the salt added as an adulterant and to the reduction in intercrystalline cohesion.

When relatively pure hemihydrate is mixed with minimal amounts of water, the working time is short and the setting expansion unduly high. However, as just noted, dental gypsum products contain additives that reduce the setting expansion, increase the working time, and provide a rapid final set. The addition of more chemicals can upset the delicate balance of these properties. Thus if a change is desired in the setting time, it should be controlled by modest alterations in the W/P ratio and/or the spatulation time.

? CRITICAL QUESTION

Which properties are used to classify the various types of gypsum products?

TYPES OF GYPSUM PRODUCTS

ADA Specification No. 25 classifies five types of gypsum products, as shown in Table 9-5, with the property requirement for each type. Some gypsum materials are formulated for special purposes such as for pouring orthodontic casts or attaching casts to an articulator. The criterion for selecting any particular gypsum product depends on the intended use and the physical properties necessary for that particular use. For example, a dental stone is a poor material for use as an impression material because, if teeth are present, it would be impossible, because of the high strength of the stone, to remove the impression over the undercuts in the teeth without injury to the patient.

IMPRESSION PLASTER (TYPE I)

These impression materials are composed of plaster of Paris (β-hemihydrate; Figure 9-2, *A*) to which modifiers have been added to regulate the setting time and setting expansion. Impression plaster is rarely used any longer for making dental impressions because it has been replaced by less rigid materials such as the hydrocolloids and elastomers. Descriptions of the impression plaster and applications are given in Chapter 8.

MODEL PLASTER (TYPE II)

This model plaster or laboratory Type II plaster is now used principally to fill a flask used in denture construction when setting expansion is not critical and the strength is adequate according to the limits cited in the ADA specification or ISO standard. It is usually marketed in the natural white color, thus, contrasting with stones, which are generally colored.

DENTAL STONE (TYPE III)

With the advent of hydrocolloid impression material (Chapter 8), the improved hardness of α-hemihydrate (Figure 9-2, *B*) made stone dies workable and the indirect wax pattern possible.

Type III stone has a minimal 1-hour compressive strength of 20.7 MPa (3000 psi), but it does not exceed 34.5 MPa (5000 psi). It is intended for the construction of casts in the fabrication of full dentures to fit soft tissues. For this application, a slight setting expansion can be tolerated in casts that reproduce soft tissues, but not when teeth are involved. Type III stones are preferred for casts used to process dentures because the stone has enough strength for this purpose and the denture is easier to remove after processing.

There are at least two methods for the construction of the cast. One method is to construct a mold by wrapping soft flat wax strips around the impression so that they extend approximately 12 mm beyond the tissue side of the impression. This process is called *boxing*, which forms the base of the cast. The mixture of stone and water is then poured into the impression under vibration. The mixture is allowed to flow slowly in a controlled pathway along the impression so that it forces the air forward as it fills all tooth impressions without entrapment of air bubbles.

Another method is to fill the impression first as described. The remainder of the stone-water mixture is poured on a glass plate. The filled impression is then inverted over a mound of stone, and the base is shaped with the spatula before the stone sets. Such a procedure is not indicated if the impression can easily be deformed or if the stone is "runny." The cast should

not be separated from the impression until it has hardened. The minimal time allowed for setting varies from 45 to 60 minutes, depending on the rate of setting of the stone or plaster and the type of impression material used.

DENTAL STONE, HIGH STRENGTH (TYPE IV)

The principal requisites for a die material are strength, hardness, and minimal setting expansion. To obtain these properties, modified α-hemihydrate (Figure 9-2, *C*) is used. The cube-shaped particles and the reduced surface area produce such properties without undue thickening of the mix. This material is also called *die stone*.

A hard surface is necessary for a die stone because the tooth preparation is covered with wax and carved flush with the margins of the die. A sharp instrument is used for this purpose; therefore, the stone must be resistant to abrasion. Gypsum hardening solutions, silver plating, coating with cyanoacrylate adhesive, and other methods of increasing the abrasion resistance are discussed in Chapter 10. It is fortunate that the surface hardness increases more rapidly than the compressive strength because the surface dries more rapidly. This is a real advantage in that the surface resists abrasion, whereas the core of the die is tough and less subject to accidental breakage. The average dry surface hardness of the Type IV stones is approximately 92 (Rockwell hardness) and that of Type III stone is 82. Even though the surface of the Type IV stone is harder, care should be taken when the pattern is being carved.

? CRITICAL QUESTION

Under what conditions might a Type V dental stone be used?

DENTAL STONE, HIGH STRENGTH, HIGH EXPANSION (TYPE V)

This gypsum product exhibits an even higher compressive strength than the Type IV dental stone. The improved strength is attained by making it possible to lower the W/P ratio even further than that used for Type IV stone. In addition, the setting expansion has been increased from a maximum of 0.10% to 0.30% (Table 9-5). The rationale for increasing setting expansion is that certain newer alloys, such as base metal, have a greater casting shrinkage than do the traditional noble metal alloys (Chapter 16). Thus, higher expansion is required in the stone die to aid in compensating for the alloy solidification shrinkage. The use of a Type V stone may also be indicated when the expansion achieved during the fabrication of cast crowns is inadequate. One should avoid the use of Type V stones for producing dies for inlays and onlays since the higher expansion may lead to an unacceptably tight fit. Additional information on the use of Type IV and V stones is provided in the discussion of die materials in Chapter 10.

SPECIAL GYPSUM PRODUCTS

The orthodontist prefers a white stone or plaster for study models and may even treat the surface with soap to increase their sheen. These products generally have a longer working time, which reduces void formation and facilitates trimming.

The use of an articulator makes it necessary to mount the casts using a gypsum-producing product. These materials are referred to as "mounting" stones or plasters. They are fast setting and have low setting expansion. The mounting plaster has a sufficiently low strength to permit easy trimming and facilitate separating the cast from the articulator mounting plates.

Some products are designed to save time. One type is extremely fast setting and is ready to use in 5 minutes, but it has little working time. Another product changes color to indicate when it is ready for use. In addition, one specialty product contains a small amount of plastic or resin to reduce brittleness and improve resistance to abrasion during the carving of wax patterns.

Usually, when one feature is improved, another is sacrificed. A faster set is accepted in return for less working time. An improved resistance to carving is accepted in return for more difficult manipulation, decreased detail reproduction, or the need to box the impression because of excessive runniness. Improvements in materials and testing equipment have made it possible to use silicone-stone combinations that can reproduce spaces between lines as fine as 10 μm or less. Current specifications or standards require an accuracy of only 50 μm.

At present many gypsum products are available to suit almost all individual requirements or combinations thereof.

MANIPULATION OF GYPSUM PRODUCTS

So far, we have discussed the types of gypsum products based on their crystal form, their applications and their setting processes, which may affect the dimensions and strength of the set material. In practice, clinicians and technicians must not only produce a cast using a gypsum-producing material, but they must also store the powder properly and maintain the cast in its best condition for subsequent procedures.

CARE OF GYPSUM PRODUCTS

The hemihydrate of gypsum absorbs water from the air readily. For example, if the relative humidity of the surroundings exceeds 70%, the plaster absorbs sufficient moisture from the air to start a setting reaction. The first hydration probably produces a few crystals of gypsum on the surface of the exposed hemihydrate crystals. These gypsum crystals can act as nuclei of crystallization and accelerate the setting reaction when they are mixed with water. If the hydration is allowed to continue, this process results in the hemihydrate crystals being completely covered with dihydrate crystals. Under these conditions, the water penetrates the dihydrate coating with difficulty and the setting time is prolonged.

Therefore, it is important that all gypsum products be stored in a dry atmosphere. The best means of storage is to seal the product in a moisture-proof metal container. When gypsum products are stored in closed containers, the setting time is generally retarded only slightly, approximately 1 or 2 min per year. This may be counteracted by a slight increase in the mixing time if necessary.

PROPORTIONING

The recommended W/P ratio should be used. The water and powder should be measured by using an accurate graduated cylinder for the water volume and a weighing balance for the weight of powder. The powder should not be measured by volume (as by using a scoop) as it does not pack uniformly. This characteristic may vary from product to product, and it will pack more densely if the container remains undisturbed. When the container is shaken, the packed particles will be loosened and the volume will increase as a result of air entrapment. Preweighed envelopes are very popular because they promote accuracy, reduce waste, and save time. However, this preweighed, packaged material adds to the cost of producing models and casts.

MIXING AND POURING

If mixing is performed by hand, the bowl should be parabolic in shape, smooth, and resistant to abrasion. The spatula should have a stiff blade and a handle that is convenient to hold. A measured amount of water is placed in the bowl and the weighed powder is sifted into the water as initial hand mixing is performed. The mixture is then vigorously stirred, with periodic wiping of the inside of the bowl with the spatula to ensure wetting of all of the powder and breaking up of any agglomerates or lumps. The mixing should continue until a smooth mix is obtained, usually within a minute. A longer spatulation time drastically reduces the working time, which is of particular importance when pouring models. Entrapment of air in the mix must be avoided, since porosity can lead to weak spots and surface inaccuracies. After mixing, the use of a vibrator of high frequency and low amplitude is helpful in reducing air entrapment.

The preferred method of mixing is to use a mechanical mixer under vacuum. First, the measured water is added to the bowl, followed by gradual addition of the preweighed powder. The powder is incorporated during approximately 15 s of mixing with a hand spatula, followed by 20 to 30 s of mechanical mixing under vacuum. The strength and hardness obtained from such vacuum mixing usually exceed that obtained by 1 minute of hand mixing. Repeatedly adding water and powder by guesswork to achieve the proper consistency should be avoided. This yields a lower strength and may cause distortion.

The mixing bowl with the dental stone mixture is then placed on top of a vibrator to eliminate entrapped air bubbles and the impression tray is held in one hand against the vibrator. The surface of the impression should be free of excess water. With the metal spatula, a small amount of dental stone is added to one open end of the impression (e.g., in the last molar of a full arch impression). The speed of the vibrator should be adjusted high enough to make the stone flow slowly into adjacent spaces. If the speed of vibration is too high, it can generate air bubbles within the stone mixture. The impression may be tilted to control the movement of the stone into the tooth depression. Additional stone is added behind the moving front to promote the flow of stone and to ensure that the previously filled area does not lose much of its volume. Once the tooth depressions are completely filled, larger amounts of dental stone can be added under light vibration to fill the remaining impression up to the mucobuccal fold or rim of the boxed area around the impression tray. The impression is then briefly placed on the vibrator for a few seconds to distribute the stone evenly across the impression.

If the inversion method is used, a mound of stone about 20 mm high is made on a flat surface, such as glass plate, with the remainder of the mixture or with a new mix using a lower W/P ratio. The filled impression, which should exhibit the initial set but not the final set, is then inverted over the mound of stone and the base is shaped with the spatula before the stone sets. The dental stone model should be left undisturbed for 45 to 60 min until the material has set completely. The dental stone model is now separated from the impression. When tooth preparations are involved, a smaller spatula may be used to deliver a much smaller amount of stone to fill the sites of the preparations and ensure complete filling before the remaining portion of the impression is poured.

? CRITICAL QUESTION

What storage conditions are necessary to maintain the dimensional accuracy of a gypsum cast?

CARE OF THE CAST

Once the setting reactions in the cast have been completed, its dimensions will be relatively constant under ordinary conditions of room temperature and humidity. However, it is sometimes necessary to soak the gypsum cast in water in preparation for other procedures. When a dry cast is immersed in water, negligible expansion may occur if the water is saturated with calcium sulfate. If the water is not saturated, dissolution of gypsum will occur. For example, a stone cast immersed in a container under running water will lose approximately 0.1% of its linear dimension for every 20 min of immersion. The safest method for soaking the cast is to place it in a water bath with gypsum debris remaining on the bottom of the container to provide a saturated solution of calcium sulfate.

If the storage temperature is raised to between 90 °C and 110 °C (194 °F to 230 °F), shrinkage occurs, along with loss of strength as the water of crystallization is removed and the dihydrate reverts to the hemihydrate form. As a rule of thumb, it is not safe to store or heat a stone cast in air at a temperature higher than 55 °C (130 °F).

? CRITICAL QUESTION

What procedure should be followed if it is uncertain whether the impression or the gypsum cast has been disinfected?

INFECTION CONTROL

Concern over possible cross-contamination of dental office personnel by microorganisms, including hepatitis B virus and human immunodeficiency virus, via dental impressions has prompted study of the effect of spray and immersion-disinfecting techniques on impression materials (Chapter 8).

The effect of such agents on the surface quality and accuracy of the resulting gypsum casts is an important consideration.

If an impression has not been disinfected or if the laboratory had no assurance that an appropriate disinfection protocol was followed, it will be necessary to disinfect the stone cast. Disinfection solutions can be used that do not adversely affect the quality of the gypsum cast. Alternatively, disinfectants can be incorporated either in the powder or dissolved in the mixing water. Addition of a disinfectant in the gypsum products would undoubtedly have an effect on some of the properties of certain products, such as strength, setting expansion, and setting time. The precise effect depends on the types of gypsum and antimicrobial agents used. Nonetheless, the disinfected stones apparently compare favorably with nondisinfected controls.

The same microwave irradiation used in drying gypsum casts has also been evaluated in infection control. One study showed that a 5-min irradiation at 900 W reduced microorganism counts (cfu/mL) with a median log value of six to median counts (cfu/mL) of zero. Data on the effectiveness of microwave irradiation on different microorganism species, based on the power setting, the duration needed, and the influence of prolonged irradiation on the properties of the gypsum cast, are not available.

The widespread availability of a spectrum of disinfected dental stone casts (Type II to Type V) with proven efficacy and unimpaired physical properties will undoubtedly strengthen the barrier system of infection control in the dental laboratory.

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CHAPTER
10

Dental Waxes, Casting Investments, and Casting Procedures

OUTLINE

History of Dental Wax

Types of Inlay Waxes

Composition of Dental Waxes

Desirable Properties of Wax

Flow of Dental Wax

Thermal Properties of Dental Waxes

Manipulation of Inlay Wax

Wax Distortion

Specialty Waxes

Gypsum-Bonded Investment

Phosphate-Bonded Investment

Ethyl Silicate–Bonded Investment

Clinical Evaluation of Casting Fit

Compensation for Solidification Shrinkage

Preparation of the Master Die

Variables and Principles of Optimal Sprue Design

Casting Ring Liner

Investing Procedure

Casting Procedure

Technical Considerations for Phosphate-Bonded Investment

Causes of Defective Castings

KEY TERMS

Baseplate wax—Dental wax provided in sheet form to establish the initial arch form in the construction of complete dentures. This product typically contains approximately 75% paraffin or ceresin wax, beeswax other waxes, and resins.

Bite wax—A wax form used to record the occlusal surfaces of teeth as an aid in establishing maxillomandibular relationships.

Boxing wax—A wax sheet form used as a border at the perimeter of an impression to provide an enclosed boundary for the base of the cast to be made from a poured material such as gypsum or resin.

Burnout—Process of heating an invested mold to eliminate the embedded wax or plastic pattern.

Corrective wax (dental impression wax)—A thermoplastic wax that is used to make a type of dental impression.

Dental wax—(1) A low-molecular-weight ester of fatty acids derived from natural or synthetic components, such as petroleum derivatives, that soften to a plastic state at a relatively low temperature. (2) A mixture of two or more waxes and additives used as an aid for the production of gypsum casts, production of nonmetallic denture bases, registering of jaw relations, and laboratory work.

Direct wax technique—A process whereby a wax pattern is prepared in the mouth directly on prepared teeth.

Divesting—Process of removing investment from a cast metal or hot-pressed ceramic.

Elastic memory—Tendency of a solid wax form to partially return to its original shape when it is stored at a higher temperature than that to which it was cooled.

Flow—Relative ability of wax to plastically deform when it is heated slightly above body temperature.

Hygroscopic expansion—Amount of setting expansion that occurs when a gypsum-bonded casting investment is immersed in water, which is usually heated to approximately 38 °C. (See Chapter 9 for more information on this process.)

Indirect wax technique—Procedure in which a wax pattern is prepared on a die.

Inlay wax—A specialized **dental wax** that can be applied to dies to form direct or indirect patterns for the lost-wax technique, which is used for the casting of metals or hot pressing of ceramics.

Refractory—Capable of sustaining exposure to a high temperature without significant degradation.

Sprue—The mold channel through which molten metal or ceramic flows into a mold cavity.

Sprued wax pattern—A wax form consisting of the prosthesis pattern and the attached sprue network.

Sticky wax—A type of dental wax that exhibits high adhesion to dry, clean surfaces when it is heated to a plastic condition.

CRITICAL QUESTION

A wax pattern of an inlay made using the direct technique may result in a looser-fitting inlay than one made using the indirect technique. Why?

HISTORY OF DENTAL WAX

Wax has been a valuable commodity for over 2000 years. In ancient times beeswax was used for softening skin, binding together reeds used for flutes, coating and preserving valuable objects, candle production, and making sculptures and statues of highly regarded public figures. Beeswax was derived from secretions that bees use to build honeycombs. Although beeswax is still used today, modern waxes, such as those used to preserve furniture and automobile surfaces and those designed for dental procedures, are made from natural plant and animal sources; some types are derived synthetically from petroleum products and distillates. Synthetic waxes are typically composed of hydrogen, carbon, oxygen, and chlorine. Synthetic waxes are more uniform than natural waxes in their organic structure and more homogeneous in composition.

Carnauba is one of the hardest and most durable waxes. It is derived from the fronds of carnauba palm trees and is one of the main components of dental **inlay wax**. Candelilla wax, a major component of some dental waxes, is obtained from plants growing in Costa Rica, Guatemala, Mexico, Nicaragua, Panama, and the southwestern United States. In comparison to plant-derived carnauba and candelilla waxes, animal-derived beeswax, smd mineral-derived paraffin and ceresin waxes, other dental waxes are produced from components of fats, gums, oils, and resins.

TYPES OF INLAY WAXES

The wide variety of dental waxes can be classified into two groups, those used primarily in the clinic and those used in commercial dental laboratories. Clinical products include bite registration wax, disclosing wax (also known as pressure-indicating paste), utility waxes for altering and adapting impression trays, and low-melting type I inlay waxes used in the mouth for direct-waxing processes for pattern production. Laboratory products include **boxing wax**, **baseplate wax**, **sticky wax**, beading wax, utility wax, and hard, medium, and soft type II inlay-type waxes for making patterns on patients' models using the **indirect wax technique**. Type II waxes are required for the lost-wax processing of cast prostheses and frameworks. Each of these waxes has a melting range over which the temperature must be adjusted by means of a burner flame to control the **flow** properties for each specific application.

Dental waxes can also be classified in one of three types, pattern wax (inlay, casting, and baseplate types), processing wax (boxing, utility, and sticky types), and impression wax (bite registration and correction types). Casting wax is used for partial denture frameworks and other metal frameworks. One of the correction types includes waxes for repairing ceramic margin defects on all-ceramic inlays and crowns.

Inlay waxes are used to prepare patterns. These patterns are reproduced in gold via a casting process and in ceramic by hot-isostatic-pressing procedures. Inlay wax is sometimes referred to as casting wax, although other types of pattern waxes also fall into this category. Inlay wax must exhibit excellent adaptability to model or die surfaces, and it must be free from distortion, flaking, or chipping during the preparation of patterns. It must also be able to disintegrate, volatilize, and be eliminated completely from an investment mold during the **burnout** or wax elimination procedure. For **direct wax techniques** type I inlay wax must soften at a temperature that is not hazardous to the pulp tissue, and it must harden at a temperature above mouth temperature.

The colors of inlay waxes should contrast with the hues of teeth and dies. Dental waxes are supplied in a variety of colors including blue, green, yellow, red, and ivory. The colors are useful to provide a suitable contrast against a die that is an accurate replica of a prepared tooth or dental arch form. Ivory-colored wax is useful for aesthetic case presentations to patients. If applied as a veneer in a sufficient thickness, its opacity must be sufficient to mask colored die stones.

Inlay waxes may be softened over a flame or in water at 54 °C to 60 °C to enable their flow in the liquid state and their adaptation to the prepared tooth or die. These waxes are designed to maintain uniform workability over a wide temperature range and to facilitate accurate adaptation to the tooth or die under pressure. Additive layers and corrections may be applied to produce a relatively homogeneous pattern. These fused layers can be carved easily without chipping or flaking. A regular or soft type of wax is typically used for indirect work at room temperature or in cool weather. A harder or medium type with a low flow property is indicated for use in warmer climates.

The first procedure in the casting of an inlay or crown for the lost-wax process is the preparation of a **dental wax** pattern. The cavity is prepared in the tooth and the pattern is carved directly on a die that is a reproduction of the prepared tooth and dental tissues (indirect technique). The direct technique for producing wax inlay patterns within prepared teeth is rarely used because of the wax's sensitivity to changes in pressure, temperature, and heating and cooling rates during manipulation. Because the thermal expansion coefficient of wax is extremely high compared with the values for other dental materials, a wax pattern made in the mouth (direct technique) will shrink appreciably as it is cooled to room temperature. A pattern made by the indirect method may not shrink as much, although the amount depends on whether or not the pattern is allowed to reach room temperature before it is removed from the die. Dipping waxes are used occasionally to facilitate the wax pattern preparation process. This wax is kept molten to provide a station for mass production of patterns.

Type I is a *medium wax* employed in direct techniques and type II is a *soft wax* used in the indirect techniques. No matter how a pattern is prepared, it should be an accurate

reproduction of the missing tooth structure or part of a prosthesis that is adapted to soft tissues. The wax pattern forms the outline of the mold into which an alloy is cast or a ceramic is hot-isostatically pressed. Consequently, the resulting appliance, device, prosthesis, or framework can be no more accurate than the wax pattern regardless of the care observed in subsequent procedures. Therefore, the pattern should be well adapted to the prepared cavity or replica cavity and properly carved without any significant distortion. Before the adaptation of the wax pattern within a tooth or a die, a separating medium must be used to ensure the complete separation of the wax pattern without distortion. After the pattern is removed from the prepared cavity, it is encased in a gypsum- or phosphate-based material or other type of **refractory** material known as an *investment*. This process is called *investing the pattern*.

After investing anatomically accurate wax or resin patterns for inlays, onlays, crowns, bridges, and frameworks for removable partial dentures, the invested material must be eliminated completely before molten metal is cast or core ceramic is hot-pressed into the mold cavity. Wax patterns are used in the production of several types of complex removable devices or prostheses in addition to single-tooth restorations. However, this chapter is limited primarily to the construction of prostheses employed in operative dentistry and fixed prosthodontics.

COMPOSITION OF DENTAL WAXES

The primary components of dental waxes are derived from synthetic waxes and natural waxes (hydrocarbons of the paraffin and the microcrystalline groups, carnauba wax, candelilla wax, and resins). As stated earlier, natural waxes are derived from mineral, vegetable, and animal origins. Synthetic waxes are chemically synthesized from natural wax molecules. Most synthetic waxes are more homogeneous than pure natural waxes. Coloring agents are added for contrast of wax patterns against tooth, die, and model surfaces or to provide an ivory-colored or other natural tooth color as demonstration models used for educating patients about treatment options. Some formulations contain a compatible filler to control expansion and shrinkage of the wax product.

Most dental waxes contain 40% to 60% paraffin by weight, which is derived from high-boiling fractions of petroleum. They are composed mainly of a complex mixture of hydrocarbons of the methane series together with minor amounts of amorphous and microcrystalline phases. The wax can be obtained in a wide range of melting or softening temperatures depending on the molecular weight and distribution of the constituents. The melting range can be determined by a temperature versus-time cooling curve, as shown in Figure 10-1, for a paraffin-based inlay wax. The temperature-time relationship during cooling indicates the successive solidification of progressively lower-molecular-weight fractions. This condition promotes moldability of the wax below its melting temperature. Paraffin that is used for type I waxes has a higher melting point than the paraffin used for type II waxes.

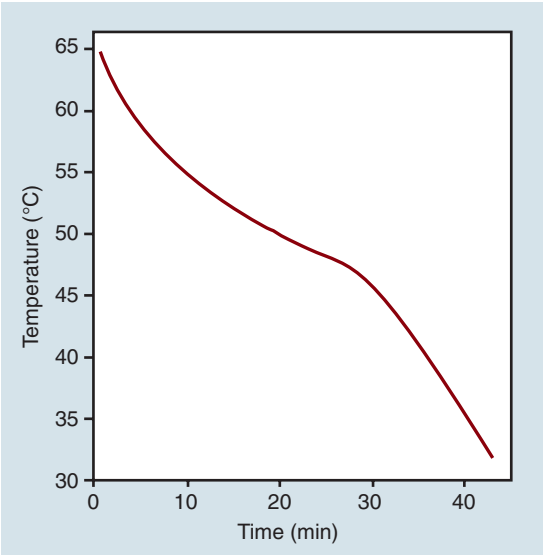


FIGURE 10-1 Time-temperature cooling curve for type I inlay wax.

Paraffin wax is likely to flake when it is trimmed, and it does not produce a smooth, glossy surface, which is a desirable requisite for an inlay wax. Thus, other waxes and natural resins must be added as modifying agents.

Gum dammar, or dammar resin, is a natural resin. It is added to the paraffin to improve the smoothness in molding and to render it more resistant to cracking and flaking. It also increases the toughness of the wax and enhances the smoothness and luster of the surface.

Carnauba wax occurs as a fine powder on the leaves of certain tropical palms. This wax is very hard, and it has a relatively high melting point and it has an agreeable odor. It is combined with the paraffin to decrease flow at mouth temperature. Carnauba wax contributes greater glossiness to the wax surface than dammar resin.

Candelilla wax can also be added partially or entirely to replace carnauba wax. Candelilla wax provides the same general qualities as carnauba wax but its melting point is lower and it is not as hard as carnauba wax. Ceresin (see below) may replace part of the paraffin to modify the toughness and carving characteristics of the wax.

Ceresin is typically a white wax extracted from ozokerite, a waxy mineral mixture of hydrocarbons that is colorless or white when pure, but it has a somewhat unpleasant odor.

Carnauba wax is often replaced in part by certain synthetic waxes that are compatible with paraffin wax. At least two waxes of this type can be used. One is a complex nitrogen derivative of the higher fatty acids and the other contains esters of acids derived from montan wax, a derivative hard wax that is obtained by solvent extraction of certain types of lignite or brown coal. Approximately a third of all montan wax produced is used in automobile polishing pastes.

For an impression compound, a synthetic wax is preferable to a natural wax because it has greater uniformity. Because of the high melting point of the synthetic waxes, more paraffin can be incorporated to improve the general working qualities of the product.

DESIRABLE PROPERTIES OF WAX

Control of the properties of dental wax is accomplished by a combination of factors. For example, certain wax formulations may be based on the amount of carnauba wax, the desired melting range of the hydrocarbon wax, and the addition of resin to achieve desirable properties.

Depending on the specific application of a given wax, the melting range, viscosity, adaptability, flow, elastic recovery, carvability, and burnout properties of these materials control the quality and reproducibility of the final prostheses and restorations. The most important properties of inlay waxes are as follows:

1. The wax should be uniform when softened. It should be compounded with ingredients that blend with each other so that there are no granules on the surface and no hard spots within the surface when the wax is softened.
2. The color should contrast with die materials or prepared teeth. Since it is necessary to carve the wax margins against the die surface, the wax must exhibit a definite contrast in color and sufficient opacity in thin layers to facilitate proper finishing of the margins.
3. The wax should not fragment into flakes or similar surface particles when it is molded after softening. Such flakiness is likely to be present in paraffin wax, so modifiers must be added to minimize this effect.
4. Once the wax pattern has solidified, it is necessary to carve the original tooth anatomy and the margins so that the pattern conforms precisely to the surface of the die. The latter procedure sometimes requires that the wax be carved to a very thin layer. The wax must not be pulled away by the carving instrument or chip as it is carved or such precision cannot be achieved.
5. For lost-wax casting of metals, an investment mold is formed around a wax pattern. After the mold containing the wax pattern has been formed, the wax must be eliminated from the mold. Elimination of the **sprued wax pattern** is usually accomplished by heating the mold to melt and ignite the wax. If the wax leaves a residue or an impervious coating on the walls of the mold, the cast metal inlay may be adversely affected. Consequently, the wax should burn out completely by oxidizing residual carbon to volatile gases. Ideally, when wax melts and is vaporized at 500 °C, it should not leave a solid residue that amounts to more than 0.10% of the original weight of the specimen.

Expansion and shrinkage of casting wax are extremely sensitive to temperature. Normally soft wax shrinks more than hard wax. High-shrinkage wax may cause significant pattern distortion when it solidifies. It is necessary to avoid excessive shrinkage and expansion caused by a temperature change. For this reason, organic filler is added to certain wax formulations. Such fillers should be completely miscible with the components of the inlay wax during manufacture, and they should not leave an undesirable residue after burnout.

FLOW OF DENTAL WAX

One of the desirable properties of type I inlay wax is that it should exhibit a marked plasticity or flow at a temperature slightly above that of the mouth. The temperatures at which the wax is plastic are indicated by the time-temperature cooling curve for a typical type I wax, as shown in Figure 10-1. The wax begins to harden slowly below 65 °C and becomes solid below approximately 48 °C; below which it cools rapidly at a constant rate.

Different types of casting waxes exhibit characteristic flow curves as a function of temperature. Each wax exhibits a sharp transition temperature at which it loses its plasticity. Soft wax exhibits a transition point at a lower temperature than hard wax. Inlay waxes do not solidify with a space lattice, as does a metal. Instead, the structure likely exhibits a combination of crystalline and amorphous structures, with limited short-range order of the molecules. The wax lacks rigidity and may flow under applied pressure even at room temperature.

Requirements for the flow properties of inlay waxes at specific temperatures are summarized in Table 10-1. The flow is measured by subjecting cylindrical specimens to a designated load at the stated temperature and measuring the percentage of reduction in length. The maximum flow permitted for type I waxes at 37 °C is 1%. Their low flow at this temperature permits carving and removal of the pattern from the prepared cavity at oral temperature without distortion. In addition, both type I and type II waxes at 45 °C must have a minimal flow of 70% and a maximum flow of 90%. At this temperature, the wax is inserted into the prepared cavity. If the wax does not have sufficient plasticity, it will not flow into all of the areas in the preparation and reproduce the details that were established by the invested wax pattern.

THERMAL PROPERTIES OF DENTAL WAXES

Inlay waxes are softened with heat, forced into the prepared tooth cavity in either the tooth or the die, and cooled. The

TABLE 10-1 Requirements for Inlay Wax Flow (%)

Type of Wax	T = 30 °C Maximum	T = 37 °C Maximum	T = 40 °C Minimum	T = 40 °C Maximum	T = 45 °C Minimum	T = 45 °C Maximum
I	—	1	—	20	70	90
II	1	—	50	—	70	90

thermal conductivity of the waxes is low (e.g., $k_{paraffin} = 0.25$ W/mK), and sufficient time must be allowed both to heat them uniformly throughout and to cool them to body or room temperature.

Another thermal characteristic of inlay waxes is their high coefficient of thermal expansion. As shown in Figure 10-2, the wax may expand as much as 0.7% with an increase in temperature of 20 °C or contract as much as 0.35% when it is cooled from 37 °C to 25 °C. The average linear thermal expansion coefficient over this temperature range is 350×10^{-6}/K, with values ranging from 217 to 512×10^{-6}/K.

A comparison of the thermal expansion coefficients of dental materials given in the chapters on physical properties and ceramics indicates that inlay wax expands and contracts thermally more per degree temperature change than any other dental material. This property is less significant when the wax is used in the indirect technique because the pattern is not subjected to a change from mouth to room temperature.

The thermal dimensional change may be affected by the previous treatment of the wax. Curve A in Figure 10-2 represents the thermal expansion of inlay wax as a function of temperature. The expansion rate increases abruptly above approximately 35 °C. The temperature at which a change in rate occurs is known as the *glass transition temperature*. Some constituents of the wax probably change in their crystalline form at this temperature, and the wax is more plastic at higher temperatures. Not all waxes exhibit transition temperatures. The transition point shown in Figure 10-2 appears to be characteristic of an inlay wax with a high paraffin wax content. If the wax is allowed to cool without being placed under pressure, the transition temperature region is not as pronounced when it is reheated, nor is there much change in the thermal expansion coefficient, as shown in curve B of Figure 10-2.

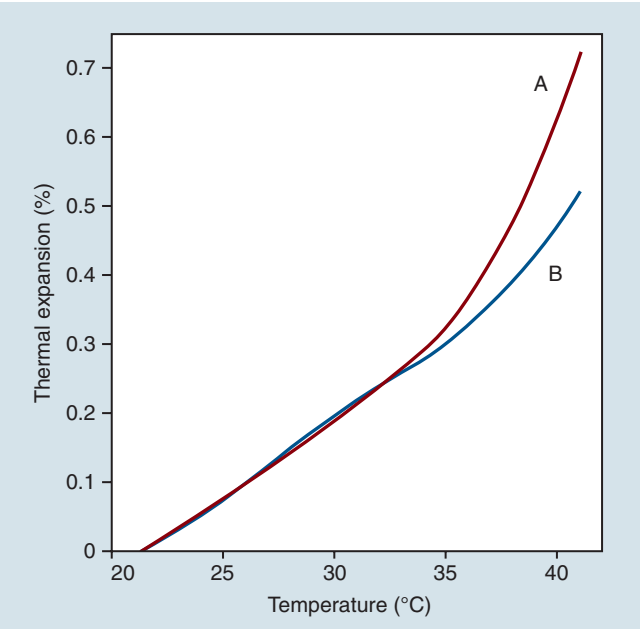


FIGURE 10-2 Thermal expansion of inlay wax. Curve A represents the thermal expansion when the wax was held under pressure while it was cooling from the liquid state. When the same wax was allowed to cool without pressure and again heated, the behavior shown by curve B occurs.

MANIPULATION OF INLAY WAX

The higher flow of softer waxes produces larger cast metal or hot-isostatically-pressed (HIP) ceramic prostheses than harder waxes because the soft waxes expand more as the investment heats up during setting and they offer less resistance to the expanding investment during setting. Waxes oxidize on heating, and on prolonged heating some waxes evaporate, so that the storage container for melted wax will be coated by gummy deposits. Therefore, care should be exercised to use the lowest temperature possible and to clean the wax pot and replace the wax periodically.

To manipulate inlay wax, dry heat is preferred to the use of a water bath. The latter can result in the inclusion of droplets of water, which can splatter on flaming, smear the wax surface during polishing, and distort the pattern during temperature changes. To avoid distortion during removal of the pattern, it should be penetrated slightly with an explorer point and carefully removed from the cavity. A mesial-occlusal-distal (MOD) pattern can best be removed by inserting a staple-like wire within the surface so that each prong is positioned above the proximal wall areas of the pattern. It should be removed with dental floss looped through the staple and withdrawn in a direction parallel to the axial walls and with minimum distortion. After removal, touching the pattern with the fingers should be avoided as much as possible to prevent any temperature changes and distortion.

To fabricate indirect patterns, the die should be lubricated, preferably with a lubricant containing a wetting agent. Any excess must be avoided because it will prevent intimate adaptation to the die. The melted wax may be added in layers with a spatula or a waxing instrument. The prepared cavity should be overfilled, and the wax then carved to the proper contour. When the margins are being carved, care should be taken to avoid abrading any surface of the stone die. A silk or other fine cloth may be used for a final polishing of the pattern, rubbing toward the margins. Theoretically, applying pressure is undesirable, as shown by change in shape of the the stick of wax in Figure 10-3. However, some clinicians prefer to apply finger pressure as the wax is cooling to help fill the cavity and prevent distortion during cooling. The fingers also accelerate the cooling rate. Although temperature changes should be avoided, some technicians prefer to repeatedly remelt small areas along the margins and examine them under a low-power microscope. Regardless of the method chosen, the most practical method for avoiding any possible delayed distortion is to invest the pattern immediately after removal from the mouth or die, as noted earlier. Once the investment hardens (sets), no distortion of the pattern will occur.

? CRITICAL QUESTION

How can one best minimize potential distortion effects associated with **elastic memory** and temperature changes?

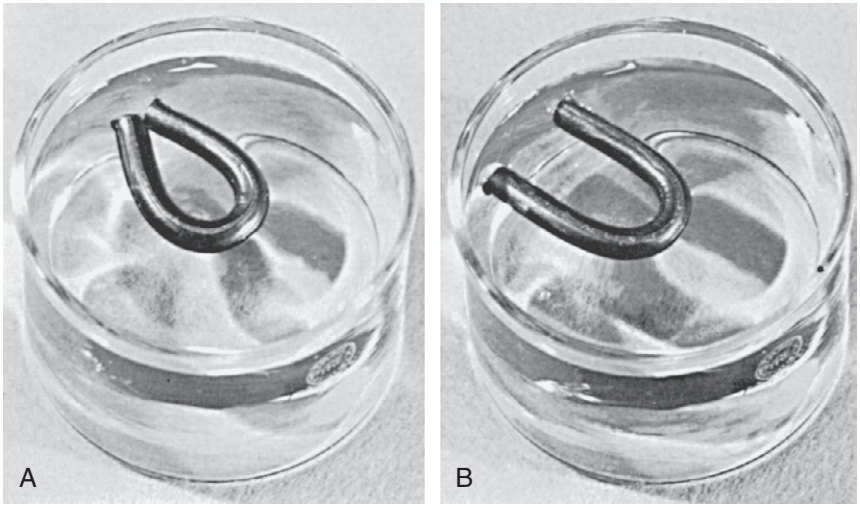


FIGURE 10-3 **A,** A stick of inlay wax is bent into the shape of a horseshoe and floated on water at room temperature. **B,** After 24 hours the same stick of wax tends to relax and distortion occurs.

WAX DISTORTION

Distortion of wax patterns is the most serious problem one can experience in forming and removing the pattern from a tooth or die. Distortion of a wax pattern results from occluded air in the pattern, physical deformation (during molding, carving, or removal), release of stresses "trapped" during previous cooling, excessive storage time, and extreme temperature changes during storage.

A newly made wax pattern tends to change its shape and size over time. Upon cooling it contracts and, after attaining equilibrium, reaches a state of dimensional stability. It is important that the wax pattern be retained on the die for several hours to avoid distortion and ensure that equilibrium conditions are established.

Like other thermoplastics, waxes tend to return partially to their original shape after manipulation. This is known as *elastic memory*. To demonstrate this effect, a stick of inlay wax can be softened over a Bunsen burner, bent into a horseshoe shape, and chilled in this position. If it is then floated in room-temperature water for a number of hours, the horseshoe will open, as shown in Figure 10-3, *A* and *B*. This is more critical for inlay waxes than for other impression materials because the metal or hot-pressed ceramic restorations made from the wax must fit onto unyielding hard tooth tissue.

The elastic memory of waxes is further illustrated during measurement of the thermal expansion of a wax held under pressure during cooling. The expansion increases above the glass transition temperature more than when it is cooled without pressure, as shown in curve B of Figure 10-2. Again, this illustrates the tendency of wax to return to its normal undisturbed state. In recalling Figure 10-3, *A*, when the wax is bent into a horseshoe, the inner molecules are under compression and the outer ones are in tension. Once the stresses are gradually relieved at room temperature, the wax tends to recover its elastic strain.

The components of a casting ring with a wax pattern surrounded by casting investment are shown in Figure 10-4. A sprued wax pattern is shown in the center of the investment

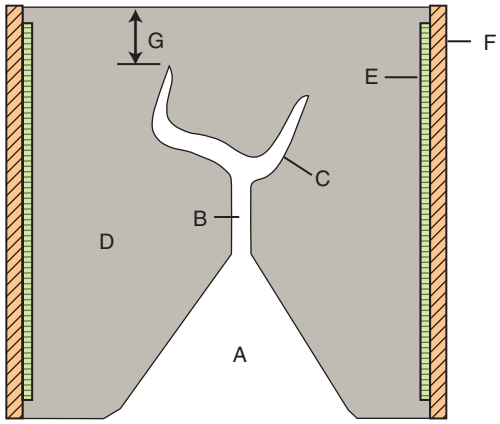


FIGURE 10-4 Diagrammatic representation of a dental casting mold: **A,** Crucible former. **B,** Sprue. **C,** Cavity formed by wax pattern after burnout. **D,** Investment. **E,** Liner. **F,** Casting ring. **G,** Recommended maximum investment thickness of approximately 6 mm between the end of the mold cavity and the end of the invested ring to provide pathways for sufficient gas escape during casting.

ring. Examples of properly sprued wax patterns for a single crown and for a three-unit bridge are shown in Figure 10-5. Note the spherical reservoir that is attached to the single crown pattern. The purpose of the reservoir is to maintain a molten pool of metal to ensure complete filling of the crown area of the mold cavity. For the bridge pattern on the right side of Figure 10-5, a runner bar is used as a reservoir. Additional details are presented later in this chapter.

Storage of a wax pattern for too long can lead to a distortion of its form because of stress relaxation effects. A casting will fit most accurately when the pattern is invested immediately after its removal from the preparation.

? CRITICAL QUESTION

Under what conditions should medium and hard waxes be used?

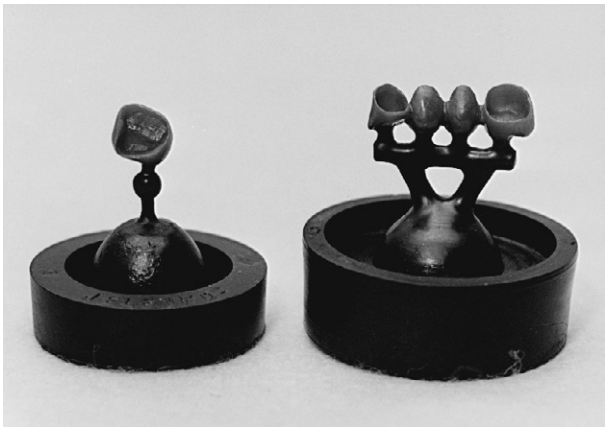


FIGURE 10-5 Primary sprue oriented directly toward the wax pattern (*left*). Note the spherical reservoir on the vertical sprue. Indirect sprue design showing a horizontal reservoir runner bar that is positioned near the heat center of the invested ring (*right*).

SPECIALTY WAXES

A pattern made of hard wax is less sensitive to temperature conditions than one made of soft wax. The exothermic heat generated during the setting of an investment affects the pattern selectively. A soft wax pattern may result in a slightly larger and relatively rougher casting than a hard wax pattern. This tendency of softer inlay waxes to expand during setting in a hygroscopic bath at 37.8 °C (100 °F) may contribute to the phenomenon of **hygroscopic expansion**, described further in Chapter 9.

Other types of waxes are employed for different purposes than those described for the inlay waxes. The composition of each type is adjusted for the particular requirements. One of the most common is baseplate wax.

Baseplate wax is used to establish the initial arch form in the construction of complete dentures. Supplied in 1- to 2-mm-thick red or pink sheets, the wax is approximately 75% paraffin or ceresin with additions of beeswax and other resins or waxes. The harder the wax, the less the flow at a given temperature. The difference in flow of the three types may be advantageous for a particular application. Type I, a soft wax, is used for building veneers. Type II, a medium wax, is designed for patterns to be placed in the mouth in normal climatic conditions. Type III, a hard wax, is used for trial fitting in the mouth in tropical climates. Because residual stress is present within the wax from contouring and manipulating the wax, the finished denture pattern should be flasked as soon as possible after completion of all adjustments and manipulations.

The *impression waxes*, also referred to as ***bite waxes*** or ***corrective waxes***, tend to distort if they are withdrawn from undercut areas. Thus, they are limited to use in edentulous sites of the mouth or in occlusal surface areas. Although corrective waxes are relatively soft at mouth temperature, they have sufficient body to register the detail of soft tissues, and they are rigid at room temperature.

Other types of dental waxes include *sticky wax,* an orange-colored stick wax, which is tacky when melted but firm and brittle when cooled. Sticky waxes are used to temporarily fasten gypsum model components, join and temporarily stabilize the components of a bridge before soldering, or attach pieces of a broken denture prior to a repair.

Boxing wax is another useful material for enclosing an impression before the plaster or stone cast is poured. Typically provided in pink-colored flat sheets, this wax is relatively soft and pliable and can easily be pressed to the desired contour around the perimeter of an impression and self-sealed at the overlapped area with firm pressure.

Carving wax and *presentation wax* are used for demonstration purposes. Such waxes contain synthetic and polymeric materials with additives such as fillers and coloring agents.

CRITICAL QUESTION

Why should gypsum-bonded investment not be heated above 700 °C?

GYPSUM-BONDED INVESTMENT

The most common method used to form metal inlays, onlays, crowns, bridges, and other metal frameworks is to cast molten alloys by centrifugal force, under pressure, or under vacuum and pressure into a mold cavity. The material used for the mold must be sufficiently refractory and thermally stable that it can withstand exposure to the high temperatures of molten metal as the metal solidifies and cools to room temperature. In addition, the mold or investment material must not interact chemically with the metal surface, and it must be easy to remove from the metal casting.

The mold cavity is produced by eliminating a wax or resin pattern by heating the mold to a specific temperature and for a specific time. This is called the *burnout process*. To provide a pathway to the mold cavity for molten metal, the wax or resin pattern must have one or more cylindrical wax segments attached at the desired point(s) of metal entry; this arrangement is termed a *sprued wax pattern*. A **sprue** is the channel in a refractory investment mold through which molten metal flows. After the wax pattern has been made, either directly on a prepared tooth or on a replica die of the tooth, a sprue former base is attached to the sprued wax pattern, an investment ring is pressed into the sprue former base, and an investment slurry is vibrated into the ring to embed the wax pattern in the investment. Examples of sprued wax patterns on a sprue former base are shown in Figure 10-5. The investment material is mixed in the same manner as plaster or dental stone, poured around the pattern, and allowed to set. After the investment hardens, the sprue-former base is removed. The molten metal is then forced through the sprue or ingate created by the sprue former base into the mold cavity left by the wax.

The remainder of this chapter deals with refractory investments and casting methods used for the fabrication of

small dental crown and bridge prostheses either by casting metal or by hot-pressing ceramic. Generally two types of investments—gypsum-bonded and phosphate-bonded—are employed, depending on the melting range of the alloy to be cast. The gypsum-based materials represent the type traditionally used for conventional casting of gold alloy inlays, onlays, crowns, and larger fixed dental prostheses (FDPs). Phosphate-based investments are designed primarily for alloys used to produce copings or frameworks for metal-ceramic prostheses (Chapter 18) and some base metal alloys. It can also be used for pressable ceramics. A third type is the ethyl silicate–bonded investment, which is used principally for the casting of removable partial dentures made from base metals (cobalt-based and nickel-based alloys). Commercially pure titanium and titanium alloys require a special investment as well as a controlled atmosphere to achieve satisfactory castings.

The type of investment used depends on whether the appliance to be fabricated is fixed or removable and on the method of obtaining the expansion required to compensate for the contraction of the molten alloy during solidification. Type I investments are those employed for the casting of inlays or crowns when the compensation for alloy casting shrinkage is accomplished principally by thermal expansion of the investment. Type II investments are also used for casting inlays, onlays, or crowns, but the major mode of compensation for alloy shrinkage during solidification is by hygroscopic expansion achieved by immersing the invested ring in a warm water bath. Burnout of the investment is performed at a lower temperature than that used for the high-heat burnout technique. Type III investments are used rarely in the construction of partial dentures because they are designed for casting gold alloys. This chapter focuses primarily on type I and type II investments.

COMPOSITION

The ingredients of dental inlay investments employed with conventional gold casting alloys are α-hemihydrate of gypsum, and quartz, or cristobalite, which are forms of silica. Most investments contain the α-hemihydrate of gypsum because of its greater strength. This gypsum product serves as a binder for the other ingredients and to provide rigidity. The strength of the investment is dependent on the amount of binder used. The investment powder may contain 25% to 45% of calcium sulfate hemihydrate. The remainder consists of silica allotropes and controlling chemicals.

GYPSUM-BONDED INVESTMENTS

The α-hemihydrate form of gypsum is generally the binder for investments used in casting gold-containing alloys with melting ranges below 1000 °C. When this material is heated at temperatures sufficiently high to completely dehydrate the investment and to ensure complete castings, it shrinks considerably and occasionally fractures.

The thermal expansion curves for the three common forms of gypsum products are shown in Figure 10-6. All forms shrink considerably after dehydration between 200 °C and 400 °C. A slight expansion takes place between 400 °C and approximately 700 °C, and a large contraction then occurs. This latter shrinkage is most likely caused by decomposition and the release of sulfur dioxide. This decomposition not only causes shrinkage but also contaminates the castings with the sulfides of the nonnoble alloying elements, such as silver and copper. Thus, it is imperative that gypsum investments not be heated above 700 °C. However, for gypsum products containing carbon, the maximum temperature is 650 °C. In this way proper fit and uncontaminated alloys are obtained.

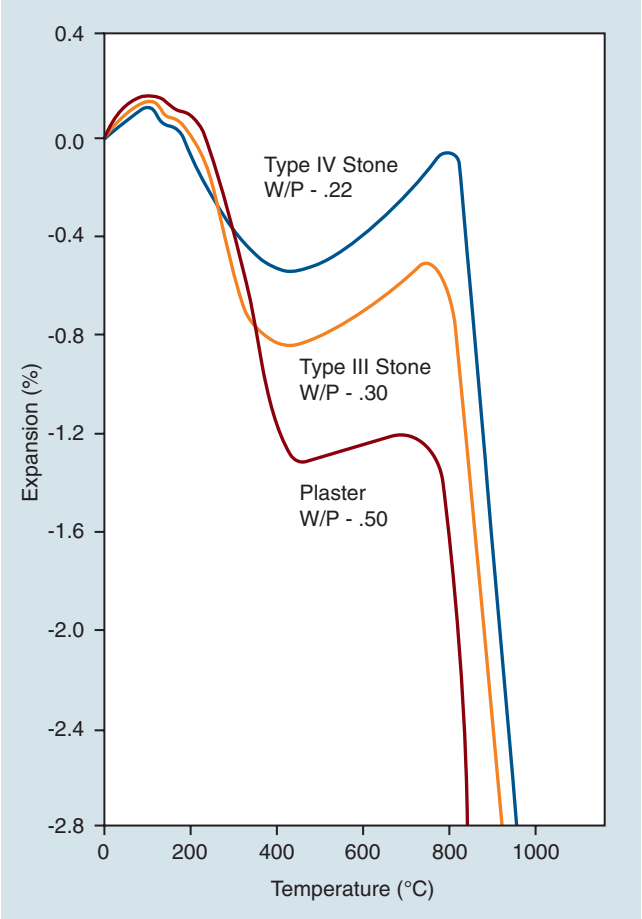


FIGURE 10-6 Dimensional change of three forms of gypsum when heated. (Courtesy of R. Neiman, Whip-Mix Corporation, Louisville, KY.)

Usually castings made from *pure gypsum* ($CaSO_4 \cdot 2H_2O$) molds are extremely undersized. The α-hemihydrate product, which requires less mixing water and shrinks less, is the optimal choice as a binder.

SILICA

The wax pattern is usually eliminated from the mold by heat. During heating, the investment is expected to expand thermally to compensate partially or totally for the casting shrinkage of the solidifying alloy. As shown in Figure 10-5, gypsum shrinks considerably when it is heated. If the proper forms of silica are employed in the investment, this contraction during heating can be eliminated and changed to an expansion. Silica exists in at least four allotropic forms: quartz, tridymite,

cristobalite, and fused quartz. Quartz and cristobalite forms are of particular dental interest.

When quartz, tridymite, or cristobalite is heated, a change in crystalline form occurs at a transition temperature characteristic of the particular form of silica. For example, when quartz is heated, it inverts (transforms) reversibly from a "low" room-temperature crystal form, known as α quartz, to a "high" form, called β quartz, at a temperature of 573 °C. This α to β phase transformation is called an *inversion,* and it is accompanied by a linear expansion of 0.45%. In a similar manner, cristobalite undergoes an analogous transition between 200 °C and 270 °C from "low" (α cristobalite) to "high" (β cristobalite). Two inversions of tridymite occur at 117 °C and 163 °C, respectively. The β-allotropic forms are stable only above the transition temperature noted, and an inversion to the lower α form occurs on cooling in each case. In powdered form, the inversions occur over a range of temperature rather than instantaneously at a specific temperature.

The density decreases as the α form changes to the β form, with a resulting increase in volume that occurs by a rapid increase in the linear expansion as indicated in Figure 10-7. Consequently, the shrinkage of gypsum shown in Figure 10-6 can be counterbalanced by the inclusion of one or more of the crystalline silicas. Fused quartz is amorphous and glass-like in character, and it exhibits no inversion at any temperature below its fusion point. It has an extremely low linear coefficient of thermal expansion and is of little use in dental investments. Quartz, cristobalite, or a combination of the two forms may be used in a dental investment. Both are available in the pure form. Tridymite is no longer an expected impurity in cristobalite. On the basis of the type of silica principally employed, dental investments are often classified as quartz or cristobalite investments.

MODIFIERS

In addition to silica, certain modifying agents, coloring matter, and reducing agents, such as carbon and powdered copper, are present. The reducing agents are used in some investments to provide a nonoxidizing atmosphere in the mold when a gold alloy is cast.

Unlike the dental stones, a setting expansion is usually desirable to assist in compensating for the contraction of the alloy. Some of the added modifiers—such as alkali-earth and transition-metal chlorides, boric acid, and sodium chloride—not only regulate the setting expansion and the setting time but also prevent most of the shrinkage of gypsum when it is heated above 300 °C. In some instances, the modifiers are needed to regulate the setting time and setting expansion, as described for the dental stones. The microstructure of a set gypsum-bonded investment can be seen in Figure 10-8.

SETTING TIME

The setting time of an investment can be measured in the same manner as plaster. Furthermore, it can be controlled in the same manner. The setting time for dental inlay casting investment should not be less than 5 or more than 25 minutes. Usually the modern inlay investments set initially in 9 to 18 minutes. Sufficient time should be allowed for mixing and investing the pattern before the investment sets.

NORMAL SETTING EXPANSION

A mixture of silica and calcinated gypsum powder (calcium sulfate hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$) results in setting expansion greater than that of the gypsum product used alone. The silica particles probably interfere with the intermeshing and interlocking of the crystals as they form. Thus, the thrust of the crystals is outward during growth, and they increase expansion. Generally the resulting setting expansion in such

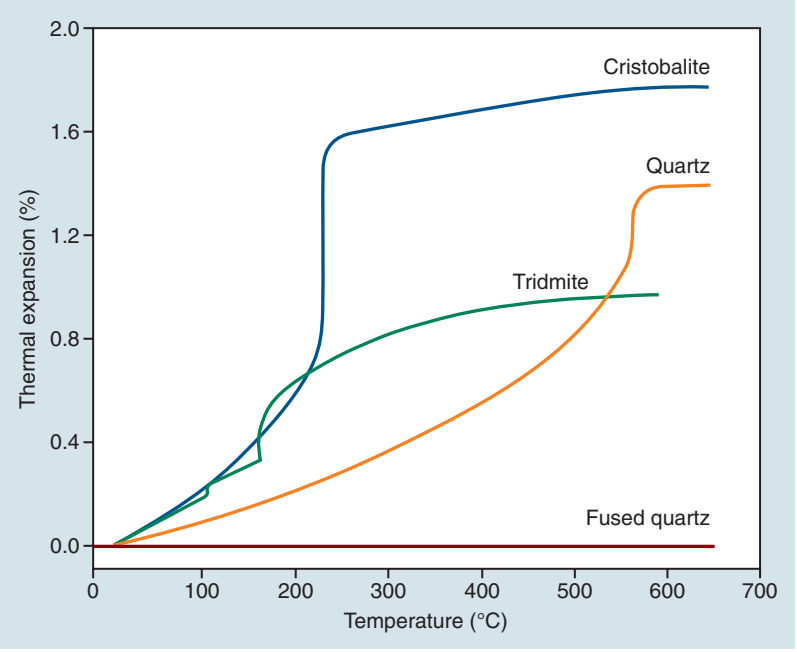


FIGURE 10-7 Thermal expansion of four forms of silica. (Courtesy of R. Neiman, Whip-Mix Corporation, Louisville, KY.)

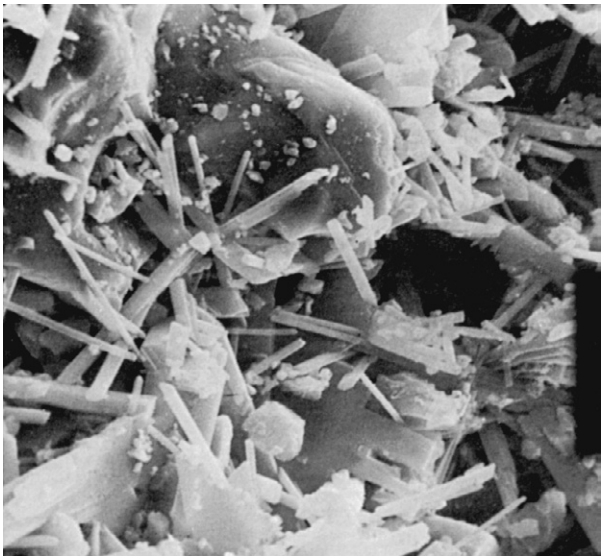


FIGURE 10-8 Microstructure of the surface of a set cristobalite investment. The large irregular particles are silica and the rodlike particles are cristobalite (×3000). (Courtesy of R. Earnshaw.)

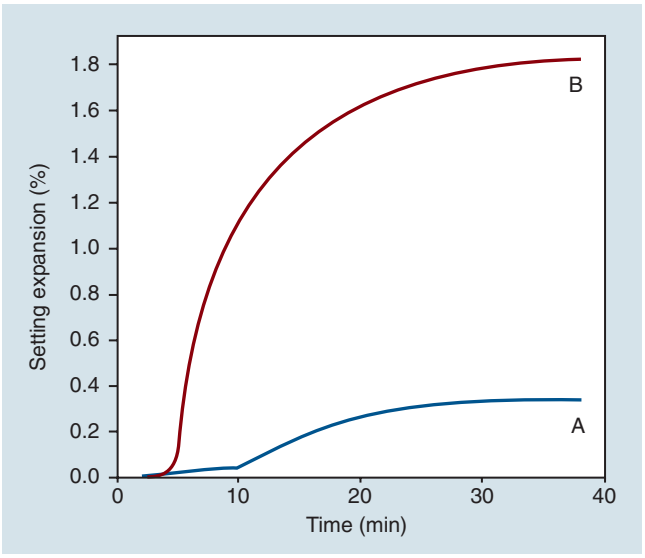


FIGURE 10-9 Setting expansion and hygroscopic expansion of a gypsum-bonded investment. **A,** Normal setting expansion of dental investment. **B,** Hygroscopic setting expansion. The investment was immersed in water 5 minutes after the beginning of mixing; the water/powder ratio was 0.30.

a case is high. Type I investments should exhibit a maximum setting expansion in air of 0.6%. The purpose of the setting expansion is to aid in enlarging the mold to compensate partially for the casting shrinkage of the alloy. Typically, the setting expansion of these investments is approximately 0.4%. This expansion is controlled by retarders and accelerators.

Variables other than the exothermic heat of reaction also influence the effective setting expansion. As the investment sets and setting expansion occurs, it eventually gains sufficient strength to produce a dimensional change in the wax pattern and mold cavity. The inner core of the investment adjacent to a mesial-occlusal-distal (MOD) wax pattern can actually force the proximal walls outward to a certain extent. If the pattern has a thin wall, the effective setting expansion is somewhat greater than for a pattern with thicker walls because the investment can move the thinner wall more readily. Also, the softer the wax, the greater is the effective setting expansion, because the softer wax is more readily moved by the expanding investment. If a wax softer than a type II inlay wax is used, the setting expansion may cause an excessive distortion of the pattern.

HYGROSCOPIC SETTING EXPANSION

The theory of hygroscopic setting expansion was previously described in connection with the setting of dental plaster and stone. Hygroscopic setting expansion, which is greater in magnitude than normal setting expansion, differs from normal setting expansion in that it occurs when the gypsum product is allowed to set when placed in contact with heated water.

Hygroscopic setting expansion was first discovered in connection with an investigation of the dimensional changes of a dental investment during setting. As illustrated in Figure 10-9, the hygroscopic setting expansion may be six or more times greater than the normal setting expansion of a dental investment. In fact, it may be as high as 5 linear percent. The hygroscopic setting expansion is one of the methods for expanding the casting mold to compensate for the casting shrinkage of gold alloys.

Commercial investments exhibit different amounts of hygroscopic expansion. Although all investments appear to be subject to hygroscopic expansion, the expansion in some instances is not as great as in others. For this reason, certain investments are specially formulated to provide a substantial hygroscopic expansion when the investment is permitted to set in contact with water. Type II investments should exhibit a minimum setting expansion in water of 1.2%. The maximum expansion permitted is 2.2%. As discussed in the following sections, a number of factors are important in the control of hygroscopic expansion.

VARIABLES THAT AFFECT HYGROSCOPIC EXPANSION

The magnitude of the hygroscopic setting expansion of a dental investment is generally proportional to the silica content of the investment, other factors being equal. The finer the particle size of the silica, the greater is the hygroscopic expansion. In general, α-hemihydrate is apt to produce a greater hygroscopic expansion in the presence of silica than is the β-hemihydrate, particularly when the expansion is unrestricted.

A dental investment should have enough hemihydrate binder with the silica to provide sufficient strength after hygroscopic expansion. Otherwise shrinkage occurs during the subsequent drying of the set investment. At least 15% of binder is necessary to prevent drying shrinkage.

With most investments, as the mixing time is reduced, the hygroscopic expansion is decreased. This factor is also important in the control of the effective setting expansion.

The older the investment, the lower is its hygroscopic expansion. Consequently the amount of investment purchased at one time should be limited. The greatest amount of hygroscopic setting expansion is observed if the immersion takes place before the initial set. The longer the immersion of the investment in the water bath is delayed beyond the time of the initial set of the investment, the lower is the hygroscopic expansion.

Both the normal and hygroscopic setting expansions are confined by opposing forces, such as those exerted by the walls of the container in which the investment is poured or by the walls of the wax pattern. However, the confining effect on hygroscopic expansion is more pronounced than the similar effect on the normal setting expansion. Therefore, the effective hygroscopic setting expansion is likely to be less relative to the expected expansion compared with the normal setting expansion.

When the dimensional change in the wax pattern itself is measured after investing, the increase in the effective setting expansion during immersion of investment in a 37.7 °C (100 °F) water bath is apparently not only the result of hygroscopic expansion. Rather, it may be caused mainly by heating and expanding the wax pattern and softening the pattern at the water temperature, permitting an increase in effective setting expansion. The latter results from a combination of thermal expansion of the wax pattern plus the softened condition of the wax, reducing its confining effect on the expansion of the setting investment. This is substantiated by the fact that immersion in water at room temperature (rather than 37.7 °C) reduces the effective expansion.

The magnitude of the hygroscopic setting expansion can be controlled by the amount of water added to the setting investment. It has been proved that the magnitude of the hygroscopic expansion is proportional to the amount of water added during the setting period until maximal expansion occurs. No further expansion is then evident regardless of the amount of water added.

The effects of some of the factors previously discussed (W/P ratio, mixing, and shelf life) on the maximal hygroscopic setting expansion are illustrated in Figure 10-9 relative to the amount of water added. As shown in Figure 10-9, the magnitude of the hygroscopic setting expansion below the maximal expansion value is dependent only on the amount of water added and independent of the W/P ratio, the amount of mixing, and the age or shelf life of the investment. This finding is the basis for the mold expansion technique.

Hygroscopic setting expansion is a continuation of ordinary setting expansion because the immersion water replaces the water of hydration, thus preventing confinement of the growing crystals by the surface tension of the excess water. Because of the dilution effect of the quartz particles, the hygroscopic setting expansion in these investments is greater than that of the gypsum binder when used alone. This effect is the same as previously described for normal setting expansion. This phenomenon is purely physical. The hemihydrate binder is not necessary for hygroscopic expansion because investments with other binders exhibit a similar expansion when they are allowed to set under water. Expansion can be detected when water is poured into a vessel containing only small smooth quartz particles. The water is drawn between the particles by capillary action, thereby causing the particles to separate, creating an expansion. The effect is not permanent after the water is evaporated unless a binder is present.

The greater the amount of the silica or the inert filler, the more rapidly the added water can diffuse through the setting material and the greater the expansion. The W/P ratio affects the hygroscopic expansion for the same reason that it affects the normal setting expansion. Once setting starts, the later that water is added to the investment, the less the hygroscopic setting expansion will be, because part of the crystallization has already started in a "normal" way. Some of the crystals have intermeshed, inhibiting further crystal growth when the water is added.

THERMAL EXPANSION OF GYPSUM-BONDED INVESTMENTS

To achieve sufficient expansion of gypsum-bonded investment, the silica must be increased to counterbalance the contraction of the gypsum during heating. However, when the quartz content of the investment is increased to 60%, with the balance being the calcium sulfate hemihydrate binder, the initial contraction of the gypsum is not eliminated. The contraction of the gypsum is entirely balanced when the quartz content is increased to 75% (Figure 10-10). If a sufficient amount of setting expansion had been present, a casting made at 700 °C would probably have fit the die reasonably well. The thermal expansion curves of quartz investments are influenced by the particle size of the quartz, the type of gypsum binder, and the resultant W/P ratio necessary to provide a workable mix.

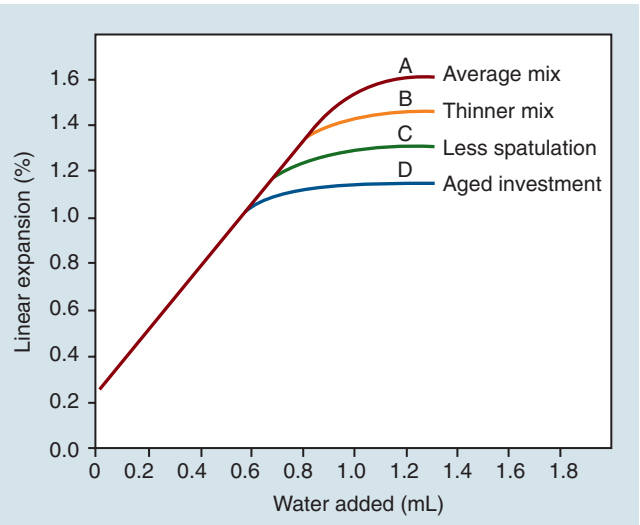


FIGURE 10-10 Relationship of the linear hygroscopic setting expansion and the amount of water added as influenced by certain manipulative factors. (Data from Asgar K, Mahler DB, Peyton FA: Hygroscopic technique for inlay casting using controlled water additions. *J Prosthet Dent* 5:711, 1955.)

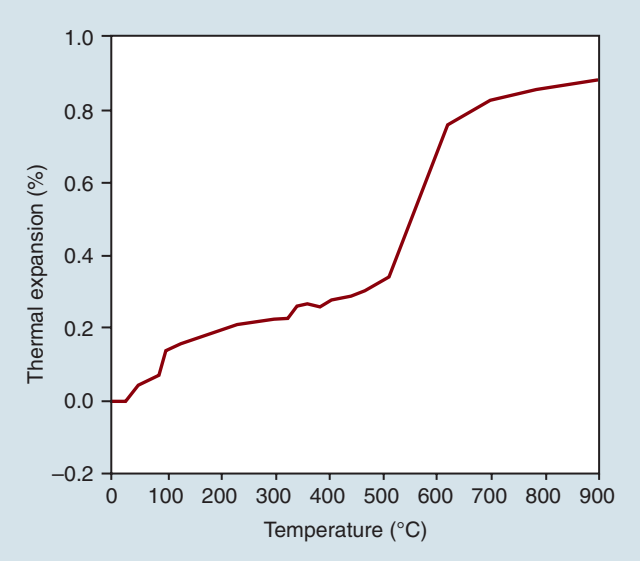


FIGURE 10-11 Thermal expansion of an investment that contains 25% plaster of Paris and 75% quartz. (Courtesy of G. C. Paffenbarger.)

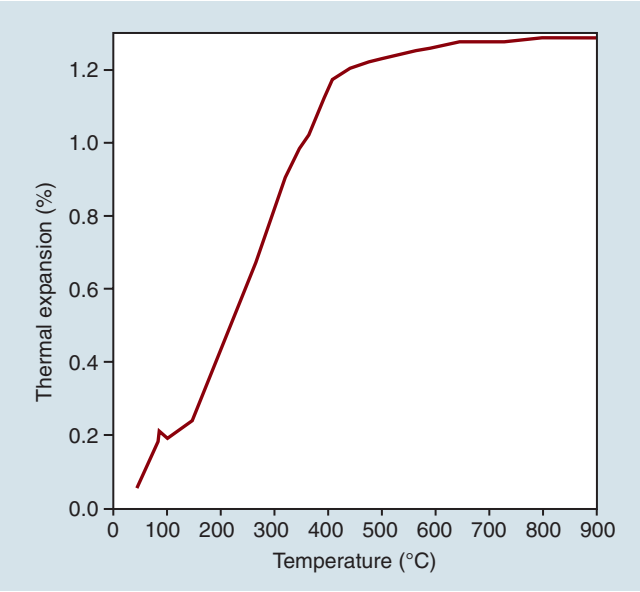


FIGURE 10-12 Thermal expansion of an investment that contains cristobalite rather than quartz. (Courtesy of G. C. Paffenbarger.)

The effect of cristobalite compared with that of quartz is demonstrated in Figure 10-11. Because of the much greater expansion that occurs during the inversion of cristobalite, the normal contraction of the gypsum during heating is readily eliminated. Furthermore, the expansion occurs at a lower temperature because of the lower inversion temperature of the cristobalite in comparison with that of quartz. A reasonably good fit of the castings is obtained when a gold alloy is cast into the mold at temperatures of 500 °C and higher. The thermal expansion curves of an investment provide some idea of the form of the silica that is present. As can be seen from Figures 10-11 and 10-12, the investments containing cristobalite expand earlier and to a greater extent than those containing quartz. Some of the modern investments are likely to contain both quartz and cristobalite.

The desired magnitude of the thermal expansion of a dental investment depends on its use. If the hygroscopic expansion is to be used to compensate for the contraction of the gold alloy, as for the type II investments, thermal expansion should be between 0% and 0.6% at 500 °C. However, for type I investments, which rely principally on thermal expansion for compensation, the thermal expansion should not be less than 1% or greater than 1.6%.

The magnitude of thermal expansion is related to the amount of solids present. Therefore, it is apparent that the more water used in mixing the investment, the less is the thermal expansion that is produced during subsequent heating. This effect is demonstrated by the curves shown in Figure 10-13. Although the variations in the W/P ratios shown are rather extreme, the curves indicate that it is imperative to measure the water and powder accurately if the proper compensation is to be achieved.

EFFECT OF CHEMICAL MODIFIERS

A disadvantage of an investment that contains sufficient silica to prevent any contraction during heating is that the weakening effect of the silica in such quantities is likely to be too great. The addition of small amounts of sodium, potassium, or lithium chlorides to the investment eliminates the contraction caused by the gypsum and increases the expansion without the need for an excessive amount of silica.

Boric acid has a similar effect. It also hardens the set investment. However, it apparently disintegrates during the heating of the investment and a roughened surface on the casting may result. Silicas do not prevent gypsum shrinkage but counterbalance it, whereas chlorides actually reduce gypsum shrinkage below temperatures of approximately 700 °C.

THERMAL CONTRACTION

When an investment is cooled from 700 °C, its contraction curve follows the expansion curve during the inversion of the β quartz or β cristobalite to its stable α form at room temperature. Actually, the investment contracts to less than its original dimension. This contraction below the original dimension is unrelated to any property of the silica; it occurs because of the shrinkage of gypsum when it is first heated.

As the investment is reheated, it expands thermally to the same peak value reached when it was first heated. However, in practice the investment should not be heated a second time because internal cracks can develop.

STRENGTH

The fracture resistance of the investment must be adequate to prevent cracking, bulk fracture, or chipping of the mold during heating and casting of gold alloys. Although a certain minimal strength is necessary to prevent fracture of the investment mold during casting, the compressive strength should not be unduly high. It has been found that all castings for the standardized MOD die used by the National Institute

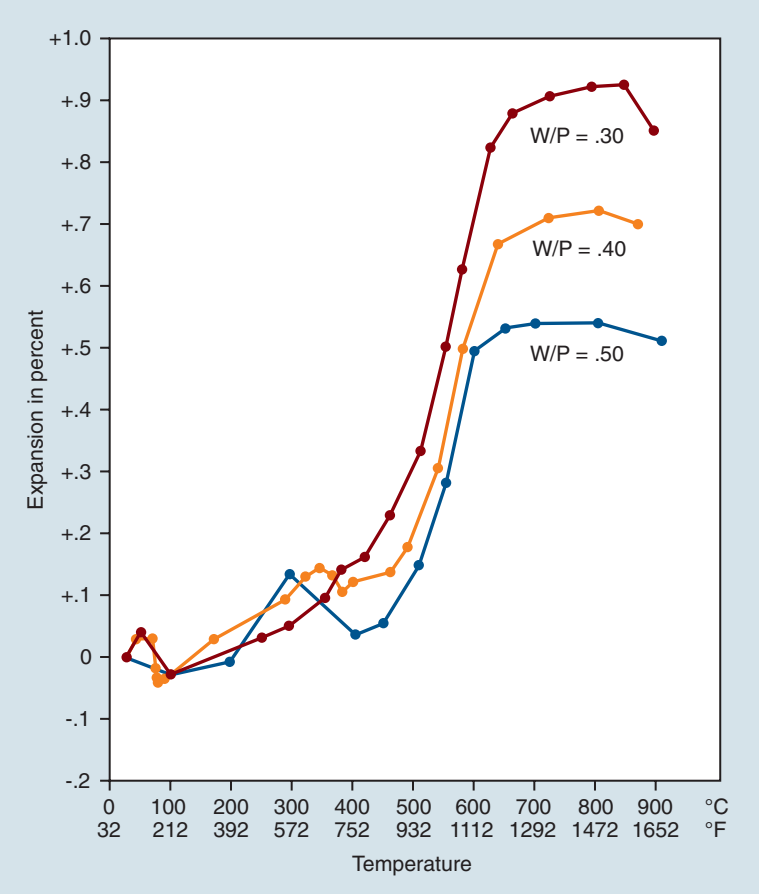


FIGURE 10-13 Effect of water/powder ratio on the thermal expansion of an investment containing 20% plaster of Paris and 80% quartz. (Courtesy of G. C. Paffenbarger.)

of Standards and Technology showed a constant pattern of distortion. The distortion apparently results from a directional restraint by the investment to the thermal contraction of the alloy casting as it cools to room temperature.

The strength of the investment is affected by the W/P ratio in the same manner as any other gypsum product; the more water that is employed in mixing, the lower is the compressive strength. Heating the investment to 700 °C may increase or decrease the strength as much as 65%, depending on the composition. The greatest reduction in strength on heating is found in investments containing sodium chloride. After the investment has cooled to room temperature, its strength decreases considerably, presumably because of fine cracks that form during cooling.

Although the total thermal contraction of the investment is similar to that of gold alloys from the casting temperature to room temperature, the contraction of the investment is fairly constant until it cools to below 550 °C. Thus, when the alloy is still hot and weak, the investment can resist alloy shrinkage by virtue of its strength and constant dimensions. This can cause distortion and even fracture of the casting if the hot strength of the alloy is low. Although this is rarely a factor with gypsum-bonded investments, it can be important with other types of investments.

The strength of an investment is usually measured under compressive stress. The compressive strength is increased according to the amount and the type of the gypsum binder present. For example, the use of α-hemihydrate instead of plaster definitely increases the compressive strength of the investment. The use of chemical modifiers increases strength because more of the binder can be used without a marked reduction in thermal expansion.

The compressive strength for the inlay investments should not be less than 2.4 MPa when tested 2 hours after setting. Any investment that meets this requirement should have adequate strength for casting of an inlay. However, when larger, complicated castings are made, greater strength is necessary, as required for type III partial denture investments.

FINENESS OF GYPSUM INVESTMENT

The fineness of the investment may affect its setting time, the surface roughness of the casting, and other properties. A fine silica results in a higher hygroscopic expansion than does a coarser silica. A fine particle size is preferable to a coarse one because the finer the investment, the smaller the surface irregularities on the casting.

? CRITICAL QUESTION

What are two measures that may be taken to minimize porosity in dental castings?

POROSITY OF THE GYPSUM-BASED CASTING INVESTMENT

As the molten metal enters the mold under pressure during casting, the trapped air must be forced out ahead of the inflowing metal. If the air is not completely eliminated, a back pressure builds up to prevent the molten alloy from completely filling the mold. The simplest method for venting the mold is through the pores of the investment. Thus, it is important that the end of a wax pattern that is nearest to the end of the investment ring not be covered by more than 6 mm of investment to allow sufficient interconnectivity of the porous network for escape of gas from the mold cavity during filling of the mold with molten metal.

In general, the more gypsum crystals that are present in the set investment, the less is its porosity. Thus, the lower the amount of calcium sulfate hemihydrate and the more gauging water used in mixing the investment, the more porous it will be.

The particle size of the investment is also a factor. The more uniform the particle size, the greater is its porosity. This factor is of greater importance than is the particle size. A mixture of coarse and fine particles exhibits less porosity than an investment composed of a uniform particle size.

CRITICAL QUESTION

Why are premeasured packets of investments sometimes more cost-effective?

STORAGE OF GYPSUM-BASED CASTING INVESTMENT

Gypsum-based investments should be stored in the same manner as that followed for storage of plaster or dental stone. In storage rooms with high relative humidity, the setting time may change. The setting expansion and the hygroscopic expansion may be altered such that the entire casting procedure may be adversely affected. Thus the investments should be stored in airtight and moisture-proof containers. During use, the containers should be opened for as short a time as possible. All investments are composed of a number of ingredients, each of which possesses a different specific gravity. There is a tendency for these components to separate as they settle, according to their specific gravity. This separation may influence the setting time and other properties of the investment. Because of this settling and the danger of accidental moisture contamination, it is advisable to purchase prepackaged investments in relatively small quantities. If investments are needed on an infrequent basis, prepackaged products are more cost-effective because less waste is likely, especially in storage areas with relatively high humidity.

The selection of a casting investment is dependent partly on the specific techniques for which the investment is designed. Some investments are formulated for casting inlays and crowns employing thermal expansion as the main factor for casting shrinkage compensation and some are designed for hygroscopic setting expansion. Acceptable castings for the range of typical dental cavity preparations can be made with a number of investments and techniques.

The investment supplied in bulk packages should be weighed and the water should be measured according to the proportion of the investment mix. In this manner one can control the setting or the thermal expansion in relation to the compensation needed for the casting shrinkage and other important properties. One need only measure the gauging water.

Manufacturers also supply preweighed packets of investment powder. However, one should be aware of slight variations in the weight of premeasured packets of powder. The quality control of investment products is related not only to the homogeneity of particulate components but also to variations in the weight of powder in the packets. Products with weight variations of 2% or less between packets in a box of of preweighed investment powder packets represent excellent quality control. Weight variations of 5% or more among packets may have serious consequences in terms of the flow characteristics of the investment slurry, setting time, setting expansion, and fracture resistance.

PHOSPHATE-BONDED INVESTMENT

Rapid growth in the use of metal-ceramic and hot-pressed ceramic prostheses has resulted in the increased use of phosphate-bonded or silicate-bonded investments. Although these investments are more difficult to remove from castings than are gypsum-based investments, this problem has been reduced recently, and the phosphate-bonded investments now produce satisfactory results with conventional gold alloys.

Phosphate-bonded investments are becoming more widely used than gypsum-bonded investments. The tremendous increase in the use of metal-ceramic prostheses necessitates the use of higher-melting gold alloys that do not cast well into gypsum investments. Likewise, with the recent increase in the cost of the noble metals and silver (starting in 2010), there will likely be a recurrent trend toward the use of the less expensive base metal alloys, most of which require phosphate investments. Commercially pure titanium and titanium alloys require specially formulated investments to minimize the interaction of the molten metal with the investment.

COMPOSITION

Like gypsum-based investments, phosphate-based investments contain refractory fillers and a binder. The silica filler, typically 80% by weight, is in the form of cristobalite, quartz, or a mixture of the two forms. The purpose of the filler is to provide thermal shock resistance (refractoriness) and a high thermal expansion. The particle size varies from a submicron level to that of a fine sand. The sandy feel of the investment does not necessarily relate to casting smoothness or affect the ease of removing the casting from the investment.

The binder consists of magnesium oxide (basic) and a phosphate that is acid in nature. Originally phosphoric acid was used, but monoammonium phosphate has replaced it because it can be incorporated into the investment powder.

Because several of the newer gold-containing alloys and other alloys used for metal-ceramic restorations have higher melting temperature ranges than traditional gold alloys, it usually follows that their contraction during solidification is also greater. This necessitates a greater expansion of the investment. In this regard, colloidal silica suspensions in place of water are beneficial for mixing the phosphate investments.

Because colloidal silica liquid suspensions can freeze and become unusable, these suspensions and their investment powders should be stored in a frost-free environment. Some suspensions are available as freeze-stable products. Although they freeze solid at low temperatures, they become useful again after they have been thawed out and shaken. Some phosphate investments are made to be used with water for the casting of alloys. In addition, for predominantly base metal alloys, a 33% dilution of the colloidal silica is required.

Carbon is often added to the powder to produce clean castings and facilitate the **divesting** of the casting from the investment mold. This addition is appropriate when the casting alloy is gold, but there is disagreement regarding the effects of carbon in phosphate investments used for casting silver-palladium alloys, palladium-silver alloys, or base metal alloys. It is believed that carbon can embrittle the alloys, even though the investment is heated to temperatures that burn out the carbon. Some evidence indicates that palladium reacts with carbon at temperatures above 1504 °C. Thus, if the casting temperature of an alloy with high palladium content exceeds this critical point, a phosphate investment without carbon should be used. Also, a carbon crucible should not be employed for melting the alloy. Generally even gold alloys used with porcelain should not be premelted or fluxed on charcoal blocks because trace elements that provide high strength may be removed or are reduced below the desired level.

SETTING REACTION

The chemical reaction for the phosphate-based binder system that causes the investment to set and harden is described below.

$$NH_4H_2PO_4 + MgO + 5H_2O \rightarrow NH_4MgPO_4 + 6H_2O \quad (1)$$

For example, in some products the magnesium ammonium phosphate formed is polymeric. Although the stoichiometry suggests the use of equal quantities or equal molecules of magnesia and monoammonium phosphate, an excess of magnesia is usually present, and some of it is never fully reacted. The product formed is the predominantly colloidal multimolecular $(NH_4MgPO_4{\cdot}6H_2O)_n$ aggregate around excess MgO and fillers. On heating, the binder of the set investment undergoes thermal reactions as suggested by the following sequence:

$$\begin{array}{ll}
MgO + NH_4H_2PO_4 + H_2O & \\
\downarrow & \text{Room temperature} \\
(NH_4MgPO_4 + 6H_2O)_n & \\
MgO & \\
NH_4H_2PO_4 & \text{Colloidal-type particles} \\
H_2O & \\
\downarrow & \text{Prolonged set at 25 °C/} \\
(NH_4MgPO_4 + 6H_2O)_n & \text{Dehydration at 50 °C} \\
\downarrow & \text{Dehydrated at 160 °C} \\
(NH_4MgPO_4 + H_2O)_n & \\
\downarrow & \text{Heated from 300 to 650 °C} \\
(Mg_2P_2O_7)_n & \\
\downarrow & \text{Noncrystalline polymeric phase} \\
Mg_2P_2O_7 & \\
\downarrow & \text{Heated above 1040 °C} \\
Mg_3(P_2O_4)_2 &
\end{array} \quad (2)$$

The resulting reaction products of phosphate-bonded investments are crystalline $Mg_2P_2O_7$, excess MgO, and essentially unchanged quartz, cristobalite, or both. In addition, $Mg_3(P_2O_4)_2$ may be formed if the investment is grossly overheated or if the molten metal contacts the mold cavity surfaces.

SETTING AND THERMAL EXPANSION OF PHOSPHATE-BONDED INVESTMENT

In theory, the setting reaction should result in shrinkage, as is also expected for gypsum-based investments. However, a slight expansion actually occurs, which can be increased considerably by using a colloidal silica solution (sometimes called a special liquid) instead of water. This solution allows phosphate investments to expand considerably rather than shrink according to predictions. Figure 10-14 shows the effect of the concentration of colloidal silica in aqueous suspension on increasing the setting and thermal expansion.

Shown in Figure 10-15 is the thermal expansion of a typical phosphate investment mixed with water as compared with the same investment mixed with its accompanying special liquid. When phosphate investments are mixed with water, they shrink over the same temperature range as gypsum-bonded investments (200 °C to 400 °C). This contraction is practically eliminated when a colloidal silica solution replaces water. Some users of phosphate-bonded investment prefer to decrease expansion by increasing the L/P ratio rather than by decreasing the concentration of the special liquid, or they may use a combination of these methods.

The early thermal shrinkage of phosphate investments is associated with decomposition of the binder, magnesium ammonium phosphate, and is accompanied by evolution of ammonia, which is readily apparent by its odor. For gypsum investments the shrinkage is caused by the transformation of calcium sulfate from the hexagonal to the rhombic form. However, some of the shrinkage is masked because of the expansion of the refractory filler, especially for cristobalite.

WORKING AND SETTING TIME

Unlike gypsum investments, phosphate investments are markedly affected by temperature. The warmer the mix, the faster it sets. The setting reaction itself gives off heat, and this further accelerates the rate of setting. Increased mixing time and mixing efficiency, as determined by the type of mixer and speed of mixing, result in a faster set and a greater rise in temperature. In general the more efficient the mixing, the better is the smoothness and accuracy of the casting. The ideal technique is to mix as long as possible yet have just enough time for investing. Mechanical mixing under vacuum is preferred.

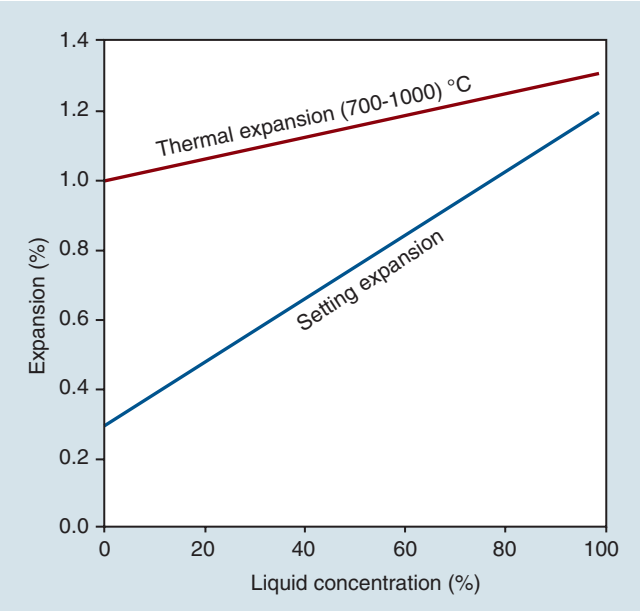


FIGURE 10-14 Influence of liquid concentration on the setting and thermal expansion of a phosphate-bonded investment. (Courtesy of R. Neiman, Whip-Mix Corporation, Louisville, KY.)

A third variable that has a considerable effect on the working and setting time is the L/P ratio, which often varies considerably depending on user preference. An increase in the L/P ratio increases the working time, which can be very short (2 minutes or less) when the investment is mixed at the manufacturer's recommended L/P ratio at high speed (1750 rpm) for the recommended time. Prolonged working time occurs at higher laboratory temperatures and also when the liquid has not been chilled.

SURFACE QUALITY OF CAST METALS

In the past, detail reproduction and surface smoothness of a metal-ceramic gold alloy restoration cast in a phosphate-bonded investment were considered inferior to those characteristic of a conventional gold alloy that had been cast in a gypsum-bonded investment. However, increasing the ratio of special liquid to water used for the mix markedly enhances casting surface smoothness, but it can lead to oversized extracoronal castings. Improvement in the technique and also in the investment composition now make it possible to fabricate castings having few surface imperfections when phosphate-bonded investment is used with either a low-fusing gold alloy, a high-fusing gold alloy, or a base-metal alloy. Phosphate-bonded investments now approach the surface quality or fineness of the gypsum investments. However, their ability to improve the smoothness is dependent on the alloy and casting procedure employed.

ETHYL SILICATE–BONDED INVESTMENT

The use of ethyl silicate–bonded investments has declined because of the more complex and time-consuming procedures involved with their use; however, they are still used in the construction of high-fusing base metal partial denture alloys. In this case, the binder is a silica gel that reverts to silica (cristobalite) on heating. Several methods may be used

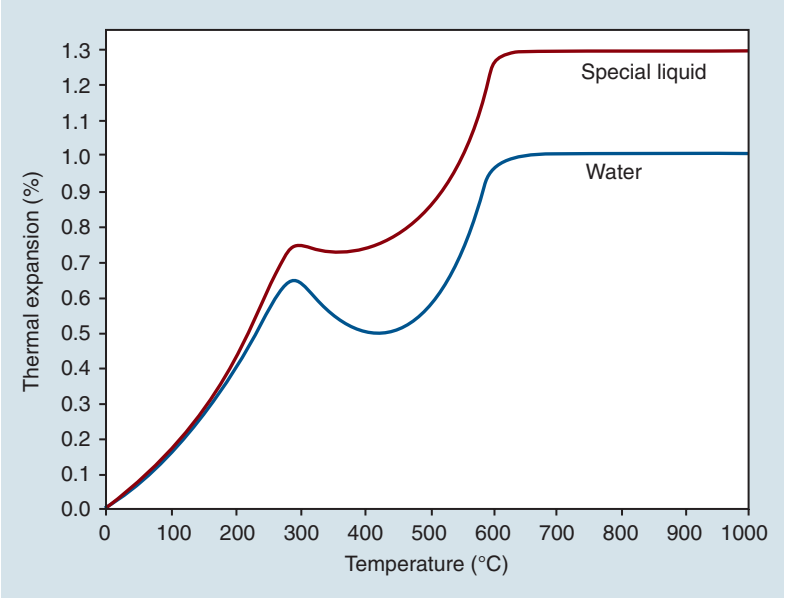


FIGURE 10-15 Thermal expansion of a phosphate-bonded investment mixed with water as compared with the special liquid. (Courtesy of R. Neiman, Whip-Mix Corporation, Louisville, KY.)

to produce the silica or silicic acid gel binders. When the pH of sodium silicate is lowered by the addition of an acid or an acid salt, a bonding silicic acid gel forms. The addition of magnesium oxide strengthens the gel. An aqueous suspension of colloidal silica can also be converted to a gel by the addition of an accelerator, such as ammonium chloride.

Another system for binder formation is based on ethyl silicate. A colloidal silicic acid is first formed by hydrolyzing ethyl silicate in the presence of hydrochloric acid, ethyl alcohol, and water. In its simplest form, the reaction can be expressed follows:

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH \quad (3)$$

Since an ethyl silicate polymer is used, a colloidal sol of polysilicic acids is expected instead of the simpler silicic acid sol shown in the reaction. The sol is then mixed with quartz or cristobalite, to which is added a small amount of finely powdered magnesium oxide to render the mixture alkaline. A coherent gel of polysilicic acid then forms, accompanied by a setting shrinkage. This soft gel is dried at a temperature below 168 °C. During the drying process, the gel loses alcohol and water to form a concentrated, hard gel. As might be expected, a volumetric contraction accompanies the drying, which reduces the size of the mold. This contraction is known as green shrinkage, which is additive to the setting shrinkage.

Gelation is likely to be slow and time-consuming. A faster method for the production of the silica gel can be used. Certain types of amines can be added to the solution of ethyl silicate so that hydrolysis and gelation occur simultaneously. The mold enlargement before casting must compensate not only for the casting shrinkage of the metal but also for the green shrinkage and the setting shrinkage of the investment.

Investments of this type are designed to reduce the silica gel layer around the particles. They have a specific particle-size gradation and are handled in a different manner. The powder is added to the hydrolyzed ethyl silicate liquid, mixed quickly, and vibrated into a mold that has an extra collar to increase the height. The mold is placed on the platform of a special type of vibrator that provides a so-called tamping action. This allows the heavier particles to settle quickly while the excess liquid and some of the fine particles rise to the top. In about 30 minutes, the accelerator in the powder hardens the settled part and the excess at the top is poured off. Thus, the L/P ratio in the settled part is greatly reduced and the setting shrinkage is reduced to 0.1%.

The remaining cast is somewhat fragile because the amount of binder is quite low and it is essentially composed of silica. The wax pattern is formed on the cast and invested in a manner similar to other investments. However, the process for an ethyl silicate–bonded investment is a little more complicated than that for the phosphate type in that care must be exercised during handling and burnout because flammable alcohol is given off. If the ethyl silicate–bonded investment is heated to a sufficiently high temperature, some silica converts to quartz and provides added expansion. This type of investment can be heated to between 1090 °C and 1180 °C and is compatible with the higher-fusing alloys. Its low setting expansion minimizes distortion.

? CRITICAL QUESTION

Why is the marginal fit of cast crowns on a prepared tooth essential to the long-term clinical success of metal prostheses?

CLINICAL EVALUATION OF CASTING FIT

Dental castings can be produced in any size (from a denture base to the smallest inlay). The procedures employed for the construction of small restorations, such as an inlays, onlays, crowns, and endodontic posts, are the primary topic of this chapter. The fundamental principles are the same, regardless of the size of the casting, and the techniques differ only in sprue design, type of investment, and method of melting the alloy.

The casting process is designed to provide a metallic duplication of missing tooth structure with as much accuracy as possible. The tolerance limits for the fit and marginal adaptation of a cast restoration are not known. In a clinical study, 10 experienced dentists were asked to evaluate the marginal adaptation of a group of inlays, using an explorer and radiographs. After the cemented restorations were graded, they were microscopically measured at the marginal openings of various areas. For "acceptable" restorations, the mean opening was 21 µm at the occlusal surface and 74 µm at the gingival region, which is not as accessible visually. There was little agreement among these 10 dentists on the acceptability of the marginal openings when evaluated by either explorers or radiographs.

The difficulty in detecting small discrepancies at the margins of cemented restorations is associated with the use of explorers that have a relatively large radius of curvature at the tip compared with the width of margin gaps that are being evaluated. As shown in Figure 10-16, the tip of this unused explorer may not "catch" a 60-µm margin gap, whose width is the diameter of a human hair, as it traverses along a path perpendicular to the gap. If this explorer tip substantially penetrates into a gap during probing, the fit of a crown, inlay, or onlay will not be clinically acceptable. The illustration poses the question of how readily a hairline gap can be detected by running an explorer over the margins of the restoration, especially in interdental areas that must often be probed at a small angle to the surface. It is obvious that the accuracy of the inlay or crown should be greater than can be detected by the eye or by the conventional methods of clinical testing. At the margins of the cemented restoration, a thin line of cement is always present, even though it may not be readily visible. With the exception of resin-based luting materials, the present dental cements are somewhat soluble and can deteriorate in the oral cavity. Thus, the less accurate the casting fit and the greater the amount of cement exposed, the more likely it is that the cement will degrade. Certainly a high degree of accuracy in marginal adaptation of 25 µm or less

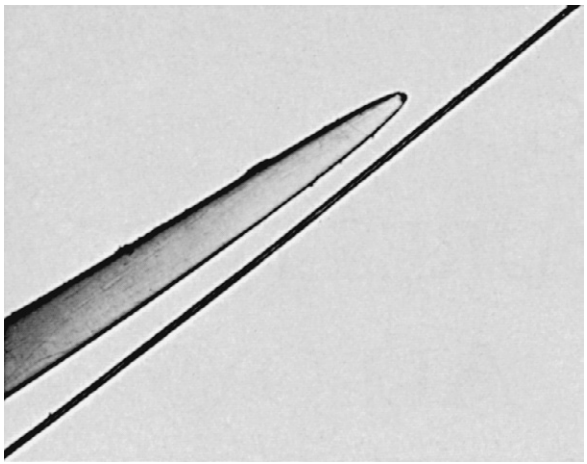


FIGURE 10-16 Cross-section of an unused explorer tip (*top*) and a 60-µm hair (×25). (From McLean JW, Van Fraunhofer JA: The estimation of cement film thickness by an in vivo technique. *Br Dent J* 131:107, 1971.)

cannot be guaranteed for all cast restorations. It stands to reason that the more accurate the fit of the casting, the less the likelihood of leakage, plaque accumulation on the cement, and secondary caries.

Assuming that the wax pattern is satisfactory, the procedure then becomes a matter of enlarging the mold uniformly and sufficiently to compensate for the casting shrinkage of the alloy. Theoretically, if the shrinkage of the wax and the alloy are known, the mold can be expanded enough to compensate for such shrinkage. Unfortunately there are variables in the behavior of the materials and the wax that cannot be precisely controlled. The overall dimensional accuracy possible with current techniques has not been clearly defined. Thus, neither the allowable tolerance of accuracy in the fit of the casting nor that obtainable during the casting procedure is known. In the final analysis, the casting procedure is partly empirical and previous experience is very beneficial.

There are many steps in the procedure for which a considerable number of facts are known. In addition, certain variations in the techniques described here produce equally satisfactory results. However, any technique involves strict adherence to certain fundamental principles common to all metals. These are the fundamentals emphasized subsequently.

COMPENSATION FOR SOLIDIFICATION SHRINKAGE

Compensation for the shrinkages inherent in the dental casting procedure may be obtained by controlling either (l) the setting or hygroscopic expansion of the investment or (2) the thermal expansion of the investment. Both of these techniques are currently in use and are commonly referred to as the hygroscopic expansion (low-heat) method and the thermal expansion (high-heat) method. As their names alone might indicate, the high-heat method requires thermal expansion of the investment between room temperature and a high temperature (650 °C to 700 °C) for gypsum-bonded investments and up to 1050 °C for phosphate-bonded investments).

Despite these differences, the overall procedures involved in investing and casting are quite similar; therefore, they are described simultaneously. If not stated to the contrary, the reader can assume that the procedures mentioned are common to both the high-heat and the low-heat techniques. For best results, the manufacturer's recommendations for the specific alloy used should be followed.

RINGLESS CASTING SYSTEM

A ringless system that provides maximum expansion of investment is available commercially. This system, called the PowerCast Ringless System (Whip-Mix Corporation, Louisville, KY), consists of three sizes of rings and formers, preformed wax sprues and shapes, investment powder, and a special investment liquid. The tapered plastic rings allow for removal of the investment mold after the material has set. This system is suited for the casting of alloys that require greater mold expansion than traditional gold-based alloys.

CRITICAL QUESTION

What methods can be used to increase the abrasion resistance of master dies?

PREPARATION OF THE MASTER DIE

The most commonly used die materials are type IV (dental stone, high-strength) and type V (dental stone, high-strength, high-expansion) improved stones. These materials are relatively inexpensive, easy to use, and generally compatible with all impression materials. Type IV stones should have a setting expansion of 0.1% or less, whereas the harder type V stones may expand as much as 0.3%. This greater expansion is useful in compensating for the relatively large solidification shrinkage of base metal alloys.

The chief disadvantage of the type IV gypsum die is its susceptibility to abrasion during carving of the wax pattern. Gypsum dies are sometimes modified to (1) make them more abrasion-resistant, (2) change the dimensions of the dies, (3) increase the refractoriness of the dies, or (4) produce a combination of these effects. Several means are used to increase the abrasion resistance, including silver plating, coating the surface with cyanoacrylate adhesive, and adding a die hardener to the gypsum. However, each of these methods can also increase the die dimensions slightly, thus reducing accuracy (Table 10-2).

METHODS OF ALTERING DIE DIMENSIONS

Additional accelerator (potassium sulfate) and retarder (borax) can be added to the gauging water to reduce the setting expansion of the type IV die stone to less than 0.1% and, therefore, to reduce the diameter of the die. To produce

TABLE 10-2 Dimensional Change in Dies Made from a Silicone Impression Compared with a Standardized Die

	DIMENSIONAL CHANGE (%)	
Die Material	**Occlusal**	**Cervical**
Type IV die stone	0.06	0.00
Type IV stone plus hardener A	0.16	0.08
Type IV stone plus hardener B	0.10	0.10
Silica-filled epoxy resin	–0.15	–0.26
Aluminum-filled epoxy resin	–0.14	–0.19
Electroformed silver	–0.10	–0.20

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relief space for cement, clinicians commonly use a die spacer that is coated on a stone die. The most common die spacers are resins. Although proprietary paint-on liquids are sold for this purpose, model paint, colored nail polish, and thermoplastic polymers dissolved in volatile solvents are also used. Such spacers are applied in several coats to within 0.5 mm of the preparation finish line to provide relief for the cement luting agent and ensure complete seating of an otherwise precisely fitting casting or coping.

DIE STONE/INVESTMENT COMBINATION

Another technique employs a die material and the investing medium with a comparable composition. One of the commercial gypsum-bonded materials (Divestment, Whip-Mix Corporation, Louisville, KY) is mixed with a colloidal silica liquid. The die is made from this mix, and the wax pattern is constructed on it. Then the entire assembly (die and pattern) is invested in a mixture of the investment and water, thereby eliminating the possibility of distortion of the pattern on removal from the die or during the setting of the investment. When it is heated to 677 °C, the setting expansion of the material is 0.9% and the thermal expansion is 0.6%. Because this type of investment is a gypsum-bonded material, it is not recommended for high-fusing alloys used for metal-ceramic restorations. However, it is a highly accurate technique for use with conventional gold alloys, especially those selected for extracoronal preparations.

A phosphate-bonded investment is used in the same manner as gypsum-based material, and it is suitable for use with high-fusing alloys. Phosphate-bonded die-investment materials formulated for use in making ceramic prostheses can also be used when casting high-fusing alloys.

OTHER DIE MATERIALS

Non-gypsum die materials are also available, such as acrylic, polyester, and epoxy resins. These materials are limited in their compatibility with impression materials, which would ordinarily be nonaqueous elastomers rather than hydrocolloid or compound. Compatibility is specific and germane only to the particular brand rather than to chemical types of impression materials. Moreover, in the case of filled autopolymerizing acrylic resins, the curing contraction is excessive (0.6 linear percent for one material). Therefore, acrylic resin cannot be used when an accurate die is required. The same is true for polyester resin materials.

Various epoxy die materials are reliable with respect to the 0.1% to 0.2% dimensional change on polymerization (Table 10-2). Even though epoxy dies are generally undersized in comparison with the prepared tooth, especially in the axial direction, they are used successfully by some commercial dental laboratories, presumably because of their superior abrasion resistance.

In some cases the resin die should be no more undersized than the stone die is oversized. However, this issue must be taken into consideration, because it may be necessary to adjust the investing and casting technique accordingly. A cast crown that is fabricated on a slightly undersized resin die may not seat completely on the tooth compared with one made on a slightly large stone die.

The high-strength stones (types IV and V) appear to be the most successful die materials available. With care, abrasion during carving of the wax pattern can be avoided. However, in the construction of a metal-ceramic crown that is made with a metal foil coping (such as Captek), the metal is burnished on the die. This process requires the application of high localized pressure to adapt the metal foil intimately on the die surface. Gypsum dies may be readily damaged, so a less brittle material, such as resin or metal, is sometimes preferred.

Recently several gypsum die stones have been compounded with resins to provide the advantages of both materials. These modified die stones maintain the low expansion of stone, but they also have the increased toughness and resistance to carving imparted by the resins.

? CRITICAL QUESTION

Why is the term "silver-plated die" technically incorrect?

ELECTROFORMED DIES

Metal dies produced from electroplated impression material have moderately high strength, adequate hardness, and excellent abrasion resistance. Detail reproduction of a line 4 μm or less in width is readily attainable on the resulting metal-covered die when a nonaqueous elastomeric impression material is used.

Copper-plated compound dies first became popular in the early 1930s, and silver-plated dies became more popular in later years. Several modifications of the fabrication technique are used, but the following description is typical.

The first step in the procedure is to treat the surface of the impression material so that it conducts electricity. This process is referred to as metallizing. In this process, a thin layer of metal, such as silver powder, is deposited on the surface of the impression material. This metal layer determines to a large extent the surface character of the finished

die. Various metallizing agents are available, including bronzing powder and aqueous suspensions of silver powder and powdered graphite. These agents can be deposited on the surface of the impression with a camel-hair brush.

The electroplating bath itself is primarily a solution of silver cyanide. Care must be taken to avoid the addition of acids to the cyanide solution, which can cause the release of cyanide vapor, a "death chamber" gas. Chemical deposition of silver from a silver nitrate solution can be used if greater surface detail reproduction is desired.

In the silver-plating process, the greater the concentration of silver in the bath, the faster the silver is deposited. The acid content increases the throwing power, a term that refers to the penetration of current into a concave structure, such as an impression for a full crown. Impressions of teeth generally have walls with significant depth relative to the location of the occlusal area. Therefore a considerable amount of throwing power is desirable. An electrical contact is made with the metallized surface of the impression, which is the cathode in the electroplating bath. A plate of silver is used as the anode. A direct current is applied for approximately 10 hours.

Hydrocolloid impressions are extremely difficult to electroplate, and the process is not feasible for dental use. Electroformed dies made from polysulfide rubber impressions are clinically acceptable when a silver cyanide bath is used, although they are generally slightly less accurate than a properly constructed stone die.

Polysulfide rubber impressions are cleaned thoroughly and dried. They are then metallized with a fine silver powder. Although other metallizing agents can be used, the silver powder results in a superior surface on the electroformed die. An anode of pure silver, at least twice the size of the area to be plated, is employed, and the electroplating is carried out as before for approximately 10 hours, using 5 to 10 mA/cm^2 of cathode surface.

An impression that contains the electroformed die surface is then filled with dental stone. When the stone hardens, it is mechanically locked into the rough interior of the electroformed metal shell. The impression material is then removed to provide a die with greater surface hardness and resistance to abrasion than one of gypsum. The model and die are prepared in the normal manner, and the margins of the die are trimmed with a finishing disk. It should be clear to the reader that the terms "electroplated die" and "silver-plated die" are technically incorrect because it is the impression material surface that receives the electrodeposited metal.

? CRITICAL QUESTION

What casting deficiencies may result when (1) the sprue former is too small in diameter, (2) the sprue former is attached without flaring to thinner areas, (3) the sprues are oriented toward thin areas of a wax pattern, or (4) the sprues are of inadequate length to position the wax pattern within 6 mm of the end of the invested ring?

VARIABLES AND PRINCIPLES OF OPTIMAL SPRUE DESIGN

The purpose of a sprue former, or sprue pin, is to provide a channel through which molten alloy can reach the mold in an invested ring after the wax has been eliminated. With large restorations or prostheses, such as removable partial denture frameworks and fixed dental prostheses, the sprue formers are made of wax.

The diameter and length of the sprue former (also referred to simply as the sprue) depend to a large extent on the type and size of the pattern, the type of casting machine to be used, and the dimensions of the flask or ring in which the casting will be made. Prefabricated sprue formers are available in a wide range of gauges or diameters (Table 10-3).

WAX PATTERN REMOVAL

The sprue former should be attached to the wax pattern with the pattern on the master die provided that the pattern can be removed directly in line with its path of withdrawal from the die. Any motion that might distort the wax pattern should be avoided during removal. The gauge selection and design for the sprue former are often empirical, but optimal performance during the casting process is based on the following five general principles.

SPRUE DIAMETER

Select a sprue former with a diameter that is approximately the same size as the thickest area of the wax pattern. If the pattern is small, the sprue former must also be small, because attaching a large sprue former to a thin, delicate pattern could cause distortion. On the other hand, if the sprue former's diameter is too small, this area will solidify before the casting itself and localized shrinkage porosity ("suck-back" porosity) may develop. As shown in Figure 10-5, reservoir sprues are used to help overcome this problem.

SPRUE POSITION

The position of the sprue former attachment is often a matter of individual judgment and intuition, based on the shape and

TABLE 10-3 Wire Gauge Numbers and Diameters

	DIAMETER	
Brown & Sharpe Gauge Number	mm	in.
6	4.115	0.1620
8	3.264	0.1285
10	2.588	0.1019
12	2.053	0.0808
14	1.628	0.0641
16	1.291	0.0508
18	1.024	0.0403

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form of the wax pattern. Some clinicians prefer placement at the occlusal surface, whereas others choose sites such as a proximal wall or just below a nonfunctional cusp to minimize subsequent grinding of occlusal anatomy and contact areas. As indicated earlier, the ideal area for the sprue former is the point of greatest bulk in the pattern to avoid distorting thin areas of wax during attachment to the pattern and permit complete flow of the alloy into the mold cavity.

SPRUE ATTACHMENT

The sprue former connection to the wax pattern is generally flared for high-density gold alloys but often restricted for lower-density alloys. Flaring of the sprue former may act in much the same way as a reservoir, facilitating the entry of the fluid alloy into the pattern area. If possible, the sprue former should be attached to the portions of the pattern with the largest cross-sectional areas. It is best for the molten alloy to flow from a thick section to surrounding thin areas (e.g., the margins) rather than the reverse. This design minimizes the risk of turbulence. Also, the orientation of the sprue former should minimize the risk for metal flow onto flat areas of the investment or onto small areas such as line angles.

The sprue former should be long enough to position the pattern properly in the casting ring within 6 mm of the trailing end (see Figure 10-4) and yet short enough so that the molten alloy does not solidify before it fills the mold. The type of sprue former selected influences the burnout technique used. Wax sprue formers are more common than plastic. It is advisable to use a two-stage burnout technique whenever plastic sprue formers or patterns are involved to ensure complete carbon elimination because plastic sprues soften at temperatures above the melting point of inlay waxes. Patterns may be sprued either directly or indirectly. For direct spruing, the sprue former provides a direct connection between the pattern area and the sprue base or crucible former area (see Figure 10-4). With indirect spruing, a connector or reservoir bar is positioned between the pattern and the crucible former (see Figure 10-4). It is common to use indirect spruing for multiple single units and fixed partial dentures, although several single units can be sprued with multiple direct sprue formers.

A reservoir should be added to a sprue network to prevent localized shrinkage porosity (Figure 10-17). When the molten alloy fills the heated casting ring, the pattern area should solidify first and the reservoir last. Because of its large mass of alloy and position in the heat center of the ring, the reservoir remains molten to furnish liquid alloy into the mold as it solidifies. Assuming that the reservoir bar is larger in volume than that of the patterns, and that the sprue formers attached to those patterns were of the correct diameter and placed in the appropriate position, the resulting solidification shrinkage occurs in the reservoir bar and not in the prosthesis.

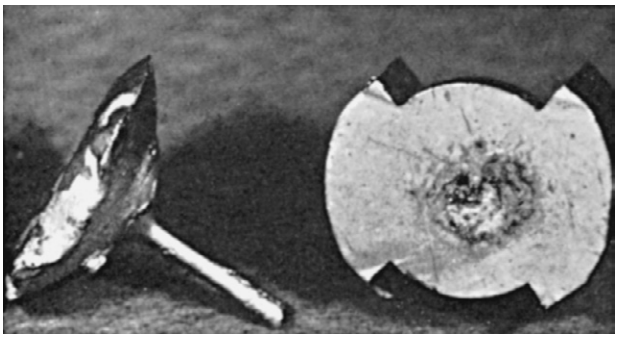


FIGURE 10-17 Localized shrinkage caused by using a sprue of improper diameter.

SPRUE DIRECTION

The sprue former should be directed away from any thin or delicate parts of the pattern because the molten metal may abrade or fracture investment in this area and result in a casting failure. The sprue former should not be attached to a broad flat surface at a right angle. Such an orientation leads to turbulence within the mold cavity and severe porosity in this region (Figure 10-18, *A*). When this same pattern is sprued at a 45° angle to the proximal area, a satisfactory casting is obtained (Figure 10-18, *B*).

SPRUE LENGTH

The length of the sprue former depends on the length of the casting ring. If the sprue is too short, the wax pattern may be so far removed from the end of the casting ring that gases cannot be adequately vented to permit the molten alloy to fill

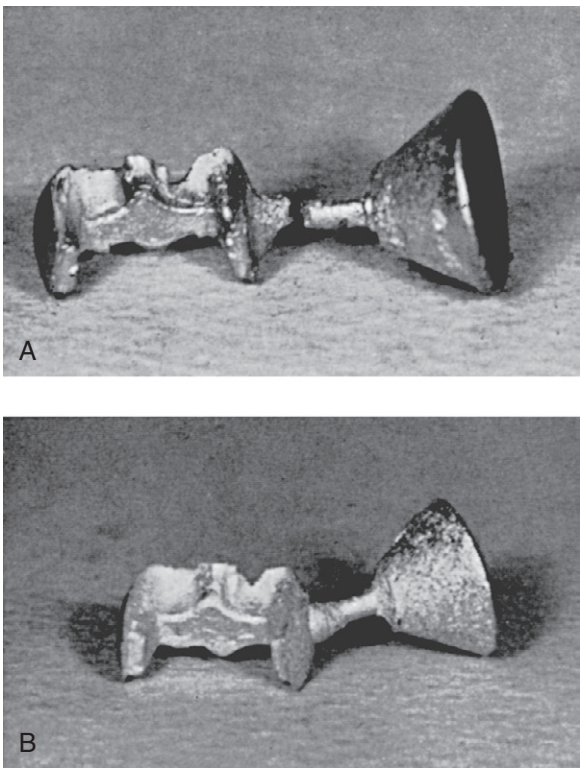


FIGURE 10-18 A, Detached sprue indicates severe porosity at the point of attachment because of turbulence caused by an improper sprue angle. **B,** Sound casting results with sprue at approximately 45° to the proximal wall.

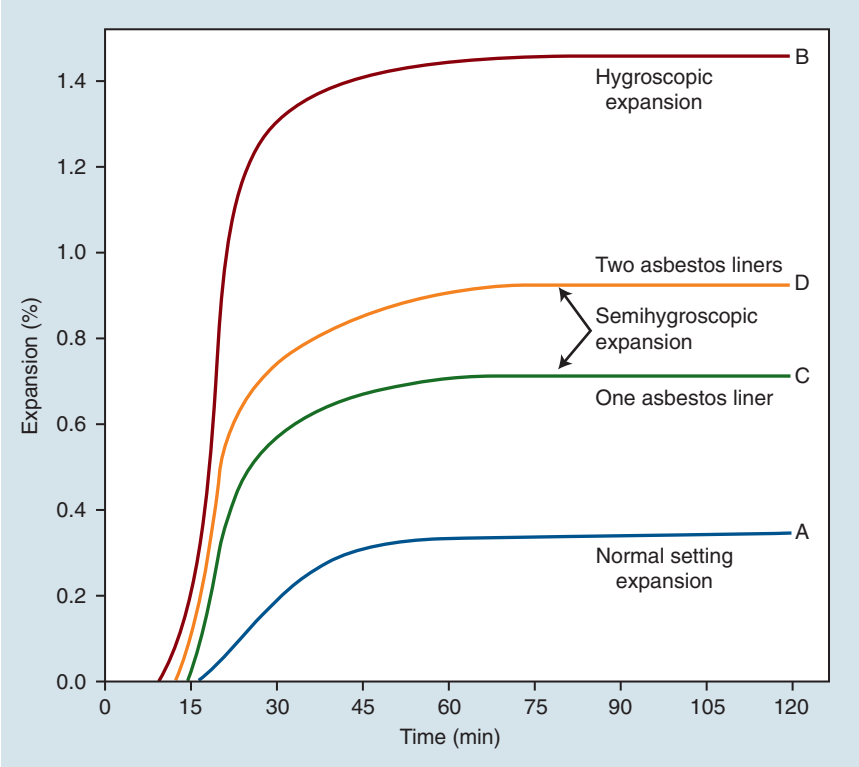


FIGURE 10-19 **A,** Normal setting. **B,** Hygroscopic expansion of an investment compared with the somewhat restricted expansion that occurs in an inlay ring containing (**C**) one liner and (**D**) two liners. (Courtesy of R. Neiman, Whip-Mix Corporation, Louisville, KY.)

the ring completely. When these gases are not completely eliminated, porosity may result. Therefore, the sprue length should be adjusted so that the top of the wax pattern is within 6 mm of the open end of the ring for gypsum-bonded investments (Figure 10-19). With the higher-strength phosphate-bonded investments, it may be possible to position the wax pattern within 3 to 4 mm of the top of the investment. For reproducibility of casting accuracy, the pattern should be placed as close as possible to the center of the ring. However, the position of the wax pattern for vacuum pressure casting may be different.

? CRITICAL QUESTIONS

How does nonuniform investment expansion occur? How can excessive longitudinal expansion be minimized?

CASTING RING LINER

With the use of solid metal rings or casting flasks, provision must be made to permit investment expansion. The mold may actually become smaller rather than larger because of the reverse pressure resulting from the confinement of the setting expansion. This effect can be overcome by using a split ring or flexible rubber ring that permits the setting expansion of the investment.

However, the most commonly used technique to provide investment expansion is to line the walls of the ring with a ring liner. Traditionally, asbestos was the material of choice, but it can no longer be used because its carcinogenic potential makes it a biohazard. Two types of nonasbestos ring liner materials have been produced: an aluminosilicate ceramic liner and a cellulose (paper) liner.

To ensure uniform expansion, the clinician or technician cuts the liner to fit the inside diameter of the casting ring with no overlap. The dry liner is tacked in position with sticky wax, and it is then used either dry or wet. With a wet liner technique, the lined ring is immersed in water for a time, and the excess water is shaken away. Squeezing the liner should be avoided, because this leads to variable amounts of water removal and nonuniform expansion. Although a ceramic liner may not absorb water like a cellulose liner, its network of fibers can retain water on the surface.

The liner affords greater normal setting expansion in the investment and the absorbed water causes a semihygroscopic expansion as it is drawn into the investment during setting, as shown for gypsum investments in Figure 10-9. The use of one liner (C) increases the normal setting expansion compared with no liner. Using a thicker liner material or two layers of liner (D) provides even greater semihygroscopic expansion and also affords a more unrestricted normal setting expansion of the investment. As shown in Figure 10-20, two layers of liner can be used to increase the expansion slightly compared with that obtained from one liner. In any case, the thickness of the liner should not be less than approximately 1 mm.

Because cellulose liners are paper products, they are burned away during the burnout procedure and a technique must be found to secure the investment in the ring. However, the desired length of the liner remains a matter of

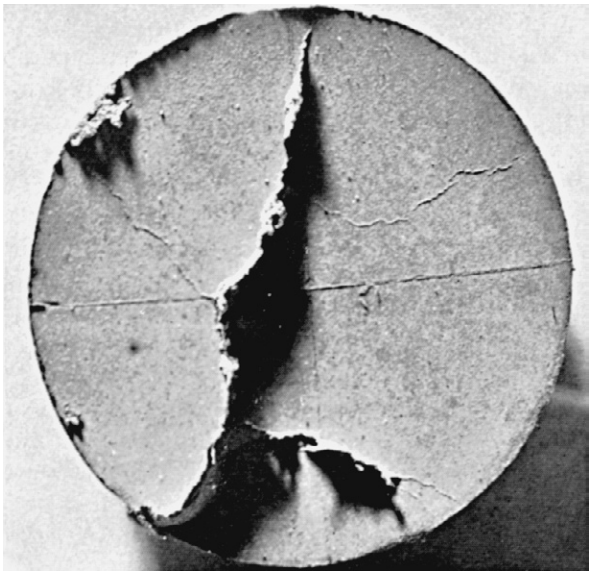


FIGURE 10-20 Fins on the surface of a casting that formed as a result of cracks in the investment before casting of the metal.

controversy. If the length of the liner is somewhat shorter than that of the ring itself, the investment will be confined at one or both ends of the ring. The longitudinal setting and hygroscopic expansion are thereby restricted as compared with an arrangement where the liner is flush with the ends of the ring.

The expansion of the investment is always greater in the unrestricted longitudinal direction than in the radial direction—that is, toward the ring. Therefore, it is desirable to reduce the expansion in the longitudinal direction. Placing the liner somewhat short (3.25 mm) of the ends of the ring tends to produce a more uniform expansion; thus there is less chance for distortion of the wax pattern and the mold.

INVESTING PROCEDURE

The wax pattern should be cleaned of any debris, grease, or oils. A commercial wax pattern cleaner or a diluted synthetic detergent may be used. Any excess liquid is shaken off, and the pattern is left to air-dry while the investment is being prepared. The thin film of cleanser left on the pattern reduces the surface tension of the wax and permits better "wetting" of the investment to ensure complete coverage of the intricate portions of the pattern.

While the wax pattern cleaner is air-drying, the appropriate amount of distilled water (gypsum investments) or colloidal silica special liquid (phosphate investments) is dispensed. The liquid is added to a clean dry mixing bowl, and the powder is gradually added to the liquid, using the same care and caution to minimize air entrapment as was discussed for the mixing of dental stones. Mixing is performed gently until all the powder has been wet; otherwise the unmixed powder may inadvertently be pushed out of the bowl. Although hand-mixing is an option, it is far more common to mix all casting investments mechanically under vacuum.

VACUUM MIXING

Mechanical mixing under vacuum removes air bubbles created during mixing and evacuates any potentially harmful gases produced by the chemical reaction of the high-heat investments. Once mixing is complete, the pattern may be hand-invested or vacuum invested. For investing by hand, the entire pattern is painted (inside and out) with a thin layer of investment. The casting ring is positioned on the crucible former, and the remainder of the investment is vibrated slowly into the ring. With vacuum investing, the same equipment used to mix the investment is employed to invest the pattern under vacuum.

As noted, the amount of porosity in the investment is reduced by vacuum investing. As a result, the texture of the cast surface is somewhat smoother with better detail reproduction. The tensile strength of vacuum-mixed investment is also increased. In one study, it was found that 95% of vacuum-invested castings were free of nodules, whereas only 17% of castings made in hand-invested molds were entirely free of defects. Freedom of any surface imperfections is highly important, because even a small nodule on a casting may damage a fragile enamel margin when the casting is evaluated for fit in the prepared cavity. The finished casting should always be checked under magnification for such defects before fitting it on the die.

Air bubbles that remain in the mix, even with vacuum mixing, can be entrapped on flat or concave surfaces that are not oriented suitably for air evacuation. Tilting the ring slightly aids in releasing these bubbles so that they can rise to the surface. Excessive vibration should be avoided because it can cause solids in the investment to settle and may lead to free-water accumulation adjacent to the wax pattern, resulting in surface roughness. Excessive vibration can also dislodge small patterns from the sprue former (Figure 10-18), resulting in a miscast.

If the hygroscopic technique is employed, the filled casting ring is immediately placed in a 37 °C water bath with the crucible former's side down. For the thermal expansion or high-heat technique, the invested ring is allowed to bench set undisturbed for the time recommended by the manufacturer.

COMPENSATION FOR SHRINKAGE

Occasionally it may be desirable to alter the mold dimensions of a full cast crown compared with a small inlay. A number of factors influence mold size. As previously discussed, two liners allow for greater setting and thermal expansion than does a single liner. Also the setting, hygroscopic, and thermal expansions of investments can be controlled to a certain extent by varying the L/P ratio of the investment. The lower the L/P ratio, the greater the potential for investment expansion. Conversely, thinner mixes reduce the expansion. With some investments, however, the effect of minor adjustments to the L/P ratio is insignificant.

There is a limit to how much the L/P ratio can be altered. If the mix is too thick, it cannot be applied to the pattern without a likelihood of distorting the pattern and producing

air voids during investing. On the other hand, if the mixture is too thin, a rough surface may result on the casting.

Another possible problem is too much expansion of the mold when the thermal expansion technique is used with a cristobalite investment. A thermal expansion of 1.3% may take place. If an effective setting expansion of 0.3% to 0.4% is added to such a thermal expansion, a total linear expansion as high as 1.7% may be obtained, higher than the average casting shrinkage of a gold alloy. As a result, a cast crown may be too large.

In addition to controlling the hygroscopic expansion by the L/P ratio, the clinician can regulate expansion by reducing the time of immersion of the setting investment or by controlling the amount of water to be added during the setting process. The longer the delay before the investment is immersed in the water bath, the less is the amount of hygroscopic expansion that can occur.

The modern hygroscopic investment technique generally provides the precise expansion for most types of patterns. However, some patterns may require a variation in expansion. By using higher burnout and water bath temperatures one increases the expansion, and vice versa.

In one technique, the shrinkage compensation is controlled by the addition of water during the setting of the investment. This method is usually referred to as the controlled water-added technique.

CONTROLLED WATER-ADDED TECHNIQUE

The linear hygroscopic expansion increases directly with the amount of water added until maximum expansion is attained. The compositions of investments used with with the water-added hygroscopic casting technique ensure maximal expansion during immersion in water. The amount of hygroscopic expansion needed for compensation is then obtained by adding only enough water to provide the desired expansion.

A soft, flexible rubber ring is used instead of the usual asbestos-lined metal ring. The pattern is invested as usual. A specified amount of water is then added on top of the investment in the rubber ring, and the investment is allowed to set, usually at room temperature. The controlled water-added technique is rarely used, however, because the hygroscopic expansion method described earlier provides adequate expansion in most cases.

CASTING PROCEDURE

Once the investment has set for an appropriate period—approximately 1 hour for most gypsum- and phosphate-bonded investments—it is ready for burnout. The procedures for the two types of investments are similar, so the following discussion focuses on gypsum investments. The crucible former and any metal sprue formers are carefully removed. Any debris from the ingate area (funneled opening at the end of the ring) is cleaned with a brush. If the burnout procedure does not immediately follow the investing procedure, the invested ring is placed in a humidor at 100% humidity. If possible, the investment should not be permitted to dry out. Rehydration of a set investment that has been stored for an extended period may not replenish all of the lost water.

WAX ELIMINATION AND HEATING

The invested rings are placed in a room-temperature furnace and heated to the prescribed maximum temperature. For gypsum-bonded investments, this temperature can be either 500 °C for the hygroscopic technique or 700 °C the thermal expansion technique. With phosphate-bonded investments, the maximum temperature setting may range from 700 °C to 1030 °C, depending on the type of alloy selected. The temperature setting is more critical with gypsum-bonded investments than for the phosphate type because the gypsum investments are more prone to investment decomposition. During burnout, some of the melted wax is absorbed by the investment and residual carbon produced by ignition of the liquid wax becomes trapped in the porous investment. It is also advisable to begin the burnout procedure while the mold is still wet. Water trapped in the pores of the investment reduces the absorption of wax, and as the water vaporizes, it flushes wax from the mold. This process is facilitated by placing the ring with the sprue hole down over a slot in a ceramic tray in the burnout furnace. When the high-heat technique is used, the mold temperature generates enough heat to convert carbon to either carbon monoxide or carbon dioxide. These gases can then escape through the pores in the heated investment.

HYGROSCOPIC LOW-HEAT TECHNIQUE

Hygroscopic expansion of gypsum-bonded investments was described earlier in this chapter. This technique (Figure 10-19) obtains its compensation expansion from three sources: (1) the 37 °C water bath expands the wax pattern, (2) the warm water entering the investment mold from the top adds some hygroscopic expansion, and (3) the thermal expansion at 500 °C provides the needed thermal expansion. The low-heat technique offers the advantages of less investment degradation, a cooler surface for smoother castings, and the convenience of placing the molds directly in the 500 °C furnace. The last benefit makes it possible to keep one or more furnaces at the burnout temperature so that molds may be put in as they are ready. This is particularly useful in large laboratories where molds are ready for burnout at various times. Care must nevertheless be taken to allow sufficient burnout time because the wax is more slowly oxidized (eliminated) at the low temperature.

The molds should remain in the furnace for at least 60 minutes, and they may be held up to 5 hours longer with little damage. Since the temperature of the furnace is lowered each time a mold is placed, extra time should be allowed to ensure complete wax elimination when molds are placed at intervals. Even though the mold is usually held at this temperature for 60 to 90 minutes, sufficient residual fine carbon may be retained to reduce the venting of the mold. Because of this potential for reduced venting, back-pressure porosity is a greater hazard in the low-heat

technique than in the high-heat technique, since the investments generally employed with the low-heat technique may be more dense.

The standardized hygroscopic technique was developed for alloys with a high gold content; the newer noble alloys may require slightly more expansion. This added expansion may be obtained by making one or more of the following changes:

1. Increasing the water bath temperature to 40 °C
2. Using two layers of liner
3. Increasing the burnout temperature to a range of 600 °C to 650 °C

HIGH-HEAT THERMAL EXPANSION TECHNIQUE

This approach depends almost entirely on using a high-heat burnout to obtain the required expansion while at the same time eliminating the wax pattern. Additional expansion results from the slight heating of gypsum investments on setting, thus expanding the wax pattern, and the water entering the investment from the wet liner adds a small amount of hygroscopic expansion to the normal setting expansion.

CASTING METAL IN GYPSUM INVESTMENTS

These casting investments are relatively fragile and require the use of a metal ring for protection during heating. The molds are usually placed in a furnace at room temperature, slowly heated to 650 °C to 700 °C in 60 minutes, and held for 15 to 30 minutes at the upper temperature.

The rate of heating has some influence on the smoothness and, in some instances, the overall dimensions of the investment. Initially the rapid heating can generate steam, which can cause flaking or spalling of the mold walls. Too many patterns in the same plane within the investment often cause separation of a whole section of investment because the expanding wax creates excessive pressure over a large area.

Too rapid a heating rate may also cause cracking of the investment. In such a case, the outside layer of the investment expands much more than the center sections. Consequently the outside layer starts to expand thermally, resulting in compressive stress in the outside layer, which counteracts tensile stresses in the middle regions of the mold. Such a stress distribution causes the brittle investment to crack from the interior outward in the form of radial cracks. These cracks, in turn, produce a casting with fins or spines similar to those shown in Figure 10-20. This condition is especially likely to be present with a cristobalite investment. The comparatively low inversion temperature of the cristobalite and the rapid rate of expansion during the inversion make it especially important to heat the investment slowly.

Breakdown of the dental investment and the resulting contamination and brittleness of the gold alloy casting probably occur more frequently than is generally realized. The mechanism of this investment decomposition and alloy contamination is related to a chemical reaction between the residual carbon and calcium sulfate binder. Calcium sulfate per se does not decompose unless it is heated above 1000 °C. However, the reduction of calcium sulfate by carbon takes place rapidly above 700 °C in accordance with the following reactions:

$$\begin{aligned} CaSO_4 + 4C &\rightarrow CaS + 4CO \\ 3CaSO_4 + CaS &\rightarrow 4CaO + 4SO_2 \end{aligned} \qquad (4)$$

This reaction takes place whenever gypsum investments are heated above 700 °C in the presence of carbon. The sulfur dioxide as a product of this reaction contaminates gold castings and makes them extremely brittle. This fact emphasizes the need for completely eliminating the wax and avoiding burnout temperatures above 700 °C, particularly if the investment contains carbon. Furthermore, sulfur gases are generated by the gypsum investment when it is heated above 700 °C.

After the casting temperature has been reached, the casting should be made immediately. Maintaining a high temperature for a considerable length of time may result in sulfur contamination of the casting and also in a rough surface on the casting because of the disintegration of the investment. To avoid this problem, some technicians use furnaces with heating elements on all four sides, thereby reducing the burnout time.

Despite all of these precautions and reasons for using a slow burnout technique, the desire for rapid results has led to improved investment formulations. A few gypsum investments, some with a considerable amount of cristobalite, are now offered for use with a much more rapid burnout procedure. Some suggest placing the mold in a furnace at 315 °C for 30 minutes and following this with very rapid heating to the final burnout temperature. In addition, a few investments may be placed directly into a furnace at the final burnout temperature, held for 30 minutes, and cast. Because of the furnace design, the proximity of the mold to the heating element, and the availability of air in the muffle may affect size and smoothness, it is advisable to examine these factors carefully before a casting is made in this manner.

CASTING IN PHOSPHATE INVESTMENTS

Many of the earlier statements about gypsum investments also apply to phosphate investments. There are several differences, however, because the setting mechanism and reactions on heating are quite different.

Phosphate investments obtain their expansion from the following sources:

1. Expansion of the wax pattern—this is considerable because the setting reaction raises the mold temperature substantially.
2. Setting expansion—this is usually higher than in gypsum investments, especially because special liquids are used to increase such expansion.
3. Thermal expansion—this is greater when taken to temperatures higher than those used for gypsum-bonded investments.

A total expansion of 2% or more is required for alloys used to produce metal-ceramic prostheses, since these gold-based, palladium-based, and base metal alloys have higher melting and solidification temperatures.

Although phosphate investments are usually much harder and stronger than gypsum investments, they are nevertheless quite brittle and are subject to the same unequal expansion of adjacent sections as phase changes occur during heating.

The usual burnout temperatures for phosphate-bonded investments range from 750 °C to 1030 °C. The highest temperatures are required for base metal alloys. The heating rate is usually slow to 315 °C and is quite rapid thereafter, reaching completion after a hold at the upper temperature for 30 minutes. Most burnout furnaces are capable of being programmed for heating rates and holding times.

Because the entire process involving phosphate investments takes a long time, the demand for time-saving changes is strong. Again, investment manufacturers have attempted to answer this demand, resulting in the availability of some investments that can be subjected to two-stage heating more rapidly, by being placed directly in the furnace at the top temperature, held for 20 to 30 minutes, and then cast. To save more time, manufacturers have also eliminated the use of a metal ring and liner, the metal ring being replaced with a plastic ring that is tapered, so that once the investment has set, it can be pushed out of the ring, held for a specified time to ensure complete setting, and then placed directly into the hot furnace. Obviously the expansion on setting for this method is different from that when a lined ring is used and changes in overall fit must be considered. The required expansion may be adjusted by varying the liquid concentration.

TIME ALLOWABLE FOR CASTING

The investment contracts thermally as it cools. When the thermal expansion or high-heat technique is used, the investment loses heat after the heated ring is removed from the furnace and the mold contracts. Because of the liner and the low thermal conductivity of the investment, a short time can elapse before the temperature of the mold is appreciably affected. Under average conditions of casting, approximately 1 minute can pass without a noticeable loss in dimension.

In the low-heat casting technique, the temperature gradient between the investment mold and the room is not as great as that employed with the high-heat technique. Also, the thermal expansion of the investment is not as important to the shrinkage compensation. However, the burnout temperature lies on a fairly steep portion of the thermal expansion curve rather than on a plateau portion, as in the high-heat technique. Therefore, in the low-heat casting technique, the alloy should also be cast soon after removal of the ring from the oven; otherwise a significant variation from the desired casting dimensions may occur.

CASTING MACHINES

Alloys are melted in one of the four following ways, depending on the available types of casting machines:

1. The alloy is melted in a separate crucible by a torch flame and cast into the mold by centrifugal force (Figure 10-21).
2. The alloy is melted electrically by a resistance heating or induction furnace and then cast into the mold centrifugally by motor or spring action. A representative casting machine of this type is shown in Figure 10-22.

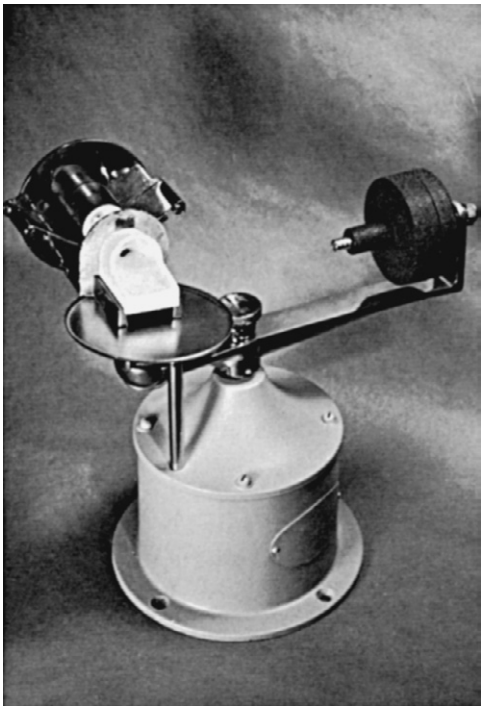


FIGURE 10-21 Centrifugal casting machine, spring-wound.

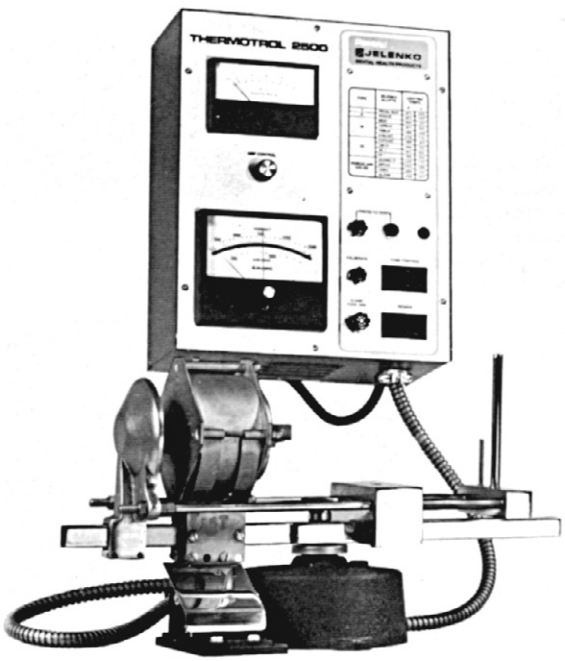


FIGURE 10-22 Spring-wound casting machine with electrical resistance melting furnace.

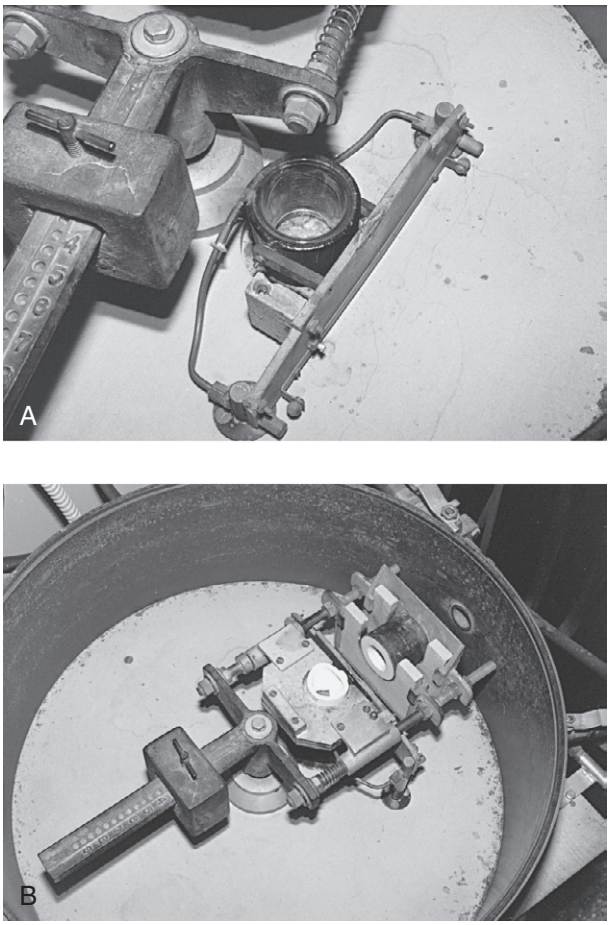


FIGURE 10-23 Induction melting casting machine. **A,** Water-cooled induction coil. **B,** Vertical crucible (*white area*) positioned within the induction coil.

3. The alloy is melted by induction heating and then cast into the mold centrifugally by motor or spring action. A representative casting machine of this type is shown in Figure 10-23.
4. The alloy is vacuum-arc melted and cast by pressure in an argon atmosphere.

In addition to these three melting methods, the molten metal may be cast by air pressure, vacuum, or both. The general procedure for each is described in the following sections, with certain advantages and disadvantages cited. However, it is important to follow the manufacturer's directions precisely for any of these devices.

TORCH MELTING/CENTRIFUGAL CASTING MACHINE

The casting machine spring is first wound from two to five turns (depending on the particular machine and the speed of casting rotation desired). The alloy is melted by a torch flame (Figure 10-24) in a glazed ceramic crucible attached to the "broken arm" of the casting machine. The torch flame is generated from a gas mixture of propane and air, natural gas and air, acetylene and air, or acetylene and oxygen. The broken-arm feature accelerates the initial rotational speed of the crucible and casting ring, thus increasing the linear speed of the liquid casting alloy as it moves into and through the mold. Once the metal has reached the casting temperature and the heated casting ring is in position, the machine is released and the spring triggers the rotational motion.

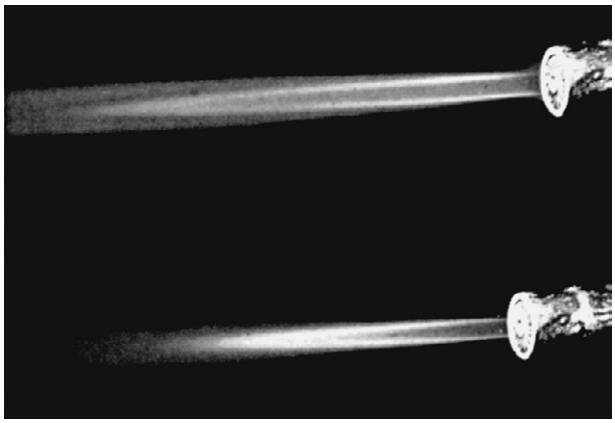


FIGURE 10-24 Two types of nonluminous flames showing combustion areas. The upper flame should be employed for fusing the noble metal alloy. The lower flame results from too much air in the mixture.

As the metal fills the mold, a hydrostatic pressure gradient develops along the length of the casting. The pressure gradient from the tip of the casting to the bottom surface is quite sharp and parabolic in form, reaching zero at the button surface. Ordinarily the pressure gradient at the moment before solidification reaches about 0.21 to 0.28 MPa at the tip of the casting. Because of this pressure gradient, there is also a gradient in the heat transfer rate such that the greatest rate of heat transfer to the mold is at the high pressure end of the gradient (i.e., the tip of the casting). Because this end also is frequently the sharp edge of the margin of a crown, there is further assurance that the solidification progresses from the thin margin edge to the button surface.

ELECTRICAL RESISTANCE–HEATED CASTING MACHINE

In this device, current is passed through a resistance heating conductor, and automatic melting of the alloy occurs in a graphite or ceramic crucible. This is an advantage, especially for alloys such as those used for metal-ceramic prostheses, which are alloyed with base metals in trace amounts that tend to oxidize on overheating. Another advantage is that the crucible in the furnace is located flush against the casting ring. Therefore, the alloy button remains molten slightly longer, again ensuring that solidification progresses completely from the tip of the casting to the button surface. A carbon crucible should not be used in the melting of high-palladium alloys, palladium-silver alloys, nickel-chromium alloys, or cobalt-chromium base metal alloys. An example of the electrical resistance casting machine is shown in Figure 10-22.

INDUCTION MELTING MACHINE

With this unit, the alloy is melted by an induction field that develops within a crucible surrounded by water-cooled metal tubing (see Figure 10-23). The electric induction furnace is a

transformer in which an alternating current flows through the primary winding coil and generates a variable magnetic field in the location of the alloy to be melted in a crucible. Once the alloy reaches the casting temperature in air or in vacuum, it is forced into the mold by centrifugal force, air pressure, or vacuum. The device has become popular in the casting of jewelry, but it has not been used as much as the other two techniques for noble alloy castings. It is more commonly used for melting base metal alloys.

There is little practical difference in the properties or accuracy of castings made with any of the three types of casting machines. The choice is a matter of access to specialized equipment and personal preference.

DIRECT-CURRENT ARC MELTING MACHINE

The direct-current arc is produced between two electrodes: the alloy and the water-cooled tungsten electrode. The temperature within the arc exceeds 4000 °C and the alloy melts very quickly. This method poses a high risk of overheating the alloy, and damage may result after only a few seconds of prolonged heating.

VACUUM- OR PRESSURE-ASSISTED CASTING MACHINE

For this method, the molten alloy is heated to the casting temperature, drawn into the evacuated mold by gravity or vacuum, and subjected to additional pressure to force the alloy into the mold. For titanium and titanium alloys, vacuum arc heated-argon pressure casting machines are required.

CASTING CRUCIBLES

Generally four types of casting crucibles are available: clay, carbon, quartz, and zirconia-alumina. Clay crucibles are appropriate for many of the crown and bridge alloys, such as the high noble and noble types. Carbon crucibles can be used not only for high noble crown and bridge alloys but also for the higher-fusing gold-based metal-ceramic alloys.

Crucibles made from alumina, quartz, or silica are recommended for high-fusing alloys of any type. These are especially suited for alloys that have a high melting temperature or those that are sensitive to carbon contamination. Crown and bridge alloys with a high palladium content—such as palladium-silver alloys for metal-ceramic copings and any of the nickel-based or cobalt-based alloys—are included in this category.

TORCH MELTING OF NOBLE METAL ALLOY

This type of alloy is best melted by placing it on the inner sidewall of the crucible. Thus, the operator can better observe the progress of the melting and there is a better opportunity for any gases in the flame to be reflected from the surface of the alloy rather than being absorbed.

The fuel used in most instances is a mixture of natural or artificial gas and air, although oxygen-air and acetylene can also be used. The temperature of the gas-air flame is greatly influenced by the nature of the gas and the proportions of gas and air in the mixture. Considerable care should be taken to obtain a nonluminous brush flame with the different combustion zones clearly differentiated. Two types of flames can be obtained with a casting torch, as shown in Figure 10-24. The air supply for the lower flame (Figure 10-25) is excessive, so that incomplete combustion and a lower temperature will result. This type of flame is likely to be favored by the beginner because the roaring sound that accompanies this flame adjustment "sounds" hot. The upper brush flame indicates the proper adjustment for maximal efficiency and temperature.

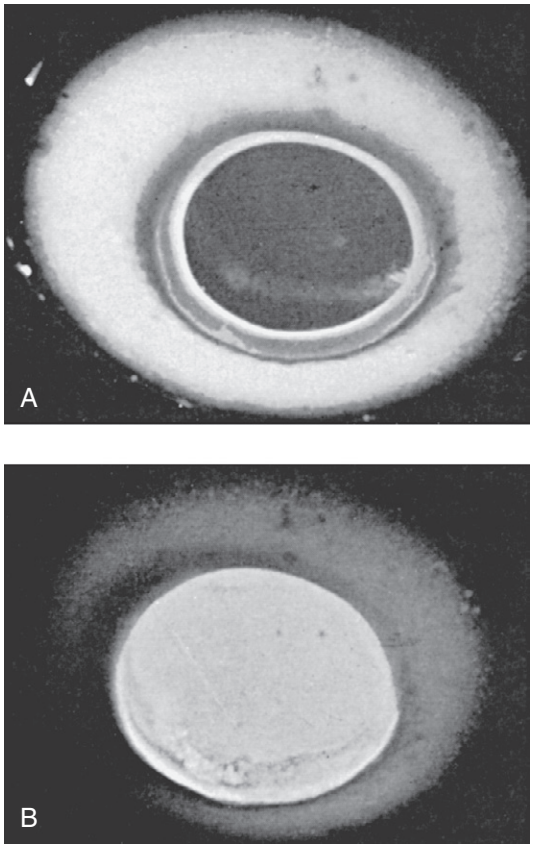


FIGURE 10-25 **A,** Mirrorlike surface of the metal indicates proper fusion. **B,** Cloudy surface indicates surface oxidation by improper positioning of the torch flame.

The parts of the flame can be identified by the conical areas in Figure 10-24. The first long cone emanating directly from the nozzle is the zone in which the air and gas are mixed before combustion. No heat is present in this zone. The next cone, which is green and immediately surrounding the inner cone, is known as the combustion zone. Here, the gas and air are partially burned. This zone is definitely oxidizing and should always be kept away from the molten alloy during fusion.

The next zone, dimly blue and located just beyond the tip of the green combustion zone, is the reducing zone. This is the hottest part of the flame, and it should be kept constantly on the alloy during melting. The outer cone (oxidizing zone) is the area in which combustion occurs with the oxygen in the air. Under no circumstances should this portion of the flame be used to melt the alloy. Not only is its temperature

lower than that of the reducing zone but it also oxidizes the alloy.

With a little practice, the clinician can readily detect whether the proper zone of the flame is in contact with the metal by observing the condition of the alloy surface. When the reducing zone is in contact, the surface of the gold alloy is bright and mirrorlike, as indicated in Figure 10-25, *A*. When the oxidizing portion of the flame is in contact with the alloy, a dull film of "dross" develops over the surface, as seen in Figure 10-25, *B*. Although care should be taken not to overheat the alloy, there is generally more likelihood of underheating when the gas-air flame is used. The alloy first appears to be spongy and then small globules of fused alloy appear. The molten alloy soon assumes a spheroidal shape, as indicated in Figure 10-25, *A*. At the proper casting temperature, the molten alloy is light orange and tends to spin or follow the flame when the latter is moved slightly. At this point, the alloy should be approximately 38 °C to 66 °C above its liquidus temperature. The casting should be made immediately when the proper temperature is reached. As previously discussed, various devices are also available for melting the alloy electrically.

It is desirable to use a flux for gold crown and bridge alloys to aid in minimizing porosity. When properly used, the flux increases the fluidity of the alloy and the film of flux formed on the surface of the molten alloy helps prevent oxidation. Reducing fluxes containing powdered charcoal are often used, but small bits of carbon may be carried into the mold and cause a deficiency at a critical margin. Although such reducing fluxes are excellent for cleaning old alloy, a better flux for the casting procedure may be made from equal parts of fused borax powder ground with boric acid powder. The boric acid aids in retaining the borax on the surface of the alloy. The flux is added when the alloy is completely melted and should be used with both old and new alloy. Old sprues and buttons from the same alloy may be recast if they are not contaminated.

CLEANING THE CASTING

When a type III or IV gold alloy has been cast and it has solidified, the ring should be quenched in water as soon as the button exhibits a dull-red glow. Two advantages are gained in quenching: (1) the noble metal alloy is left in an annealed condition for burnishing, polishing, and similar procedures and (2) when the water contacts the hot investment, a violent reaction ensues, resulting in a soft, granular investment that is easily removed.

Often the surface of the casting appears dark because of oxides and tarnish. Such a surface film can be removed by a process known as pickling, which consists of heating the discolored casting in an acid. One of the best pickling solutions for gypsum-bonded investments is a 50% hydrochloric acid (HCl) solution. The HCl aids in the removal of any residual investment, as well as of the oxide coating. The disadvantage of HCl is that the fumes from the acid are likely to corrode laboratory metal furnishings. In addition, these fumes are a health hazard and should be vented via a fume hood. However, the pickling process can be performed ultrasonically while the prosthesis is sealed in a Teflon container. A solution of sulfuric acid (H_2SO_4) may also be more advantageous in this respect. Ultrasonic devices are useful for cleaning the casting, as are commercial pickling solutions made of acid salts. Abrasive blasting devices are also useful for cleaning the surface of castings.

The best method for pickling is to place the casting in a test tube or dish and to pour the acid over it. It may be necessary to heat the acid, but boiling should be avoided because of the considerable amount of acid fumes involved. After pickling, the acid is poured off and the casting is removed. The pickling solution should be renewed frequently, because it is likely to become contaminated after reusing the solution several times.

In no case should the casting be held with steel tongs so that both the casting and the tongs come into contact with the pickling solution, because this may contaminate the casting. The pickling solution usually contains small amounts of copper dissolved from previous castings. When the steel tongs contact this electrolyte, a small galvanic cell is created and copper is deposited on the casting at the point where the tongs grip it. This copper deposition extends into the alloy and is a future source for discoloration in the area.

If gold-based and palladium-based metal-ceramic alloys and base metal alloys are bench-cooled to room temperature before the casting is removed from the investment, these alloys are generally not pickled.

MELTING OF BASE METALS

Although torch melting can be used in some cases, most base metals of Ni-Cr, Ni-Cr-Be, Co-Cr, Co-Ni-Cr, commercially pure Ti, and Ti-Al-V require special melting equipment, such as induction melting machines, vacuum melting devices, or arc-melting units. The procedures required are designed to minimize the risk for excessive oxidation or an interaction of the molten alloys with the recommended casting investments. It is beyond the scope of this book to discuss these methods; the reader is referred to specialized instruction manuals developed by the manufacturers of these products.

TECHNICAL CONSIDERATIONS FOR PHOSPHATE-BONDED INVESTMENT

The procedure for investing a wax pattern in a phosphate-bonded investment is essentially the same as that for a gypsum-bonded investment. As previously mentioned, the working time can vary depending on the L/P ratio, special liquid concentration, temperature, mixing time, mixing rate, and operator skill and experience.

As with any investment that has a high thermal expansion, especially when marked changes in expansion or contraction occur, it is necessary to use a slow heating rate during burnout to prevent possible cracking or spalling. Some furnaces provide slow rates of heating. For those that do not, it is advisable to use a two-stage burnout, holding at 200 °C to 300 °C for at least 30 minutes before completing the burnout.

Recommendations for the rate of heating vary, so it is wise to follow the instructions for the specific investment used.

Although phosphate investments appear strong, they are still susceptible to a number of disrupting influences during burnout. When the wax softens, it expands much more than does the investment. When investing, it is desirable to leave 3 to 6 mm of investment around each pattern and to stagger the patterns if several are placed in the same ring. A number of patterns positioned along a plane can exert tremendous pressure and fracture almost any investment, but particularly the phosphate-bonded materials. The rapid expansion of cristobalite investment at approximately 300 °C requires slow heating to prevent fracture. After the temperature reaches 400 °C, the rate of heating can be safely increased. After burnout, usually at a final temperature of 700 °C to 1030 °C depending on the alloy melting range, the casting is made. The permeability of the phosphate investment is low compared with that of a gypsum-bonded investment. Therefore, the required casting pressure should be greater than that for a gypsum mold.

Recovery and cleaning of the casting are more difficult when a phosphate-bonded investment is used because such materials do not contain the soft gypsum products. Also, the particles usually include large grains of quartz. In some instances, such as with gold-containing alloys, the investment adheres rather tenaciously, usually requiring cleaning in an ultrasonic device. Neither the phosphate binder nor the silica refractory is soluble in HCl or H_2SO_4. Old hydrofluoric acid (HF) dissolves the silica refractory quite well without damage to a gold-based or a palladium-silver alloy, but this acid must be used carefully with other alloys. In fact, even dilute HF should not be used unless the necessary neutralizing solutions are immediately at hand and the clinician is familiar with the correct handling techniques. However, once tissue injury has occurred, it cannot be reversed with such solutions. Alternative commercially available solutions can be used with greater safety.

Base metal alloys require a light sandblasting, usually with fine alumina. Chromium-based partial dentures are usually sandblasted to remove the investment. Acid should not be used for cleaning base metal alloys.

The selection of the appropriate phosphate-bonded investment must be made on the basis of the composition of the alloy to be used. Carbon-containing investments are well suited for gold-based crown and bridge casting alloys and metal-ceramic alloys. However, if the alloy is carbon-sensitive (such as in silver-palladium, high palladium, palladium-silver, nickel-chromium-beryllium, nickel-chromium, and cobalt-chromium alloys), a noncarbon investment should be used.

CAUSES OF DEFECTIVE CASTINGS

An unsuccessful casting results in considerable trouble and loss of time. In almost all instances, defects in castings can be avoided by strict observance of procedures governed by certain fundamental rules and principles. Seldom is a defect in a casting attributable to factors other than the carelessness or ignorance of the operator. With present techniques, casting failures should be the exception, not the rule.

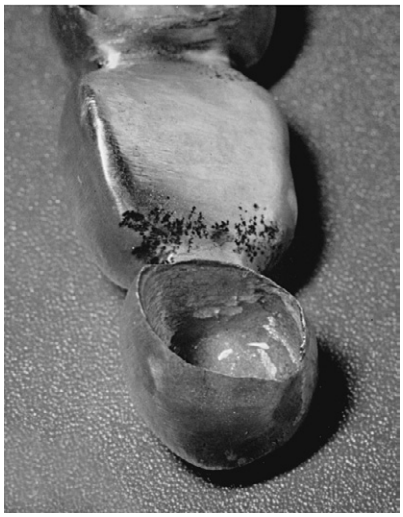


FIGURE 10-26 Localized shrinkage porosity in pontic of three-unit bridge caused by delayed solidification and lack of a chill-set sprue.

Defects in castings can be classified under four headings: (1) distortion; (2) surface roughness and irregularities; (3) porosity (Figure 10-26); and (4) incomplete or missing detail. The porosity in the pontic area of Figure 10-26 was caused by the retention of heat by the pontic because of its bulk and because it was located in the heat center of the ring. This problem can be solved simply by attaching one or more small-gauge sprues (e.g., 18-gauge) at the surface most distant from the main sprue attachment and extending the sprue(s) laterally within 5 mm of the edge of the ring. These small chill-set sprues ensure that solidification begins within the sprues, and they act as cooling pins to carry heat away from the pontic. Other types of casting porosities are described in a later section.

DISTORTION

Any marked distortion of the casting is probably related to a distortion of the wax pattern, as described in the section on inlay wax. This type of distortion can be minimized or prevented by proper manipulation of the wax and handling of the pattern.

Unquestionably some distortion of the wax pattern occurs as the investment hardens around it. The setting and hygroscopic expansions of the investment may produce a nonuniform expansion of the walls of the pattern. This type of distortion occurs in part from the nonuniform outward movement of the proximal walls. The gingival margins are forced apart by the mold expansion, whereas the solid occlusal bar of wax resists expansion during the early stages of setting. The configuration of the pattern, the type of wax, and the thickness influence the distortion that occurs, as has been discussed. For example, distortion increases as the thickness of the pattern decreases. As would be expected, the lower is the setting expansion of the investment, the less lower is distortion. Generally this is not a serious problem, but it

accounts for some of the unexplained inaccuracies that may occur in small castings.

SURFACE ROUGHNESS, IRREGULARITIES, AND DISCOLORATION

The surface of a dental casting should be an accurate reproduction of the surface of the wax pattern from which it is made. Excessive roughness or irregularities on the outer surface of the casting necessitate additional finishing and polishing, whereas irregularities on the cavity surface prevent proper seating of an otherwise accurate casting.

Surface roughness should not be confused with surface irregularities. Surface roughness is defined as relatively finely spaced surface imperfections whose height, width, and direction establish the predominant surface pattern. Surface irregularities are isolated imperfections, such as nodules, that are not characteristic of the entire surface area.

Even under optimal conditions, the surface roughness of the dental casting is invariably somewhat greater than that of the wax pattern from which it is made. The difference is probably related to the particle size of the investment and its ability to reproduce the wax pattern in microscopic detail. With proper manipulative techniques, the normal increased roughness in the casting should not be a major factor in dimensional accuracy. However, improper technique can lead to a marked increase in surface roughness as well as to the formation of surface irregularities.

AIR VOIDS

Small nodules on a casting are caused by air bubbles that become attached to the pattern during or subsequent to the investing procedure. Such nodules can sometimes be removed if they are not in a critical area. However, for nodules on margins or on internal surfaces, removal of these irregularities might alter the fit of the casting. As previously noted, the best method to avoid air bubbles is to use the vacuum investing technique.

If a manual method is used, various precautions can be taken to eliminate air from the investment mix before the investing. As previously outlined, a mechanical mixer with vibration both before and after mixing should be used routinely. A wetting agent may be helpful in preventing the collection of air bubbles on the surface of the pattern, but it is by no means a certain remedy. As previously discussed, it is important that the wetting agent be applied in a thin layer. It is best to air-dry the wetting agent, because any excess liquid dilutes the investment, possibly producing surface irregularities on the casting.

WATER FILMS

Wax is repellent to water; if the investment becomes separated from the wax pattern in some manner, a water film may form irregularly over the surface. Occasionally this type of surface irregularity appears as minute ridges or veins. If the pattern is slightly moved, jarred, or vibrated after investing or if the painting procedure does not result in intimate contact of the investment with the pattern, such a condition may result. A wetting agent is useful for the prevention of such irregularities. Too high an L/P ratio may also produce these surface irregularities.

LIQUID/POWDER RATIO

The amount of water and investment should be measured accurately. The higher the L/P ratio, the rougher the casting. However, if too little water is used, the investment may be unmanageably thick, so that it cannot be properly applied to the pattern. In vacuum investing, the air may not be sufficiently removed. In either instance, a rough surface on the casting may result.

COMPOSITION OF THE INVESTMENT

The ratio of the binder mass to that of the quartz influences the surface texture of the casting. In addition, a coarse silica causes surface roughness.

FOREIGN BODIES

When foreign substances get into the mold a surface roughness may be produced. For example, a rough crucible former with investment clinging to it may roughen the investment on its removal so that bits of investment are carried into the mold with the molten alloy. Carelessness in the removal of the sprue former may also be a cause.

Usually contamination results not only in surface roughness but also in incomplete areas or surface voids. Any casting that shows sharp, well-defined deficiencies indicates the presence of some foreign particles in the mold, such as pieces of investment and bits of carbon from a flux. Bright-appearing concavities may be the result of flux being carried into the mold with the metal.

Surface discoloration and roughness can result from sulfur contamination. An example of this effect may be seen in Figure 10-27, either from investment breakdown at elevated temperatures or from a high sulfur content of the torch flame. The interaction of the molten alloy with sulfur produces a black or gray layer on the surface of gold alloys that is brittle and does not clean readily during pickling.



FIGURE 10-27 A black-coated noble metal alloy casting resulting from sulfur contamination or oxidation during melting of the alloy.

IMPACT OF MOLTEN ALLOY ON THE MOLD WALL

The direction of the sprue former should be such that the molten gold alloy does not impact a weak portion of the mold surface. Occasionally the molten alloy may fracture or abrade the mold surface on impact, regardless of its bulk. It is unfortunate that sometimes the abraded area is smooth, so that it cannot be detected on the surface of the casting. Such a depression in the mold is reflected as a raised area on the casting, often too slight to be noticed yet sufficiently large to prevent complete seating of the casting. This type of surface roughness or irregularity can be avoided by proper spruing so as to prevent the direct impact of the molten metal at an angle of 90° to the investment surface. A glancing impact is likely to be less damaging, and at the same time an undesirable turbulence is avoided.

PATTERN POSITION

If several patterns are invested in the same ring, they should not be placed too close together. Likewise, positioning too many patterns in the same plane in the mold should be avoided. The expansion of wax is much greater than that of the investment, and this may cause breakdown or cracking of the investment if the spacing between patterns is less than 3 mm.

CARBON INCLUSIONS

Carbon from a crucible, an improperly adjusted torch, or a carbon-containing investment, can be absorbed by the alloy during casting. These particles may lead to the formation of carbides or even create visible carbon inclusions.

? CRITICAL QUESTION

How can the risk for porosity and incomplete castings be minimized?

POROSITY

Cast metal prostheses such as inlays, onlays, crowns, and bridges represent the most durable and long-lasting materials and devices used for dental restorations. They are quite costly, so dental patients should expect a high degree of precision and quality in their manufacture. In this regard, extreme care should be taken to prevent the casting defects already mentioned. In addition, care should also be taken to avoid producing one of the most common types of defects, i.e., casting porosity.

Where is porosity most likely to occur? It may occur both within the interior region of a casting and in the external surface. The latter effect results in surface roughness, but it is also a manifestation of internal porosity. Not only does the internal porosity weaken the casting, but it also extends to the surface, which may also cause discoloration. If severe, it can cause plaque accumulation at the tooth-restoration interface, and secondary caries or periodontal disease may result within the adjacent tooth structure. Although porosity in a casting cannot be prevented entirely, it can be minimized by the use of proper techniques.

Porosities in noble metal alloy castings are classified below. Illustrations of some of these defects are also noted.

I. Solidification defects
   A. Localized shrinkage porosity (Figure 10-26)
   B. Microporosity (Figure 10-28, *A*)
   C. Suck-back porosity (Figure 10-29)
II. Trapped gases
   A. Pinhole porosity (Figure 10-28, *A*)
   B. Gas inclusions
   C. Subsurface porosity (Figure 10-28, *B*)
   D. Back pressure porosity (Figure 10-30)

Localized shrinkage is generally caused by premature termination of the flow of molten metal during solidification. The linear contraction of noble metal alloys from a liquid state to a solid state is at least 1.25%. Therefore, continual feeding of molten metal through the sprue must occur to make up for the shrinkage of metal volume during solidification. If the sprue freezes in its cross section before this flow is completed to the casting proper, a localized shrinkage void will occur in the last portion of the casting that solidifies. Four types of porosities are shown in Figure 10-28, *A* and *B*: (a) localized shrinkage porosity, (b) microporosity, (c) pinhole porosity, and (d) subsurface porosity. Localized shrinkage porosity is shown in Figure 10-28, *C*. Localized shrinkage generally occurs near the sprue-casting junction, but it may occur anywhere between dendrites, as shown in Figure 10-28, *C*, where the last part of the casting to solidify was between the dendrite branches as they developed.

Microporosity also occurs from solidification shrinkage, but it is generally present in fine-grain alloy castings when

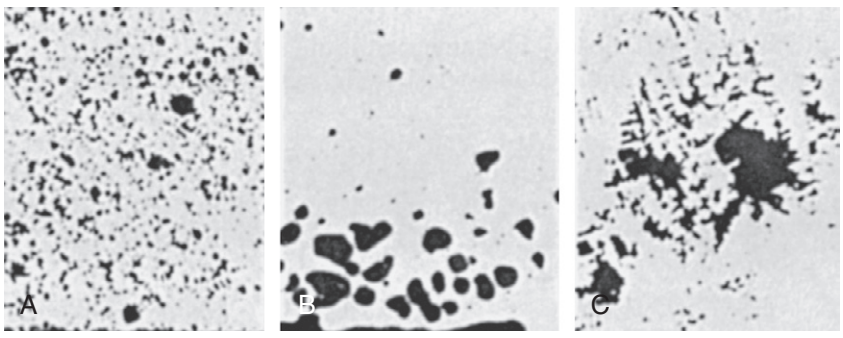


FIGURE 10-28 **A,** Microporosity, pinhole porosity, and gas inclusions. Microporosity voids are irregular in shape, whereas the two other types tend to be spherical; the largest spherical voids are gas inclusions. **B,** Subsurface porosity. **C,** Localized shrinkage porosity. (Courtesy of G. Ryge.)

the solidification is too rapid for the microvoids to segregate to the liquid pool. This premature solidification causes the formation of small, irregular voids. Such phenomena can occur from rapid solidification if the mold or casting temperature is too low. Unfortunately, this type of defect is not detectable unless the casting is sectioned. In any case, it is generally not a serious defect. The effects of various factors involved in formation of microporosity and other types of porosities are summarized in Table 10-4.

Oxygen is dissolved by some of the metals, such as silver, in the alloy while they are in the molten state. During solidification, the gas is expelled to form blebs and pores in the metal. As was pointed out earlier, this type of porosity may be attributed to abuse of the metal. Castings that are severely contaminated with gases are usually black when they are removed from the investment and do not clean easily on pickling (see Figure 10-27). The porosity that extends to the surface is usually in the form of small pinpoint holes (see Figure 10-28, *A*). When the surface is polished, other pinholes appear.

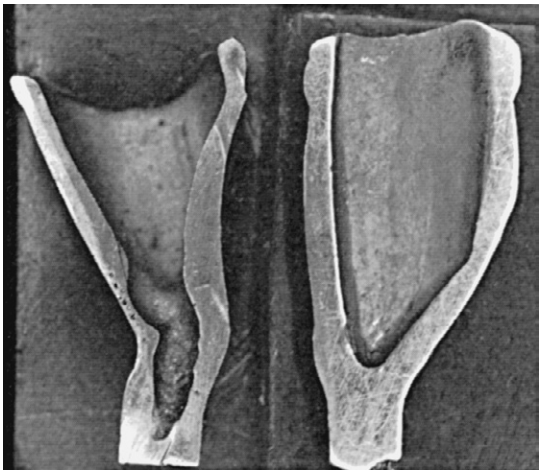


FIGURE 10-29 Examples of suck-back porosity. The coping on the left was cast at 1370 °C. The coping on the right side was cast at 1340 °C. (Courtesy of J. Nielsen.)



FIGURE 10-30 Surface irregularity on the cavity side of a casting caused by back-pressure porosity.

Both pinhole and gas inclusion porosities are related to the entrapment of gas during solidification. Both are characterized by a spherical contour but are decidedly different in size. The gas inclusion porosities are usually much larger than pinhole porosity, as indicated in Figure 10-28, *A*. Many metals dissolve or occlude gases while they are molten. For example, both copper and silver dissolve oxygen in large amounts in the liquid state. Molten platinum and palladium have a strong affinity for hydrogen as well as oxygen. On solidification, the absorbed gases are expelled and pinhole porosity results. The larger voids (Figure 10-28, *A*) may also result from the same cause, but it is more logical to assume that such voids are caused by gas that is mechanically trapped by the molten metal in the mold or by gas that is incorporated during the casting procedure.

Larger spherical porosities can be caused by gas occluded from a poorly adjusted torch flame or by use of the mixing or oxidizing zones of the flame rather than the reducing zone (Figure 10-28, *A*). If the alloy has been used before, these types of porosities can be minimized by premelting the gold alloy on a graphite crucible or a graphite block and correctly adjusting and positioning the torch flame during melting.

Subsurface porosity occurs on occasion, as shown in Figure 10-28, *B*. At other times it may be particularly evident. The reasons for such voids are not well understood. They may be caused by the simultaneous nucleation of solid grains and gas bubbles at the first moment that the alloy freezes at the mold walls. As has been explained, this type of porosity can be diminished by controlling the rate at which the molten metal enters the mold.

As described previously in this chapter, suck-back porosity, another type of localized shrinkage porosity, may also occur externally, usually in the interior of a crown near the area of the sprue, if a hot spot has been created by the hot metal impinging from the sprue channel on a point of the mold wall. This hot spot causes the local region to freeze last and results in what is called suck-back porosity, as shown in

TABLE 10-4 Effects of Technical Variables on Solidification Porosity

Type of Porosity	Increased Sprue Thickness	Increased Sprue Length	Increased Melt Temperature	Increased Mold Temperature
Localized shrinkage	Decreased	Increased	Decreased	Decreased
Subsurface porosity	Increased	Decreased	Increased	Increased
Microporosity	No effect	No effect	Decreased	Decreased

From Ryge G, Kozak SF, Fairhurst CW: *J Am Dent Assoc* 54:746, 1957.

Figure 10-29 (left). Suck-back porosity often occurs at an occlusoaxial line angle or incisoaxial line angle that is not well rounded. The entering metal impinges onto the mold surface at this point and creates a higher localized mold temperature in this region, known as a hot spot. A hot spot may retain a localized pool of molten metal after other areas of the casting have solidified. This, in turn, creates a shrinkage void or suck-back porosity. This type of porosity defect can be eliminated by flaring the point of sprue attachment and reducing the mold-melt temperature differential—that is, lowering the casting temperature by about 30 °C. Such a result is shown on the right side of Figure 10-29.

Entrapped air bubbles on the inner surface of the casting, are sometimes referred to as back-pressure porosity, can produce large concave depressions such as those seen in Figure 10-30. This is caused by the inability of the air in the mold to escape through the pores in the investment or by the pressure gradient that displaces the air pocket toward the end of the investment via the molten sprue and button. The entrapped air voids are frequently found in a "pocket" at the cavity surface of a crown or mesio-occlusal-distal casting. Occasionally it is found even on the outside surface of the casting when the casting temperature or mold temperature is so low that solidification occurs before the entrapped air can escape. The incidence of entrapped air can be increased by use of the dense modern investments, by an increase in mold density produced by vacuum investing, and by the tendency for the mold to clog with residual carbon when the low-heat technique is used. Each of these factors tends to slow the venting of gases from the mold during casting.

All castings probably contain a certain amount of porosity, as exemplified by the photomicrographs shown in Figure 10-31. This porosity should be kept to a minimum because it may adversely affect the physical properties of the casting. Proper burnout, an adequate mold and casting temperature, a sufficiently high casting pressure, and proper L/P ratio can minimize or eliminate eliminate entrapped-air porosity. It is good practice to make sure that the thickness of investment between the tip of the pattern and the end of the ring is not greater than 6 mm.

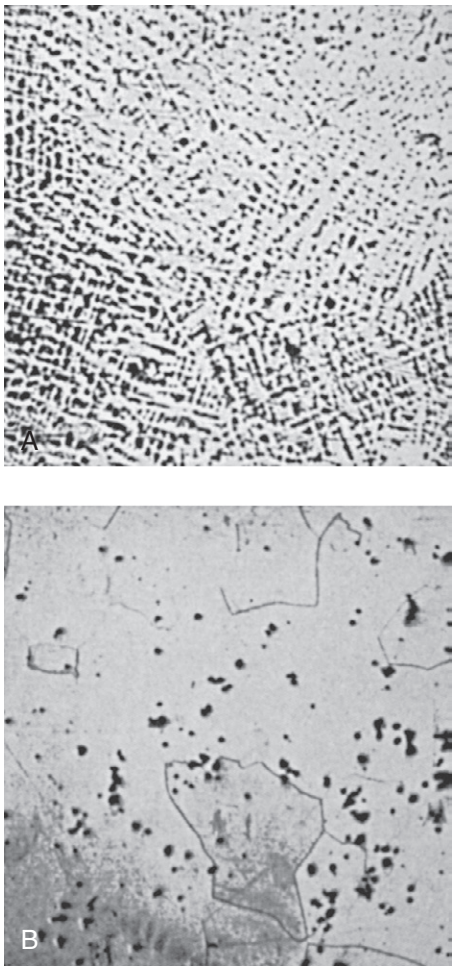


FIGURE 10-31 **A,** Grain structure of an as-cast type III noble metal alloy. **B,** Same alloy after a homogenization heat treatment at 725 °C for 70 minutes. Pinhole porosity is visible. (Courtesy of B. Hedegard.)

INCOMPLETE CASTING

Occasionally only a partially complete casting or perhaps no casting at all is found. The obvious cause is that the molten alloy has been prevented in some manner from completely filling the mold. At least two factors that may inhibit the ingress of the liquefied alloy are insufficient venting of the mold and high viscosity of the fused metal.

The first consideration, insufficient venting, is directly related to the back pressure exerted by the air in the mold. If the air cannot be vented quickly, the molten alloy does not fill the mold before it solidifies. In such a case, the magnitude of the casting pressure should be suspected. If insufficient casting pressure is used, the back pressure cannot be overcome. Furthermore, the pressure should be applied for at least 4 seconds. The mold is filled and the alloy solidified in 1 second or less, yet it is quite soft during the early stages.

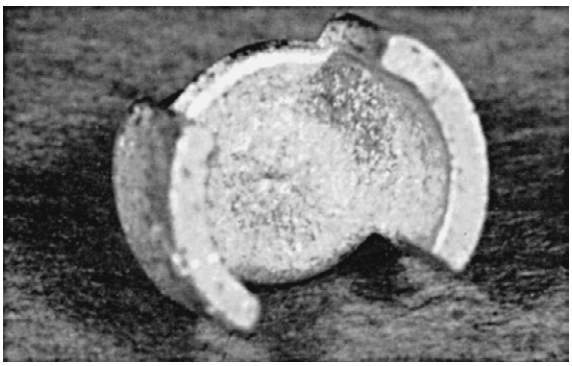


FIGURE 10-32 Rounded, incomplete margins are evidence of insufficient casting pressure.

Therefore, the pressure should be maintained for a few seconds beyond this point. An example of an incomplete casting that is caused by insufficient casting pressure is shown in Figure 10-32. These failures are usually exemplified by rounded, incomplete margins.

A second common cause of an incomplete casting is incomplete elimination of wax residues from the mold. If too

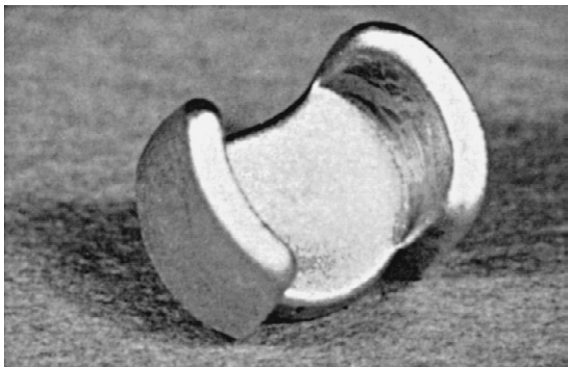


FIGURE 10-33 Incomplete casting resulting from incomplete wax elimination is characterized by rounded margins and shiny appearance.

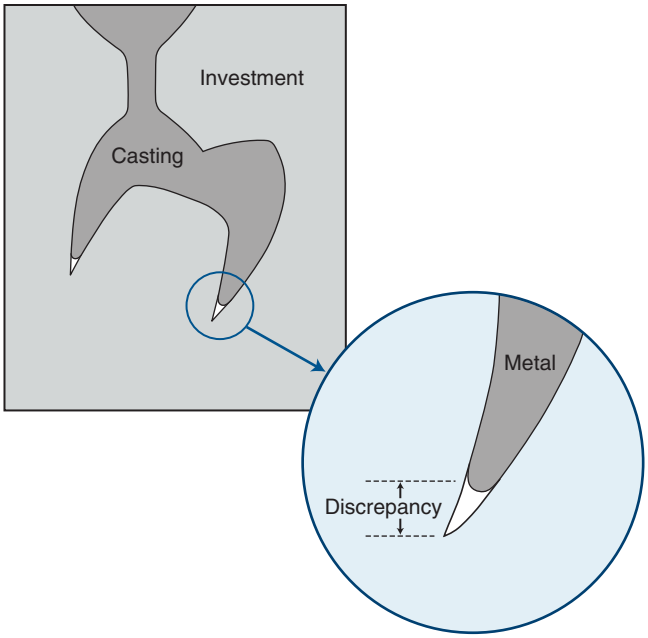


FIGURE 10-34 Schematic illustration of an incomplete casting.

many products of combustion remain in the mold, the pores in the investment may become filled, so that the air cannot be vented completely. If moisture or particles of wax remain, the contact of the molten alloy with these foreign substances produces an explosion that may lead to sufficient back pressure to prevent the mold from being filled. An example of a casting failure caused by incomplete wax elimination can be seen in Figure 10-33 and is shown schematically in Figure 10-34. Although the rounded margins in Figure 10-34 are similar to those of the incomplete casting in Figure 10-32, they are quite shiny rather than dull. This shiny condition of the metal is caused by the strong reducing atmosphere created by carbon monoxide left by the residual wax.

The influence of the L/P ratio of the investment has already been discussed. A lower L/P ratio is associated with less porosity of the investment. An increase in casting pressure during casting can also solve this problem.

Casting alloys probably exhibit varying viscosities in the molten state, depending on composition and temperature. Since both the surface tension and the viscosity of a molten alloy increase with a decrease in temperature, incomplete casting results from too great a viscosity that is attributed to insufficient heating. The temperature of the alloy should be raised higher than its liquidus temperature so that its viscosity and surface tension are decreased so that it does not solidify prematurely as it enters the mold. Such premature solidification may account for the greater susceptibility of the white gold alloys to porosity because their liquidus temperatures are higher. Thus, white gold alloys are more difficult to melt with a gas-air torch flame.

OTHER CAUSES

Certain surface discolorations and roughness may not be evident when the casting is completed but may appear during service. For example, various gold alloys—such as solders, bits of wire, and mixtures of different casting alloys—should never be melted together and reused. The resulting mixture would not possess the proper physical properties and might form a eutectic phase with low corrosion resistance. Discoloration and corrosion can also occur.

An often overlooked source of discoloration is the surface contamination of a gold alloy restoration by mercury. Mercury penetrates rapidly into the alloy and causes a marked loss in ductility and a greater susceptibility to corrosion. Thus it is not a good practice to place a new amalgam restoration adjacent to a high-noble-alloy restoration. In addition, these dissimilar metals form a galvanic cell that can lead to breakdown of the anode (amalgam) relative to the cathode (noble alloy).

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Total expansion, setting expansion, and thermal expansion of the investment setting against a smooth dry surface was 1.7%; against a dry ceramic liner, 1.6% to 1.7%; and against wet cellulose or wet asbestos, 2.2% to 2.3%. The ceramic liner can be used wet if it is treated with a surfactant instead of water.

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CHAPTER 11

Materials and Processes for Cutting, Grinding, Finishing, and Polishing

OUTLINE

A Brief History of Abrasives

Applications of Abrasives in Dentistry

Benefits of Finishing and Polishing Restorative Materials

Principles of Cutting, Grinding, Finishing, and Polishing

Abrasion and Erosion

Abrasive Instrument Design

Types of Abrasives

Finishing and Polishing Procedures

Dentifrices

Summary and Recommendations

KEY TERMS

Abrasive—A sharp, hard, natural or synthetic substance used for grinding, finishing, or polishing a softer surface.

Air-particle abrasion—Process of removing material, contaminants, stain, or carious tissue by use of air pressure and abrasive particles appropriate for the substrate being treated.

Buffing—Process of producing a lustrous surface through the abrading action of fine abrasives bound to a nonabrasive carrier with or without a liquid or paste medium.

Bulk reduction—Process of removing excess material (natural tooth or synthetic structure) by cutting or grinding with rotary instruments to provide a desired anatomic form.

Contouring—Process of producing a desired anatomic form by cutting or grinding away excess material.

Cutting—Process of removing material from the substrate by use of a bladed bur or an abrasive embedded in a binding matrix on a bur or disc.

Finished and polished restoration—A prosthesis or direct restoration whose outer surface has been progressively refined to a desired state of surface finish.

Finishing—Process of removing surface defects or scratches created during the contouring process through the use of cutting or grinding instruments or both.

Glaze ceramic—A specially formulated ceramic powder that, when mixed with a liquid, applied to a ceramic surface, and heated to an appropriate temperature for a sufficient time, forms a smooth glassy layer on a dental ceramic surface (see *natural glaze*).

Grinding—Process of removing material from a substrate by abrasion with relatively coarse particles.

Natural glaze—A vitrified layer that forms on the surface of a dental ceramic containing a glass phase when the ceramic is heated to a glazing temperature for a specified time.

Overglaze—Thin surface coating of glass formed by fusing a thin layer of glass powder that becomes a viscous liquid at a lower temperature than that associated with the ceramic substrate.

Polish—Luster or gloss produced on a finished surface.

Polishing—Process of providing luster or gloss on a material surface.

A BRIEF HISTORY OF ABRASIVES

Abrasive processes have been used since prehistoric times. Hunting and gathering instruments were shaped and sharpened by chipping and abrading one surface against another over 10,000 years ago to produce sharp edges on hard natural materials. Spear points, arrowheads, scraper tools, and hoes were made by chipping, **grinding**, and honing the surfaces and edges of relatively hard rocklike materials. Sandstone was used to produce smoother surfaces on the Egyptian pyramids.

Grinding wheels of a primitive type were created over 4000 years ago by taking a cylindrical stone with an **abrasive** surface and spinning it against metals and ceramics to adjust their shapes, reduce rough areas, and produce smoother surfaces. These processes were refined over subsequent millennia to produce, by the Middle Ages, metal

daggers, swords, spears, and shields of relatively high quality. The Chinese introduced the first coated abrasives in the thirteenth century by embedding seashell fragments in natural gums that were spread on a parchment backing.

In the early 1900s, abrasive technology advanced further through the development and use of alumina grains, diamond particles, and silicon carbide grit. New products in the form of powders, slurries, particle-embedded discs and wheels, and burs of different types soon emerged for use in dentistry. The further refinement of dental handpieces, air or abrasive technology, and methods of bonding abrasives to various binders has led to major processing breakthroughs that have rapidly advanced the quality of treatment in the current era of restorative dentistry, particularly with adhesive and esthetic dentistry.

APPLICATIONS OF ABRASIVES IN DENTISTRY

The intraoral surfaces of virtually every direct and indirect restoration must be contoured by grinding, **finishing**, and **polishing** procedures. The goal of these procedures is to produce the smoothest surface possible in a limited time. A single type of abrasive cannot be used effectively for all types of dental materials. Different abrasives are used for the three major classes of materials: ceramics, metals, and resin-based composites.

Why are abrasives different? The abrasive instruments used for metals must be able to remove metal particles quickly and efficiently without generating excessive heat or becoming clogged with debris. Although the flexible discs used for resin composites can be used for metals, they are incapable of removing large amounts of metal quickly. Instead, silicon carbide discs are required for **cutting** metal sections such as casting sprues, and bonded abrasive wheels or points are used for rapid adjustment of surface contours. Likewise, although diamond burs have been developed for grinding and finishing zirconia frameworks, specialized Zir-Cut (Axis/SybronEndo, Coppell, Texas) coarse blue wheels with embedded diamond particles may be more effective because they may not wear out as fast as diamond burs and they can remove relatively large amounts of zirconia from framework surfaces rather efficiently. Therefore, suitable finishing and polishing instruments should be utilized for the respective dental materials.

The form of polishing instruments also affects the rate of material removal and the surface finish. For example, regular and extra-thin Sof-Lex (3M ESPE St. Paul, MN) **contouring** and polishing discs, useful for finishing and polishing resin-based materials, are provided in the stiff and flexible disc forms to allow either light or heavy pressure to be applied, depending on the amount of composite that needs to be removed. The polymer backing allows the discs to be used either in the dry or wet condition. The regular Sof-Lex discs are available in four grades of abrasiveness, coarse (black), medium (dark blue), fine (medium blue), and superfine (light blue). The extra-thin discs and gapped strips are also provided in these four abrasive grades, but their colors are different. A word of caution is important here. The abrasive discs and strips of other manufacturers may not follow the same convention for Sof-Lex discs (i.e., darker colors corresponding to coarser abrasives and lighter colors to finer abrasives).

The Astropol finishing and polishing system (Ivoclar Vivadent, Amherst, NY) for composites and ceromers is also provided in different forms and levels of abrasiveness. Astropol is a comprehensive finishing and polishing set that consists of four differently shaped polishers in three grit sizes for interdental and occlusal applications, small flame, large flame, cup, and disc forms. The grit sizes are designated as (1) finish (Astropol F for the removal of excess material and prepolishing); (2) **polish** (Astropol P, for polishing of restorations: especially those made from microfilled composite materials); and (3) high-gloss polish (Astropol HP, that is best suited for hybrid composites). Similar types of abrasive tools are available from other manufacturers and suppliers of dental products.

In summary, dental abrasives are used for tooth cleaning (dental prophylaxis), occlusal adjustment of tooth enamel and restoration surfaces, contouring of material (acrylic, composite, metal, and ceramic) surfaces, finishing and debris removal (grinding and **air-particle abrasion**), and fine polishing to produce glossy surfaces. The abrasives can be provided in the form of powders, pastes, diamond burs, and abrasive stones, discs, wheels, points, and cups. The best choice for any dental application depends on the initial surface quality, material type, and specific purpose or need. The specific need can vary from cutting or rough grinding to final polishing to achieve a desired luster or gloss.

CRITICAL QUESTIONS

What are the six main benefits of finishing and polishing the surfaces of restorative materials? What are the goals of finishing and polishing?

BENEFITS OF FINISHING AND POLISHING RESTORATIVE MATERIALS

Finished and polished restorations provide four benefits of dental care: better gingival health, chewing efficiency, patient comfort, and esthetics. Patients can detect a surface roughness change of less than 1 μm (Jines et al., Research Brit Dent J, 196:42–45, 2004) by tongue proprioception. Surface changes greater than 1 μm can also lead to increased bacterial adhesion as well as surface staining. A well-contoured and polished restoration promotes gingival health by resisting the accumulation of food debris and pathogenic bacteria. This is accomplished through a reduction in total surface area and reduced roughness of the restoration surface. Smoother surfaces have less retention areas and are easier to maintain in a hygienic state when preventive oral home care is practiced because dental floss and the toothbrush bristles can gain more complete access to all surfaces and marginal areas.

Tarnish and corrosion activity of some metallic materials can be significantly reduced if the entire metal restoration is highly polished. Oral function is enhanced with a well-polished restoration because food glides more freely over occlusal and embrasure surfaces during mastication. More

importantly, smooth restoration surfaces minimize wear rates on opposing and adjacent teeth. This is particularly true for restorative materials such as ceramics, which contain phases that are harder than tooth enamel and dentin.

Rough material surfaces lead to the development of high, two-body contact stresses that can cause the loss of functional and stabilizing contacts between teeth or a reduction in the vertical dimension of occlusion. Rough surfaces on ceramics also act as stress concentration points. Finishing and polishing these surfaces can improve the strength of the restoration, especially in areas that are under tension, such as the perimeter of ceramic-ceramic crowns where unsupported areas of veneering ceramic are present. Finally, esthetic demands may require the dentist to finish and polish highly visible surfaces of restorations differently from those that are not accessible. Although a mirrorlike polish is preferred for previously mentioned reasons, this type of surface may not be esthetically compatible with adjacent teeth in highly visible areas, such as the facial surfaces of maxillary anterior teeth. Fortunately, these surfaces are not subject to high contact stresses and they are easily accessible for cleaning. Subtle anatomic features and textures may be added to these areas without affecting oral health or function.

In summary, the goals of finishing and polishing procedures are to obtain the desired anatomy, proper occlusion, and reduction of roughness and the depth of gouges and scratches produced by the contouring and finishing instruments. The instruments available for finishing and polishing restorations include fluted carbide burs, diamond burs, stones, coated abrasive discs and strips, polishing pastes, and soft and hard polymeric cups, points, and wheels impregnated with specific types and sizes of abrasive particles. The polished surface should be smooth enough to be well tolerated by oral soft tissues and to resist bacterial adhesion and excessive plaque accumulation. When plaque deposits exist on restorative material surfaces, they should be easily removable by brushing and flossing.

? CRITICAL QUESTION

What are the similarities of and differences between the mechanisms responsible for the cutting action of carbide burs and abrasive wheels?

PRINCIPLES OF CUTTING, GRINDING, FINISHING, AND POLISHING

Particles of a substrate material (workpiece) are removed by the action of a harder material that makes frictional contact with the substrate. This contact must generate sufficient tensile and shear stresses to break atomic bonds and release particles from the substrate. With rotary instrumentation, the blades of a carbide bur or the tips of abrasive particles transfer the force to the substrate. These tensile and shear stresses are induced in both the substrate and the rotary instrument. The instrument will fail to cut, grind, or polish if the stress that develops in any part of the cutting or grinding surface exceeds the strength of the instrument blade edges or particle bond strength to the binder compared with the strength of the substrate (workpiece). As a result, blade edges will become dull, and abrasive particles will fracture or tear away from their binder. Such degradation of finishing instruments is discussed in more detail in a later section.

Subtle differences distinguish the cutting, grinding, and polishing processes. A cutting operation usually involves the use of a bladed instrument or any other instrument in a bladelike fashion. Substrates may be divided into large separate segments, or they may sustain deep notches and grooves by the cutting operation. High-speed tungsten carbide burs have numerous regularly arranged blades that remove small pieces or segments of the substrate as the bur rotates. As shown in Figure 11-1, *A*, the unidirectional cutting pattern reflects the action of the regularly arranged blades on a tungsten carbide bur. The pattern produced by a diamond bur is shown in Figure 11-1, *B*. The surface of a coarse diamond bur is shown in Figure 11-1, *C*. When 30-fluted finishing burs have been used on a surface, the regular pattern of the cutting blades is discernible only if the surface is magnified for inspection. On the other hand, a separating wheel is an example of an instrument that can be used in a bladelike fashion. A separating wheel does not contain individual blades, but its thin blade design allows it to be used in a rotating fashion to grind through cast metal sprues and die stone materials.

A grinding operation removes small particles of a substrate through the action of bonded or coated abrasive instruments. Grinding instruments contain many randomly arranged abrasive particles. Each particle may contain several sharp points that run along the substrate surface and remove particles of material. For example, a diamond-coated rotary instrument may contain many sharp diamond particles (see Figure 11-1, *C*) that pass over a tooth during each revolution of the instrument. Because these particles are randomly arranged, many unidirectional scratches are produced within the material surface, as illustrated in Figure 11-1, *B*, which shows a tooth surface ground by a diamond bur. Cutting and grinding are both considered predominantly unidirectional in their action. This means that a cut or ground surface exhibits cuts and scratches oriented in one predominant direction.

Different types of burs have unique effects on surfaces. In general, a carbide bur with more blades will produce a smoother surface than a carbide bur containing fewer blades. For example, a 16-fluted carbide bur produces a smoother finish than an 8-fluted carbide bur, but the latter removes material more rapidly. Similarly, the coarsest diamond bur removes material more quickly but leaves a rougher surface. (See Figure 11-2 for scanning electron microscopy [SEM] images of carbide and diamond burs.)

BULK-REDUCTION PROCESS

Bulk reduction can be achieved through the use of instruments such as diamond burs, tungsten carbide burs, steel burs, abrasive wheels, and separating discs. Whereas diamond burs and abrasive wheels provide this action by grinding, steel and carbide burs remove materials through a cutting action of the hard blades. Abrasive-coated discs are popular instruments for bulk reduction of resin-based

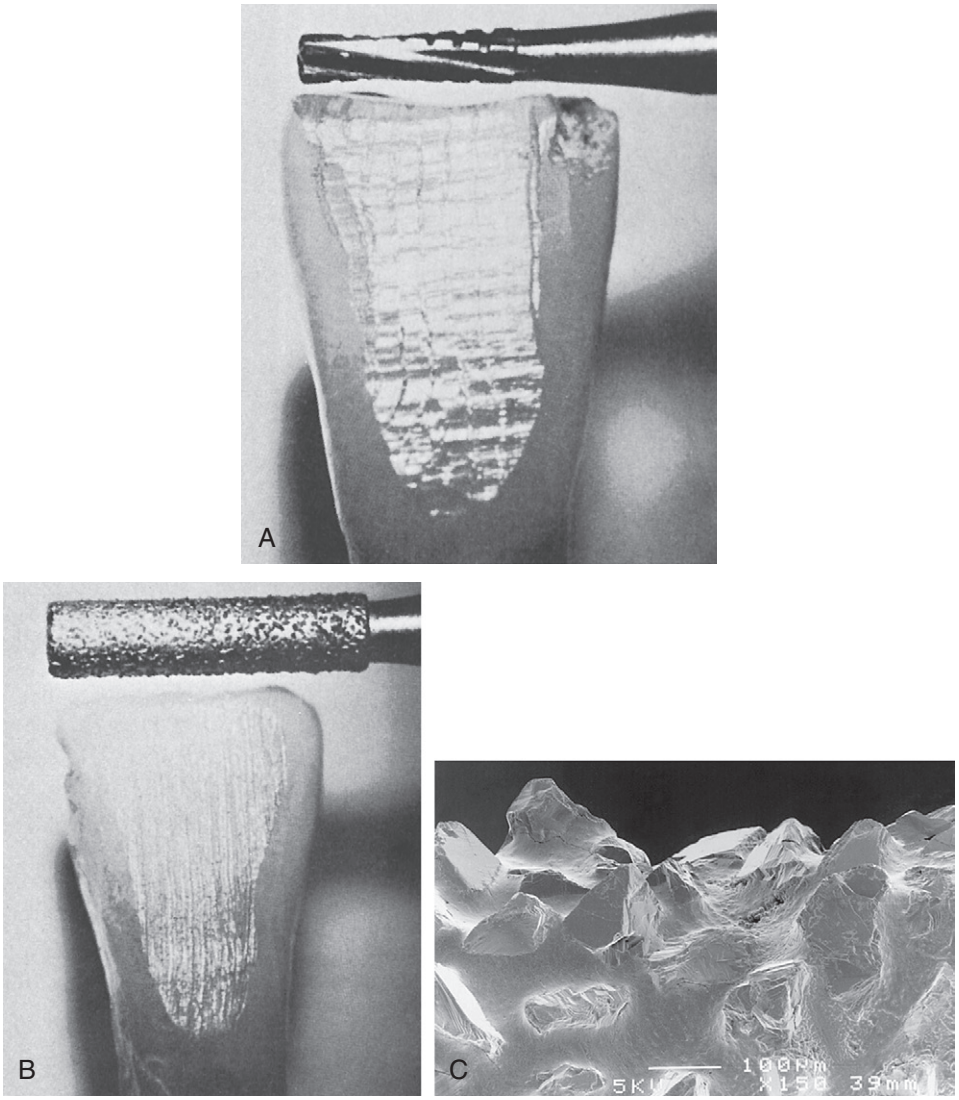


FIGURE 11-1 **A,** Tooth cut by a carbide bur. Note the regular pattern of removal of tooth structure, which corresponds to the regular arrangement of blades on the bur. **B,** Tooth ground by a diamond bur. Note the multiple scratches formed by the random arrangement of abrasive particles on the diamond bur. **C,** Magnified image of the bonded diamond particles on a coarse diamond bur (×150).

composite restorations. For bulk reduction of composites, the clinician should choose 8- to 12-fluted carbide burs or abrasives with a particle size of 100 µm or larger and sufficient hardness (9 to 10 Mohs hardness). SEM images of the surface finishes produced on a resin-based composite by a coarse diamond, a 12-fluted carbide bur, a 16-fluted carbide bur, and two types of finishing or polishing systems are shown in Figure 11-3. For bulk reduction of ceramics and metals, the user should follow the manufacturers' instructions to minimize the time required. In some cases, instruments used in the dental lab may be different from those used chairside, so the abrasiveness of an unknown instrument should be tested on a scrap piece of the material that will be used for a specific task.

CONTOURING

Even though contouring can be achieved during the bulk-reduction process, in some cases, it requires finer cutting instruments or abrasives to provide better control of contouring and surface details. At the end of this process, the desired anatomy and margins should be established. The smoothness of the surface at this stage depends on the instrument used and may require extra steps to establish a smoother surface. Usually 12- to 16-fluted carbide burs or abrasives ranging in size from 30 to 100 µm provide a fine contouring action.

FINISHING

In general, finishing and polishing processes require a stepwise approach, introducing finer scratches to the surface of the substrate to methodically remove deeper scratches. This process may require several steps to reach the desired surface smoothness. Surface imperfections can be an integral part of the internal structure, or they can be created by the instruments that are used for gross removal because of the size of

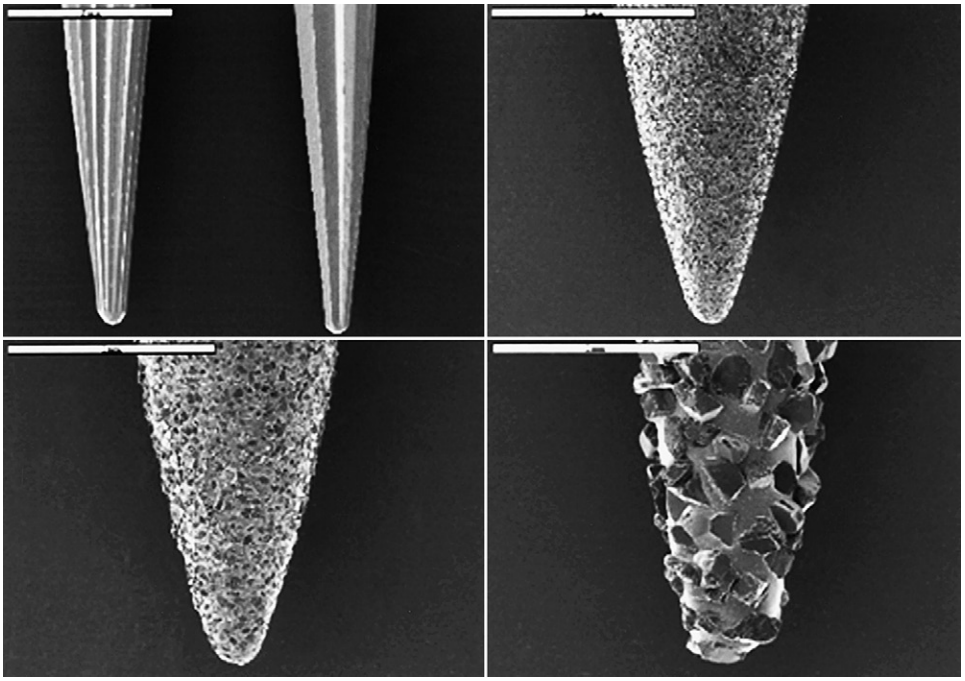


FIGURE 11-2 Scanning electron microscopy (SEM) images. *Upper left*, 16-fluted (*left*) and 8-fluted (*right*) tungsten carbide finishing burs. *Upper right*, Fine diamond bur. *Bottom left*, Medium-grit diamond bur. *Bottom right*, Coarse-grit diamond bur.

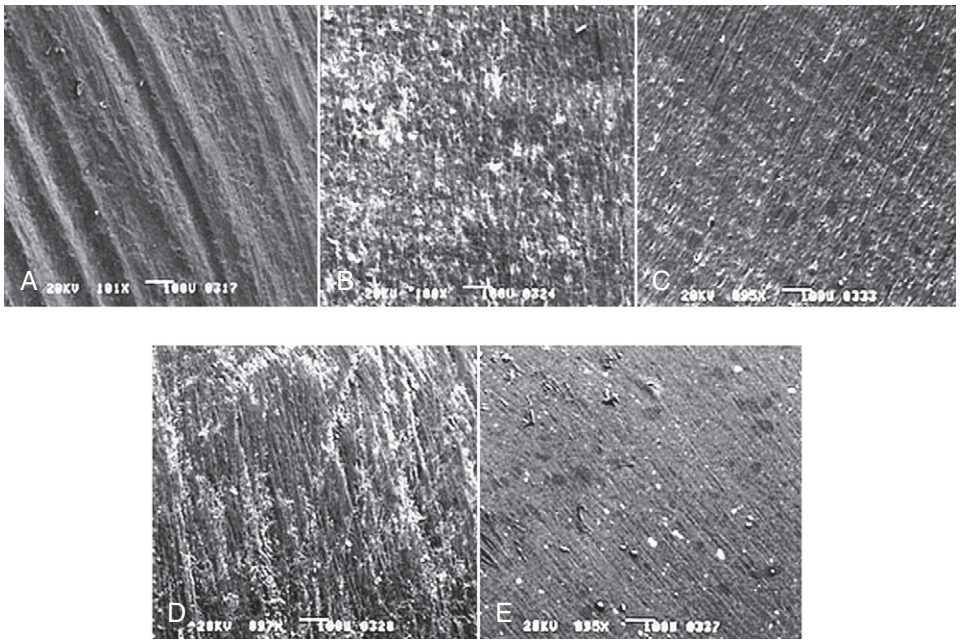


FIGURE 11-3 Scanning electron microscopy (SEM) images of the surface of a resin-based composite after the grinding, finishing, and polishing processes using five instruments: **A,** A coarse diamond. **B,** A 12-flute carbide bur. **C,** A 16-flute carbide bur. **D,** An abrasive impregnated finishing disc. **E,** An abrasive impregnated polishing disc.

the abrasives or the flute geometry. Finishing provides a relatively blemish-free smooth surface. The finishing action is usually accomplished using 18- to 30-fluted carbide burs, fine and superfine diamond burs, or abrasives that are between 8 and 20 μm in size.

CRITICAL QUESTION

How does a clinician know when the smoothest surface has been achieved?

POLISHING

The purpose of polishing is to provide an enamel-like luster to the restoration. Smaller particles provide smoother and shinier surfaces. The speed of achieving a luster, however, depends on the hardness and size of the abrasive particles and the method of abrasion (e.g., two-body abrasion or three-body abrasion). Ideally, abrasive particles in the range of particle sizes up to 20 μm provide luster at a low magnification. At the end of this process, there should be no visible scratches. However, there will always be scratches that are detectable at higher magnification. The surface must be cleaned between steps because abrasive particles left on the surface from the previous step can cause deep scratches.

The quality of the surface finish and polish can be characterized by the measurement of the surface roughness using a profilometer, an optical microscope, or an SEM. In clinical practice, the surface luster is usually judged without magnification. Most of the time, surface smoothness is correlated with the luster, as in cases such as resin-based composite restorations. However, the smoothest surface does not necessarily provide the most lustrous surface. For industrial applications, reflectometers are used to measure the luster. However, it is difficult to use them successfully for dental applications because of the irregular contour and small size of dental restorations.

Polishing procedures, the most refined of the finishing processes, remove the finest surface particles. Each type of polishing abrasive acts on an extremely thin region of the substrate surface. Polishing progresses from the finest abrasive that can remove scratches from the previous grinding procedure and is completed when the desired level of surface smoothness is achieved. Each step is followed by the use of progressively finer polishing media until no further improvement in surface finish is observed. The final stage produces scratches so fine that they are not visible unless greatly magnified. Polishing should be terminated when no further change in surface luster or glossiness occurs during the application of the finest abrasive that is used for that application. Further attempts to improve the surface appearance may actually degrade the surface by generating heat and by smearing dislodged material across the surface.

Examples of polishing instruments are rubber abrasive points, fine-particle discs and strips, and fine-particle polishing pastes. Polishing pastes are applied with soft felt points, muslin (woven cotton fabric) wheels, prophylaxis rubber cups, or **buffing** wheels. A nonabrasive material should be used as an applicator while using polishing pastes. Felt, leather, rubber, and synthetic foam are popular applicator materials for buffing. A common feature of some of these materials is their porous texture, which allows fine abrasive particles to be retained during the buffing procedure.

Polishing is considered multidirectional, which means that the final surface scratches are oriented in many directions. Some examples of ground and polished surfaces are shown in Figure 11-3. Note that the differences in surface appearance are subtle because of the transitional nature of the grinding and polishing processes. If there were larger differences in the size of particles removed, the surface change would be more easily detected.

Heat generation during the cutting, contouring, finishing, and polishing processes of direct restorations is a major concern. To avoid adverse effects to the pulp, the clinician must cool the surface with a lubricant, such as an air–water spray, and avoid continuous contact of high-speed rotary instruments with the substrate. Intermittent contact during operation is necessary not only to cool the surface but also to remove debris formed between the substrate and the instrument. The effectiveness and the speed of the contouring, finishing, and polishing procedures will be greatly improved by the removal of debris.

CRITICAL QUESTIONS

What precautions should be taken to minimize the generation of aerosols? What precautions should be taken to minimize exposure to and inhalation of aerosols?

BIOLOGICAL HAZARDS OF GRINDING, FINISHING, AND POLISHING PROCESSES

Dispersions of solid particles are generated and released into the breathing space of laboratories and dental clinics whenever finishing operations are performed. These airborne particles may contain tooth structure, dental materials, and microorganisms. Such aerosols have been identified as potential sources of infectious and chronic diseases of the eyes and lungs and present a hazard to dental personnel and their patients. Silicosis, also called *grinder's disease*, is a major illness caused by inhalation of aerosol particles released from any of a number of silica-based materials that are used in the processing and finishing of dental restorations. Silicosis is a fibrotic pulmonary disease that severely debilitates the lungs and doubles the risk for lung cancer. The risk for silicosis is substantial, because 95% of generated aerosol particles are smaller than 5 μm in diameter and can readily reach the pulmonary alveoli during normal respiration. Additionally, 75% of airborne particles are potentially contaminated with infectious microorganisms. Furthermore, aerosols can remain airborne for more than 24 hours before settling and are, therefore, capable of cross-contaminating other areas of the treatment facility. Aerosol sources, in both the dental operatory and laboratory environments, must be controlled whenever finishing procedures are performed. A concise and informative source of information on aerosol hazards has been written by Cooley (see Selected Reading).

Aerosols produced during finishing procedures may be controlled in three ways: First, they may be controlled at the source through the use of adequate infection control procedures, water spray, and high-volume suction. Second, personal protective equipment (PPE) such as safety glasses and disposable face masks can protect the eyes and respiratory tract from aerosols. Masks should be chosen to provide the best filtration along with ease of breathing for the wearer. Third, the entire facility should have an adequate ventilation system that efficiently removes any residual particulates from the air. Many systems are also capable of controlling chemical

contaminants such as mercury vapor from amalgam scrap and monomer vapor from acrylic resin.

CRITICAL QUESTION

How can the amount of lubricant either increase or decrease cutting efficiency?

ABRASION AND EROSION

ABRASION

Wear is a material removal process that can occur whenever surfaces slide against each other. The process of finishing a restoration involves abrasive wear through the use of hard particles. In dentistry, the outermost particles or surface material of an abrading instrument is referred to as the *abrasive*. The material being finished is called the *substrate*. In the case of a diamond bur abrading a tooth surface, as illustrated in Figure 11-4, the diamond particles bonded to the bur represent the abrasive, and the tooth is the substrate. Also, note that the bur in the high-speed handpiece rotates in a clockwise direction as observed from the head of the handpiece.

The rotational direction of a rotary abrasive instrument is an important factor in controlling the instrument's action on the substrate's surface. When a handpiece and bur are translated in a direction opposite to the rotational direction of the bur at the surface being abraded, a smoother grinding action is achieved. However, when the handpiece and bur are translated in the same direction as the rotational direction of the bur at the surface, the bur tends to "run away" from the substrate, thereby producing a more uncontrolled grinding action and a rougher surface.

Abrasion is further divided into the processes of two-body and three-body wear. *Two-body abrasion* occurs when abrasive particles are firmly bonded to the surface of the abrasive instrument and no other abrasive particles are used. A diamond bur abrading a tooth represents an example of two-body wear. *Three-body abrasion* occurs when abrasive particles are free to translate and rotate between two surfaces. An example of three-body abrasion involves the use of nonbonded abrasives such as those in dental prophylaxis pastes. These nonbonded abrasives are placed in a rubber cup, which is rotated against a tooth or material surface. These two processes are not mutually exclusive. Diamond particles may debond from a diamond bur and cause three-body wear. Likewise, some abrasive particles in the abrasive paste can become trapped in the surface of a rubber cup and cause two-body wear. Lubricants are often used to minimize the risk of these unintentional shifts from two-body to three-body wear, and vice versa. Thus, the efficiency of cutting and grinding will be improved with the use of lubricants such as water, glycerin, or silicone. Intraorally, a water-soluble lubricant is preferred. Excessive amounts of lubricant may reduce the cutting efficiency by reducing the contact between the substrate and the abrasive. Too little lubricant results in increased heat generation and reduced cutting efficiency.

EROSION

Erosive wear is caused by hard particles impacting a substrate surface, carried by either a stream of liquid or a stream of air, as occurs in sandblasting a surface. Figure 11-5 illustrates schematically the processes of two-body abrasion, three-body abrasion, and hard-particle erosion. Most dental laboratories

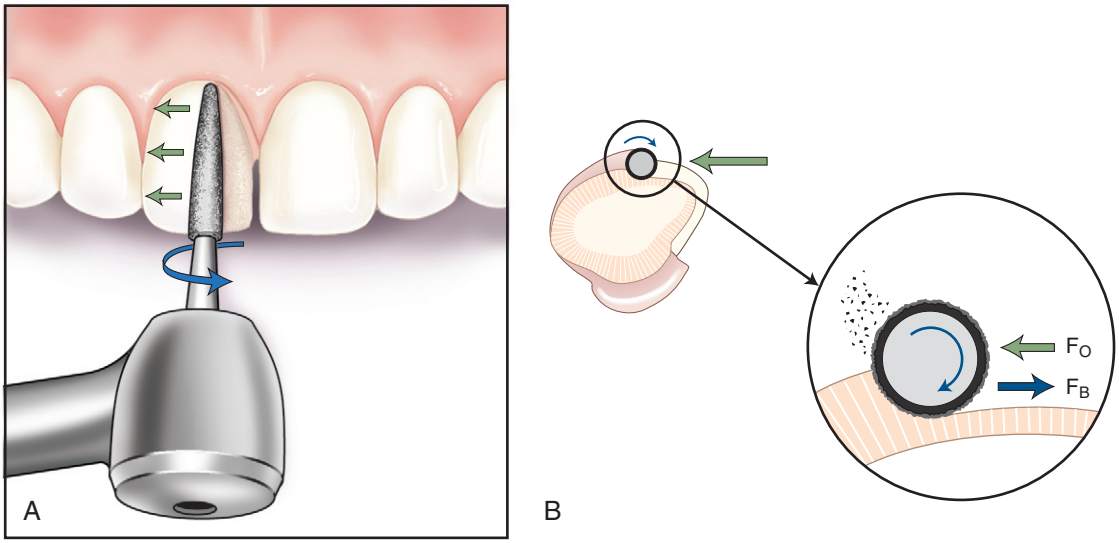


FIGURE 11-4 The mechanics of high-speed rotary instrumentation. **A,** The blue circular arrow indicates that the high-speed diamond bur rotates in a clockwise direction when viewed from the head of the handpiece. The green arrows indicate the direction that the instrument should be drawn to counteract the rotational force of the bur and achieve the most rapid abrasive action of the bur. **B,** Incisal view of the forces generated during high-speed rotary tooth preparation. As the bur rotates in a clockwise direction, it generates a rotational force at the tooth surface, F_B (*large blue arrow* that represents schematically the force of tooth structure against the bur). The operator of the instrument must generate an opposing force, F_o (*green arrow*), which will exceed the rotational force of the bur, F_B, and carry the instrument against the tooth surface where the surface will be abraded.

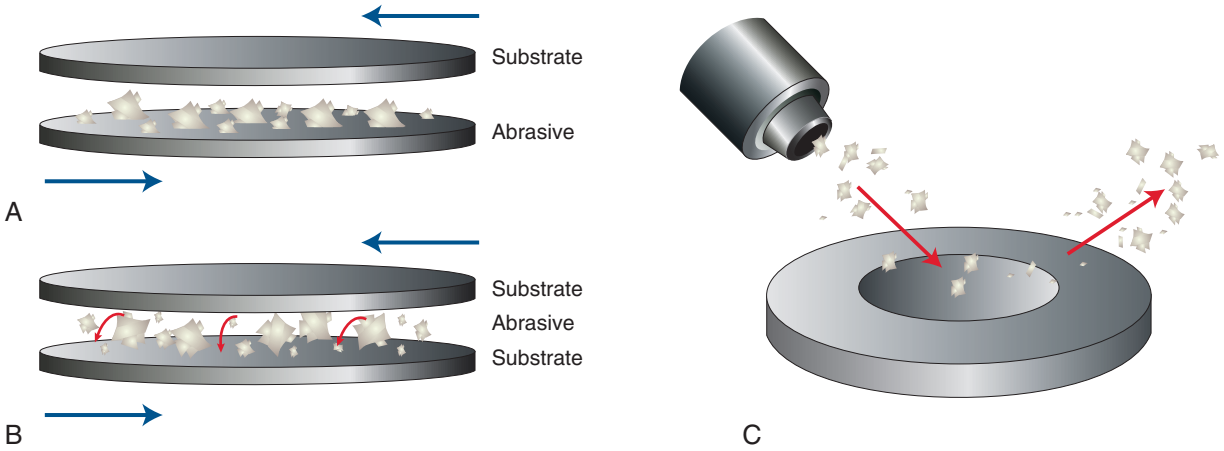


FIGURE 11-5 Illustrations of two-body abrasion, three-body abrasion, and hard-particle erosion. **A,** Two-body abrasion occurs when abrasive particles are tightly bonded to the abrasive instrument that is removing material from the substrate surface. **B,** Three-body abrasion occurs when abrasive particles are free to translate and rotate between two surfaces. **C,** Hard-particle abrasion (also called "air abrasion") is produced when abrasive particles are propelled against a substrate by air pressure.

have air-driven grit-blasting units that employ hard-particle erosion to remove surface material. A distinction must be made between this type of erosion and chemical erosion, which involves chemicals such as acids and alkalis instead of hard particles to remove substrate material. Chemical erosion, more commonly called *acid etching* in dentistry, is not used as a method of finishing dental materials. It is used primarily to prepare tooth surfaces to enhance bonding or coating.

HARDNESS OF ABRASIVES

As stated previously, the inherent strength of cutting blades or abrasive particles on a dental instrument must be great enough to remove particles of substrate material without becoming dull or fracturing too rapidly. The durability of an abrasive is related to the hardness of its particles or surface material. Hardness is a surface measurement of the resistance of one material to be plastically deformed by indenting or scratching another material. The first ranking of hardness was published in 1820 by Friedrich Mohs, a German mineralogist. He ranked 10 minerals by their relative scratch resistance in relation to one another. The least scratch-resistant mineral, talc, received a score of 1 and the most scratch-resistant mineral, diamond, received a score of 10.

Knoop and Vickers hardness tests are based on indentation methods that quantify the hardness of materials. The tip of a Knoop diamond indenter has an elongated pyramidal shape, whereas the Vickers diamond indenter has an equilateral pyramidal design. Both tests involve the application of the indenter to a test surface under a known load (usually 100 Newtons, or 100 N). The depth of surface penetration is reported as hardness in units of force per unit area. Although a number of other factors affect a material's abrasiveness, the farther apart a substrate and an abrasive are in hardness, the more efficient is the abrasion process. On the basis of a comparison of hardness values for several dental materials listed in Table 11-1, it is expected that silicon carbide and diamond abrasives will abrade dental porcelain more readily compared with garnet, even though the abrasive particles for all three materials have very sharp edge characteristics.

? CRITICAL QUESTION

Why is it sometimes inappropriate to select the hardest abrasive to reduce the time required for finishing and polishing a prosthesis?

ABRASIVE INSTRUMENT DESIGN

ABRASIVE GRITS

Abrasive grits are derived from materials that have been crushed and passed through a series of mesh screens (sieves) to obtain different particle size ranges. Table 11-2 lists grit and particle sizes for commonly used dental abrasives. Dental abrasive grits are classified as coarse, medium coarse, medium, fine, and superfine, according to particle size. Experience generally indicates which grades of an abrasive give the best results in finishing a given material. Keep in mind that the rate of material removal is not the only important factor. The surface finish obtained with each abrasive is just as important. If too hard an abrasive is used or if the grain size is too coarse for use on a given material, deep scratches result in the substrate that cannot be removed easily in subsequent finishing operations. Additionally, if an abrasive does not have the proper particle shape or does not break down in a manner that creates or exposes new sharp-edged particles, it will tend to gouge the substrate.

? CRITICAL QUESTION

How can one differentiate between high-quality and low-quality bonded abrasive tools?

TABLE 11-1 Hardness Values of Dental Materials, Tooth Structure, and Abrasives

Material	Mohs Hardness	Knoop Hardness (kg/mm^2)	Vickers Hardness (kg/mm^2)
Talc	1	—	—
Gypsum	2	—	12
Denture base resin	2–3	20	—
Cementum	—	40	—
Calcite	3	135	—
Metal-reinforced glass ionomer		14–24	40
Dentin	3–4	70	57–60
Type III gold alloy	3	—	122–180 (softened)/155–250 (hardened)
Type IV gold alloy	4	220	150–194 (softened)/248–280 (hardened)
Amalgam	4–5	90	120 (Ag_2Hg_3 phase)
Enamel (apatite)	5	340–431	294–408
Rouge	5–6	—	—
Glass (glass–ceramics)	5–6	360	—
Microfilled composite	5–7	30	37–160
Hybrid composite	5–7	55	61–159
Titanium (Ti)	—	—	210
Ti-6Al-4V	—	—	320
Nickel–chromium (Ni-Cr) alloy (as cast)	—	153–328	200–395
Cobalt–chromium (Co-Cr) alloy (as cast)	—	—	280–380
Layered gold alloy (for porcelain fused to metal [PFM])	—	—	35
Pressed lithia disilicate core	—	—	640
Tripoli	6	—	—
Pumice	6–7	460–560	—
Porcelain	6–7	560	430
Tin oxide	6–7	—	—
Sand	7	—	—
Cuttle	7	800	—
Quartz	7	820	—
Zirconium silicate	7.5	—	—
Garnet	8–9	1,350	—
Emery	7–9	2,000	—
Corundum	9	2,000	—
Aluminum oxide	9	2,100	1,200
Tungsten carbide	9.8	1,900	—
Silicon carbide	9–10	2,500	—
Diamond	10	7,000–10,000	—

BONDED ABRASIVES

Bonded abrasives consist of abrasive particles incorporated through a binder to form grinding tools such as points, wheels, separating discs, coated thin discs, and a wide variety of other abrasive shapes. Particles are bonded by four general methods: (1) sintering, (2) vitreous bonding (glass or ceramic), (3) resinous bonding (usually phenolic resin), and (4) rubber bonding (latex-based or silicone-based rubber). Because most of the rubber wheels, cups, and points contain latex, a known allergen, all residues must be removed from polished surfaces.

Abrasive discs are used for bulk reduction, contouring, finishing, and polishing of restoration surfaces. Most types of discs are coated with aluminum oxide abrasive. Abrasive

TABLE 11-2 Abrasive Particle Sizes*

Grit/Mesh (USA)	Aluminum Oxide, Silicon Carbide, and Garnet (μm)	Grade†	Coated Disc Diamond (μm)	Abrasive descriptions for Diamond Burs and Diamond Polishing Paste
120	142	Coarse	142	Supercoarse–coarse
150	122		122	Coarse–regular
180	70–86		86	Coarse–regular
240	54–63		60	Fine
320	29–32	Medium	52	Fine
400	20–23		40	Fine–superfine–coarse finishing
600	12–17	Fine	14	Superfine–medium finishing
800	9–12		8	Ultrafine–fine finishing
1200	2–5	Superfine	6	Milling pastes
1500	1–2		4	Polishing pastes (2–5 μm)
2000	1		2	Polishing pastes (2–5 μm)

*Average particle sizes. Grades vary among manufacturers.
†Four grades used for a popular brand for aluminum oxide–coated discs. Silicon carbide (SiC) and garnet may vary among manufacturers.

strips with either a plastic or metal backing are also available to smooth and polish the proximal surfaces of all direct and indirect bonded restorations. Metal strips are usually limited to situations in which very tight proximal contacts are involved. They are particularly useful for ceramic restorations but are also used for resin composites and amalgams. However, care must be taken to avoid lacerating the gingival tissues. Metal-backed strips are more costly, but they can be autoclaved and used several times if they are not damaged. Plastic-backed strips are used primarily for resin composites, compomers, hybrid ionomers, and resin cements.

Sintered abrasives are the strongest type because the abrasive particles are fused together. Vitreous-bonded abrasives are mixed with a glassy or ceramic matrix material, cold-pressed to the instrument shape, and fired to fuse the binder. Resin-bonded abrasives are cold-pressed or hot-pressed and then heated to cure the resin. Hot pressing yields an abrasive binder with extremely low porosity. Rubber-bonded abrasives are made in a manner similar to that for resin-bonded abrasives.

The type of bonding method employed for the abrasive greatly affects the grinding behavior of the tool on the substrate. Bonded abrasives that tend to disintegrate rapidly against a substrate are too weak and result in increased abrasive costs because of the reduced instrument life. Those that tend to degrade too slowly get clogged with grinding debris, which results in loss of abrasive efficiency, increased heat generation, and increased finishing time. An ideal binder holds the abrasive particles in the tool long enough to cut, grind, or polish the substrate, and yet it releases the particles either before cutting efficiency is lost or before heat buildup causes thermal damage to the substrate. Binders are specially formulated for substrate-specific applications. Several examples of bonded abrasives are shown in Figure 11-6.

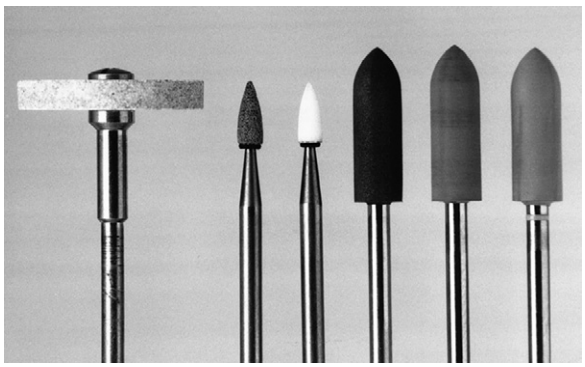


FIGURE 11-6 Typical bonded abrasive instruments used in the dental laboratory include vitreous bonded abrasive wheels and points (*three instruments on left*) and rubber-bonded abrasive bullets (*three instruments on right*).

? CRITICAL QUESTION

What are the purposes of truing a grinding instrument?

A bonded abrasive instrument should always be trued and dressed before use. *Truing* is a procedure by which the abrasive instrument is run against a harder abrasive block until the abrasive instrument rotates in the handpiece without eccentricity or runout when placed on the substrate. The *dressing* procedure, like truing, is used to shape the instrument, but it accomplishes two different purposes as well. First, the dressing procedure reduces the instrument to its correct working size and shape. Second, it is used to remove clogged debris from the abrasive instrument to restore grinding efficiency during the finishing operation. The clogging of the abrasive instrument with debris is called *abrasive blinding*. Abrasive blinding occurs when the debris generated from grinding or polishing occludes the small spaces between the

abrasive particles on the tool and reduces the depth that particles can penetrate into the substrate. As a result, abrasive efficiency is lost and greater heat is generated. A blinded abrasive appears to have a coating of the substrate material on its surface. Frequent dressing of the abrasive instrument during the finishing operation on a truing instrument, as illustrated in Figure 11-7, maintains the efficiency of the abrasive in removing the substrate material.

Binders for diamond abrasives are manufactured specifically to resist abrasive particle loss rather than to degrade at a certain point and release particles. One reason for this is that diamond is the hardest material known—so hard that diamond abrasive particles do not lose their cutting efficiency against substrates and, therefore there is no need for new abrasive particles to be exposed during the grinding process. Another reason is that diamond grits are expensive and must be used in limited quantities for instrument manufacture. Special bonding processes have been designed to allow for extended instrument life by keeping the abrasive particles firmly bound to the instrument shank with maximum particle exposure.

Diamond particles are bonded to metal wheels and bur blanks with special heat-resistant resins such as polyimides. The supercoarse through fine grades are then plated with a refractory metal film such as nickel. The nickel plating provides improved particle retention and acts as a heat sink during grinding. Titanium nitride coatings are used as an additional layer on some of the recent diamond abrasive instruments to further extend their longevity. Finishing diamonds used for resin-based composites contain diamond particles 40 μm or less in diameter, and many are not nickel-plated. Therefore, they are highly susceptible to debonding and should always be used with light force and copious water spray to ensure retention of the very fine diamond particles. Diamond burs should always be used in the presence of water spray and at rotational speeds of less than 50,000 revolutions per minute (rpm).

Diamond instruments are preshaped and trued; they are not treated like other bonded abrasives. Diamond cleaning stones are used on the supercoarse through fine grades to remove debris buildup and to maintain grinding efficiency. An example of a diamond cleaning stone is shown in

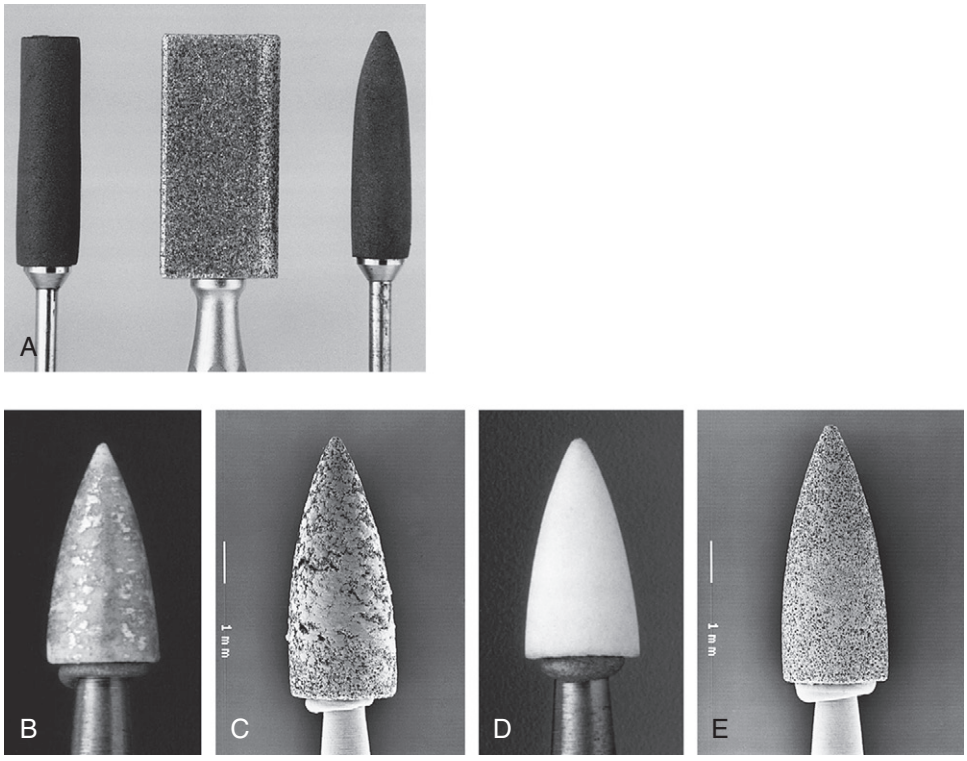


FIGURE 11-7 A dressing tool is used to true, shape, and clean bonded abrasive instruments both before and during the finishing procedure. **A,** A rubber-bonded abrasive cylinder (*left*) shows irregular external contours, which will cause it to run eccentrically. The cylinder is first trued against a diamond-coated abrasive dressing tool (*center*) to make it rotate around the central axis of the instrument. Once trued, the abrasive is further dressed to a desired working shape (*right*). **B,** Instruments that are blinded with debris lose their cutting efficiency and generate more heat during operation. Note the coating of debris on the abrasive surface. **C,** A scanning electron micrograph of the same instrument reveals the significant amount of debris that is clogging the instrument surface. **D,** Frequent dressing of the abrasive on the dressing tool shown in the first photograph removes accumulated debris and restores cutting efficiency. **E,** A scanning electron micrograph of the blinded abrasive after dressing reveals that the debris has been removed and the abrasive surface restored.

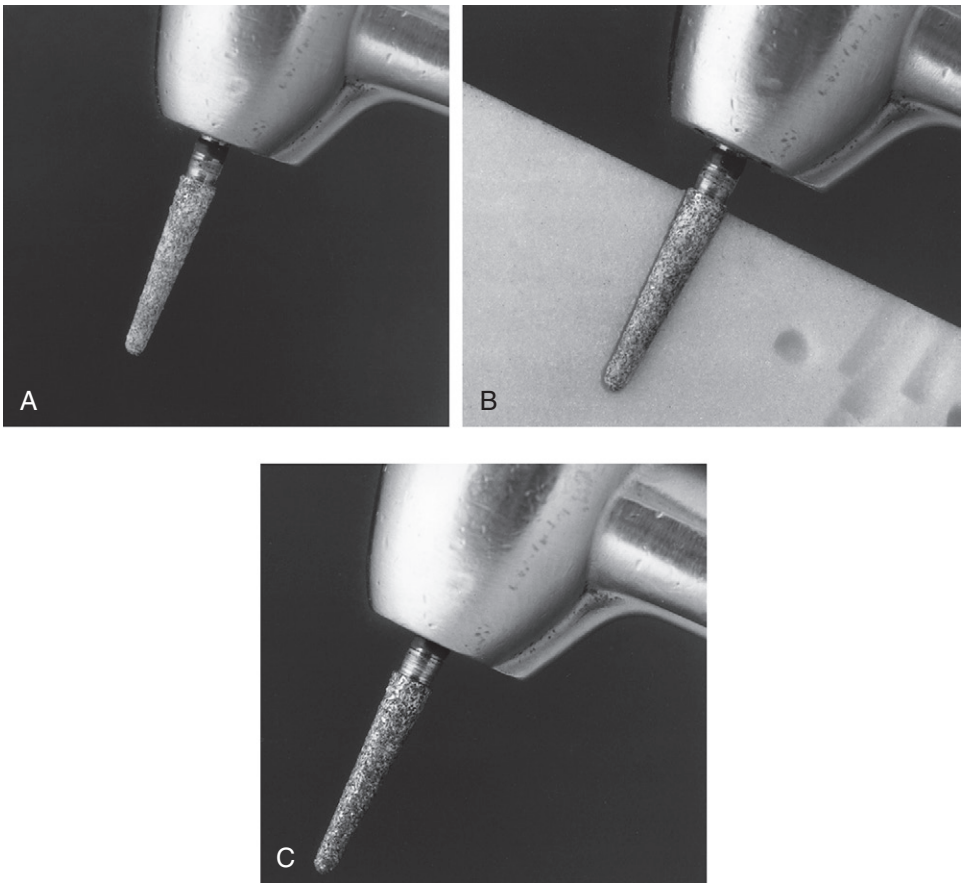


FIGURE 11-8 A diamond cleaning stone is used to remove debris from diamond instruments. **A,** Diamond bur in high-speed rotary handpiece before cleaning. Note the accumulated debris. **B,** The bur is cleaned by running it against the moistened diamond cleaning stone for 2 to 4 seconds. **C,** The cleaned diamond bur has no debris remaining between the diamond abrasive particles.

Figure 11-8. Cleaning stones should not be used on finishing diamonds because their bonded particles are quickly removed. Manufacturers provide special operating and cleaning instructions for these instruments.

COATED ABRASIVE DISCS AND STRIPS

Coated abrasives are fabricated by securing abrasive particles to a flexible backing material (heavyweight paper, metal, or Mylar) with a suitable adhesive material. These abrasives typically are supplied as discs and finishing strips. Discs are available in different diameters and with thin and very thin backing thicknesses. A further designation is made in regard to whether or not the disc or strip is moisture-resistant. It is advantageous to use abrasive discs or strips with moisture-resistant backings because their stiffness is not reduced by water degradation. Furthermore, moisture acts as a lubricant to improve cutting efficiency. Examples of coated abrasives are shown in Figure 11-9.

Different manufacturers use various coding conventions to allow the user to differentiate between coarse, medium, and fine abrasive grits. This situation was explained earlier for Sof-Lex discs. Examples of different types of abrasive instruments and abrasive grades are shown in Figures 11-10 through Figure 11-15.

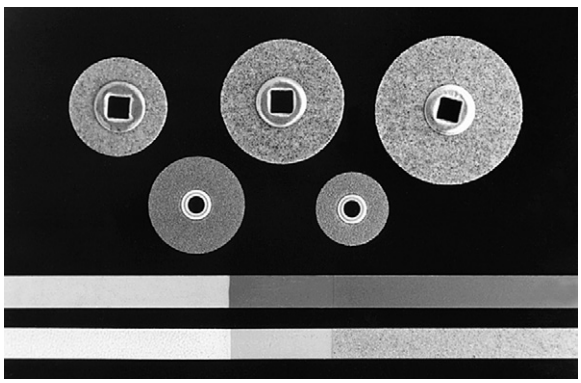


FIGURE 11-9 Coated abrasive discs and strips. Discs are available in several sizes and with both paper and moisture-resistant backings. Paper-backed discs are represented by the top row of discs; moisture-resistant Mylar-backed discs are shown in the second row. Mylar-backed abrasive strips may be coated with two different grades of abrasive. The coatings are separated in the center of the strip by an uncoated area, which allows the strip to be passed between teeth.



FIGURE 11-10 Specialized diamond burs for occlusal reduction of tooth surfaces. The color-coded bands refer to the depth of the cutting portion. The depths are as follows: 1.0 mm (white), 1.5 mm (green), 1.8 mm (orange), 2.0 (yellow), 2.2 mm (blue), and 2.4 mm (red).



FIGURE 11-11 Astropol (Ivoclar Vivadent) polishing kit with wheel, point, and cup shapes.

NONBONDED ABRASIVES

Polishing pastes are considered nonbonded abrasives and are primarily used for final polishing. They must be applied to the substrate with a nonabrasive device such as synthetic foam, rubber, felt, or chamois cloth. The abrasive particles are dispersed in a water-soluble medium such as glycerin for dental applications. Aluminum oxide and diamond are the most popular nonbonded abrasives.

ABRASIVE MOTION

The motion of abrasive instruments is classified as rotary, planar, or reciprocal. In general, burs act in a rotary motion and discs in a planar motion, and reciprocating handpieces provide a cyclic motion and are reciprocal in relationship to their direction of motion. Different sizes of abrasives can be incorporated with each motion. Reciprocating handpieces



FIGURE 11-12 Kit for laboratory grinding and finishing of metals. Typically, green mounted stones contain silicon carbide and are useful for shaping, adjusting, finishing, and fine grinding of high-noble and noble cast alloys. The blue, brown, and white mounted stones are useful for noble and base metal alloys that are used for metal–ceramic prostheses. The pink mounted points and cylinder are used for hard metals such as cobalt–chromium alloys. The user should check whether these devices are intended for benchtop lathes or for handpieces.

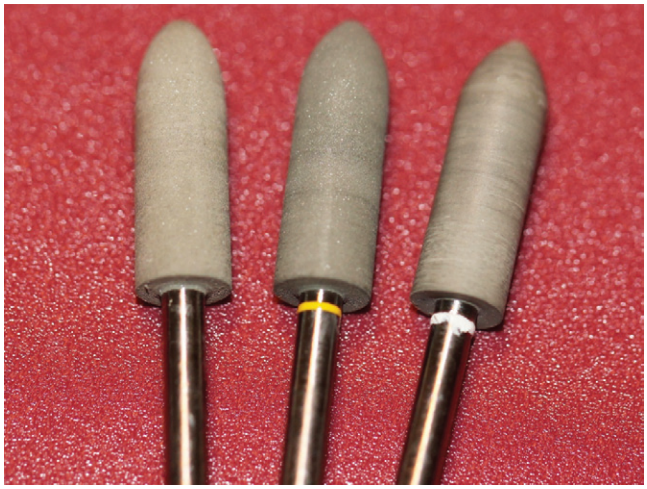


FIGURE 11-13 Rubberized abrasive points with color-coded bands or no band to indicate relative levels of abrasiveness. Because of variability in color coding, the websites of the manufacturer or supplier should be referred to for the color codes and indications for use.

especially provide the benefit of accessing interproximal and subgingival areas to remove overhangs, finish subgingival margins without creating ditches, and create embrasures.

TYPES OF ABRASIVES

Many types of abrasive materials are available, but only those commonly used in dentistry are discussed in this section. Natural abrasives include Arkansas stone, chalk, corundum, diamond, emery, garnet, pumice, quartz, sand, tripoli, and zirconium silicate. Cuttle and kieselguhr are derived from the

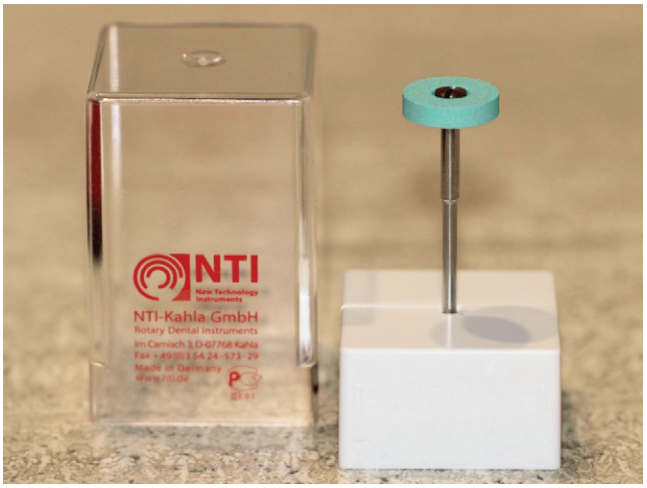


FIGURE 11-14 Abrasive wheel for grinding zirconia and other ceramics.

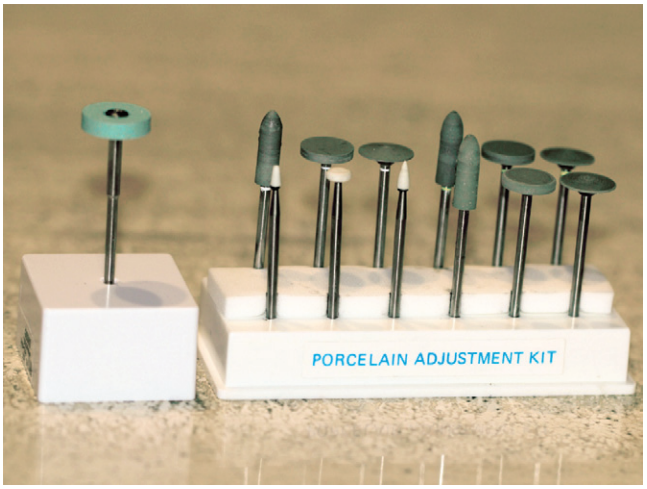


FIGURE 11-15 Porcelain finishing kit. Note the yellow and white bands on the mandrels (shanks) to distinguish the levels of abrasiveness.

remnants of living organisms. Manufactured abrasives are synthesized materials, which are generally preferred because of their more predictable physical properties. Silicon carbide, aluminum oxide, synthetic diamond, rouge, and tin oxide are examples of manufactured abrasives.

ALUMINUM OXIDE

Fused aluminum oxide was the second synthetic abrasive to be developed. Synthetic aluminum oxide (alumina) is made as a white powder and can be somewhat harder than corundum (natural alumina) because of its purity. However, corundum has a Mohs hardness of approximately 9 (on a scale of 1 to 10. Alumina can be processed with different properties by slight alteration of the reactants in the manufacturing process. Several grain sizes of alumina are available, and alumina has largely replaced emery for several abrasive uses. Aluminum oxide is widely used to make bonded abrasives, coated abrasives, and air-propelled grit abrasives for dental applications.

Sintered aluminum oxide is used to make white stones, which are popular for adjusting dental enamel and finishing metal alloys, resin-based composites, and ceramic materials.

Pink and ruby variations of aluminum oxide abrasives are made by adding chromium compounds to the original melt. These variations are sold in a vitreous-bonded form as non-contaminating mounted stones for the preparation of metal–ceramic alloys to receive porcelain. Remnants of these abrasives and other debris should be removed from the surface of metals used for metal–ceramic bonding so as not to prevent optimal bonding of porcelain to the metal alloy. A review by Yamamoto (see Selected Reading) suggests that carbide burs are the most effective instruments for finishing this type of alloy because they do not contaminate the metal surface with entrapped abrasive particles.

ARKANSAS STONE

This abrasive material is a semi-translucent light-gray siliceous sedimentary rock mined in Arkansas. It contains microcrystalline quartz and is dense, hard, and uniformly textured. Small pieces of this mineral are attached to metal shanks and trued to various shapes for fine grinding of tooth enamel and metal alloys.

CHALK

One of the mineral forms of calcite is chalk, a white abrasive composed of calcium carbonate. Chalk is used as a mild abrasive paste to polish tooth enamel, gold foil, amalgam, and plastic materials.

CUTTLE

Commonly referred to as *cuttlefish*, *cuttlebone*, or *cuttle*, this abrasive is a white calcareous powder made from the pulverized internal shell of a Mediterranean marine mollusk of the genus *Sepia*. Cuttle is available as a coated abrasive and is useful for delicate abrasion operations such as the polishing of metal margins and dental amalgam restorations.

CORUNDUM

This mineral form of aluminum oxide is usually white. Its physical properties are inferior to those of manufactured alpha (α) aluminum oxide (Al_2O_3), which has largely replaced corundum in dental applications. Corundum is used primarily for grinding metal alloys and is available as a bonded abrasive in several shapes. It is most commonly used in an instrument known as a white stone.

? CRITICAL QUESTION

What are the advantages and disadvantages of natural diamond abrasives compared with synthetic diamond abrasives?

NATURAL DIAMOND

Diamond is a transparent colorless mineral composed of carbon. It is the hardest known substance. Diamond is called a *superabrasive* because of its ability to abrade any other known substance. Diamond abrasives are supplied in several

forms, including bonded abrasive rotary instruments, flexible metal-backed abrasive strips, and diamond polishing pastes. They are mostly used on ceramic and resin-based composite materials.

SYNTHETIC DIAMOND ABRASIVES

The advantages of synthetic diamonds over natural diamonds include their consistent size and shape as well as their lower cost. The shape of the diamond determines the binder needed for its use, which can be either resin or metal. Resin-bonded diamonds have sharp edges. During use, the sharp edges break down and expose new sharp edges and corners. However, metal-bonded diamonds are regular and more consistent in size. They function as cutting points or edges primarily through the benefit of their hardness rather than their shape.

Larger synthetic diamond particles appear greenish because of the chemical reaction with nickel during the manufacturing process. Manufactured diamond is used almost exclusively as an abrasive and is produced at five times the quantity of natural diamond abrasive. This abrasive is used in the manufacture of diamond saws, wheels, and burs. Blocks with embedded diamond particles are used to true other types of bonded abrasives. Diamond polishing pastes are also produced from particles smaller than 5 μm in diameter. Synthetic diamond abrasives are used primarily on tooth structure, ceramic materials, and resin-based composite materials.

EMERY

This abrasive is a grayish-black corundum prepared in a fine-grain form. Emery is used predominantly in coated abrasive discs and is available in a variety of grit sizes. It may be used for finishing metal alloys or acrylic resin materials.

GARNET

The term *garnet* includes a number of different minerals that possess similar physical properties and crystalline forms. These minerals are the silicates of aluminum, cobalt, iron, magnesium, and manganese. The garnet abrasive used in dentistry is usually dark red. Garnet is extremely hard and, when fractured during the grinding operation, it forms sharp, chisel-shaped plates, making it a highly effective abrasive. Garnet is available on coated discs and arbor bands. It is used in grinding metal alloys and acrylic resin materials.

KIESELGUHR

This material is composed of the siliceous remains of minute aquatic plants known as *diatoms*. The coarser form of kieselguhr is called *diatomaceous earth* and is used as a filler in many dental materials such as the hydrocolloid impression materials. Kieselguhr is an excellent mild abrasive; however, the risk of respiratory silicosis caused by chronic exposure to airborne particles of this material is significant, so appropriate precautions should always be taken.

PUMICE

Volcanic activity produces this light-gray highly siliceous material. It is used mainly in grit form but can be found in some rubber-bonded abrasives. Both pumice forms are used on acrylic resin materials. Flour of pumice, an extremely fine-grained volcanic rock derivative from Italy, is used in polishing tooth enamel, direct-filling gold, dental amalgam, and acrylic resins.

QUARTZ

The most commonly used form of silica (SiO_2) is quartz, a very hard (Mohs hardness of 7), colorless, and transparent mineral. It is the most abundant and widespread of minerals. Quartz crystalline particles are pulverized to form sharp, angular particles that are useful in making coated abrasive discs. Quartz abrasives are used primarily to finish metal alloys, and they may also be used to grind dental enamel.

SAND

This abrasive is a mixture of small mineral particles predominantly composed of silica. These particles represent a mixture of colors, making sand abrasives distinct in appearance. Sand particles have a rounded to angular shape. They are applied under air pressure, through a process called *sandblasting*, to remove refractory investment materials from base metal alloy castings. They are also coated onto paper discs for grinding metal alloys and acrylic resin materials.

TRIPOLI

This abrasive is derived from a lightweight, friable siliceous sedimentary rock. Tripoli can be white, gray, pink, red, or yellow. The gray and red types are most frequently used in dentistry. The rock is ground into very fine particles and formed with soft binders into bars of polishing compound. Tripoli is used for polishing metal alloys and some acrylic resin materials.

ROUGE

Iron oxide is the fine red abrasive component of rouge. Like tripoli, rouge is blended with various soft binders into a cake form. It is used to polish high noble metal alloys such as yellow gold alloys.

SILICON CARBIDE

This extremely hard abrasive was the first of the synthetic abrasives to be produced. Green and blue-black types of silicon carbides are produced; both types have equivalent physical properties. The green form is often preferred because substrates are more visible against the green color. Silicon carbide is extremely hard and brittle. The particles are sharp, and they break to form new sharp particles. This results in highly efficient cutting of a wide variety of materials, including metal alloys, ceramics, and acrylic resin materials. Silicon carbide is available as an abrasive in coated discs and as vitreous- and rubber-bonded instruments.

TIN OXIDE

This extremely fine abrasive material is used extensively as a polishing agent for polishing teeth and metallic restorations

such as dental amalgams in the mouth. It is mixed with water, alcohol, or glycerin to form a mildly abrasive paste.

ZIRCONIUM SILICATE

Zircon or zirconium silicate ($ZrSiO_4$) is supplied as an off-white mineral. It is ground to various particle sizes and used to make coated abrasive discs and strips. It is frequently used as a component of dental prophylaxis pastes.

ABRASIVE PASTES

The most commonly used abrasive pastes contain either aluminum oxide (alumina) or diamond particles. Alumina pastes should be used with a rotary instrument and increasing amounts of water as the polishing process proceeds from the use of coarser to finer abrasive particles. Diamond abrasive pastes are used in a relatively dry condition. The instruments that apply the paste to the material surface are equally important. These include ribbed prophy cups (the ribbed type or the more flexible nonribbed type), brushes, and felt wheels. Abrasive pastes have several disadvantages: First, they are relatively thick and cannot gain access to embrasures. Second, the pastes tend to splatter when they spin off of the instruments at excessive rotational speeds or if they become wet. Third, heat is generated when insufficient coolant is used or when continuous polishing pressure is applied without allowing coolant to reach the surface.

? CRITICAL QUESTION

Which procedure will ensure that progressively finer abrasives completely remove scratches made by previous coarse abrasives?

FINISHING AND POLISHING PROCEDURES

RESIN-BASED COMPOSITE RESTORATIONS

Dental composites are among the most difficult types of materials to predictably finish and polish to a high luster because they contain a relatively soft resin matrix and hard filler particles in their structures. Each resin composite brand contains a different microstructure. Therefore, there are varying methods for finishing and polishing different composites and different time requirements for achieving a desirable luster (Figure 11-16). Additionally, the maintenance of the luster over time can vary considerably because of the microstructural differences (Figure 11-17). This means that there must be selective grinding associated with the soft material and the harder particles, a situation that is especially apparent with hybrid composites. In addition, the final finish of a composite restoration depends on the fillers and resin matrix, the preparation design, curing effectiveness, and postcuring time required for the material to achieve its final properties. For some composite materials, a delay of 10 minutes or more is recommended after curing to allow complete polymerization to occur. Curing lights for polymerization such as halogen lamps must produce a minimal light output of 475 nm/mm^2 for most photoinitiated composites. Chemically cured composites must be properly placed in the prepared tooth within the working time of the materials.

Exposed filler particles create peaks and valleys that prevent the surface from acquiring a high luster. During each stage of finishing and polishing, the operator should proceed in one direction only. Then, after the use of the next abrasive in the sequence, polishing should continue in a direction perpendicular to the previous one. This process ensures that

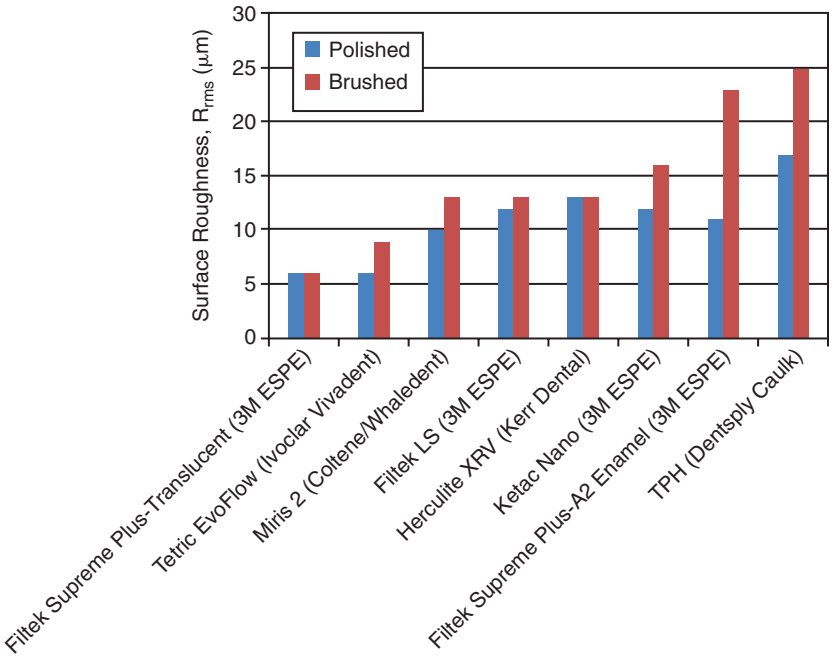


FIGURE 11-16 Influence of toothbrushing on surface roughness of various direct restorative materials. (Courtesy of Dr. J-H Phark.)



FIGURE 11-17 Maintenance of gloss for different resin composites subjected to toothbrush abrasion.

scratches become more visible and that the effectiveness of scratch removal can be assessed more rapidly. The recommended abrasives and polishing instruments should be used in the proper sequence, and intermediate abrasive steps should never be skipped. For example, following a coarse abrasive disc with a fine abrasive rather than a medium-grit abrasive would leave some of the scratches produced by the coarse abrasive. The operator can choose to use one system from start to finish (such as abrasive-coated or flexible abrasive-impregnated rubber discs) or combine different systems based on preference and the location of the restoration (such as sandpaper for anterior or a brush for posterior sites).

The finishing and polishing technique consists of three essential steps: First, contour the restoration either with 12-fluted carbide burs, 30- to 100-μm diamond burs, or coarse abrasive-coated discs, depending on the dentist's preference. Next, finish with 16- to 30-fluted carbide burs, fine and extra fine diamond burs, white stones (aluminum oxide), white Arkansas stones, or medium and fine abrasive-coated discs. Finally, polish with fine and extrafine polishing paste (aluminum oxide or diamond); extra-fine abrasive-coated discs; silicon carbide–impregnated brushes; or diamond-impregnated rubber polishing discs, cups, or points. Most finishing and polishing systems, whether impregnated or coated with abrasive, are available in a variety of color-coded kits. Manufacturers' instructions for their use must be followed to obtain the optimal outcome.

Shown in Figure 11-18 are two clinical photographs of a Class II composite restoration made of Tetric EvoCeram (Ivoclar Vivadent) resin-based composite after polishing (top left) and after 12 months of clinical service (top right). The bottom center image represents a laser-scanned image resulting from the superposition of the second surface scan over the one made at baseline. The red areas represent the loss of composite or tooth enamel during the 12-month period. The maximum wear depths at two of the sites were 160 and 190 μm.

DENTAL AMALGAM

Burnishing prior to carving provides the removal of the excess mercury and improves marginal adaptation, and burnishing after carving improves smoothness. However, burnishing alone will not provide a completely scratch- and retention-free surface for amalgam restorations. Slow-speed handpieces should be used for finishing and polishing amalgam restorations. In the past, a recommendation was made to wait 24 hours before polishing the amalgam restorations to allow amalgam to set completely. However, if the restoration's surface is finished initially with a very fine prophylaxis paste applied with a cotton pellet or a nonribbed rubber prophy cup rotated at slow speed and light pressure, a smooth, velvety finish is achieved that will acquire a luster as it is abraded normally in the mouth. Spherical amalgams set faster and can be finished and polished sooner.

If amalgam has hardened to an advanced stage in which the abrasion by a fine prophylaxis paste is no longer effective, the following procedure may be used at the next dental appointment: (1) Contour with slow-speed green stones or diamond burs or brown and green rubber points; and (2) apply a mixture of fine pumice and water or alcohol with a rotary brush or felt wheel to polish the surface.

GOLD ALLOY

Pure gold is a very soft and ductile metal. Therefore, it requires a different approach from that used for many other metals used in dentistry. Slow-speed handpieces should be used for finishing and polishing gold alloys. This technique consists of the following steps: (1) Contour with carbide burs, green stones (silicon carbide), or heatless stones; (2) finish with pink stones (aluminum oxide) or medium-grade abrasive-impregnated rubber wheels and points (brown and green); (3) apply fine abrasive-impregnated rubber wheels, cups, and points; and, if necessary, (4) apply tripoli or rouge with rag or leather wheels.

? CRITICAL QUESTION

What are the differences between finishing and polishing a ceramic restoration extraorally and intraorally?

CERAMIC RESTORATIONS

The ideal surface for ceramic restorations is a polished and glazed one. However, the production of a **glaze ceramic** through a **natural glaze** or **overglaze** process will not necessarily yield a smooth surface if the initial ceramic surface has significant roughness. The smoothest surfaces can be achieved extraorally before a prosthesis is cemented. In the mouth, minor roughness can be successfully polished without compromising the surface quality. In addition, polishing can improve the strength within the surface region of a ceramic prosthesis because it removes pores, microcracks, and other microscopic flaws. Adequate cooling is important when ceramic restorations are finished and polished in vivo. The use of an air–water spray device and maintaining intermittent contact between the restoration and the rotary instrument is critical during the operation.

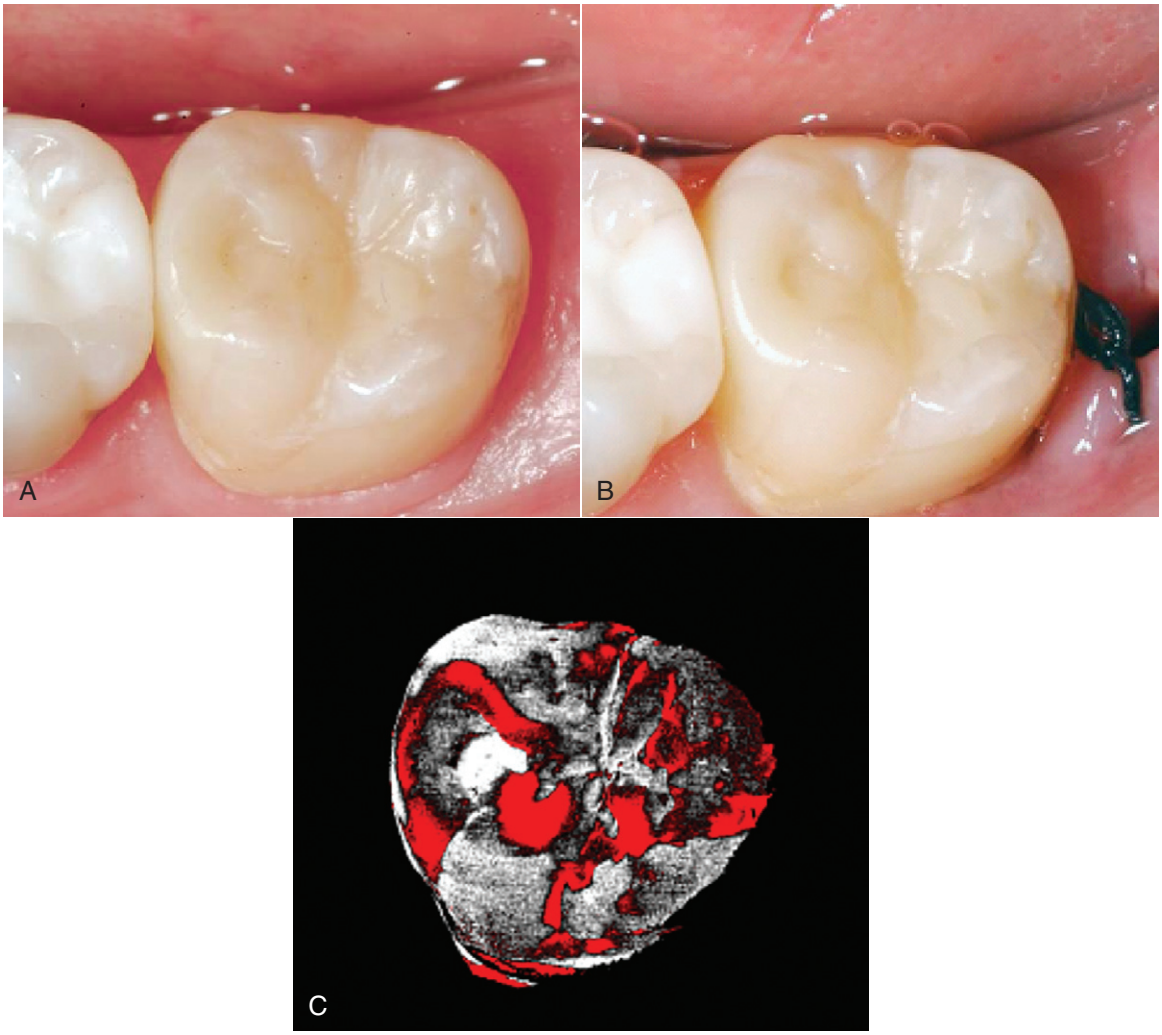


FIGURE 11-18 Class II composite restoration made of Tetric EvoCeram (Ivoclar Vivadent) resin-based composite. (**A**) Baseline view of occlusal and buccal surfaces after polishing. (**B**) View of occlusal and buccal surfaces after 12 months. The material loss (red areas) between these surfaces (**C**) is revealed by superposing the two scanned images. The red areas indicate the loss of enamel or composite. Two areas with maximum wear depths of 160 and 190 µm that was measured via laser scanning, were not detectable by visual examination. (Photos provided courtesy of Dr. Siegward Heintze.)

Continuous contact between the restoration and the rotary instrument should be avoided. A heatless stone (silicon carbide) provides heat reduction and can be used as an alternative. Several kits are available for finishing and polishing ceramic restorations. Manufacturers' instructions should be followed when these systems are used. Depending on the dentist's preference, a general technique is as follows: (1) Contour the ceramic surface with flexible diamond discs, diamond burs, heatless or polymer stones, or green stones (silicon carbide); (2) finish with white stones or abrasive-impregnated rubber discs, cups, and points. This process may require two or three steps, depending on the system used; (3) polish with fine abrasive-impregnated rubber discs, cups, and points or, if necessary, use a diamond paste applied with a brush or felt wheel; and (4) apply an overglaze layer or natural glaze on the ceramic, if necessary. For intraoral polishing, use an intermittent application of rotating instruments with a copious amount of water as a coolant.

Monolithic zirconia has been introduced by a large commercial dental laboratory to eliminate the chipping fractures of veneers that have been reported for several types of ceramic–ceramic systems based on an yttria-stabilized tetragonal zirconia particle (Y-TZP) system. Depending on the particle-size distribution of the zirconia and the amount of surface grinding required to adjust occlusion, the surface may be very difficult to grind and polish. Therefore, intraoral finishing and polishing may take significant chair time (Figure 11-19).

This may result in a relatively rough surface, which may cause severe wear of opposing enamel or restorative material surfaces. A glaze layer may also wear rapidly, exposing the rough-milled surface of the zirconia (Figures 11-20 and 11-21).

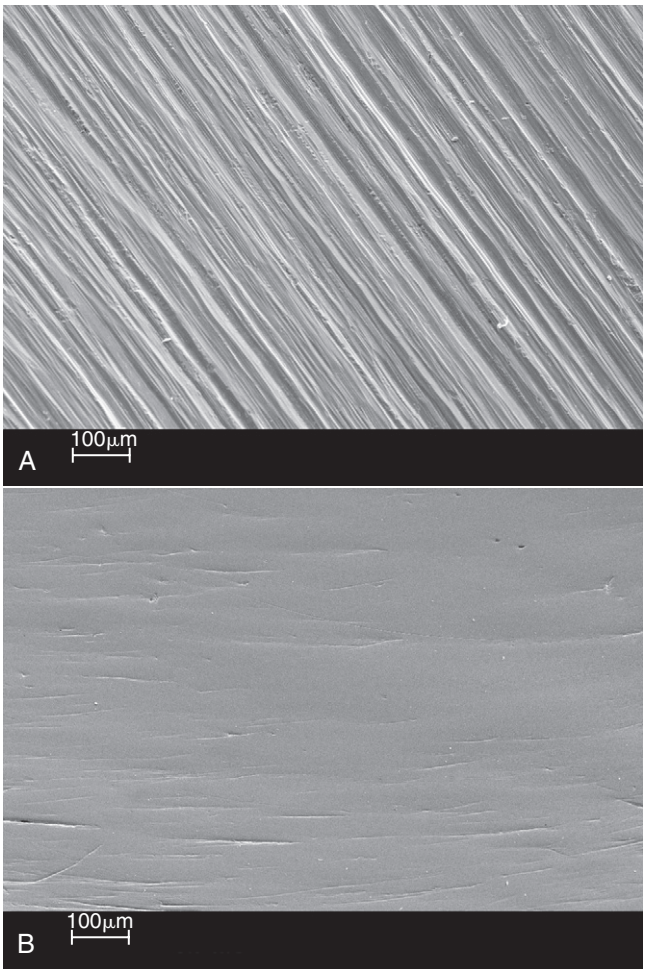


FIGURE 11-19 **A,** Zirconia surface finished with a fine diamond bur. **B,** Zirconia surface polished using the Dialite/Diashine system. (Courtesy of Dr. Siegward Heintze.)

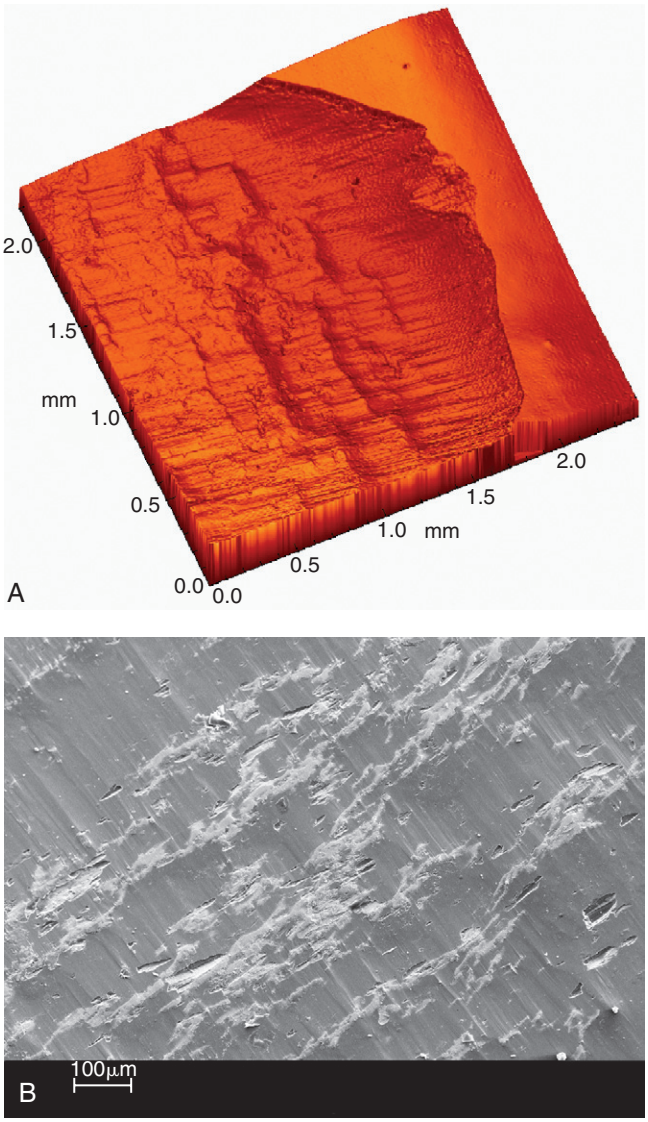


FIGURE 11-20 Wear facet of a milled and glazed ceramic after wear simulation. Three-dimensional image generated with FRT MicroProf sensor, **A,** and a scanning electron micrograph **B,** (×100 magnification). (Courtesy of Dr. Siegward Heintze.)

Limited information is available on this system or on optimal methods of producing the most minimally abrasive surface and on the durability of polished surfaces after exposure to the oral environment for several years. In addition, one can anticipate that crowns with greater zirconia thicknesses will require a much longer time for making endodontic access preparations and the removal of crowns that have failed.

ACRYLIC RESINS FOR DENTURE BASES AND VENEERS

Resins are relatively soft materials. To avoid overheating, a large amount of pumice slurry should be applied to the surface. Intermittent contact with the substrate also helps to avoid overheating. The following technique is recommended: (1) Contour with tungsten carbide burs and sandpaper; (2) use a rubber point to remove the scratches; (3) apply pumice with a rag wheel, felt wheel, bristle brush, or prophy cup, depending on the size of the area that needs to be polished; and (4) apply tripoli or a mixture of chalk and alcohol with a rag wheel.

AIR-PARTICLE ABRASION TECHNOLOGY

As an alternative to the use of rotary instrument cutting, air-particle abrasive systems can deliver a fine, precisely controlled high-pressure stream of 25- to 30-µm aluminum oxide particles to remove enamel, dentin, and restorative materials. Because air-particle abrasion generates minimal heat and vibration, there is relatively little potential for tooth chipping or microfracturing. These systems have been used for the following applications: tooth preparation, removal of defective resin-based composite restorations, endodontic access through porcelain crowns, a minimal preparation to repair crown margins, tunnel preparations, superficial removal of stains, cleaning of tooth surfaces before adhesive bonding, and roughening of internal surfaces of indirect porcelains or composite restorations before adhesive bonding.

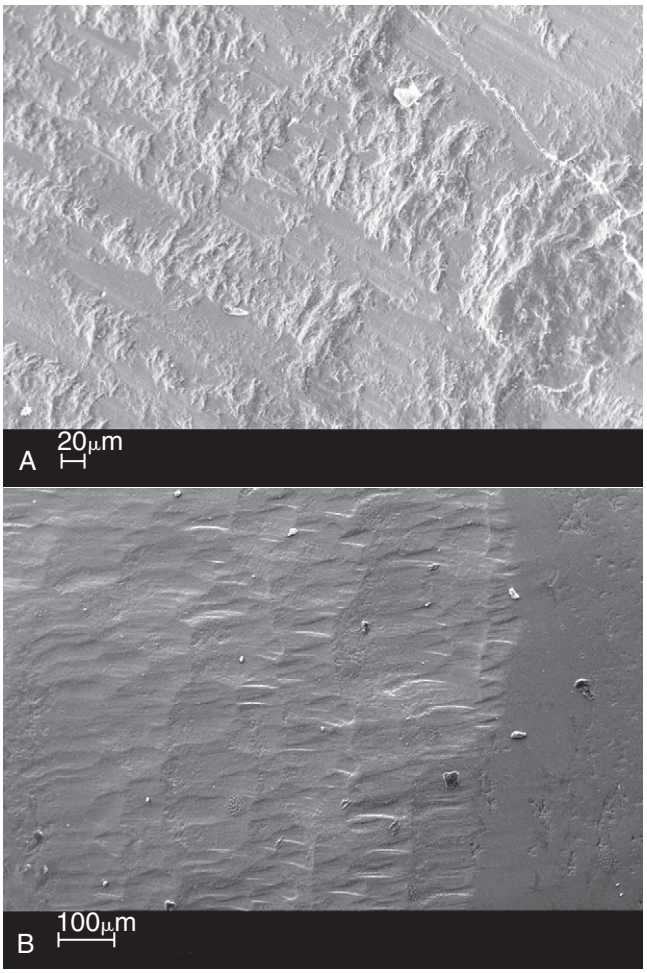


FIGURE 11-21 Scanning electron micrograph images of enamel stylus abraded by glazed crowns (**A**) and by optimally polished crowns (**B**). (Courtesy of Dr. Siegward Heintze.)

TABLE 11-3 Effect of Prophylaxis Pastes on Glazed Ceramic Surface Roughness

Product	Surface Roughness
Proxyt coarse (Ivoclar Vivadent, Amherst, NY)	0.183 ± 0.08
Proxyt fine (Ivoclar Vivadent, Amherst, NY)	0.066 ± 0.03
Nupro coarse (DENTSPLY International, York, PA)	0.209 ± 0.11
Nupro fine (DENTSPLY International, York, PA)	0.188 ± 0.07
Control (glazed surface)	0.061 ± 0.03

PROPHYLAXIS PASTE SELECTION FOR DENTAL HYGIENE PROCEDURES

It should be noted that, depending on the particle size of the abrasive and its composition, the abrasiveness of the prophy pastes may have adverse effects on exposed cementum and dentin surfaces as well as esthetic restorative materials. Table 11-3 shows the mean roughness values obtained on glazed ceramic surfaces after three rounds of 10-second application of various prophy pastes by the same operator. Only one of the pastes (Proxyt Fine) did not alter the surface smoothness significantly. Similarly, another study revealed the effect of the same prophy pastes on the gloss reduction of a polished resin composite (Table 11-4).

TABLE 11-4 Effect of Prophy Pastes on Polished Composite Surface Gloss Reduction, Measured by Gloss Units, after a 60-Second Application

Product	Mean GU ± SD
Nupro coarse	−40.86 ± 4.22[a]
Nupro fine	−40.57 ± 5.64[a]
Proxyt coarse	−41.61 ± 3.32[a]
Proxyt fine	−16.24 ± 3.34[b]

The difference between mean values of groups represented by the same superscripts are not statistically significant.

DENTIFRICES

Tooth cleaning substances such as dentifrices are available as toothpastes, gels, and powders. Dentifrices have three important functions: (1) Their abrasive and detergent actions provide more efficient removal of debris, plaque, and stained pellicle compared with use of a toothbrush alone; (2) they polish teeth to provide increased light reflectance and superior esthetic appearance, and the high polish, as an added benefit, enables teeth to resist the accumulation of microorganisms and stains better than rougher surfaces could; and (3) they act as vehicles for the delivery of therapeutic agents with known benefits—for example, fluorides, tartar control agents, desensitizing agents, and remineralizing agents.

Fluorides improve resistance to caries and may, under a proper oral hygiene regimen, enhance the remineralization of tooth surfaces with incipient noncavitated enamel lesions, thereby hardening the surface. Tartar-control agents such as potassium and sodium pyrophosphates can reduce the rate at which new calculous deposits form supragingivally. Desensitizing agents with proven clinical efficacy are strontium chloride and potassium nitrate. The therapeutic benefits of other additives such as peroxides and bicarbonates are under investigation. The products advertised as "whitening toothpastes" may contain an abrasive agent alone or both a chemical agent and an abrasive agent. The former type of additive acts through a surface stain-removal mechanism, whereas the latter additives act through a combined mechanism of abrasion and bleaching.

DENTIFRICE COMPOSITION

Typical components of some dentifrices are listed in Table 11-5. The abrasive concentrations in paste and gel dentifrices are 50% to 75% lower than those of powder dentifrices. Therefore, powders should be used more sparingly and with greater caution by patients (especially where cementum and dentin are exposed) to avoid excessive dentinal abrasion and pulpal sensitivity.

TABLE 11-5 Typical Dentifrice Components*

Component	Composition (wt%) Pastes and Gels	Composition (wt%) Powders	Materials	Purpose
Abrasive	20–55	90–98	Calcium carbonate Dibasic calcium phosphate dihydrate Hydrated alumina Hydrated silica Sodium bicarbonate Mixtures of listed abrasives	Removes plaque or stain Polishes tooth surface
Detergent	1–2	1–6	Sodium lauryl sulfate	Aids in debris removal
Colorants	1–2	1–2	Food colorants	Are used for appearance
Flavoring	1–2	1–2	Oils of spearmint, peppermint, wintergreen, or cinnamon	Provides flavor
Humectant	20–35	0	Sorbitol, glycerine	Maintains moisture content
Water	15–25	0	Deionized water	Acts as suspension agent
Binder	3	0	Carrageenan	As thickener, prevents liquid–solid separation
Fluoride	0–1	0	Sodium monofluorophosphate Sodium fluoride Stannous fluoride	Prevents dental caries
Tartar control agents	0–1	0	Disodium pyrophosphate Tetrasodium pyrophosphate Tetrapotassium pyrophosphate	Inhibits formation of calculus above the gingival margin
Desensitization agents	0–5	0	Potassium nitrate Strontium chloride	Promotes occlusion of dentinal tubules

*Some compositional information provided by Dr. George Stookey.

DENTIFRICE ABRASIVENESS

The ideal toothpaste should provide the greatest possible cleaning action on tooth surfaces with the lowest possible abrasion rate. Dentifrices do not have to be highly abrasive to clean teeth effectively. This is fortunate because exposed root-surface cementum and dentin, respectively, are abraded at rates of 35 and 25 times the rate of enamel. Standardized laboratory tests have been developed to measure the cleaning ability and abrasiveness of dentifrices. Only the abrasiveness test is discussed in this section.

Currently, the preferred means of evaluating dentifrice abrasiveness is to employ irradiated dentin specimens and brush them for several minutes with test and reference dentifrices. An abrasiveness ratio is then calculated by comparing the amounts of radioactive phosphorus (P^{32}) released by each dentifrice, and this value is multiplied by 1000. A dentifrice must obtain an abrasiveness score of 200 to 250 or less to satisfy the abrasiveness test requirements proposed by the American Dental Association (ADA) and the International Organization for Standardization (ISO). This means that a test dentifrice must abrade dentin at 20% to 25% of the rate of the reference standard to be considered safe for normal usage. A problem with this laboratory test is that it does not account for all variables that would affect abrasiveness under in vivo conditions. Some of the factors affecting dentifrice abrasiveness are listed in Box 11-1.

Another problem is that not all dentifrices respond in a similar manner under this test. For example, dentifrices that contain sodium bicarbonate yield poor test results because the particles dissolve completely approximately 1 minute into the 8-minute test. This illustrates that it is very difficult or impossible to use a laboratory test to predict the in vivo abrasiveness of various dentifrices. Patients should experience similar amounts of relative wear from the various dentifrices as those found in laboratory tests. The majority of modern dentifrices are not exceedingly abrasive. In fact, one published document has rated four dozen dentifrices with regard

BOX 11–1 Factors Affecting Dentifrice Abrasiveness

Extraoral Factors

Abrasive particle type, size, and quantity in dentifrice
Amount of dentifrice used
Toothbrush type
Toothbrushing method and force applied during brushing
Toothbrushing frequency and duration
Patient's coordination and mental status

Intraoral Factors

Saliva consistency and quantity (normal variations)
Xerostomia induced by drugs, salivary gland pathology, and radiation therapy
Presence, quantity, and quality of existing dental deposits (pellicle, plaque, calculus)
Exposure of dental root surfaces
Presence of restorative materials, dental prostheses, and orthodontic appliances

to cleaning ability and abrasiveness. The products are ranked as high, moderate, or low in abrasiveness. It is highly probable that most of the evaluated products meet the American National Standards Institute (ANSI)/ADA and ISO test requirements. Thus, these rankings should be considered a guide to products that do not exceed a maximum acceptable (safe) abrasiveness value.

TOOTHBRUSHES

The bristle stiffness of toothbrushes alone has been shown to have no effect on the abrasion of hard dental tissues. However, when a dentifrice is used, there is evidence that more flexible toothbrush bristles bend more readily and bring more abrasive particles into contact with tooth structure, albeit with relatively light forces. This interaction should produce more effective abrasion and cleaning action on the areas that the bristles can reach. Battery-powered toothbrushing devices provide a variety of cleansing actions that are claimed to improve tooth-cleaning actions even further than those achieved by manual toothbrushes.

CRITICAL QUESTION

One observes new fine scratches on a metal partial denture framework when an additional increment of the same abrasive paste is applied with a buffing wheel that was used previously. What is the cause of the new scratches?

SUMMARY AND RECOMMENDATIONS

Lab technicians, dentists, and dental hygienists should carefully select the appropriate abrasive system for each material product. Although it is convenient to use the same instruments for grinding and finishing different materials, the quality of the finished tooth or material surfaces may be far less than ideal if the optimal processes and abrasives recommended for specific materials are not followed. For in vivo processes, use liquid coolant, whenever possible. In situations where a copious supply of liquid coolant is not possible, intermittent application of polishing pressure should be performed.

To determine whether successive abrasive steps with finer and finer abrasives are used, change the orientation of the polishing path from one abrasive to the next. Polishing instruments or carriers (e.g., brushes or rag wheels) should be cleaned thoroughly between abrasive stages so that coarser particles are not incorporated with finer abrasives. If possible, use new carriers. Use lighter pressure as the final stages of each abrasive step are reached. Rinse the treated surface off periodically to remove wear debris that may interfere with the ability to produce the finest possible surface finish.

ACKNOWLEDGMENT

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PART 3

DIRECT RESTORATIVE MATERIALS

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CHAPTER 12

Bonding and Bonding Agents

OUTLINE

Terminology

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Dentin Bonding Agents

Luting Agents and Resin Cements

Orthodontic Bracket Bonding Resins

Root Canal Sealers

Glass Ionomer Restoratives

Amalgam Bonding

Pit and Fissure Sealants

KEY TERMS

Acid-etch technique—The process of cleaning and roughening a solid surface by exposing it to an acid and thoroughly rinsing the residue to promote micromechanical bonding of an adhesive to the surface.

Adherend—A material substrate that is bonded to another material by means of an adhesive.

Adhesion—A molecular or atomic attraction between two contacting surfaces promoted by the interfacial force of attraction between the molecules or atoms of two different species; adhesion may occur as chemical adhesion (formation of covalent bonds, hydrogen bonds, or polar bonds via van der Waals attraction), mechanical adhesion (structural interlocking), or a combination of both types.

Adhesive—Substance that promotes adhesion of one substance or material to another.

Adhesive bonding—Process of joining two materials by means of an adhesive agent that solidifies during the bonding process.

Bonding—A means of binding two adjoining materials, for example, dental hard tissues, metal, composite, or ceramic, and providing resistance to their separation.

Cement/Cementing—Substance that hardens from a viscous state to a solid union between two surfaces. For dental applications, cements act as a base, liner, restorative filling material, or adhesive to bond devices and prostheses to tooth structure or to each other. See also, "Luting agent."

Cohesive Strength—Molecular attraction between molecules or atoms of the same species.

Contact angle—Angle of intersection between a liquid and a surface of a solid that is measured from the solid surface through the liquid to the liquid–vapor tangent line originating at the terminus of the liquid–solid interface; used as a measure of wettability, whereby absolutely no wetting occurs at a contact angle of 180 degrees and complete wetting occurs at an angle of 0 degrees.

Dentin bonding—The process of bonding a resin to conditioned dentin.

Dentin bonding agent—A thin layer of resin between conditioned dentin and the resin matrix of a resin composite restorative material.

Dentin conditioner—An acidic agent that dissolves the inorganic structure in dentin, resulting in a collagen mesh that allows infiltration of an adhesive resin.

Filler/Reinforcing filler—A distribution of solid particles that are dispersed in a resin matrix to increase rigidity, strength, and wear resistance and to decrease thermal expansion, polymerization viscosity, shrinkage, and swelling in water and other solvents.

Hybrid layer—An intermediate layer of resin, collagen, and dentin that is produced by acid etching of dentin and infiltration of resin into the conditioned dentin.

Luting agent—A viscous cement-like material that also fills a gap between the bonded materials. See also, "Cement."

Microleakage—The flow of oral fluid and bacteria into the microscopic gap between a prepared tooth surface and a restorative material.

Micromechanical bonding—The mechanical interlocking that is associated with bonding of an adhesive to a roughened adherend surface.

Obturate/Obturation—To form an obstruction, or to obstruct. In endodontic dentistry, filling of a root canal completely and densely with a nonirritating hermetic sealing agent to prevent leakage.

Preventive-resin restoration (PRR)—A conservative, sealed, resin-based composite restoration, usually placed in a minimally prepared occlusal fissure area, with the sealant extending into contiguous uncut fissures.

Primer—A hydrophilic, low-viscosity resin that promotes bonding to an adherend substrate, such as dentin.

Resin tag—Extension of resin that has penetrated into etched enamel or dentin.

Sandwich technique—The process of restoring a prepared tooth by initially placing a layer of type II glass ionomer cement for fluoride release followed by an overlayer of resin-based composite.

Smear layer—Poorly adherent layer of ground dentin produced by cutting a dentin surface; also, a tenacious deposit of microscopic debris that covers enamel and dentin surfaces that have been prepared for a restoration.

Surface energy—The excess energy of molecules at the surfaces of materials above that of molecules found in the interior of a material.

Surface tension—The tension at the surfaces of liquids that results from the physical driving force to minimize the total energy of a system. This tension causes a liquid to minimize its surface by forming a spherical drop or a droplet with a contact angle against a solid surface. See also, "Contact angle."

Wettability—The relative affinity of a liquid for the surface of a solid.

Wetting—Relative interfacial tension between a liquid and a solid substrate that results in a contact angle of less than 90 degrees.

Wetting agent—A surface-active substance that reduces the surface tension of a liquid to promote wetting or adhesion.

TERMINOLOGY

Bonding and **adhesion** comprise a complex set of physical, chemical and mechanical mechanisms that allow the attachment and binding of one substance to another. A dental bonding system performs three essential functions: (1) provides resistance to separation of an **adherend** substrate (i.e., enamel, dentin, metal, composite, ceramic) from a restorative or **cementing** material; (2) distributes stress along bonded interfaces; and (3) seals the interface via adhesive bonding between dentin and/or enamel and the bonded material, thus increasing resistance to **microleakage** and decreasing the risk for postoperative sensitivity, marginal staining, and secondary caries.

HISTORICAL BACKGROUND

Prior to the middle of the twentieth century, dental bonding consisted of various methods of mechanical retention, such as forming undercuts in cavity preparations for amalgam restorations (see Chapter 15). **Luting**, using zinc phosphate and other nonadhesive dental cements, also falls into this category of bonding (see Chapter 14). In the late 1940s, Oskar Hagger, at the De Trey division of Amalgamated Dental, developed the first bonding agent, Sevriton Cavity Seal. This system was based on glycerophosphoric acid dimethacrylate (see Figure 12-5 on page 263) as a self-adhesive or self-etching component for both enamel and **dentin bonding**. However, this product had very limited clinical durability because of the large interfacial stresses that developed because of the high polymerization shrinkage and high thermal expansion of the unfilled methacrylate-based resins used at that time. Shortly after, Michael Buonocore investigated stronger acids and discovered that phosphoric acid provides superior enamel etching, and it is still in use today.

As shown in Figure 12-1, these discoveries of **acid etching** led to our ability to produce clean, high-energy, roughened enamel surfaces capable of establishing a durable micromechanical retentive interface with resin-based cementing and restorative materials launched the current era of **adhesive** dentistry. These events soon led to a burgeoning growth in the development of adhesive materials and bonding techniques, into the beginning of the twenty-first century. This progress is summarized in Figure 12-1 and is discussed in detail in several of the later sections of this chapter. At the present time, **adhesive bonding** can only be relied on for

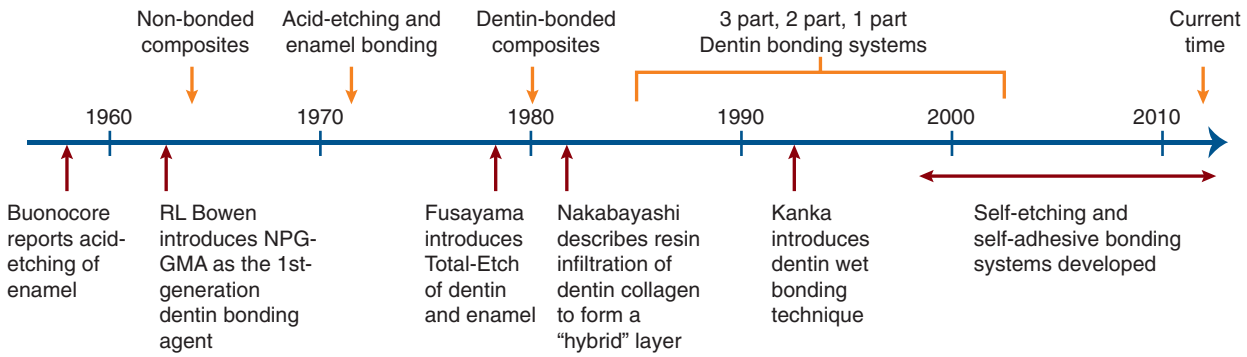


FIGURE 12-1 Major turning points and events in dental bonding technologies.

long-term retention in very select circumstances using highly specialized materials and clinical techniques, many of which are discussed in detail below. Nevertheless, dentistry is now well into the era of adhesive bonding and its associated field of esthetic dentistry.

APPLICATIONS FOR BONDING

Today, acid etching is one of the most effective ways to promote restoration retention and to ensure a sealed interfacial joint at restoration margins. This procedure has markedly expanded the use of resin-based restorative materials because it provides a strong, durable bond between resin and tooth structure and has formed the basis from many innovative dental procedures as diverse as orthodontic bracket bonding and porcelain laminate veneer bonding. Additional applications include pit and fissure sealants; amalgam bonding; both enamel and dentin bonding; adhesive cements, including glass-ionomer restorative materials; and endodontic sealers. Many of these applications are discussed in this chapter; however, other bonding applications are also discussed in greater detail throughout the book but with particular emphasis in Chapters 2, 13, 14, 15, and 18.

CRITICAL QUESTION

Why is good wetting of tooth structure by a dental adhesive not adequate for long-term adhesive bonding of a restorative material?

MECHANISMS OF ADHESION

True adhesion has been the "holy grail" of dental restorative materials for many decades. If true adhesion of restorative materials to tooth structure is to be achieved, three conditions must be satisfied:

1. Sound tooth structure must be conserved.
2. Optimal retention must be achieved.
3. Microleakage must be prevented.

The science of adhesion has been covered in Chapter 2. In this chapter, only those principles of adhesion needed for an understanding of dental bonding will be discussed.

Oral hard tissues and their environment are complex. However, the fundamental mechanism of adhesion to tooth structure can be regarded simply as an exchange by which inorganic tooth material (hydroxyapatite) is replaced by synthetic resins. This process involves two parts: (1) removing hydroxapatite to create micropores and (2) infiltration of resin monomers into the micropores and subsequent polymerization. As a result, **resin tags** are formed that micromechanically interlock or interpenetrate with the hard tissue. There may also be chemical interactions with the tooth substrate if monomers having acidic or chelating functional groups are present. In general, the following factors can play major or minor roles in achieving adhesive bonds:

1. Surface energy and wetting
2. Interpenetration (formation of a hybrid zone)
3. Micromechanical interlocking
4. Chemical bonding

Wetting is the essential first step for the success of all adhesion mechanisms. An adhesive cannot form micromechanical interlocks, chemical bonds, or interpenetrating networks with a surface unless it can form intimate contact with the surface, spread over it and penetrate by capillary attraction into any microscopic and submicroscopic irregularities. These conditions are, by definition, achieved if the adhesive wets the surface.

As explained in Chapter 2, **wettability** of a liquid on a solid can be characterized by the **contact angle** that forms between a liquid and solid, as measured within the liquid. Categories of wettability include "mostly nonwetting" (>90 degrees), "absolutely no wetting" (180 degrees), "mostly wetting" (<90 degrees), and absolute wetting (0 degrees). See Figure 2-15 for a schematic illustration of wetting situations.

Generally, wettability can be enhanced by increasing the **surface energy** of the substrates (e.g., dentin, enamel, and synthetic materials). Since a clean, microroughened tooth surface has higher surface energy than unprepared tooth surfaces, organic adhesives are inherently able to wet and spread over such a surface unless a low **surface tension** material contaminates it before the adhesive can be applied. The **acid-etch technique** (see below), by which contaminants are removed and microporosities are created, is widely used to generate high-energy tooth surfaces and promote wetting by adhesive monomers.

Although wetting is an essential requirement for intraoral adhesion, it is not sufficient to ensure durable bonding. As explained below, to achieve strong bonding through the micromechanical interlocking mechanism, wetting monomers must intimately adapt to enamel and fill enamel surface irregularities and/or infiltrate into a demineralized collagen network in dentin. Some acid monomers with a phosphate (e.g., phenyl-P) or carboxyl group (e.g., 4-MET) have the additional potential of forming chemical bonds with calcium in the residual tooth tissue. The chemical structures of these acidic monomers are shown later in Figure 12-4 and Figure 12-6.

Another requirement for achieving lasting intraoral bonds is hydrolytic stability (resistance to chemical degradation by water). Enamel and dentin are hydrated, hydrophilic, and permeable to water. Even if an enamel or dentin surface is initially dried before applying an adhesive, inadvertent contamination and diffusion can easily result in water becoming strongly bound to both the hard tissue and the adhesive. Thus, for an adhesive monomer to wet hard tooth tissue as well as form a durable bond in the moist environment of the mouth, it must be both hydrophilic for water compatibility and hydrolytically stable to ensure longevity.

SMEAR LAYER

Whenever both enamel and dentin tissues are mechanically cut, especially with a rotary instrument, a layer of adherent

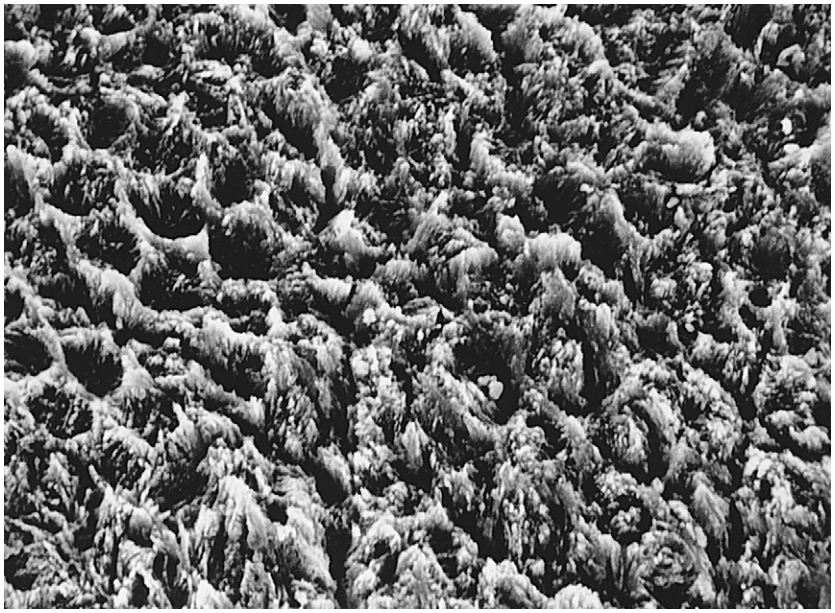


FIGURE 12-2 Surface of etched enamel in which the centers of enamel rods have been preferentially dissolved by phosphoric acid. (Courtesy of K-J. Söderholm.)

grinding debris and organic film known as a **smear layer** is left on their surfaces and prevents strong bonding. Different quantities and qualities of smear layer are produced by the various cutting and instrumentation techniques, as occurs, for example, during cavity or root canal preparation. In dentin, the smear layer becomes burnished into the underlying dentinal tubules and lowers dentin permeability, which is a protective effect. However, it is also a very weak cohesive material and interferes with strong bonding. Therefore, various cleaning or treatment agents and procedures are employed to either remove the smear layer or enhance its **cohesive strength** and other properties. As explained in greater detail below, application of acid is used to remove the smear layer from both enamel and dentin. Alternatively, in dentin the smear layer can be left partially in place and modified such that adhesive resins penetrate through it and bond to the intact dentin structures below.

ACID-ETCH TECHNIQUE

ENAMEL ETCHING

The first meaningful demonstration of intraoral adhesion was reported by Michael Buonocore (1955). Buonocore etched enamel surfaces with various acids, placed an acrylic restorative material on the micromechanically roughened surfaces, and found a great increase in the resin–enamel bond strength (~20 megapascals [MPa]). One of the surface conditioning agents he used, phosphoric acid, is still the most widely used etchant today for bonding to both enamel and dentin. Depending on the concentration, phosphoric acid removes the smear layer and about 10 microns of enamel to expose prisms of enamel rods to create a honeycomb-like, high energy retentive surface (Figure 12-2). The higher surface energy ensures that resin monomers will readily wet the surface, infiltrate into the micropores, and polymerize to form resin tags. The pattern of etching enamel may vary from selective dissolution of either the enamel rod centers (type I etching) as shown in Figure 12-2, or the peripheral areas (type II etching) as indicated by the resin tags in Figure 12-3. In either case, the resin tags are approximately 6 µm in diameter and 10 to 20 µm in length and lead to micromechanical interlocking.

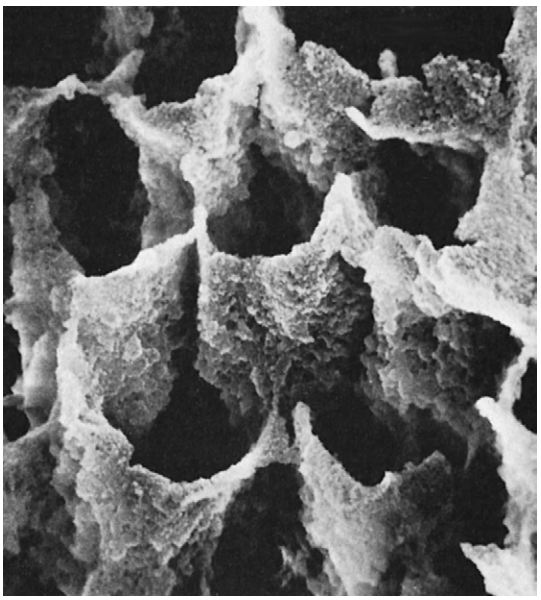


FIGURE 12-3 Scanning electron microscopy image of tags formed by the penetration of resin into etched areas of enamel. The resin was applied to the etched enamel, and enamel was then dissolved by acid to reveal the tags (×5000). (Courtesy of K-J. Söderholm.)

Prior to the introduction of enamel acid etching and the use of enamel bonding agents, restorative materials were placed directly on the smear layer of the prepared tooth. It is evident that the apparent bond strength is the cohesive

strength (5–10 MPa) of the smear layer, which is not sufficient to withstand the daily mechanical forces experienced in the mouth. As a result, debonding and leakage of oral fluids within the microscopic space between prepared teeth and restorative materials was an ongoing problem. Unlike other types of dental restorative products, resin-based composites have no mechanism to counteract the effects of marginal leakage (e.g., the corrosion of amalgam over time produces a deposit such as tin oxide and/or tin oxychloride along the tooth-restoration interface to form a relatively leakproof seal). Resin-based composites also cause problems because of the shrinkage stress (~15 MPa) generated during polymerization, exacerbating fracture of the tooth-restorative interface. Stronger and longer lasting bonds result if the smear layer is removed, because resins can then directly bond to the intact hard tissue.

DENTIN ETCHING

As illustrated in Figure 12-1, dentin etching did not gain wide acceptance until Fusayama introduced the total-etch concept in 1979. For this method, both dentin and enamel are etched simultaneously, typically using 37% phosphoric acid. His study demonstrated that not only was restoration retention substantially increased but also pulp damage did not occur as had been generally assumed. A subsequent study by Nakabayashi et al. (1984) revealed that hydrophilic resins can infiltrate the surface layer of acid-demineralized collagen fibers that is produced in etched dentin and it can form a layer of resin-infiltrated dentin with high cohesive strength. Such a **hybrid layer** structure forms very strong resin bonds through the development of an interpenetrating network of polymer and dentinal collagen, together with numerous micromechanical interlocks at the resin–hybrid layer interface. By the early 1990s, dentin etching had gained worldwide acceptance. Since the total-etch technique usually involves etching with an acid followed by rinsing to remove the acid, this technique is also known as the *etch-and-rinse technique*.

Dentin etching is more technique sensitive than enamel etching because of the complexity of the dentin structure. Unlike enamel, dentin is a living tissue, consisting of 50 vol% (volume percentage) of calcium phosphate mineral (hydroxyapatite), 30 vol% of organic material (mainly type I collagen), and 20 vol% fluid. Acid etching removes hydroxyapatite almost completely from several microns of sound dentin, exposing a microporous network of collagen suspended in water. Whereas etched enamel must be completely dry to form a strong bond with hydrophobic adhesive resins, etched dentin must be moist to form a hybrid layer. The amount of water left in etched dentin is critical. If insufficient water is present, the collagen network will collapse and produce a relatively impermeable layer that prevents resin infiltration and subsequent hybridization. If too much water remains, resin infiltration cannot fully replace the water in the collagen network and, consequently, sets the condition for later leakage into those locations. Therefore, a priming step is required to maintain a hydrated collagen network while removing excess water (see details in the following sections).

PROCESS AND PROCEDURAL FACTORS

Several aspects of the total-etch, etch-and-rinse, and related techniques are critical to the success or failure of bonding systems, as discussed below.

ETCHING TIME

The optimal application time for the etchant may vary somewhat, depending on previous exposure of the tooth surface to fluoride and other factors. For example, a permanent tooth with a high fluoride content may require a somewhat longer etching time, as do primary teeth. In the latter, increased surface conditioning time is needed to enhance the etching pattern on primary tooth enamel that is more aprismatic than permanent tooth enamel. Currently, the etching time for most etching gels is approximately 15 seconds. The advantage of such short etching times is that they yield acceptable bond strength in most instances, while conserving enamel and reducing treatment time.

RINSING AND DRYING STAGE

Once the tooth is etched, the acid should be rinsed away thoroughly with a stream of water for about 20 seconds, and the rinsed water must be removed. When enamel alone is etched and is to be bonded with a hydrophobic resin (e.g., bisphenol A glycidyl methacrylate [bis-GMA]–based resin; see Chapter 13), it must be dried completely with warm air until it takes on a white, frosted appearance. Dentin, in contrast, cannot withstand such aggressive drying, which would cause bond failure because of the formation of impermeable, collapsed collagen fibers. In the total-etch technique, a **dentin bonding agent** and **primer** must be used that are compatible with both moist dentin and moist enamel.

CLEANNESS OF THE BONDING SURFACES

The etched surfaces must be kept clean (free of contaminants) and sufficiently dry until the resin is placed to form a sound mechanical bond. Although etching raises the surface energy, contamination can readily reduce the energy level of the etched surface. Reducing the surface energy, in turn, makes it more difficult to wet the surface with a bonding resin that may have too high a surface tension to wet the contaminated surface. (Surface energy and wetting are described in detail in Chapter 2.) Thus, even momentary contact with saliva or blood can prevent effective resin tag formation and severely reduce the bond strength. Another potential contaminant is oil that is released from the air compressor and transported along the air lines to the air–water syringe. If contamination occurs, the contaminant should be removed, and the surface should be etched again for 10 seconds.

OTHER FACTORS

The acid-etch technique was not widely used in the years immediately following its introduction (see Figure 12-1). The principal reason was the inferior properties of the acrylic filling materials used at that time. With those resins, curing (>6 vol% shrinkage) and thermal dimensional changes

(coefficients of thermal expansion in excess of 100 parts per million per degree Celsius [ppm/°C]) generated interfacial stresses sufficient to rupture the bond to etched enamel. After highly filled resin-based composites were marketed beginning in the mid-1960s, the acid-etch technique was "rediscovered." Acid etching is a very effective way to improve bonding and durability as well as to ensure a sealed interface. It has markedly expanded the use of resin-based restorative materials because it provides a strong bond between resin and teeth, forming the basis for many innovative dental procedures.

? CRITICAL QUESTION

What types of bond formations result from the use of a dentin bonding agent?

DENTIN BONDING AGENTS

Dental bonding agents are designed to provide a sufficiently strong interface between restorative composites and tooth structure to withstand mechanical forces and shrinkage stress. The success of adhesives is dependent on two types of bonding:

1. Micromechanical interlocking, chemical bonding with enamel and dentin, or both
2. Copolymerization with the resin matrix of composite materials

Before the total-etch technique was adopted, enamel bonding agents were used only to enhance the wetting and adaptation of resin to conditioned enamel surfaces. Generally, enamel bonding agents are made by combining different dimethacrylates from resins of composite materials (e.g., bis-GMA) with diluting monomers (e.g., triethylene glycol dimethacrylate [TEGDMA], Figure 12-4) to control viscosity and to enhance wetting. These agents have no potential for adhesion, but they improve **micromechanical bonding** by optimal formation of resins tags within the enamel. Because enamel can be kept fairly dry, these rather hydrophobic resins work well as long as they are restricted to enamel.

During the past few years, these bonding agents have been replaced by the same systems that are used on dentin. This transition occurred because of the benefit of simultaneously bonding resin to both enamel and dentin, not because of any substantial improvement in bond strength.

A wide variety of chemistries have been explored and marketed in the search for species that can produce strong, permanent bonds to dentin. As discussed in the earlier section on adhesion mechanisms, a successful dentin bonding system must meet several requirements:

1. Adequate removal or dissolution of the smear layer from enamel and dentin
2. Maintenance or reconstitution of the dentin collagen matrix
3. Good wetting
4. Efficient monomer diffusion and penetration
5. Polymerization within tooth structure
6. Copolymerization with the resin composite matrix

Irrespective of the number of bottles or components (see Figure 12-7 and Table 12-1), a typical dentin bonding system includes etchants, resin monomers, solvents, initiators and inhibitors, fillers, and sometimes other functional ingredients such as antimicrobial agents.

COMPOSITION

Etchants

Etchants are relatively strong acids (pH = 1–2) used to remove smear layers and to dissolve the mineral phase to allow formation of micromechanical interlocking in enamel and in dentin. A number of acidic agents have been used to produce the required microporosity. However, phosphoric acid at a concentration between 30% and 50%, typically 37%, is the preferred etching agent to produce consistent etching patterns while not damaging the pulp. Concentrations greater than 50% result in the deposition of an adherent layer of monocalcium phosphate monohydrate on the etched surface, which inhibits further dissolution. Generally, the etchant is supplied as an aqueous gel to allow precise placement over a specific area. These gels are often made by adding colloidal silica (the same fine particles used in microfilled composites) or polymer beads to the acid. Brushes are used to place the acidic gel, or the acid may be supplied in a disposable syringe from which it can be expressed onto enamel and dentin. During placement, it is important to be aware of the risk for air bubbles that may be introduced at the interface. Regions with air pockets will not be etched.

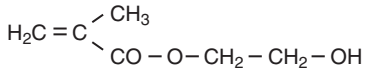
Primers

As discussed earlier, dentin etching is highly technique sensitive because the demineralized collagen network readily collapses when dried. Therefore, priming is necessary to maintain an expanded collagen network while removing residual water to allow for the infiltration of the hydrophobic adhesive monomer. Primers are solutions containing hydrophilic monomers dissolved in a solvent such as acetone, ethanol, or water. Such monomers exhibit hydrophilic properties through phosphate, carboxylic acid, alcohol, or ester functional groups. HEMA (2-hydroxylethyl methacrylate, shown in Figure 12-4) is a widely used primer monomer because of its high hydrophilicity and solvent-like nature.

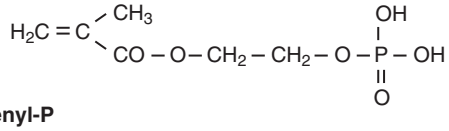
Primer mixtures have a wide pH range because of variations in the functional groups of the corresponding monomers. The rank of functional groups in their acidity is as follows: sulfonic acid > phosphonic > phosphoric > carboxylic > alcohol. If the concentration of acidic monomers is increased in a HEMA base, a primer formulation may reach a pH low enough (e.g., 1–2) to remove smear layers and etch underlying dentin. If a primer has the ability to both etch and prime, it is categorized as a self-etching primer. For this purpose, acidic monomers are frequently used to formulate self-etching primers. Representative of these are

Monomers with surface active and/or adhesive functional groups

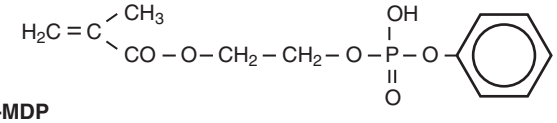
HEMA



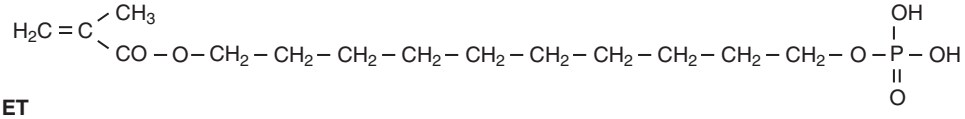
HEMA-phosphate



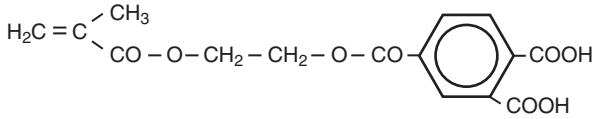
Phenyl-P



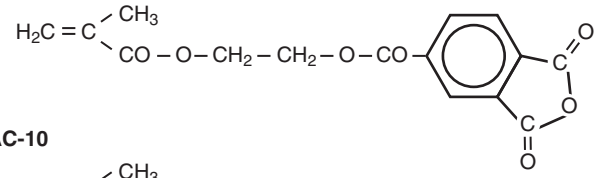
10-MDP



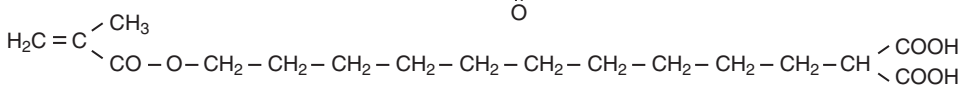
4-MET



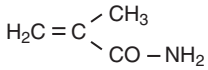
4-META



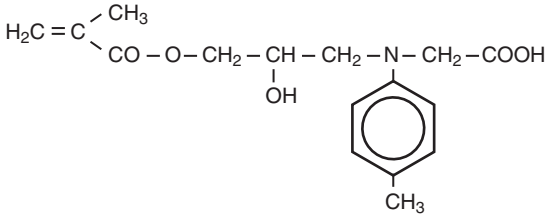
MAC-10



Methacrylamide

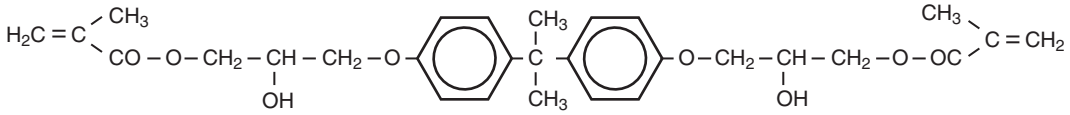


NPG-GMA

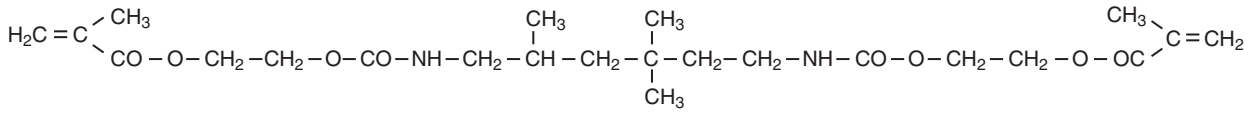


Monomers with crosslinking and copolymerizing functions

Bis-GMA



UDMA



TEGDMA

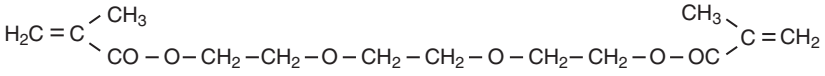


FIGURE 12-4 Structures of representative monomers used in enamel and dentin bonding agents. See also Figures 6-16, 6-17 and 6-18 in Chapter 6.

TABLE 12-1 Classification of Dental Bonding Systems and Representative Examples of Commercial Products Currently Available for Clinical Use

ETCH-AND-RINSE		SELF-ETCH	
Three-Step (Fourth generation)	**Two-Step (Fifth generation)**	**Two-Step (Sixth generation)**	**One-Step (Seventh generation)**
1. Etch Apply for 15 seconds, rinse 15 seconds gently air dry, while keeping dentin moist.	**1. Etch** Apply for 15 seconds, rinse 15 seconds, gently air dry while keeping dentin moist.	**1. Etch and Prime** One application without rinsing, gently air-dry.	**1. Etch, Prime, and Bond** Apply 1 to 5 layers without rinsing, gently air-dry, light-cure.
2. Prime Apply 1 to 5 layers, gently air-dry.	**2. Prime and Bond** Apply 1 to 5 layers, gently air-dry, light-cure.	**2. Bond** Apply one layer, gently air-dry, light-cure.	
3. Bond Apply one layer, gently air-dry, light-cure.			
REPRESENTATIVE PRODUCTS CURRENTLY MARKETED FOR CLINICAL USE			
Adper Scotchbond Multi-Purpose (3M ESPE)	DenTASTIC UNO (Pulpdent)	Adper Prompt (3M SPE)	AdheSE One (Ivoclar Vivadent)
All Bond 3 (Bisco)	Excite (Vivadent)	AdheSE (Ivoclar Vivadent)	Adper Easy Bond Self Etch (3M ESPE)
DenTASTIC All-Purpose (Pullpdent)	Gluma Comfort Bond (Heraeus Kulzer)	All-Bond SE (Bisco)	Adper Prompt L-Pop (3M ESPE)
Gluma Solid Bond (Heraeus Kulzer)	One-Step Plus (Bisco)	Clearfil Protect Bond (Kuraray)	Clearfil S3 Bond (Kuraray)
Optibond FL (Kerr)	PQI (Ultradent)	Nano-Bond (Pentron)	Futurabond DC (VOCO)
Syntac (Ivoclar Vivadent)	Prime & Bond NT (Dentsply)	One-Step P/TYRIAN (Bisco)	G-Bond (GC), XENO V (Dentsply)
	Single Bond (3M ESPE)	Peak (Ultradent)	I-Bond (Heraeus Kulzer)

HEMA-phosphate, phenyl-P (2-[methacryloyloxyethyl]phenyl hydrogen phosphate), 10-MDP (10-methacryloyloxydecyl dihydrogen phosphate), 4-MET (4-methacryloyloxyethyl trimellitic acid), 4-META (4-methacryloyloxyethyl trimellitic anhydride), and MAC-10 (11-methacryloyloxy-1,1′-undecanedicarboxylic acid). The chemical structures of these primer components and other representative bonding system monomers are illustrated in Figure 12-4.

Early dentin bonding agents were based on the successful model of silane coupling agents as used to bond the inorganic filler to the matrix resin in composites (see Chapter 13, Figure 13-3), to bond porcelain laminate veneers through resin cements to acid-etched enamel, and to repair fractured porcelain with composites (see Chapter 14). As shown in Figure 12-5 (*left*), generically, a silane coupling agent may be represented as M–R–X. M represents an unsaturated methacrylate group or groups capable of copolymerizing with the other monomers of a resin cement or composite. X represents a group capable of chemically reacting with siliceous materials such as glass and silicate filler particles in composites, and porcelain crowns and veneers, and/or the calcium ions (Ca^{++}) in dental hard tissues. R is a spacer group that provides flexibility and mobility, and thus enhanced reactivity, for the M group after the X group has been immobilized by reaction at a surface. Similarly, the adhesive phosphate monomer in Figure 12-5 (*right*) also has the M–R–X structure. This adhesive phosphate compound was the self-etching monomer used in the first dentin bonding system, Sevriton (DeTrey division of Amalgamated Dental, now Dentsply DeTrey, Konstanz, Germany), which was introduced in the 1950s. The silane monomer shown, γ-methacryloxypropyl trimethoxysilane, is currently used in all dental applications of coupling agents. An example of the surface anchoring process is illustrated for a phosphate monomer in Figure 12-6. For a silane coupling agent, see Figure 13-13 in Chapter 13.

Analogous to silane coupling agents, it was believed that dentin bonding could be achieved by forming chemical bonds between a resin system and either the inorganic or the organic components of dentin, in particular, the Ca^{++} within the hydroxyapatite mineral phases of dentin. Phosphate and carboxylic groups form chelation bonds with Ca^{++} and, therefore, are expected to form such bonds during dentin priming, as has been found with polycarboxylate cements (see Chapter 14) and illustrated in Figure 12-6. Then, during polymerization, the methacrylate group of the M–R–X molecule can react with the resin matrix of the composite material and

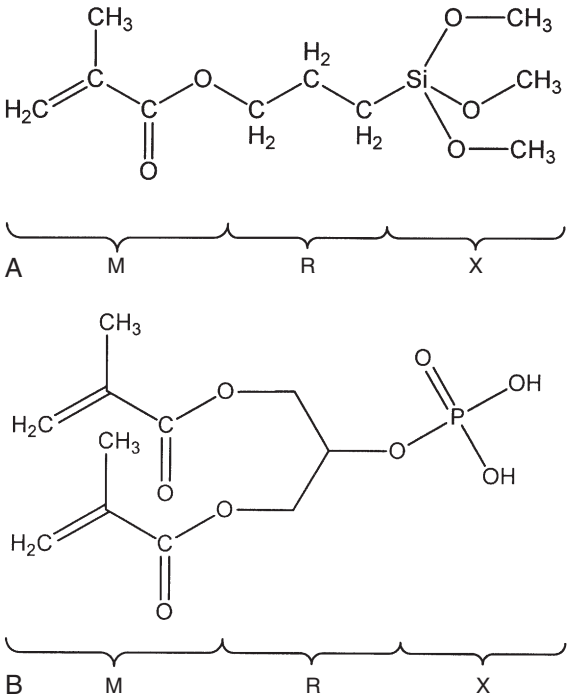


FIGURE 12-5 M-R-X structures of γ-methacryloxypropyl trimethoxysilane (*A*) and glycerophosphoric acid dimethacrylate (*B*). The surface interaction or bonding mechanism of the silane is shown in Figure 13-3. The chemical adhesion or bonding mechanism of phosphoric acid is shown in Figure 12-6.

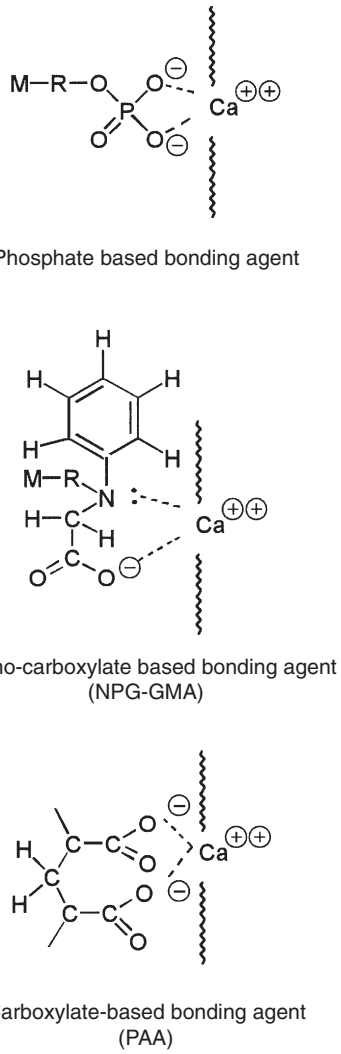


FIGURE 12-6 Chemical bonding mechanisms to hard tooth tissues through calcium salt formation with monomers having adhesive functional groups. (Courtesy of K-J. Söderholm.)

thereby form a chemical bond between composite and dentin. Several compounds that were believed to possess these properties are shown in Figure 12-4: NPG-GMA (a condensation product of *N*-phenyl glycine and glycidyl methacrylate, and the first dentin bonding agent), polymerizable phosphates (e.g., phenyl-P and 10-MDP), and carboxylate compounds (e.g., 4-MET, MAC-10, and 4-META). Also in this category are poly(alkenoic) acids as used in carboxylate and glass ionomer cements (GICs), which are discussed in more detail below and in Chapter 14. However, in spite of theoretical evidence that chemical bonding to tooth structure is possible, no convincing experimental evidence has yet been validated to prove that *significant* chemical bonding occurs between dentin adhesives and tooth structure under intraoral conditions. Rather, the adhesive functional groups facilitate surface cleaning and etching, and development of micromechanical interlocking and monomer penetration of dentin to form a hybrid layer of molecular entanglements between collagen and polymer.

Solvents

Solvents also play important roles in priming systems. The most commonly used solvents are water, ethanol, and acetone. In addition to the enhancement of wetting of hydrophilic dentin, each solvent has a specific contribution to improve bond adhesion. Water can ionize acidic monomers as well as re-expand the collapsed collagen network. Ethanol and acetone have better miscibility with relatively hydrophobic monomers, and their "water-chasing" ability facilitates water removal.

Adhesives

For dentin bonding, the primary purpose of adhesives is to fill the interfibrillar space of the collagen network, creating a hybrid layer and resin tags to provide micromechanical retention upon polymerization. In addition, adhesive layers also should prevent fluid leakage along the restorative material's margin, since they make up the major part of the intermediate layer between dentin and/or enamel and restorative composites.

It is evident that adhesives need to be hydrophobic so that fluid will not be allowed to permeate through the intermediate layer. At the same time, adhesives require a certain hydrophilicity to diffuse into the hydrophilic, primer-wetted dentin. Generally, adhesive resins are composed mainly of hydrophobic dimethacrylates such as bis-GMA, TEGDMA, and urethane dimethacrylates (UDMA), and a small amount of a

hydrophilic monomer such as HEMA. Although dimethacrylate adhesives yield strong bond strengths, the polar ester bond inevitably absorbs water and gradually hydrolyzes. Since carbamides are more hydrolytically stable than ester groups, methacrylamides have recently been adopted to replace methacrylates in several commercial products (e.g., AdheSE One F, Ivoclar Vivadent, Amherst, NY). These monomers are also shown in Figure 12-4.

Initiators

Similar initiator systems are used in both adhesives and restorative composites. Polymerization can be initiated either through a photoinitiator system consisting of a photosensitizer (e.g., camphorquinone) and an initiator (e.g., tertiary amine), through a self-cure system that includes a chemical initiator (e.g., benzoyl peroxide [BPO]), or through a dual-cure initiator system. (See Chapter 13 for details concerning initiator systems.)

Filler Particles

Nanometer-sized silica particles have been added to some adhesives to reinforce the adhesive and thereby produce higher bond strengths. However, the strengthening effect of the fillers in adhesives is uncertain because it is not clear whether these fillers can actually penetrate into the demineralized collagen networks, since the interfibrillar space of the collagen networks is within the range of 20 nanometers (nm) while the filler particles have a size of approximately 40 nm. The other reason for the addition of fillers is to effectively modify adhesive viscosity to a thicker, pastier consistency. When such an adhesive is applied to an etched dental surface, it yields a thicker bonding layer that can promote increased bond strength by preventing oxygen inhibition. Moreover, a thick adhesive layer can reduce shrinkage stress because it is more compliant compared with restorative composites. Reinforcing filler particles are described in further detail in Chapter 13.

Other Ingredients

A number of additional ingredients are used with dentin bonding agents for a variety of specific purposes. A few examples include the following: glutaraldehyde (Probond, Dentsply, York, PA) is added as a desensitizer. The monomer 12-methacryloyloxydodecylpyridinium bromide, MDPB (Clearfil Protect Bond, Kuraray America, New York, NY) and parabene (Adper Prompt-L-Pop, 3M ESPE, St. Paul, MN) are used as antimicrobials. Fluoride (Prime & Bond NT, Dentsply, York, PA) is added to prevent secondary caries. Benzalkonium chloride (e.g., Etch 37, Bisco, Schamburg, IL) and chlorhexidine (e.g., Peak LC Bond Resin, Ultradent Products, South Jordon, UT) are used to prevent collagen degradation. The latter products have recently been shown in laboratory studies to prevent protease enzymes (matrix metalloprotease enzymes or proteins [MMPs]) from being activated and subsequently denaturing the hybrid layer collagen. Unfortunately, only the early stages of long-term clinical trial results are available at this time to show whether such additives are ultimately effective.

? CRITICAL QUESTION

Why are dentin bond strength values so variable?

PROPERTIES

Measurement of Bond Strength

Evaluation of the efficacy of dentin adhesives is generally based on measurement of bond strength as determined by loading bonded test specimens in shear or in tension until fracture occurs. Such tests offer only indirect evidence of how the adhesive is likely to perform in vivo. Data published on bond strengths for a given material often vary widely, and the standard deviation of the mean value for a given bond test is usually high. This wide variance in data, that is better described by the coefficient of variation (standard deviation/mean), may be attributed to the variables inherent at the dentin surface, such as water content, the presence or absence of a smear layer, dentin permeability, orientation of the tubules relative to the surface, and differences in the in vitro test design and stress distribution adjacent to the interface. Furthermore, although no universal agreement on the minimal bond strength necessary to provide successful bonding has been established, a value of 20 MPa or higher has been proposed as a reasonable goal.

Recently, a number of studies have adopted the microtensile test methodology. By using very small specimens (approximately 1 mm^2 in cross-section), one can prepare multiple specimens from a single tooth. Even with very high indicated strengths, for example, 30 MPa or higher, failure occurs at the adhesive interface rather than within dentin. This interfacial failure has led some proponents of the method to suggest that it is the only valid measure of bond strength because significant fractions of specimens rarely fail along the tooth–resin interface using traditional test specimen geometries, such as shear-test designs.

Regardless of the numerical differences generated by different laboratory test methods, it is clear that current dentin bonding agents are capable of yielding higher bond strength values that can shift the site of clinical failure from the interface to within dentin adjacent to the restoration or, in some cases, within the restoration adjacent to the interface. Regardless of the bond test selected, it is clear that the inherent bond strength is no longer the limitation in the effectiveness of bonded restorations. The limiting factor now appears to be, at least for large restorations, induced stresses generated during curing shrinkage within the resin-based composite itself.

Measurement of Microleakage

The degree of microleakage at the restoration–tooth interface can be monitored by the penetration of tracers and staining agents. As is true for bond strength testing, there is also a large variation in leakage data from one laboratory to another, depending on the technique used and the manipulative variables adopted during placement of the bonding agents. Often, a good correlation does not exist between bond strength and microleakage. Nonetheless, the newer systems appear to be superior in inhibiting interfacial leakage between the conditioned tooth structure and adhesive resin.

Aging Effects and Degradation of the Hybrid Layer

The change of bond strength over time is a very useful indication of relative clinical lifetime and can be evaluated by accelerated aging tests in vitro. Several investigations have found that the bond strength of three-step adhesive systems show little or no decrease in contrast to two-step adhesive systems that decrease significantly during a 4- to 5-year span. Research has also shown that peripheral bonding to etched enamel, which seals the resin bond from exposure to water, can significantly increase bond durability. Transmission electron microscopy (TEM) observations have shown that collagen fibrils in the hybrid layer degrade coincidently with decreasing bond strength, suggesting that hybrid layer degradation contributes to aging of dentin bond integrity. As indicated in the above subsection on "other" bonding agent ingredients, this is likely caused by the activation of MMPs, which denature the hybrid layer collagen.

Some in vitro studies offer a degree of predictability for certain clinical situations. For example, a durable dentin bond can be expected if enamel bonding is used to seal all cavity margins.

? CRITICAL QUESTION

Do bonding agents perform the same in bonding to enamel and dentin?

CLASSIFICATION

When discussing dentin-bonding agents, it has become customary to describe the generations (first generation, second generation, etc.) of bonding agents that have led sequentially from the earliest, relatively ineffective materials to the current materials, which provide reliable functional bonds. This organization into generations of bonding agents is a somewhat artificial device to mark key advances in materials and techniques along a more-or-less continuous developmental pathway. Therefore, this chapter uses a more logical and straightforward classification for contemporary adhesive systems based rather on their mechanism of adhesion and the number of clinical steps involved. This classification was developed by van Meerbeek et al. (2003). As shown in Figure 12-7 and Table 12-1, it is based on two general approaches to etching, priming, and applying the bonding resin to dentin and enamel surfaces, and further subdivided into the number of steps in the process. Thus, the major categories of bonding systems are known as "etch-and-rinse" and "self-etch" systems, with two subcategories, each according to the number of clinical steps involved.

Etch-and-Rinse Adhesives

- *Three-step (fourth generation):* At this time, the most established, most reliable adhesion method in this category consists of three steps: (1) an acid etchant application, (2) application of the primer, and (3) application of the actual bonding agent or bonding resin. The primer contains hydrophilic functional monomers dissolved in an organic solvent such as acetone, ethanol, or water. The third step is the application of a hydrophobic resin, as mentioned earlier in the chapter.
- *Two-step (fifth generation):* A simplified method in this category combines the primer and adhesive resin into one application. This etch-and-rinse strategy is the most effective to achieve efficient and stable bonding to enamel. Etching, usually with a 30% to 40% phosphoric gel that is rinsed away, promotes the dissolution of enamel rods, creating porosities that are filled by bonding agents through capillary action and then followed by polymerization of resin.

  However, when dealing with a dentinal substrate, bonding is more difficult and less predictable than in enamel because of the organic characteristics of dentin. In this case, phosphoric acid treatment exposes a collagen

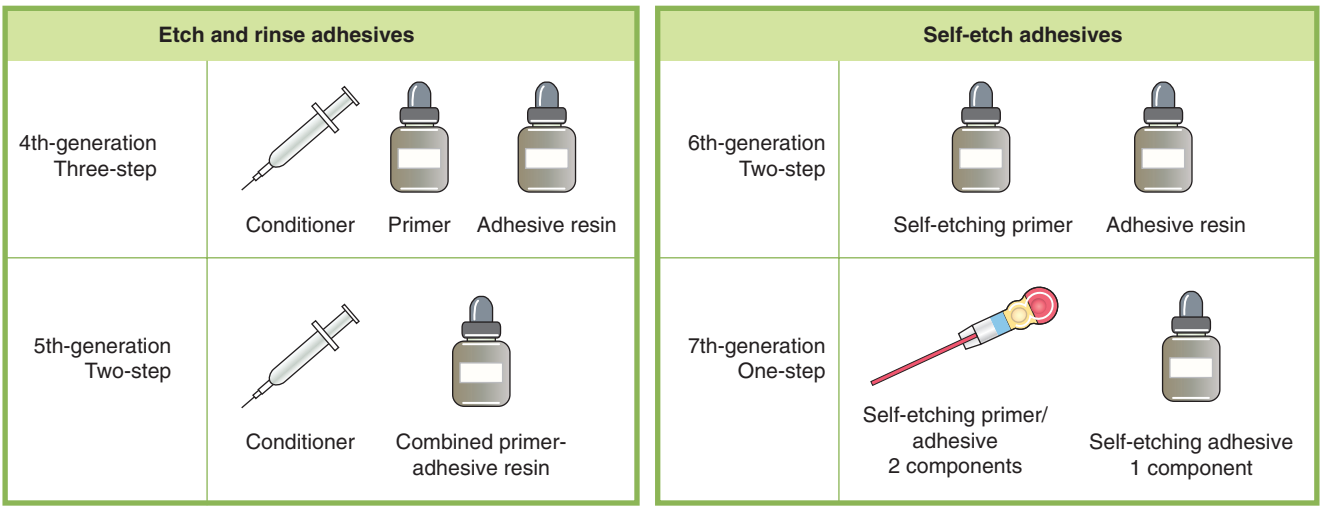


FIGURE 12-7 Classification of current adhesive systems according to van Meerbeek et al. 2003. (Figure adapted from Cardoso MV, de Almeida Neves A, Mine A, et al: Current aspects on bonding effectiveness and stability in adhesive dentistry. *Aust Dent J* 56(S1):31–44, 2011.)

network that is nearly devoid of hydroxyapatite. Bonding occurs by diffusion and infiltration of the resin within the collagen mesh, forming a hybrid layer. After in situ polymerization, this hybrid layer provides micromechanical retention to the restoration. As explained earlier, true chemical-adhesive bonding is unlikely to contribute significantly to bond strength, as the monomer functional groups have only very weak affinities for collagen. Further, in the two-step category hydrophilic and ionic monomers are combined, with the result that the bonded interface does not develop a hydrophobic resin layer and, thus, leaves the bond susceptible to water penetration and subsequent degradation, which greatly reduces bond durability.

Self-Etch Adhesives

- *Two-step (sixth generation):* This approach does not involve a separate etching step. In this case an acidic monomer which is not rinsed, is used to condition and prime the tooth at the same time. There are two types of self-etch adhesives (van Meerbeek et al., 2001), mild and strong varieties. Strong self-etch adhesives have low pH (<1) and have been documented with a bonding mechanism that resembles the etch-and-rinse adhesives. Mild self-etch adhesives (pH = 2) only partially dissolve the dentin surface, so a substantial amount of hydroxyapatite remains available within the hybrid layer. Specific carboxyl or phosphate groups of functional monomers can then chemically interact with this residual hydroxyapatite. Because this layer has some mineral content, the bond to dentin is better than that of etch-and-rinse adhesives. However, this interfacial zone can be more prone to hydrolytic degradation because the structure is more hydrophilic. The dentin bond durability of mild self-etch primer systems seems to be adequate.
- *One-step (seventh generation):* The simplified method in this category combines conditioner, primer, and bonding resin into a single step. Most one-step or "all-in-one" systems are delivered by a bottle, vial, or single-unit dose applicator, which are formulated as a single component. However, Adper Promp L-Pop (3M ESPE, St. Paul, MN) is a variation on this theme, in which two liquid components are packaged in separate "blister" compartments in a single dispenser. Bursting one blister causes the two components to blend and form a single component, which is then applied immediately using a brush that forms the handle of the blister pack. This version of one-step, two-component, self-etching primer–adhesive is illustrated in Figure 12-7.

  One-step, self-etch adhesives are an attractive approach for clinicians because of the reduced and less complex number of clinical steps required compared with multistep etch-and-rinse adhesives. There is no need for rinsing or drying of the tooth structure because of the lack of an etch step. Recently, a new self-etch adhesive bonding agent has been introduced that expands this category for use with total-etch procedures (Scotchbond Universal Adhesive, 3M ESPE, St. Paul, MN). This system contains a specific phosphate monomer and silane and is claimed to offer extended bond durability as well as versatility for use in an array of clinical applications.

  At this time, products in the one-step, self-etch category have undergone limited clinical experience, and consequently not enough is known concerning their performance and bond durability under long-term clinical conditions compared with the two-step self-etch and etch-and-rinse products. Recently, however, van Landuyt et al. (2011) showed in a randomized clinical trial that a one-step, self-etch adhesive had similar clinical performance after 3 years compared with that of an etch-and-rinse adhesive in class V restorations. However, the one-step group exhibited more incisal marginal defects and discoloration compared with the etch-and-rinse group.

These four categories are described further in Table 12-1, which also provides typical application instructions and examples of representative commercial products for each category.

The clinical application determines the best choice of an adhesive system. Some general recommendations for specific situations are given below. For bonding composite cores, three-step, etch-and-rinse (fourth-generation) systems are usually recommended. For bonding anterior and posterior composites and cementation of veneers with resin cements, two-step etch-and-rinse (fifth-generation) systems provide the best performance. For bonding posterior composites, self-etch, two-step (sixth-generation) systems are the better choice. Dual-cure one-step, self-etch (seventh-generation) systems are advised for esthetic posts and ceramic restorations bonded with resin cement, while light-cured one-step, self-etch (seventh-generation) systems are recommended for bonding posterior composite restorations.

? CRITICAL QUESTION

Can a single luting agent be used for cementation of indirect restorations in all clinical scenarios?

LUTING AGENTS AND RESIN CEMENTS

For many years, retention of indirect restorations could only be attained by the use of favorable tooth preparations and by micromechanical interlocking of the **luting agent** into irregularities present on the surface of the restoration and the tooth. Adhesive bonding completely changed the use of direct and indirect restorations. A number of materials are available for cementation, including zinc phosphate cements, polycarboxylate cements, glass-ionomer cements (GIC), RMGI cements, and resin cements that are described in more detail below and in Chapter 14. This section will concentrate on their bonding mechanism and new developments, especially regarding resin cements.

Resin cements must bond to different substrates, including tooth structure, resin composites, gold, metal alloys, titanium, and porcelain, and other ceramics. Resin cements can follow the application dentin bonding agents or not when bonding to

tooth structure. The former can be considered either as an etch-and-rinse adhesive resin cement or as a self-etch adhesive resin cement, according to its bonding agent system. Self-adhesive resin cements, for which no extra clinical step is necessary for bonding, such as RelyX Unicem (3M ESPE, St. Paul, MN), were developed in the past decade. In vitro studies have reported better enamel bonding performance for non–self-adhesive resin cements compared with self-adhesive cements. Self-adhesive resin cements do not show significant infiltration into dentin, but apparently some type of chemical interaction occurs between the calcium in hydroxyapatite and the cement monomer functional groups. With regard to biocompatibility, these cements showed no adverse pulp response according to one study (Pedro et al., 2006).

Zinc phosphate cement shows low bond strength to dentin because of the lack of adhesion and absence of chemical bond formation with tooth structure. Bonding in this case occurs primarily by mechanical interlocking at the interfaces. However, GIC can chemically bond by ionic interaction of the carboxyl groups of the polyalkenoic acid with the calcium of the hydroxyapatite that remained attached to the collagen fibrils. However, GIC and zinc phosphate cement show similar clinical results.

Most resin cements show superior mechanical properties and higher bond strengths of restorative materials to tooth structure than that of conventional luting agents. Some studies have shown that even when bonding to zirconia that has high polycrystalline content and lack of glass matrix, higher values can be achieved. Preparation of the tooth structure for cementation remains the same regardless of the indirect restoration material used. However, the preparation of an all-ceramic restoration can include, but is not limited to, sandblasting, application of hydrofluoric acid for etching, silanization, or application of a ceramic primer to improve bond strength. For cementation of all-ceramic restorations, resin cement is the material of choice. Depending on the polymerization process, resin cements can be chemically cured, light cured, or dual cured. Self-adhesive resin cements are dual-cured materials and can be used for cementation of indirect restorations in most clinical situations. The exception would be cementation of veneers, in which case a light-cured cement would be preferred.

For cementation of indirect restorations where most of the tooth structure is dentin, resin cements have shown better mechanical properties compared with conventional cements. Long-term clinical data are needed to corroborate in vitro studies.

? CRITICAL QUESTION

Why are self-adhesive cements currently not used to bond orthodontic brackets?

ORTHODONTIC BRACKET BONDING RESINS

Orthodontic treatment with fixed appliances involves the use of attachments such as brackets and bands. Bands are metal rings that go around teeth and are usually used on molars. Brackets can be welded to bands but are most commonly used today bonded to enamel. The development of bonding has contributed to a decrease in banding even in posterior teeth. A variety of luting agents have been used in orthodontics such as polycarboxylate cement, GIC, and resin-modified glass ionomer (RMGI) cements. Contemporary bonding process to enamel involves the following:

1. Prophylaxis of bonding surface
2. Etching with phosphoric acid gel or aqueous solutions
3. Rinsing with water
4. Drying with air
5. Application of sealant or primer
6. Bonding of brackets with resin cement
7. Light-curing the dual-cured or light-cured cement

Self-adhesive cements are not recommended by manufacturers as luting agents for orthodontic fixed appliances. Self-adhesive cements exhibit a lower bond strength to intact enamel in comparison with conventional orthodontic resin cements that require phosphoric acid etching. However, self-etching systems have shown acceptable results for bonding orthodontic brackets.

In orthodontic treatment, bonding most likely involves mainly enamel as the substrate. However, adults are increasingly undergoing tooth alignment. This population has larger amalgam restorations, porcelain fused to metal (PFM) crowns and all-ceramic crowns. Therefore, bonding of brackets to those surfaces also plays an important role in orthodontic treatment. It is important that the bonding of brackets be reliable, since replacing loose brackets is inefficient, time consuming, and costly.

Several types of surface treatments can be used with restorative materials to increase bond strength. For example, roughening with a diamond bur, and sandblasting enhance bonding, especially in the case of metals. These treatments create irregularities and increase surface area, promoting both micromechanical retention and chemical adhesion in the case of resins such as those containing 4-META (4-methacryloxyethyl trimellitate anhydride, 10-MDP (10-methacryloyloxydecyl dihydrogen phosphate), and others as shown in Figure 12-4. Bond strength of brackets bonded to amalgam (see below) is lower than that to etched enamel. In addition to forming a reliable bond, the ability of a resin to reduce or prevent demineralization ("white spot" caries) in the difficult-to-clean areas around orthodontic brackets and bands and to reduce damage to enamel during the treatment period are also important properties in this clinical scenario.

? CRITICAL QUESTION

What are the materials and techniques needed to overcome the root canal system environment and create a hermetic seal with endodontic obturation systems?

ROOT CANAL SEALERS

Endodontic sealers are used in conjunction with a solid or semisolid core material to fill voids and to seal root canals

during **obturation**. These sealers, sometimes called *cements*, should fill and promote a close seal between the core and the dentinal walls of the canal, preventing or minimizing leakage, entombing residual microorganisms, and possibly filling inaccessible areas of the root canal system. Sealer selection may influence the outcome of endodontic treatment. However, low levels of evidence are available in the literature, with no randomized clinical trials to corroborate this statement. Traditionally, gutta-percha has been used as the solid core material in combination with a zinc oxide and eugenol (ZOE) or calcium hydroxide cement, or an epoxy-based sealer. Clinical studies have shown predictable results with these conventional root canal sealers. GICs and resin-modified GICs are also used as root canal sealers. These can chemically bond to root canal dentin, but no bond is obtained to gutta-percha.

Recently, new materials have been introduced on the market to improve the seal of the root canal system. These include different types of core materials, the development of low-viscosity methacrylate resin-based sealers, and the incorporation of dentin bonding agents. One system uses conventional cones that are coated with a proprietary resin coating (EndoRez, Ultradent, South Jordan, UT) in combination with a methacrylate-based, dual-cured resin sealer and no dentin-bonding agent. In this case, the endodontic seal is dependent on the penetration of the hydrophilic sealer into the dentinal tubules and lateral canals following removal of the smear layer. Another system, called Resilon (SybronEndo Corporation, Orange, CA) is a thermoplastic composite polycaprolactone-based core material that contains dimethacrylate resin, radiopaque fillers, and glass-ionomer particles. Resilon cones are applied in combination with a methacrylate-based sealer to root dentin treated with self-etching primers. At the present time, obturation systems also include the use of self-etch cementing sealers.

Because of the highly complex environment of the root canal system, it is very difficult to promote adequate bond strength and low microleakage through the formation of a hybrid layer in root canal dentin, even with the latest bonding technologies. The configuration of the cavity or "C-factor" (ratio of bonded to unbonded walls as described in Chapter 13) is an especially important factor. The greater the C-factor, the greater the stress that can develop at any particular biomaterial interface. In turn, this stress can lead to interface breakdown, gap formation, microleakage, and ultimately to such problems as apical infection and caries. In the case of root canals, C-factors can be extremely high, over 1000. Thus, a resin endodontic sealer is subjected to severe polymerization shrinkage stresses during setting, which may cause debonding and gap formation along the periphery of the root canal obturation and adhesive interfaces. Gaps can form between the sealer and dentin wall or in between the solid core material (e.g., gutta-percha) and the sealer. Therefore, root canal obturation inherently requires a number of different materials and involves multiple interfaces, thereby creating a greater challenge than most other applications of adhesive dentistry.

In a long, narrow space such as the root canal, the application of self-etching adhesives or any other bonding system becomes challenging and might not be uniform throughout the entire interface. Therefore, if resin infiltration into demineralized dentin and hybrid formation is not adequate to prevent movement of fluids inward through dentin, over time, the bond will be compromised and the seal will fail. In addition, in bonding systems that contain volatile solvents, evaporation might be hindered. The canal anatomy is not only problematic to adhesive root canal obturation but also for the bonding of prefabricated posts. A further problem is that some irrigating solutions (e.g., sodium hypochlorite) and intracanal medicaments can also have adverse effects on root canal dentin collagen and, consequently, to the longevity of endodontic bonding. Different endodontic treatment protocols are currently under investigation to optimize bonding quality in root canal obturation.

? CRITICAL QUESTION

Why are glass ionomer cements (GICs) not used routinely as pit and fissure sealants?

GLASS IONOMER RESTORATIVES

Glass ionomer cements (GICs) are described in some detail in the discussion of dental cements (see Chapter 14). However, they are also pertinent to this chapter, since they represent a class of materials that exhibit chemical bonding to tooth structure. They consist of a powder, an acid-soluble aluminosilicate glass, and an aqueous solution of polyacrylic acid or an analogous polyacid. Ca^{2+} and aluminum (Al^{3+}) ions released from the powder react with the carboxylic acid (-COOH) groups to form divalent salts, which cross-link and cure the polymeric acid. The same carboxylate groups also interact strongly with surface Ca^{2+} ions in enamel or dentin to effect chemical adhesion to tooth structure. This chemical adhesion may also be beneficial in terms of resistance to hydrolytic degradation. A short polyalkenoic acid pretreatment can be used to clean the tooth surface and to remove the smear layer, exposing collagen fibrils to a depth of about 0.5 to 1 micron. Micromechanical bonding of the glass ionomer components occur by interdiffusion. Most of the current glass ionomer restorative materials also contain resin and are referred to as resin-modified glass ionomers (RMGI). They contain a light-curable acrylic resin that provides for rapid polymerization at and near the surface, together with the same bonding mechanisms as are produced with traditional glass ionomers.

Because of their fluorine-releasing capability, glass ionomer restoratives are especially useful for patients who are at a high risk for carious lesions. For teeth requiring class II restorations, a **sandwich technique** is sometimes used. This technique consists of placing a type II glass ionomer cement in the cervical area of a proximal box or the floor of other tooth preparations and building the remainder of the restoration with a resin-based composite because of its greater strength and durability in occlusal sites. Long-term clinical

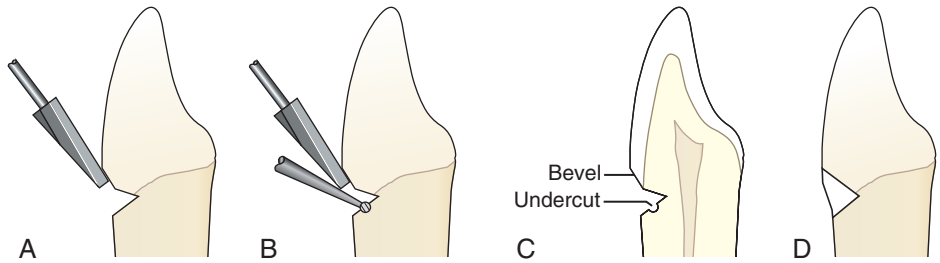


FIGURE 12-8 Glass ionomer restoration of enamel class V lesion. Because of the low curing shrinkage and thermal and mechanical stresses experienced by this material in a relatively sheltered location, clinical retention is vertically 100% despite low bond strengths of about 3 megapascals (MPa). The use of an undercut for retention may not be necessary in most cases.

studies have shown that this technique might not be advantageous for class II restorations in comparison with directly bonding composite resins in posterior restorations.

Glass ionomer cements can be used as esthetic alternatives to amalgam restorations in class V erosion lesions, as shown schematically in Figure 12-8. Although shear bond strengths measured in the laboratory are only approximately 3 MPa, clinical retention is excellent. Until recently, glass ionomers were the only materials that yielded 100% retention rates in class V lesions without mechanical retention or enamel etching, based on certain clinical studies of 3 years or more in duration.

Clinical longevity depends not just on bond strength but also on dislodging forces. Composite restoratives undergo significant polymerization shrinkage, which creates stresses adjacent to the resin–dentin interface that can rupture dentinal bonds in all but the smallest restorations. Because glass ionomers generate low stresses on setting, they are well retained even with their low bond strengths in areas such as class V sites, where occlusal forces and other external forces induce relatively little stress. However, they have also been used with somewhat limited success as pit and fissure sealants. Because of the higher stresses induced by intraoral forces in occlusal areas, a greater degree of dislodgment and fracture occur in these sites.

? CRITICAL QUESTION

How does amalgam bonding to dentin differ from composite bonding to dentin?

AMALGAM BONDING

Although mechanical retention and resistance forms were the hallmark of traditional amalgam preparation design, modern conservative philosophy has stimulated a search for improved methods for retaining and sealing amalgam restorations. Amalgam bonding or bonded amalgam restorations combine the reliability of this traditional material with a dentin bonding system, potentially reducing microleakage and increasing fracture resistance. Mechanical adjuncts, including threaded pins or retentive grooves placed in dentin, have served well for years toward these ends. More recently, bonding agents employing M–R–X-type adhesive monomers have achieved some clinical success. One system uses 4-META (see Figure 12-4). However, the mechanism responsible for bonding amalgam to resin is predominantly mechanical in nature. It is produced during condensation of the amalgam mass into the viscous plastic adhesive layer, thereby producing macroretentive areas that will interlock after polymerization. The results of controlled clinical trials have been mixed, but it is safe to say that amalgam bonding has a place as an adjunct to conventional retentive means if employed so as to maximize sealing and minimize dislodging stresses. In this regard, thicker adhesive layers or interfaces have been shown to promote greater retention under certain conditions. One example is Amalgambond Plus with HPA (high performance additive) powder (Parkell Inc., Edgewood, NY), which contains polymethylmethacrylate fibers to form a thick, viscous layer when mixed with the Amalgambond Plus base and catalyst liquids. Studies such as that of Overton (2005) have shown that amalgam bonding bond strengths range from 6 MPa to 15 MPa.

? CRITICAL QUESTION

Can sealants prevent secondary caries progression when placed over underlying carious enamel or dentin?

PIT AND FISSURE SEALANTS

Various materials and techniques have been advocated for preventing caries in the susceptible pit and fissure areas of posterior teeth, particularly in the pediatric patient or for the patient at a high caries risk in general. The most popular sealant techniques make use of resin systems that can be applied to the occlusal surfaces of teeth. The objective of sealant use is for the resin to penetrate into the pits and fissures and to seal these areas against oral bacteria and debris. A cross-section of a tooth to which a pit and fissure sealant has been applied is shown in Figure 12-9.

Several types of resins, both filled and unfilled, have been employed as pit and fissure sealants. These resin systems include those based on cyanoacrylates, UDMA, and bis-GMA. The commercially available products have been based on either the UDMA or bis-GMA monomers (see Figure 12-4) that may be polymerized by either the amine-benzoyl peroxide chemical activation-initiation system or by light activation, as discussed in Chapter 13. The unfilled resins are available as colorless or tinted transparent materials. The

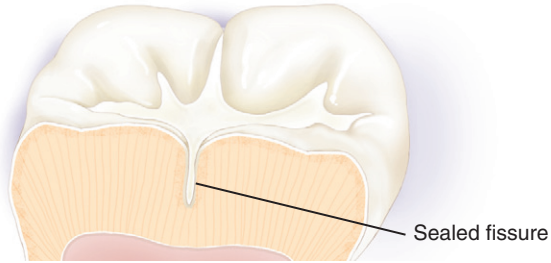


FIGURE 12-9 Schematic of a tooth cross-section, illustrating penetration of a sealant into an occlusal fissure.

filled resins are opaque and available either as tooth-colored or white materials.

The success of the sealant technique is highly dependent on obtaining and maintaining an intimate adaptation of the sealant to the tooth surface. Therefore, the sealants must be of relatively low viscosity so that they will wet the tooth and flow readily into the depths of the pits and fissures. To enhance wetting and mechanical retention of the sealant, the tooth surface is first conditioned by etching with acid, as described earlier. The physical properties of the sealants are closer to those of unfilled direct resins than to those of resin-based composites.

The reduction in occlusal caries resulting from the careful use of pit and fissure sealants has been impressive. Consequently, the American Dental Association, the American Academy of Pediatric Dentistry, the American Society of Dentistry for Children, and the American Association of Public Health Dentistry have all endorsed the use of sealants as an effective therapy. Clinical studies have shown that the failure frequency of sealants is approximately 5% per year after one single application of the sealant. In one report, at the end of 10 years, 78% of first permanent molars were free of caries when a single application of sealant had been placed compared with only 31% of caries-free teeth in the unsealed matched pairs. Mertz-Fairhurst et al. (1998) reported even more dramatic results in a study of sealed class I composite restorations where carious dentin was not removed. They showed that the lesions did not progress over a period of 10 years as long as the sealants remained intact.

If doubt exists about whether the pit or fissure is free from caries or not, it is still justified to place a sealant. Clinical trials in which sealants were intentionally placed in pits and fissures that were diagnosed as having caries have shown that as long as a sealant is well retained, no caries progression will occur. If a dentist feels uncomfortable about sealing in a potential carious lesion and believes that a visual inspection of the potential lesion is required, another conservative approach can be taken that consists of a minimal cavity preparation and the placement of an enamel–dentin bonded composite restoration combined with a sealant application. With such an approach, most of the occlusal surface is sealed. This restoration is called a **preventive-resin restoration (PRR)**. The PRR treatment has exhibited a success rate of 75% after 9 years, a remarkably high success rate, compared with traditional amalgam treatment.

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One of the pioneers in surface phenomena discusses parameters that influence wetting. Zisman was a leader in the use of contact angle measurements to screen the potential wetting of adhesives to selected adherends.

CHAPTER 13

Resin-Based Composites

OUTLINE

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Repair of Composites

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KEY TERMS

Activation—Process by which sufficient energy is provided to induce an initiator to generate free radicals and cause polymerization to begin.

Activator—Source of energy used to activate an initiator and produce free radicals. Three energy sources are currently used to dissociate an initiator into free radicals: (1) heat, which supplies thermal energy; (2) an electron-donating chemical such as a tertiary amine, which forms a complex and reduces the necessary thermal energy to that available at ambient temperature; and (3) visible light, which supplies energy for photoinitiation in the presence of a photosensitizer such as camphorquinone (CQ).

C-factor—Configuration factor. This represents the ratio between the bonded surface area of a resin-based composite restoration to the nonbonded or free surface area. The greater the C-factor, the greater the stress that develops at the restoration margin, which can lead to gap formation, marginal breakdown and leakage, and other problems, such as secondary caries.

Chemically activated resin—Resin system consisting of two pastes—(one containing an initiator (e.g., benzoyl peroxide) and the other an activator (e.g., an aromatic tertiary amine)—which, when mixed together, release free radicals that initiate polymerization.

Chemically cured composite—Particle-reinforced resin that is polymerized through a chemical activation process wherein two components are blended together just prior to placement of the composite. Also known as self-cure composite. See *chemically activated resin*.

Composite—In materials science, a solid formed from two or more distinct phases (e.g., filler particles dispersed in a polymer matrix) that have been combined to produce properties superior to or intermediate to those of the individual constituents; also a term used in dentistry to describe a dental composite or resin-based composite.

Coupling agent—A bonding agent applied to the surfaces of reinforcing particles (filler) to ensure that they are chemically bonded to the resin matrix. Organo-silane compounds are the more common class of dental composite coupling agents.

Degree of conversion (DC)—Percentage of carbon-carbon double bonds (–C=C–) converted to single bonds (–C—C–) during curing to form a polymeric resin. Also known as degree of cure and degree of monomer-to-polymer conversion.

Dental composite—Highly cross-linked polymeric materials reinforced by a dispersion of amorphous silica, glass, crystalline, mineral, or organic resin filler particles and/or short fibers bonded to the matrix by a coupling agent.

Depth of cure—Depth or thickness of a light-cured resin that can be converted from a monomer to a polymer when exposed to a light source under a specific set of conditions.

Dual-cure resin—Dental composite that contains both chemically activated and light-activated components to initiate polymerization and potentially overcome the limitations of either the chemical- or light-cure systems when used alone.

Estrogenicity—Potential of synthetic chemicals with a binding affinity for estrogen receptors to cause reproductive alterations. Bisphenol-A, a precursor of certain monomers such as *bis*-GMA, is a known estrogenic compound that is considered to have possible effects on fetal and infant brain development and behavior.

Filler—Inorganic, glass, and/or organic-resin particles that are dispersed in a resin matrix to increase rigidity, strength, and wear resistance, to decrease thermal expansion, due to water sorption, and reduce polymerization shrinkage.

Flowable composite—Hybrid composite with reduced filler level and a narrower particle size distribution that increases flow and promotes intimate adaptation to prepared tooth surfaces.

Gel point/gelation—The point in the polymerization reaction where sufficient cross-links have formed to produce a rigid, glassy state in which internal flow among the developing polymer chains has stopped. All but highly local molecular motion has stopped. After the gel point, stresses cannot be relieved but instead continue to increase and concentrate near the bonded interfaces. Thus, reducing the polymerization rate provides more time for adjacent polymer chain segments to slip among themselves, rearrange to lower energy configurations, and relieve developing stresses before the gel point is reached.

Hybrid composite—A particle-filled resin that contains a graded blend of two or more size ranges of filler particles to achieve an optimal balance among the following properties: ease of manipulation, strength, modulus (relative rigidity), polymerization shrinkage, wear resistance, appearance, and polishability. *Nanohybrids* contain at least one dispersed filler with particle sizes of 100 nm or less (see *nanofilled*, below).

Inhibitor—A chemical added to resin systems to provide increased working time and extended storage life by minimizing spontaneous polymerization, usually through free-radical scavenging mechanisms.

Initiator—A free radical–forming chemical used to start the polymerization reaction. It enters into the chemical reaction and becomes part of the final polymer compound; thus it is not a catalyst although often incorrectly labeled as such.

Lute/luting/cementing agent—Viscous material placed between two components, such as tooth structure and a restoration, that hardens to bind the two components together primarily through micromechanical interlocking, similar to the way mortar holds bricks together. Resin cements (Chapter 14) are luting agents, although some also provide chemical bonding

Light-cured/photocured/photoinitiated composite—Particle-filled resin consisting of a single paste that becomes polymerized through the use of a photosensitive initiator system (typically camphorquinone and an amine) and a light-source activator (typically visible blue light). See also *activator* and *initiator*.

Matrix—A plastic resin material that forms a continuous phase upon curing and binds the reinforcing filler particles.

Microfilled composite—Composite reinforced with colloidal silica filler particles, approximately 40 nm in size, which can be polished to a highly smooth surface. Microfillers are nondiscrete nanometer-sized particles that are agglomerated into large three-dimensional chainlike networks that drastically increase monomer viscosity.

Nanofilled composite/nanocomposite—Composites with the same-size particles as microfilled composites, but the particles have been surface-treated *before* they have agglomerated into large three-dimensional chainlike networks. Instead, they form either isolated and/or loosely bound spheroidal agglomerates (called clusters) of primary nanoparticles. The surface treatment allows an increase in filler loading by reducing the viscosity that develops when the particles are added to the monomer. Cluster size may exceed 100 nm. All of the nanocomposites currently being marketed have average primary particle sizes in the 40-nm range and so are of the same size as microfilled composites.

Ormocer—Ormocer is an acronym for organically modified ceramics, which are inorganic-organic copolymers. The organic, reactive monomers are bound to an inorganic Si-O-Si network to reinforce the resin, reduce polymerization shrinkage, and improve abrasion resistance.

Oxygen-inhibited layer—The thin surface region of a polymerized resin containing unreacted methacrylate groups arising from dissolved oxygen, which acts to inhibit the free-radical polymerization curing reaction; also known as the air-inhibited layer.

Packable composite—A hybrid resin composite designed for use in posterior areas where a stiffer consistency facilitates condensation into a cavity form in a manner similar to that used for lathe-cut amalgams, also known as condensable composite.

Polyhedral oligomeric silsesquioxane (POSS)—A molecular-sized hybrid, organic-inorganic resin containing 12-sided silicate cage structures that impart nanoparticle-like reinforcement. See also Figure 13-27.

Silorane—A tetrafunctional epoxy siloxane monomer that cures via ring-opening polymerization. When the rings open, they lengthen and occupy more space; the resulting expansion offsets a portion of the polymerization shrinkage. See also Figure 13-26.

TERMINOLOGY

Dental resin-based composites are structures composed of three major components: a highly cross-linked polymeric ***matrix*** reinforced by a dispersion of glass, mineral, or resin ***filler*** particles and/or short fibers bound to the matrix by ***coupling*** **agents**. Such resins are used to restore and replace dental tissue lost through disease or trauma and to **lute** and cement crowns and veneers and other indirectly made or prefabricated dental devices.

The gold standard of reference for these materials is amalgam. However, amalgam has its own disadvantages, such as (1) poor esthetics, (2) unfounded concerns about health hazards from the leakage of mercury, and (3) waste disposal concerns. Because resin-based composites can be made to match the natural appearance of teeth, they have become the most popular of the esthetic or tooth-colored filling materials and are widely used for a variety of dental applications.

Another key advantage of resin materials is that they can be made in a range of consistencies, from highly fluid to rigid pastes, which allows them to be conveniently manipulated and molded, to a custom-made form and then converted through a polymerization *curing* reaction to a hard, strong, attractive, and durable solid.

HISTORY

There have been remarkable developments in filler, bonding, and curing technologies in esthetic restorative materials over the past 55 years, as shown in Figure 13-1. During the first half of the twentieth century, silicates were the tooth-colored material of choice for cavity restoration. Silicates release fluoride and are excellent for preventing caries, but they are currently used almost exclusively for deciduous teeth because they become severely eroded within a few years (see Chapter 14). Acrylic resins, similar to the materials used to make dentures and custom impression trays (polymethylmethacrylate [PMMA], see Chapter 20), soon replaced silicates because of their tooth-like appearance, insolubility in oral fluids, ease of manipulation, and low cost. Unfortunately, these acrylic resins had relatively poor wear resistance and tended to shrink severely during curing, which caused them to pull away from the cavity walls, thereby producing crevices or gaps that facilitiate leakage within these gap. Excessive thermal expansion and contraction caused further stresses to develop at the cavity margins when hot or cold beverages and foods were consumed.

These problems were reduced somewhat by the addition of quartz powder particles to form a composite structure. The filler occupies space, but it does not take part in the setting reaction. In addition, commonly used fillers have an extremely low coefficient of thermal expansion, approaching that of tooth structure, thus greatly reducing thermal expansion and contraction. However, these early PMMA-based composites were not very successful, in part because the filler particles simply reduced the volume of polymer resin without being bonded (coupled) to the resin. Thus defects developed between the particles and the surrounding resin, which led to leakage, staining, and poor wear resistance.

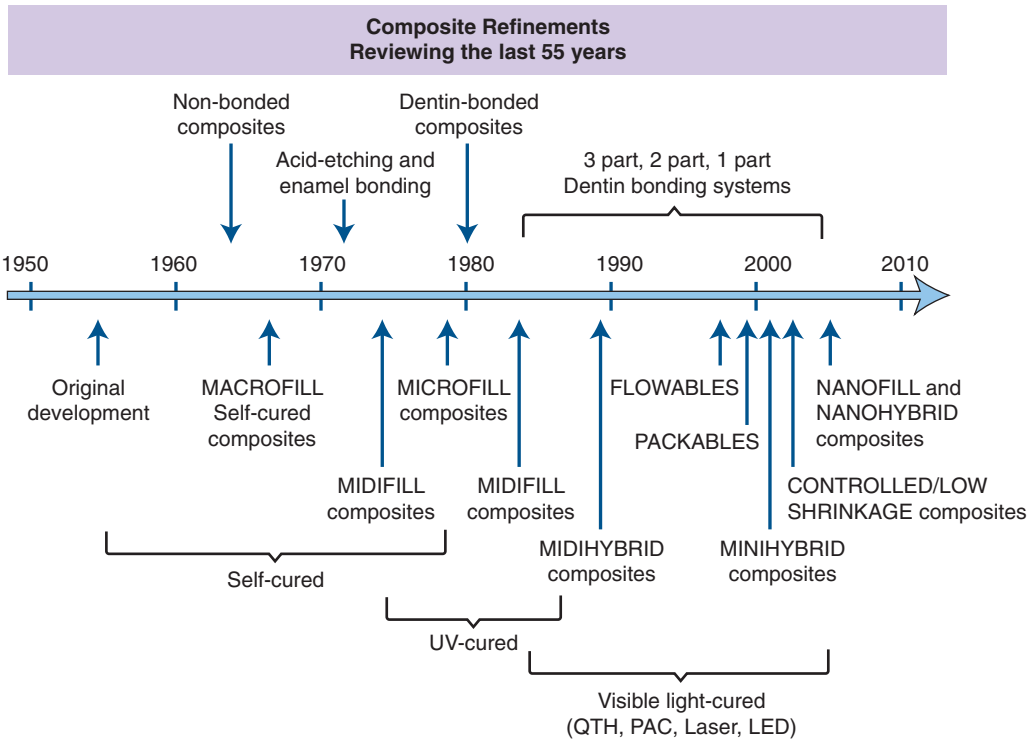


FIGURE 13-1 Chronology of dental composite developments in monomer, filler, bonding, and curing technologies. (Adapted from Figure 5 in Bayne SC: Dental biomaterials: Where are we and where are we going? *J Dent Educ* 69[5]:571–585 2005.)

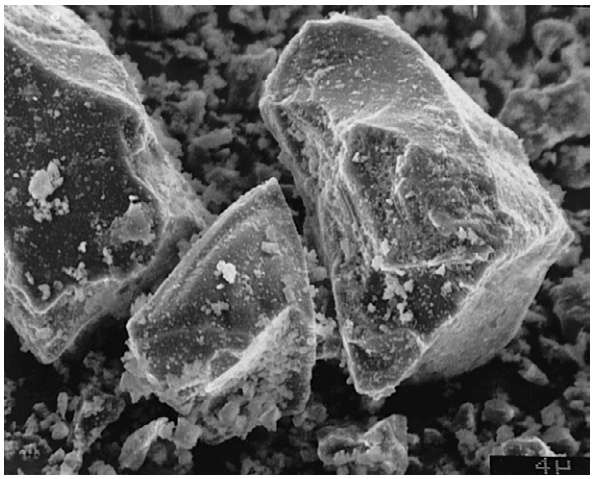


FIGURE 13-2 Ground quartz filler particles with diameters of about 1 to 30 µm. Such relatively large fillers were used in early formulations of traditional composites. The smaller particles seen in the background contribute to a broad particle size distribution. (Courtesy of K-J.M. Söderholm.)

In 1962, Bowen developed a new type of composite material that largely overcame these problems. Bowen's main innovations were bisphenol-A glycidyl dimethacrylate (*bis*-GMA), a monomer that forms a cross-linked matrix that is highly durable (see Chapter 6), and a surface treatment utilizing an organic silane compound called a *coupling agent* to bond the filler particles to the resin matrix. Current tooth–colored restorative materials continue to use this technology, but many further innovations have been introduced since 1962.

Many of these advances have occurred through developments in the filler component. The filler has evolved to ever smaller sizes, mainly in order to improve appearance and polishability. Barium and other specialty glass and inorganic mineral fillers have been developed to impart radiopacity, enhance manipulation and handling, offset curing shrinkage, and improve mechanical properties. In the 1970s a category now known as traditional composites (also known as conventional or macrofilled composites) was developed; this contained very large particles of ground amorphous silica and quartz (Figure 13-2), which imparted significant improvements in mechanical properties, water sorption, polymerization shrinkage, and thermal expansion compared with unfilled acrylic. However, these composites suffered from roughening of the surface as a result of the selective abrasion of the softer resin matrix surrounding the harder filler particles. To improve surface smoothness and retain or improve the physical and mechanical properties of traditional composites, small-particle–filled composites were developed, using inorganic fillers ground to a size range of about 0.5 to 3 µm but with a broad size distribution (Figure 13-3), allowing a higher filler loading (80% to 90% by weight and 65% to 77% by volume). This resulted not only in smoother surfaces but also greater wear resistance and some decrease in curing shrinkage. Today, further advances in the filler component have resulted in **microfilled composites** and

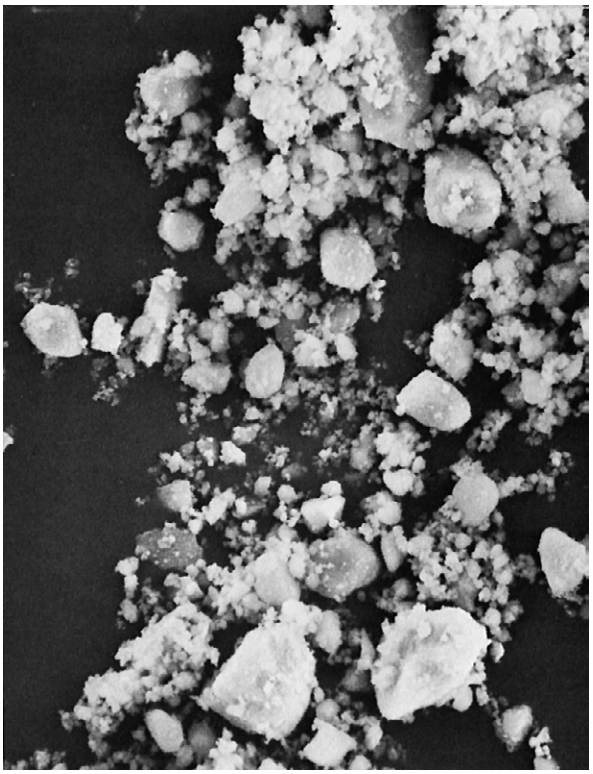


FIGURE 13-3 Typical particles of a small-particle-filled composite, with sizes in the range of 0.1 to 10 µm. (Courtesy of E.A. Glasspoole and R.L. Erickson.)

nanocomposites, **hybrid composites**, and packable and **flowable composites**, just to name a few.

Other advances involved the monomer component, providing better chemical and mechanical properties, reduced shrinkage, color and storage stability, biocompatibility, and other features. Today the monomer system is highly complex with the use of a variety of monomers and monomer blends of various molecular weights and functions. Many added innovations were later introduced in both the filler/reinforcing systems and the resin matrix-forming monomers.

Finally, advances in curing technology have yielded **light-cured** systems that make it possible to harden resins on demand as well as to improve working time and ease of manipulation. Initially an ultraviolet (UV) curing system was used, but it had several drawbacks and was soon replaced by visible blue–light curing systems, which require less than 1 minute of exposure, and they have many other advantages. These advances were soon followed by further developments in curing-lamp technology as well as in clinical techniques and training aids to optimize the advantages that light-cured resins offer.

The history and achievements in **dental composites** are outlined in Figure 13-1 and are further discussed in detail in this chapter.

APPLICATIONS

Dental applications for resin-based composites include cavity and crown restoration materials, adhesive bonding agents, pit

and fissure sealants, endodontic sealants, bonding of ceramic veneers, and cementation for crowns, bridges, and other fixed prostheses.

CLASSIFICATION

A useful classification system for composites is one based on filler particle size and size distribution, as shown in Table 13-1. Subgroups and overlaps exist, particularly for the hybrid category, which combines filler from either the small or the traditional category with micro- and nanofillers. Any resin with elongated fillers (fibers, "whiskers," filaments), with spheroidal particle fillers or fillers from two or more size ranges can in principle be considered a hybrid. Thus a single classification of hybrid composite is not very meaningful. Many modern dental composites have particle sizes less than 0.5 to 1.0 μm in combination with 10% or more by weight of micro- or nanofiller to adjust the paste to a desired viscosity/rheology so as to provide clinically useful manipulation and handling characteristics. Filler technology is discussed in detail below.

COMPOSITION AND FUNCTION

Dental composites are made up of three major components: a highly cross-linked polymeric resin *matrix* reinforced by a dispersion of glass, silica, crystalline, metal oxide or resin-reinforcing *filler* particles or their combinations and/or short fibers, which are bonded to the matrix by silane *coupling agents*. In addition, dental composites contain a number of other components, including an **activator-initiator** system that is required to convert the resin paste from a soft, moldable filling material to a hard, durable restoration. Pigments help to match the color of tooth structure. Ultraviolet (UV) absorbers and other additives improve color stability, and polymerization **inhibitors** extend storage life and provide increased working time for **chemically activated resins**. Other components may be included to enhance performance, appearance, and durability.

CRITICAL QUESTIONS

What are the three essential components of resin composite materials?

What are the potential uses of composites in dentistry?

What roles do coupling agents, fillers, *bis*-GMA, and other high-molecular-weight dimethacrylate monomers play in the function and performance of dental resins?

MATRIX

The resin matrix in most dental composites is based on a blend of aromatic and/or aliphatic *dimethacrylate* monomers such as *bis*-GMA (see Figure 7-16) and urethane dimethacrylate (UDMA, Figure 7-18) to form highly cross-linked, strong, rigid, and durable polymer structures (see Figures 7-3 and 13-16). This matrix forms a continuous phase in which the reinforcing filler is dispersed. Because of the large molecular volume of these monomers, polymerization shrinkage can be as low as 0.9% (average of 1.5% compared with a range

TABLE 13-1 Classification of Resin-Based Composites and Indications for Use

Class of Composite	Particle Size	Clinical Use
Traditional (large particle)	1- to 50-μm glass or silica	High-stress areas
Hybrid (large particle)	(1) 1- to 20-μm glass (2) 40-nm silica	High-stress areas requiring improved polishability (Classes I, II, III, IV)
Hybrid (midfilled)	(1) 0.1- to 10-μm glass (2) 40-nm silica	High-stress areas requiring improved polishability (Classes III, IV)
Hybrid (minifilled/ SPF*)	(1) 0.1- to 2-μm glass (2) 40-nm silica	Moderate-stress areas requiring optimal polishability (Classes III, IV)
Nanohybrid	(1) 0.1- to 2-μm glass or resin microparticles (2) ≤100-nm nanoparticles	Moderate-stress areas requiring optimal Polishability (Classes III, IV)
Packable hybrid	Midfilled/minifilled hybrid, but with lower filler fraction	Situations where improved condensability is needed (Classes I, II)
Flowable hybrid	Midfilled hybrid with finer particle size distribution	Situations where improved flow is needed and/or where access is difficult (Class II)
Homogeneous microfilled	40-nm silica	Low-stress and subgingival areas that require a high luster and polish
Heterogeneous microfilled	(1) 40-nm silica (2) Prepolymerized resin particles containing 40-nm silica	Low-stress and subgingival areas where reduced shrinkage is essential
Nanofilled composites	<100-nm silica or zirconia Homogeneous independent nanoparticles or nanoclusters	Anterior and noncontact posterior areas

*SPF, small particle–filled.

of 2 to 3% for most composites) when combined with inorganic particulate fillers at levels of up to 88% by weight. However, UDMA and *bis*-GMA are highly viscous (800,000 centipoise, similar to honey on a cold day) and are difficult to blend and manipulate. Thus, it is necessary to use varying proportions of lower-molecular-weight highly fluid monomers such as triethylene glycol dimethacrylate (TEGDMA, 5 to 30 centipoise, Figure 7-17) and other lower-molecular-weight dimethacrylates to blend with and dilute the viscous components to attain resin pastes sufficiently fluid for clinical manipulation and for incorporating enough filler to reinforce the cured resin. For example, a blend of 75% *bis*-GMA and 25% TEGDMA by weight has a viscosity of 4300 centipoise, whereas the viscosity of a 50% *bis*-GMA/50% TEGDMA blend is 200 centipoise (similar to thin syrup). Unfortunately, these smaller, diluent monomers undergo greater polymerization shrinkage, partially offsetting the advantage of using large monomers such as *bis*-GMA. Generally the greater the proportion of these "diluting" monomers, the greater the polymerization shrinkage and the greater the risk of eventual leakage in marginal gaps and the problems that may result.

? CRITICAL QUESTION

What are the problems that result from shrinkage and cure-induced stress during the polymerization of restorative resins?

FILLER

Various transparent mineral fillers are employed to strengthen and reinforce composites as well as to reduce curing shrinkage and thermal expansion (generally between 30% to 70% by volume or 50% to 85% by weight of a composite). These include so-called "soft glass" and borosilicate "hard glass", fused quartz, aluminum silicate, lithium aluminum silicate (beta-eucryptite, which has a negative coefficient of thermal expansion), ytterbium fluoride, and barium (Ba), strontium (Sr), zirconium (Zr), and zinc glasses. The latter five types of fillers impart radiopacity because of their heavy metal atoms.

Quartz had been used extensively as a filler in the early versions of dental composites. It has the advantage of being chemically inert but it is also very hard, making it abrasive to opposing teeth or restorations as well as difficult to grind into very fine particles; thus, it is also difficult to polish. So-called amorphous silica has the same composition and refractive index as quartz; however, it is not crystalline and not as hard, thus, greatly reducing the abrasiveness of the composite surface structure and improving its polishability.

For acceptable esthetics, the translucency of a composite restoration must be similar to that of tooth structure. Thus, the index of refraction of the filler must closely match that of the resin. For *bis*-GMA and TEGDMA, the refractive indices are approximately 1.55 and 1.46, respectively, and a mixture of the two components in equal proportions by weight yields a refractive index of approximately 1.50. Most of the glasses and quartz used for fillers have refractive indices of approximately 1.50, which is adequate for sufficient translucency.

Function of Fillers

Fillers can provide the following benefits:

- **Reinforcement**. Increased filler loading generally increases physical and mechanical properties that determine clinical performance and durability, such as compressive strength, tensile strength, modulus of elasticity (i.e., stiffness or rigidity), and toughness. As the volume fraction of filler approaches approximately 70%, abrasion and fracture resistance are raised to levels approaching those of tooth tissue, thereby increasing both clinical performance and durability.
- **Reduction of polymerization shrinkage/contraction.** Increased filler loading reduces curing shrinkage in proportion to filler volume fraction. Although shrinkage varies from one commercial composite to another, it typically ranges from slightly less than 1% up to about 4% by volume.
- **Reduction in thermal expansion and contraction.** Increased filler loading decreases the overall coefficient of thermal expansion of the composite because glass and ceramic fillers thermally expand and contract less than do polymers. As the overall expansion coefficient decreases with filler loading and approaches that of tooth tissue, less interfacial stress is produced because of differential volumetric changes while an individual consumes hot and cold foods and beverages.
- **Control of workability/viscosity.** Fluid liquid monomer + filler → a paste. The more filler, the thicker is the paste. Filler loading, filler size, and the range of particle sizes and shapes all affect markedly the consistency of a composite paste, which in turn strongly affects clinical manipulation and handling properties, such as ease of mixing and sculpting, tackiness, and the tendency to either hold a shape or to minimize slumping. Consistency and handling are more than just convenience-related properties. They determine the ease of operation, the skill and time required, and also how reliably a cavity can be restored free of errors and with the proper interproximal contact, occlusal anatomy, smoothness, and appearance.
- **Decreased water sorption**. Increased filler loading decreases water sorption. Absorbed water softens the resin and makes it more prone to abrasive wear and staining.
- **Imparting radiopacity**. Resins are inherently radiolucent. However, leaking margins, secondary caries, poor proximal contacts, wear of proximal surfaces, and other problems cannot be detected unless adequate radiographic contrast can be achieved. Thus, radiopacity is an important property. Radiopacity is most often imparted by adding certain glass filler particles containing heavy metal atoms, such as Ba, Sr, or Zn, and other heavy-metal/heavy-atom compounds such as YbF_3, which strongly absorb x-rays. For optimal diagnostic contrast, the restoration should have a

radiopacity approximately equal to that of enamel, which is about twice that of dentin. A wide range of radiopacity values have been considered to be adequate, but exceeding the radiopacity of enamel by a large degree will have the effect of obscuring radiolucent areas caused by gap formation or secondary caries.

The most commonly used glass filler is barium (Ba) glass. Although glass fillers containing metals of a high atomic number provide radiopacity, they are not as inert as quartz and amorphous silica and are slowly leached and weakened in acidic liquids such as citrus juices, high pH solutions, and other oral fluids. The glass filler is also attacked over time by caries-protective acidulated phosphate fluoride solutions or gels. Because of differences in the composition of saliva among patients, it is difficult to predict the clinical effects of exposure to saliva. However, the implication is that glass-filled composites will gradually become more susceptible to abrasive wear and hence they will have a shorter functional lifetime compared with silica-reinforced resins.

Most important properties are improved by increased filler loading. A *distribution* of particle sizes is used to maximize loading (volume fraction of filler). If particle size is uniform, no matter how tightly packed the particles are, spaces will exist among them, as illustrated by the example of the void spaces in a box filled with spheres of the same size. The maximal theoretical packing fraction for close-packed spherical structures of uniform-size is approximately 74% by volume, as shown in Figure 13-7. However, if smaller particles are inserted among the larger spheres, the void space can be reduced. By extending this process, a continuous distribution of progressively smaller particles can yield maximal filler loading.

Another advantage of using small particles is that they improve esthetics (appearance) and smoothness to the tongue (polishability). The traditional inorganic filler particles had average diameters of about 8 to 40 μm. Currently, small particles range from 0.005 μm to 2 μm. Particles larger than the wavelength of visible light cause light scattering. Scattering increases opacity and produces a visibly rough texture when the particles are exposed at the surface. A roughened surface also tends to accumulate stains and plaque. Curing produces an initially smooth surface, but finishing operations remove the resin matrix from the perimeter of filler particles, exposing particles that protrude from the surface. Oral wear mechanisms complement this process, such that the ultimate smoothness that can be maintained is highly dependent on particle size.

However, the smaller the filler particle size, the higher the surface-to-volume ratio available to form polar or hydrogen bonds with monomer molecules to inhibit their flow and increase viscosity (resistance to mixing and manipulation) thus, the less filler that can be added. The proportion of filler is limited to about 80% by volume. Therefore, there is always a tradeoff among the requirements for workability, durability, and esthetics. The clinician's challenge is to make an informed judgment concerning the claims for the many products offered and to select one that is well suited to a particular clinical application.

CLASSIFICATIONS OF FILLED RESINS

Two general classifications are used to categorize resin-based composites, one based on the size and combination of sizes of the reinforcing filler particles and another is based on the manipulation characteristics of the filled monomer paste.

Classification by Filler Particle Size

The classification by filler particle sizes is shown in Table 13-2.

Small (Fine) Particle Composites. Small-particle composites have mean particle diameters between 0.1 and 10 μm (minifiller and midifiller). These composites, while more polishable than traditional macrofilled composites (i.e., 10 to 100 μm), cannot be polished to a high gloss. However, filler loadings are as high as or higher (77% to 88%) than those of macrofilled composites, which provides a high degree of hardness and strength but also brittleness. Its excellent balance among polishability, appearance, and durability make this category suitable for general anterior use.

Microfilled Composites. Microfilled composites are agglomerates of 0.01- to 0.1-μm inorganic colloidal silica particles embedded in 5- to 50-μm resin filler particles. The problems of surface roughening and low translucency associated with traditional and small-particle composites can be overcome through the use of colloidal silica particles such as the *inorganic* filler component, with a mean particle diameter about one tenth of the wavelength of visible light (i.e., about 40 nm). Such a filler is made by a pyrolytic precipitation process where a silicon compound such as $SiCl_4$ is burned in an oxygen/hydrogen atmosphere to form macromolecular chains of colloidal silica (see Figure 13-4) resulting in *amorphous silica* (colloidal, noncrystalline SiO_2), which produces highly polishable esthetic composite restorations.

However, these particles, because of their extremely small size, have extremely large surface areas ranging from 50 to 400 m^2 per gram. In addition, the pyrolytic process results in particle "agglomeration" into long, molecular-scale chains (see Figures 13-5 and 13-6). These nondiscrete three-dimensional chainlike networks drastically increase monomer

TABLE 13-2 Classification of Reinforcing Filler Particles by Size Range

Class of Filler	Particle size
Macrofillers	10 to 100 μm
Small/fine fillers	0.1 to 10 μm
Midfillers	1 to 10 μm
Minifillers	0.1 to 1 μm
Microfillers	0.01 to 0.1 μm (agglomerated)
Nanofillers	0.005 to 0.1 μm*

*5 to 100 nm, nonagglomerated.

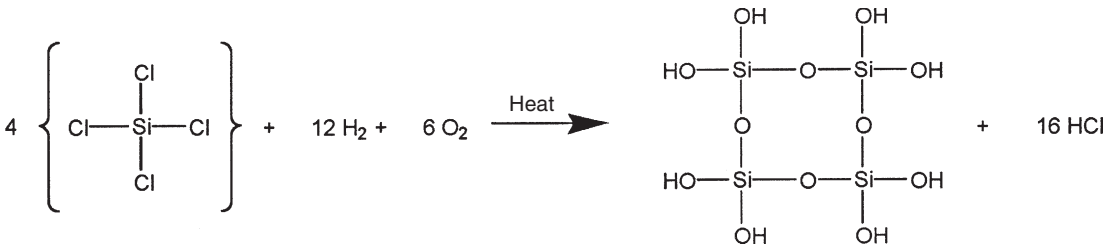


FIGURE 13-4 Pyrogenic reaction showing the initial formation of fumed silica particles in the 40-nm size range, as used in microfill resins. (Courtesy of K-J.M. Söderholm.)

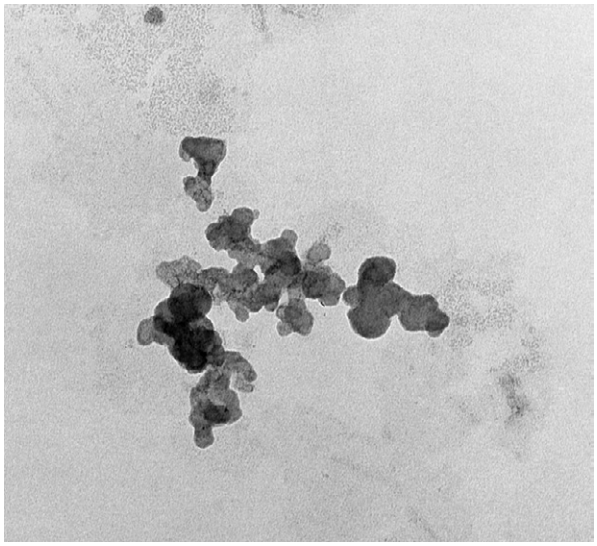


FIGURE 13-5 Transmission electron microscope image of fumed silica particles produced by the pyrogenic reaction shown in Figure 13-4. The particle diameters average approximately 0.04 µm or 40 nm. (Courtesy of K-J.M. Söderholm.)

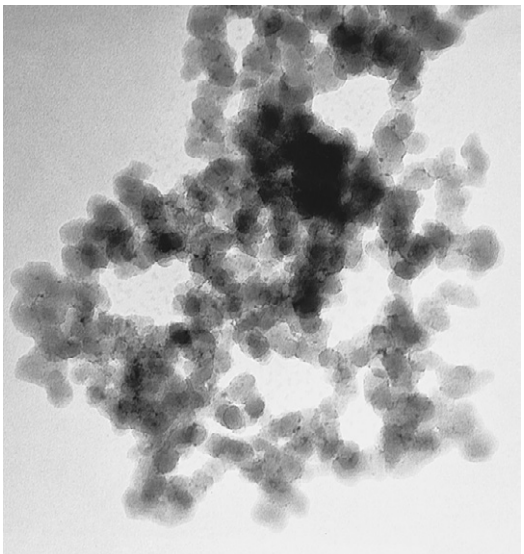


FIGURE 13-6 The pyrogenic silica used in microfilled composites has a very large total surface area because of its extremely small average particle size of about 0.04 µm/40 nm. These particles agglomerate and form long chains, as seen in this transmission electron micrograph. The chains of silica particles act similarly to resin polymer chains, as described in Chapter 6, and dramatically increase the viscosity of the monomer. (Courtesy of K-J.M. Söderholm.)

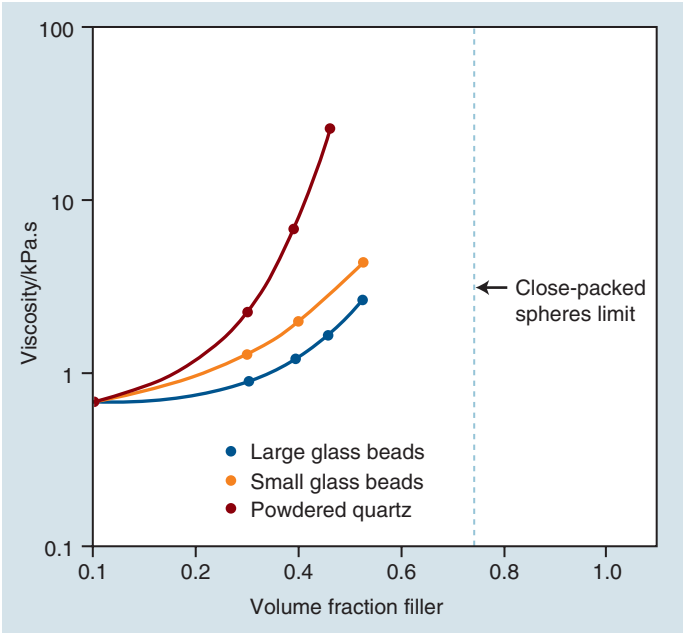


FIGURE 13-7 The effect of filler specific surface area on the viscosity (log scale) of the uncured resin matrix. The smaller the particle, the larger is the surface area and the greater the viscosity buildup. (Adapted from Darvell BW: *Materials Science for Dentistry*, ed 9, Woodhead Publishing Ltd, Cambridge, UK, 2009.)

viscosity and make clinical manipulation difficult. Filler incorporation at high enough loading to adequately reinforce the resin is also difficult with these fillers. In fact, when incorporated directly in "homogeneous" microfill composites, only about 2% by weight produces a stiff paste that is much too viscous for clinical manipulation (see Figure 13-7). However, in the manufacturing process, a resin with a very high loading (60% to 70% by weight, about 50% by volume) of silane-treated colloidal silica microfiller can be added to the monomer at a slightly elevated temperature to lower its viscosity. This is cured and then pulverized to make a filled resin powder consisting of 5- to 50-µm particles. This amorphous colloidal silica-containing resin is then used as an "organic" filler ("heterogeneous" microfill composite), which is incorporated into the monomer with additional silane-treated colloidal silica to form a workable paste. In this way the overall *inorganic* filler content of the final, cured composite is increased to about 50% by weight. However, if the composite particles are counted as filler particles, the filler content is closer to 80% by weight (approximately 60% by volume).

Thus, the *resin* particles are *themselves* composites that contain 0.01 to 0.1 μm of amorphous silica (see Figure 13-6). A diagram representing the preparation of the filler in microfilled resins of this type is shown in Figure 13-8.

One should note that because these composite particles do not shrink when the composite is cured, a microfilled composite, despite having a much lower inorganic filler loading than the traditional or small-particle composites, will not shrink as much as expected based on the total resin volume. However, a major shortcoming of these materials is that the bond between the composite particles and the clinically cured matrix is relatively weak, facilitating wear by a chipping mechanism (Figure 13-9). Because of this deficiency, with some notable exceptions, microfilled composites are not generally suitable for use as stress-bearing surfaces.

Whereas microfilled composites are among the more highly polishable restorative composites, their physical and mechanical properties are generally inferior to those of traditional composites (Table 13-3). This is to be expected, because 40% to 80% by volume of the restorative material is made up of resin, resulting in greater water sorption, a higher coefficient of thermal expansion, and decreased elastic modulus. In addition, the weak bond of the prepolymerized particles to the clinically cured resin matrix results in decreased tensile strength, similar to that of composites with nonsilanized filler particles. In addition, in the longer term, if microfilled composites are placed in wear-prone areas, they eventually break down and wear at a rate too fast for acceptable clinical performance. If placed in areas of proximal contact, anterior tooth "drifting" may occur. The wear process has also been related to fracture propagation around the poorly bonded "organic" filler particles. Thus, diamond burs, rather than fluted tungsten-carbide burs, are recommended for trimming microfilled composites so as to minimize the risk of chipping. Microfilled composites are the resins of choice for restoring teeth with carious lesions in smooth surfaces (classes III and V) but not in stress-bearing situations (classes II and IV).

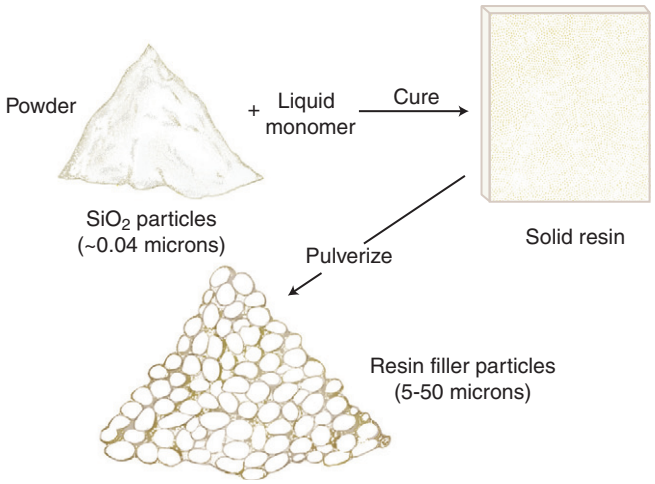


FIGURE 13-8 Preparation of resin filler particles for use in microfilled composites. The filler particles in a microfilled composite consist of pulverized "composite filler particles" dispersed in a cured resin matrix. Pyrogenic colloidal silica particles of about 0.04 μm (about 40 nm) are incorporated into both the precured resin filler particles and the curable monomer, with the precured resin containing a substantially higher concentration. (Modified from P. Lambrechts: *Basic Properties of Dental Composites and Their Impact on Clinical Performance*. Thesis. Leuven, Belgium, Katholieke University, 1983.)

? CRITICAL QUESTIONS

Why is the polymerization shrinkage of microfilled composites is not higher than that of conventional composites even though the inorganic filler loading in microfills is substantially lower?

Which properties of microfilled resins are generally inferior to those of other resin-based composite materials, and what are the clinical implications of these deficiencies?

What features of microfilled resins make them the material of choice for certain types of restorations?

Which types of restorations are produced ideally from microfilled composites?

What advantages are conferred by combining filler particles of two or more size ranges?

What are the clinical consequences of this filler combination?

Hybrid Composites. As the name implies, hybrid composites are formulated with mixed filler systems containing both microfine (0.01 to 0.1 μm) and fine (0.1 to 10 μm) particle fillers in an effort to obtain even better surface smoothness than that provided by the small-particle composites while still maintaining the desirable mechanical properties of the latter. Thus, they are a general utility class of composite that are also suitable for restoring certain high-stress-sites where esthetic considerations dominate—for example, incisal edges and small non-contact occlusal cavities. They are widely used for anterior restorations, including class IV sites (Figures 13-10 and 13-11).

Most modern hybrid fillers consist of colloidal silica and ground particles of glasses containing heavy metals, constituting a filler content of approximately 75% to 80% by weight (see Table 13-1). The glasses have an average particle size of about 0.4 to 1.0 μm, with a trend to steadily reduce this size range as improvements are made. In a typical size distribution, 75% of the ground particles are smaller than 1.0 μm and colloidal silica represents 10% to 20% by weight of the total filler content. The smaller microfiller sizes increase the surface area, which generally increases the viscosity and requires a decrease in overall filler loading as compared with small-particle composites. A polished surface is shown in Figure 13-12.

? CRITICAL QUESTIONS

How can the particle size and size distribution of resin-based composites be used to select clinical materials for various restorative situations?

Compared with amalgam, what disadvantages are associated with the use of resin composites as esthetic posterior resins?

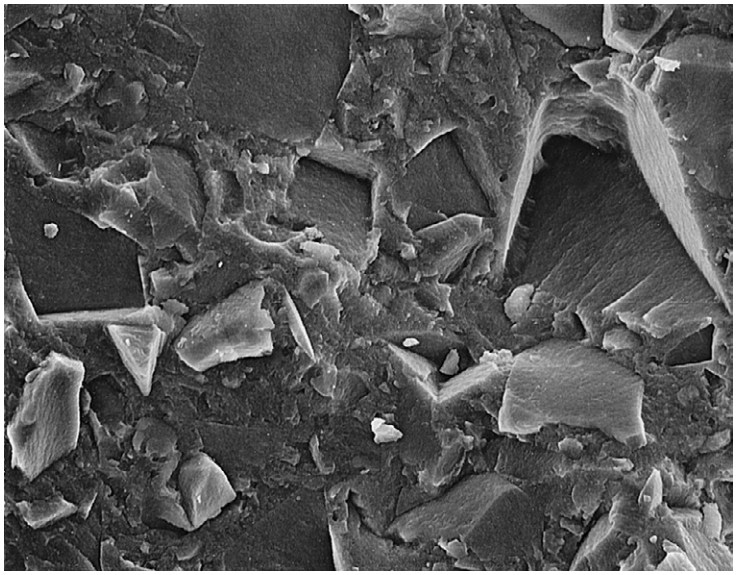


FIGURE 13-9 Fractured microfilled composite. The fractured surface shows that the organic filler (composite filler) particles have been plucked out of the matrix resin, suggesting adhesive failure due to a weak interface between the precured microfill particles and the clinically cured resin. (Courtesy of K-J.M. Söderholm.)



FIGURE 13-10 Fractured maxillary central incisor prior to restoration with a hybrid composite. (Courtesy of William Rose.)



FIGURE 13-11 Class IV restoration made with a hybrid composite. This restoration of the incisal area of the tooth produced a highly aesthetic esthetic result. (Courtesy of William Rose.)

TABLE 13-3 Properties of Composite Restorative Materials

Characteristic/ Property	Unfilled Acrylic	Traditional	Hybrid (Small-Particle)	Hybrid (All-Purpose)	Microfilled	Flowable Hybrid	Packable Hybrid	Enamel	Dentin
Size (μm)	—	8–12	0.5–3	0.4–1.0	0.04–0.4	0.6–1.0	Fibrous	—	—
Inorganic filler (vol%)	0	60–70	65–77	60–65	20–59	30–55	48–67		
Inorganic filler (wt%)	0	70–80	80–90	75–80	35–67	40–60	65–81	—	—
Compressive strength (MPa)	70	250–300	350–400	300–350	250–350	—	—	384	297
Tensile strength (MPa)	24	50–65	75–90	40–50	30–50	—	40–45	10	52
Elastic modulus (GPa)	2.4	8–15	15–20	11–15	3–6	4–8	3–13	84	18
Thermal expansion coefficient (ppm/°C)	92.8	25–35	19–26	30–40	50–60	—	—	—	—
Water sorption (mg/cm^2)	1.7	0.5–0.7	0.5–0.6	0.5–0.7	1.4–1.7	—	—	—	—
Knoop hardness (KHN)	15	55	50–60	50–60	25–35	—	—	350–430	68
Curing shrinkage (vol%)	8–10	—	2–3	2–3	2–3	3–5	2–3	—	—
Radiopacity (mm Al)	0.1	2–3	2–3	2–4	0.5–2	1–4	2–3	2	1

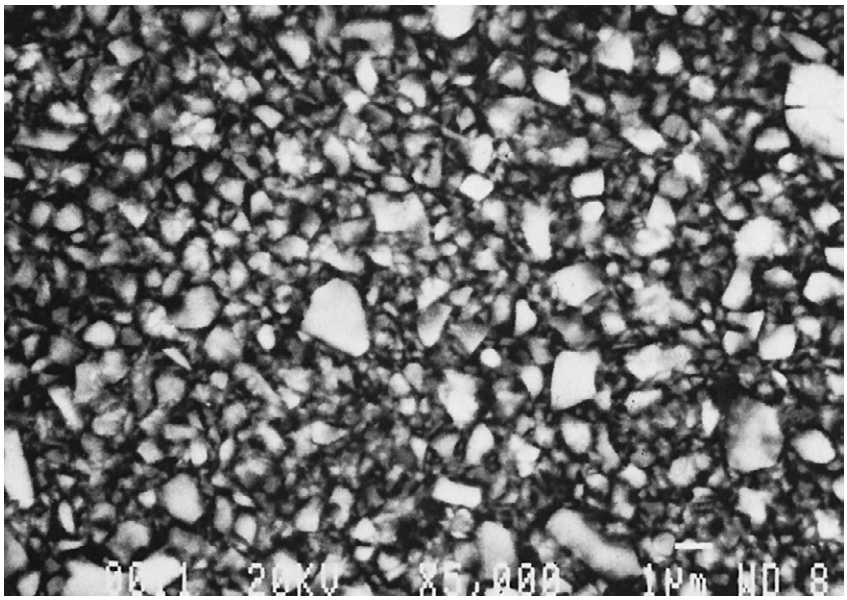


FIGURE 13-12 Polished surface of a hybrid composite similar to those shown in Figures 13-10 and 13-11. Particle sizes ranges from about 0.1 to 3 μm (SEM magnification ×5000). (Courtesy of Robert L. Erickson.)

Nanofilled Composites/Nanocomposites/Nanohybrid Composites. More recently, nanoparticles (1 to 100 nm) have been fabricated by a different method from the pyrolytic precipitation process used for colloidal silica. This allows the individual, primary particles to be surface-coated (with γ-methacryloxypropyltrimethoxysilane, for example) *prior* to becoming incorporated into three-dimensional macromolecule chains, thereby preventing or limiting particle agglomeration into large networks and driving up viscosity. In essence, the particle size is similar to that in microfilled composites, but the difference is that the particles in microfilled composites are in three-dimensional agglomerates or networks that increase viscosity whereas those in nanofilled composites are mostly discrete and have a minimal effect on viscosity. Thus, these composites have optical properties and superior polishability like those of microfilled composites, but the surface treatment reduces the increase in viscosity when incorporated into the monomer, which allows an increased filler loading of upwards of 60% by volume and 78% by weight. Filler loading in this range is expected to lead to the necessary mechanical properties for use in posterior, stress-bearing restorations, but these properties have not yet been confirmed.

One of the reasons that increased mechanical properties are not observed is that no commercial products have as yet been reported to contain only isolated, discrete, homogeneously dispersed nanoparticles as the sole filler component. In fact, few if any dental resins currently designated as nanocomposites meet the strict requirement of having essentially all filler less than 100 nm. This is because some of the nanoparticles exist as loosely bound "clusters" (loose agglomerates, such as in Filtek Supreme, 3M ESPE) of primary nanoparticles, which are sometimes reported to extend into the micron size range (e.g., 60 nm to 1.4 μm). Above 100 nm, clusters, like any particles, begin to scatter visible light and thereby reduce the translucency and the **depth of cure** of the composite. In addition, these clusters are not chemically bound to each other and act to decrease mechanical properties. Thus, while these nanocomposites with clusters have increased filler loading and hence better mechanical properties than a true homogeneous nanocomposite, they are not as strong as a hybrid composite or a microfilled composite.

To combat this deficiency, larger particles of either finely ground glass or precured nanoparticle-filled resin organic filler particles (essentially the same as those found in the microfilled composites) are combined with the monomer-dispersed nanoparticles. Thus, most, if not all, of these products are more accurately designated as "hybrid" nanocomposites or nanohybrids consisting of a blend of two or more size ranges of filler particles, one or more of which is in the nanoparticle range (see Table 13-1).

? CRITICAL QUESTION

What are the relationships and tradeoffs among particle size, composition, and percentage of filler relative to their effect on manipulation consistency, polishability, radiopacity, durability, and appearance of resin-based composite materials?

Classification of Composites by Manipulation Characteristics

Flowable Composites. A modification of the small-particle composite and hybrid composite results in the so-called flowable composites, which have become popular since 1995. These resins typically have a lower viscosity through a reduced filler loading, which enables the resin to flow readily, spread uniformly, intimately adapt to a cavity form, and produce the desired dental anatomy. This improves the clinician's ability to form a well-adapted cavity base or liner, especially in class II posterior preparations and other situations in which access is difficult. However, whereas these materials tend to be less sticky during handling than microfills and hybrids, they are

inherently inferior in mechanical properties owing to the lower filler loading and higher susceptibility to wear and other forms of attrition. Because of their greater ease of adaptation and flexibility as a cured material, flowable composites are also useful in class I restorations in gingival areas. They may also be applied in a manner similar to the use of fissure sealants as minimal class I restorations to prevent caries. Because they can flow into small crevice defects along restoration margins, some dentists refer to flowable resins as "dental caulk." The properties and clinical uses of flowable composite materials are similar to those of the so-called compomers, which are hybrids between resin composites and glass ionomer materials (Chapter 14).

Condensable (Packable) Composites. Compared with amalgam, the technique of composite placement is far more time-consuming and demanding. Because of their highly plastic, pastelike consistency in the precured state, composites cannot be packed vertically into a cavity in such a way that the material flows laterally as well as vertically to ensure intimate contact with the cavity walls. In particular, the restoration of a tooth in which a proximal contact with the adjacent tooth is required, the paste consistency of most composites dictates that a matrix band be carefully contoured and wedged to obtain an acceptable proximal contact. These are tedious, time-consuming procedures and can produce variable results without a high level of skill. Thus, condensable composites (also known as **packable composites**) were developed by adjusting their filler distribution to increase the strength and stiffness of the uncured material and provide a consistency and handling characteristics similar to those of lathe-cut amalgam.

Specifically the packable/condensable characteristics are derived from the inclusion of elongated, fibrous filler particles of about 100 μm in length and/or rough-textured surfaces or branched geometries that tend to interlock and resist flow. This causes the uncured resin to be stiff and resistant to slumping yet moldable under the force of amalgam condensers ("pluggers"). Rough surfaces and blends of fibrous and particulate fillers produce a packable consistency and enable other properties to be optimized for clinical performance. In certain products, larger than average filler particles (15 to 80 μm) are used, and the resin matrix is modified chemically to allow a slight increase in filler content over hybrids. Some have the same filler particles as their companion hybrids from the same manufacturer; the only difference is that the resin matrix is adjusted to allow approximately 1% to 2% of additional filler loading. However, many of the limitations of resin composites still prevail, and approximately twice the time required for amalgam placement is needed. At present, these materials have not demonstrated any advantageous properties or characteristics over the hybrid resins other than being somewhat similar to amalgam in their placement technique. Despite manufacturers' claims to the contrary, packable composites have not yet proven to be an answer to the general need for highly wear-resistant, easily placed posterior resins with low curing shrinkage and a depth of cure greater than 2 mm.

COUPLING AGENT

As stated previously, it is essential that filler particles be bonded to the resin matrix. This allows the more flexible polymer matrix to transfer stresses to the higher-modulus (more rigid and stiffer) filler particles. The chemical bond between the two phases of the composite is formed by a coupling agent; this is a difunctional surface-active compound that adheres to filler particle surfaces and also coreacts with the monomer forming the resin matrix. A properly applied coupling agent can impart improved physical and mechanical properties and inhibit leaching by preventing water from penetrating along the filler-resin interface.

Although titanates and zirconates can be used as coupling agents, organosilanes—such as γ-methacryloxypropyl trimethoxysilane—are used most commonly (Figure 13-13). In the presence of water, the methoxy groups ($-OCH_3$) are hydrolyzed to silanol (–Si–OH) groups, which can bond with other silanols on the filler surfaces by forming siloxane bonds (–Si–O–Si–). The organosilane methacrylate groups form covalent bonds with the resin when it is polymerized, thereby completing the coupling process. Proper coupling by means of organosilanes is extremely important to the clinical performance of resin-based composite restorative materials.

ACTIVATION/INITIATION SYSTEM

Both monomethacrylate and dimethacrylate monomers polymerize by the addition polymerization mechanism initiated by free radicals, as described in Chapter 6 on dental polymers. Free radicals can be generated by chemical **activation** or by external energy activation (heat, light, or microwave). Because dental composites for direct placement use chemical activation, light activation, or a combination of the two, only these systems are discussed here.

Chemically Activated (Self-Cure) Resins

Chemically activated resins (**chemically cured composites**) are supplied as two pastes, one of which contains the benzoyl peroxide initiator and the other an aromatic tertiary amine activator (e.g., N, N-dimethyl-p-toluidine), as previously described in Chapter 7 for the acrylic resins. When the two pastes are mixed together, the amine reacts with the benzoyl peroxide to form free radicals, and addition polymerization is initiated. One problem with chemical activation is that during mixing it is almost impossible to avoid incorporating air into the mix, thereby forming pores that weaken the structure and trap oxygen, which inhibits polymerization during curing. Another problem is that the operator has no control over the working time after the two components have been mixed. Therefore both insertion and contouring must be completed quickly once the resin components are mixed. Thus, today they are mainly used for restorations and large foundation structures (buildups) that are not readily cured with a light source.

One other problem is the formation of an **oxygen-inhibited layer**. During the initial stage of a polymerization process, the polymerization is inhibited by oxygen because the reactivity of oxygen to a radical is much higher than that of a monomer. During the inhibition period, this oxygen

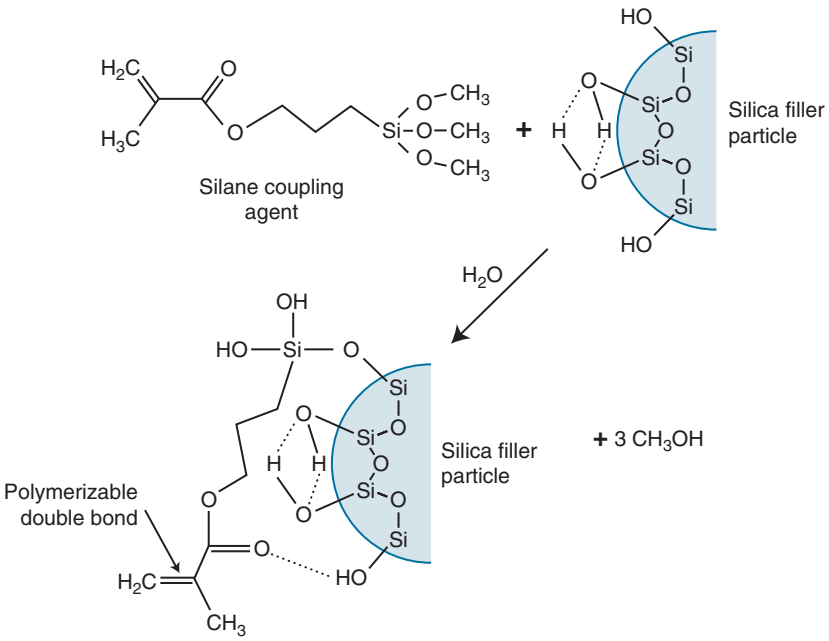


FIGURE 13-13 The chemical structure of γ-methacryloxypropyltrimethoxy silane and an idealized diagram of how a silane coupling agent is hydrolyzed and becomes attached to silica and glass filler particle surfaces. Such silanized particles are then reactive and can "couple" the particles to the resin matrix by copolymerization with the double bond in the silane propylmethacrylate group (CH_2=C(CH_3)COO–C_3H_6–Si–). (Data taken from Söderholm K-JM and Shang S-W: Molecular orientation of silane at the surface of colloidal silica. *J Dent Res* 72:1050–1054, 1993.)

TABLE 13-4 **Advantages and Disadvantages of Chemically Activated (Self-Cure) Resins**

Advantages	Disadvantages
Convenience and simplicity: no equipment needed, hazard-free	Mixing causes air entrapment, leading to porosity that weakens the material and increases susceptibility to staining. This has been reduced by the use of mixing syringes.
Long-term storage stability	
Manipulation of working/setting time by varying proportions	Aromatic amine accelerators oxidize and turn yellow with time—i.e., color instability
Degree of cure equal throughout material if mixed properly	Difficult to mix evenly, causing unequal degree of cure and consequent poor mechanical properties
Marginal stress buildup during curing is much lower than for photocured resins owing to relatively slower rates of cross-link formation	

diffuses into the liquid resin and is consumed by the radicals formed. This reaction forms an unpolymerized surface layer. The thickness of the unpolymerized film on the surface is dependent on the viscosity of the resin, the solubility of oxygen in the monomer, and the initiating system used.

Table 13-4 lists the advantages and disadvantages of chemically activated resins.

Diacrylate monomer (in both pastes) + **accelerator** (in "base" paste)
+ **initiator** (in "catalyst" paste)
↓
CROSS-LINKED POLYMER

Photochemically Activated (Light-Cure) Resins

To overcome the problems of chemical activation, manufacturers have developed resins that do not require mixing by using a photosensitive initiator system and a light source for activation. The first light-activated systems were formulated for UV light to initiate free radicals. Today, UV light–cured composites have been replaced by visible blue-light–activated systems with greatly improved depth of cure, a controllable working time, and other advantages (Table 13-5). Light-curable dental composites are supplied as a single paste contained in a lightproof syringe. The free radical initiating system, consisting of a photosensitizer and an amine initiator, is contained in this paste. As long as these two components are not exposed to light, they do not interact. However, exposure to light in the blue region (wavelength of about 468 nm) produces an excited state of the photosensitizer, which then interacts with the amine to form free radicals that initiate addition polymerization (Figure 13-14). Camphorquinone (CQ) is a commonly used photosensitizer that absorbs blue light with wavelengths between 400 and 500 nm. Only small quantities of CQ are required (0.2% by weight or less in the paste). A number of amine initiators are suitable for interaction with CQ, such as dimethylaminoethyl methacrylate (DMAEMA), which is also present at low levels of about 0.15% by weight.

In addition to avoiding the porosity of chemically activated resins, light-cured materials allow the operator to complete insertion and contouring before curing is initiated. Furthermore, once curing is initiated, an exposure time of 40 seconds or less is required to light-cure a 2-mm-thick layer, as compared with several minutes for chemically-cured materials. Finally, light-cured systems are not as sensitive to oxygen inhibition as are the chemically cured systems. Because of these advantages, visible light–activated composites are more widely used than chemically activated materials.

TABLE 13-5 Advantages and Disadvantages of Light-Activated (Photoinitiated) Resins

Advantages	Disadvantages
No mixing needed: thus low porosity, less staining, stronger.	Limited cure depth: necessary to build up in layers of about 2 mm.
	Marginal stress buildup during curing is much higher than in self-cured resins. This is due to faster cross-linking and thus reduced time for chains to slide among themselves and relax interfacial stress build-up due to cure shrinkage.
No aromatic amine accelerator: thus greatly improved color stability.	Mildly sensitive to normal room illumination (thus a crust will form when exposed too long to an examination light).
"Command" setting (upon exposure to an intense blue light). This means that working time is controlled, at will, by the clinician.	Special lamp is needed to photoinitiate curing.
	Poor lamp accessibility in posterior and interproximal areas; requires extra exposure time and care in placement and maintaining lamp tip angle and distance for optimal results.
	Darker shades require longer exposure times.
Small increments of composite can be polymerized at a time allowing the use of multiple shades within a single restoration and accommodating for shrinkage within each increment as opposed to bulk shrinkage.	Cure is affected by additives such as ultraviolet absorbers for color stabilization, fluorescent dyes for clinical aesthetics, or excessive inhibitor concentration. They all absorb light or prevent reaction.
	Problems with lamps:
	Glare is harmful to clinic personnel; use protective glasses or filters.
	Except for LED lamps, curing light generates substantial heat and will cause pain at 2 to 3 mm in about 20 seconds.
	QHT bulbs dim with age; therefore use proper instrumentation to monitor output intensity.
	Lamp wavelength must be matched with resin photoinitiation system.
	Intensity of light decreases with distance to the log scale.
	Curing angle critical; maximal intensity is delivered perpendicular (90°) to resin surface.
	Training is required to develop best practice techniques for optimum intraoral exposure to maximize degree of cure.
	Incomplete curing owing to the above problems with lamps.

However, light-cured composites have substantial limitations. First, they must be placed incrementally when the bulk exceeds approximately 2 to 3 mm because of the limited depth of light penetration. Thus, light-cured composites can actually require more time when producing large restorations (e.g., in class II cavity preparations). Other drawbacks include the cost of the light-curing unit, the need for eye protection, and several complicating factors associated with light sources and photocuring. These are listed in Table 13-5 and discussed in detail below (also see sections entitled Factors Involved in Photocuring and Properties of Composites).

Diacrylate monomer + photoinitiator + blue light (468 nm)
↓
CROSS-LINKED RESIN

Factors Involved in Photocuring

Curing Lamps. Most curing lamps are handheld devices that contain the light source and are equipped with a relatively short, rigid light guide made up of fused optical fibers. A few lamps have the power unit connected to the dental handpiece by a long flexible liquid-filled light guide. At present the most widely used light source is a quartz bulb with a tungsten filament in a halogen environment, similar to those used in automobile headlights and digital projectors. More recently, other types have been introduced with advantages that have made them increasingly popular. Four types of lamps may be used for photoinitiation of the polymerization process. The following section lists these lamps in order of lowest intensity to highest intensity.

1. **Light-emitting diode (LED) lamps.** Using a solid-state electronic process, these light sources emit radiation only in the blue part of the visible spectrum, between 440 and 480 nm, and do not require filters. LEDs require low wattage, can be battery-powered, generate no heat, and are quiet because a cooling fan is not needed. Although they inherently produce the lowest intensity radiation, the latest versions are more intense and utilize two or more LED units to both increase intensity and extend the wavelength range.
2. **Quartz-tungsten-halogen (QTH) lamps.** QTH lamps have a quartz bulb with a tungsten filament that irradiates both UV and white light, which must be filtered to

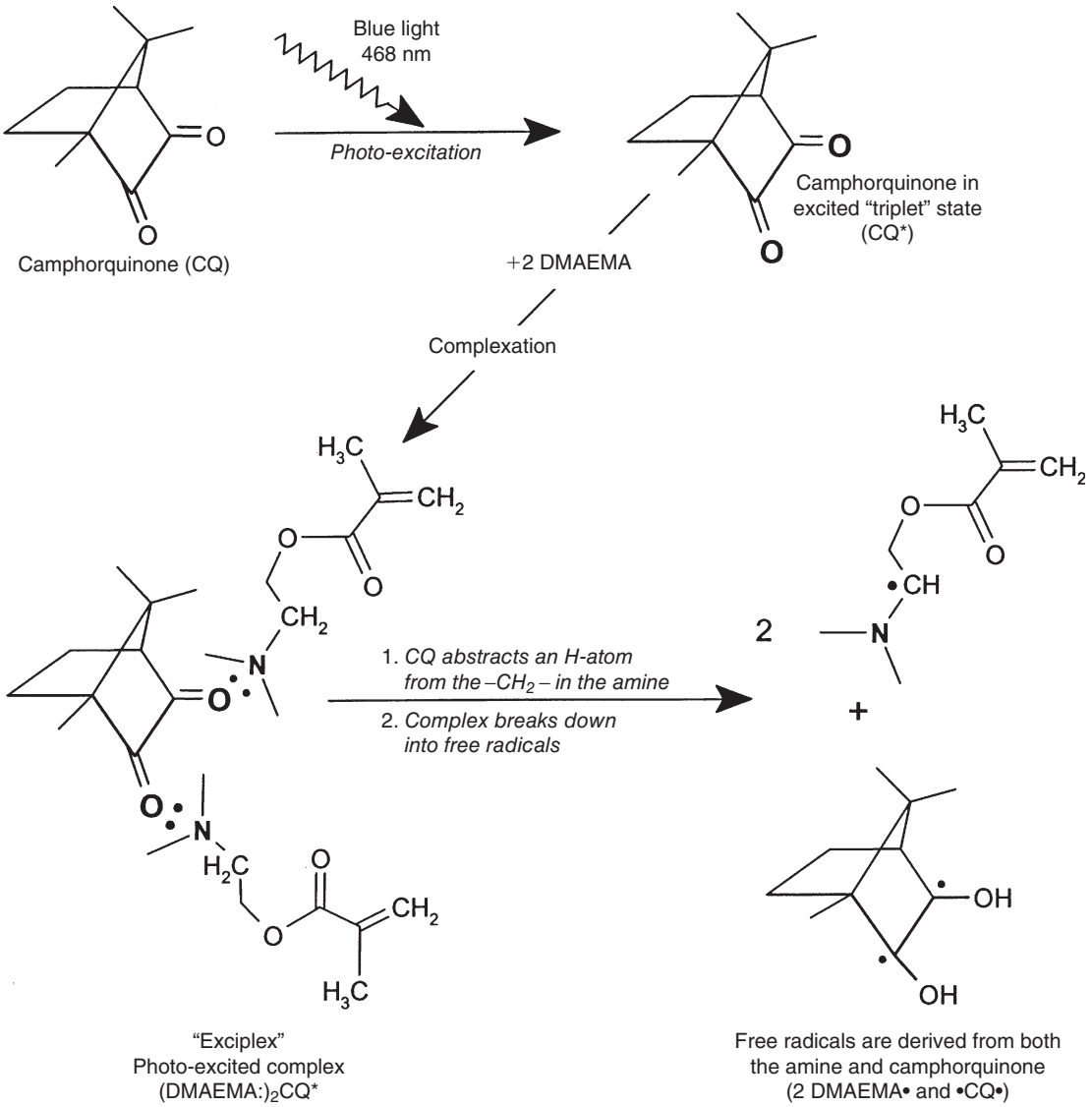


FIGURE 13-14 The light-cure process is activated when a diketone photosensitizer such as camphorquinone (CQ) absorbs a quantum of blue light and forms an excited-state complex (exciplex) with an electron donor such as an amine (e.g., dimethylaminoethyl methacrylate [DMAEMA]). In the figure "⁚" denotes the unshared pair of electrons "donated" by the amines to the > C = O (ketone) groups in CQ. While in this activated complex, CQ extracts a hydrogen atom from the α-carbon adjacent to the amine group, and the complex decomposes into amine and CQ free radicals. The CQ free radical is readily inactivated. Thus, in photoinitiation only the amine free radicals act to initiate the addition polymerization reaction (see Figure 6-8).

remove heat and all wavelengths except those in the violet-blue range (about 400 to 500 nm). The intensity of the bulb diminishes with use, so a calibration meter is required to measure the intensity.

3. **Plasma arc curing (PAC) lamps.** PAC lamps use a xenon gas that is ionized to produce a plasma. The high-intensity white light is filtered to remove heat and to allow blue light (about 400 to 500 nm) to be emitted.
4. **Argon laser lamps.** Argon laser lamps have the highest intensity and emit at a single wavelength. Lamps currently available emit light at wavelength of about 490 nm.

The tungsten and plasma arc lamps are filtered to transmit light only in the part of the violet-blue region of the spectrum that matches the photoabsorption range of CQ. CQ, as explained earlier, is a photosensitizer that is widely used for dental resins. Currently available LED and laser dental curing lamps are designed to emit light only in the blue spectral range within the 400- to 500-nm photoabsorption range of CQ. Thus, they do not require filters. A few photosensitizers and light sources have been introduced that absorb or emit, respectively, at wavelengths outside the 400- to 500-nm range, which will provide inadequate curing unless the lamp and resin/photosensitizer are matched to each other.

Polymerization is initiated when a critical concentration of free radicals is formed. This requires that a particular number of photons be absorbed by the initiator system, which is directly related to the wavelength, intensity, and time of exposure. There can be substantial differences in the wavelength range and intensity among various brands and types of manufactured lamps. Commonly available QTH lamps emit a radiant power density that ranges from approximately 300 to 1200 milliwatts/cm^2 (mW/cm^2) in the violet-blue region, and it is not unusual for two brands to vary in intensity by a factor of 2 or more.

For maximum curing, a radiant energy influx of approximately 16,000 millijoules/cm^2 (16 J/cm^2) is required for a 2-mm-thick layer of resin. This can be delivered by a 40-second exposure to a lamp emitting 400 mW/cm^2 (40 seconds × 400 mW/cm^2 = 16,000 mJ/cm^2 or 16 J/cm^2). The same result can be produced by a 20-second exposure at 800 mW/cm^2, or an exposure of about 13 seconds with a 1200-mW/cm^2 lamp. Thus, increasing the power density of the lamp increases the rate and degree of cure. However, faster curing with higher-intensity light sources can increase shrinkage stress, as discussed below.

Depth of Cure and Exposure Time. Recently QTH, PAC, laser, and LED lamps have been introduced with substantially increased intensities (greater than 1000 mW/cm^2), thus opening the possibility of reduced exposure times and/or greater depth of cure. These are highly desirable benefits that can greatly reduce restoration treatment time and associated cost to the patient. However, light absorption and scattering in resin composites reduces the power density and **degree of conversion (DC)** exponentially with depth of penetration. Intensity can be reduced by a factor of 10 to 100 in a 2-mm-thick layer of composite. This reduces monomer conversion to an unacceptable level at depths greater than 2 to 3 mm. Thus, the surface must be irradiated for a longer time to deliver sufficient power density well below the surface. Given the limits imposed by the light scattering and absorption inherent in current restorative resins, the tradeoffs are such that increased intensity will allow either shorter curing times for a given depth of cure or increased depth of cure for a given exposure time, but there is little advantage in attempting to achieve both simultaneously. The practical consequence is that curing depth is limited to 2 to 3 mm unless excessively long exposure times are used, regardless of lamp intensity. Solutions to this problem are more likely to come through advances in the chemistry and technology of composite structures rather than through advances in clinical technique or the technology of curing lamps. Some recent efforts in this direction are discussed at the end of this chapter (under Innovations in Composites).

Light attenuation can also vary considerably from one type of composite to another, depending, for example, on the opacity, filler size, filler concentration, and pigment shade. As described earlier, darker shades and/or more opaque resins require longer curing times. For these reasons, manufacturers usually recommend curing times based on a particular curing device for each shade and type of resin. *These recommended times are typically the absolute minimum required*. To maximize both degree of polymerization and long-term clinical durability, the clinician should adjust the exposure time and curing technique to the intensity of the light source used. Light is also absorbed and scattered as it passes through tooth structure, especially dentin, thereby causing incomplete curing in such critical areas as proximal boxes. Therefore, when one attempts to polymerize the resin through tooth structure, the exposure time should be increased by a factor of 2 to 3 to compensate for the reduction in light intensity.

For the halogen (QHT) lamps, light intensity is particularly susceptible to aging of the light source. For all types, faulty orientation of the light tip and too great a distance between the light tip and restoration will reduce light output. Several surveys have shown that the curing units in many dental offices worldwide do not deliver an adequate light output. The bulbs, LEDs, reflectors, and internal filters in dental light-curing units of all types have been shown to degrade with use. In addition, autoclaving, the use of disinfectant chemicals, or restorative material adhering to the light tip can dramatically reduce light output.

Consequently the lamp's output intensity should be checked regularly and the operator should always place the light tip as close as possible perpendicular to the restorative material *and maintain this distance and orientation throughout the exposure time*. In studies reported in 2010 and 2011, Price and colleagues showed that specialized training in these technique-related details substantially improves the intraoral degree of monomer-to-polymer conversion that is obtained. (See also later section on recent advances.)

In summary, technique and lamp maintenance are critical:

- A curing lamp with a wavelength range strongly overlapping the absorbance range of the resin photoinitiation system must be selected.
- Intensity of light decreases with distance to the log scale; therefore, the lamp tip must be placed and held at the minimal distance possible throughout the exposure interval (20 seconds or more).
- Curing angle is critical, since maximal intensity is delivered perpendicular (90°) to the resin surface therefore, the lamp tip must be placed and held as close as possible to 90° throughout the exposure interval.
- Lamp intensity should be evaluated frequently and adjustments made to ensure sufficient radiant energy influx (about 16 J/cm^2) for adequate curing.
- Training is required to develop the best practice techniques for optimal intraoral curing.

Safety Precautions for Using Curing Lamps. The light emitted by curing units can cause retinal damage if a person looks directly at the beam for an extended period or even for short periods in the case of lasers. To avoid such damage, never look directly into the light tip and minimize observation of the reflected light for longer periods. Protective eyeglasses and various types of shields that filter the light are

available for increased protection for both clinical personnel and patients.

CRITICAL QUESTIONS

What are the similarities and differences in the mechanisms involved in chemically activated and light-activated dental resins?

What are the tradeoffs among the several types of light sources used to photoactivate dental restorative resins?

Can increasing the intensity of curing lamps shorten the time needed to adequately cure resin-based composites? How does lamp intensity affect the depth of cure?

What are the most important factors that affect depth of cure for a lamp with a given intensity?

What are the critical exposure technique and lamp maintenance practices required for optimal curing and ensuring maximal longevity of resin-based composite restorations?

Dual-Cured Resins

One way to overcome limits on curing depth and some of the other problems associated with light curing is to combine chemical curing and visible-light curing components in the same resin. **Dual-cure resins** are commercially available and consist of two light-curable pastes, one containing benzoyl peroxide and the other containing an aromatic tertiary amine accelerator. They are formulated to set up very slowly when mixed via the self-cure mechanism. The cure is then accelerated on "command" via light-curing promoted by the amine/CQ combination. The major advantage of this system is assurance of completion of cure throughout, even if photocure is inadequate. The major disadvantage is porosity caused by the required mixing. But this has been greatly alleviated by the use of mixing syringes. There is also less color stability than with the photocure resins owing to the aromatic amine accelerators, but this is still better than for self-cure systems, since the concentration of the accelerators is reduced compared with self-cure resins. Finally, as with the chemically cured resins, air inhibition and porosity are problems with dual-cure resins. Dual-cure materials are intended for any situation that does not allow sufficient light penetration to produce adequate monomer conversion—for example, cementation of bulky ceramic inlays.

INHIBITOR

Inhibitors are added to resin systems to minimize or prevent spontaneous or accidental polymerization of monomers. Inhibitors have a strong reactivity potential with free radicals. If a free radical is formed, for example, by brief exposure to room lighting when the material is dispensed, the inhibitor reacts with the free radical faster than the free radical can react with the monomer. This prevents chain propagation by terminating the reaction before the free radical is able to initiate polymerization. After all of the inhibitor is consumed, chain propagation can begin. A typical inhibitor is butylated hydroxytoluene (BHT), which is used in concentrations on the order of 0.01% by weight. BHT and similar free radical scavengers are also used as food preservatives to prevent oxidation and rancidity. Thus, inhibitors have two functions: to extend the resin's storage life and to ensure sufficient working time.

OPTICAL MODIFIERS

For a natural appearance, dental composites must have visual shading and translucency similar to the corresponding properties of tooth structure. Shading is achieved by adding various pigments, usually consisting of minute amounts of metal oxide particles. Translucency and opacity are adjusted as necessary to simulate enamel and dentin. For example, if a class IV incisal area is reconstructed, the translucency of an unmodified composite might allow too much light to pass through the restoration. As a result, less light is reflected or scattered back to the observer, who perceives the incisal edge as too dark. This deficiency can be corrected by adding an opacifier. However, if an excessive amount of opacifier is added, too much light may be reflected and the observer then perceives that the restoration is "too white," or more correctly, "too high in value" (Chapter 3). To increase the opacity, the manufacturer adds titanium dioxide and aluminum oxide to composites in minute amounts (0.001% to 0.007% by weight).

It is important to realize that all optical modifiers affect light transmission through a composite. Thus, darker shades and greater opacities have a decreased depth of light-curing ability and require either an increased exposure time or a thinner layer when cured. Studies have shown that for optimal polymerization, resins with darker shades and opacifiers should be placed in thinner layers. This consideration has added importance when a bonding agent covered by a composite layer is being cured.

PROPERTIES OF RESIN-BASED COMPOSITES

DEGREE OF CONVERSION (DC)

The DC is a measure of the percentage of carbon-carbon double bonds that have been converted to single bonds to form a polymeric resin (Figure 13-15). The higher the DC, the better the strength, wear resistance, and many other properties essential to resin performance. A conversion of 50% to 60%, typical of highly cross-linked *bis*-GMA–based composites, implies that 50% to 60% of the methacrylate groups have polymerized. However, this does not imply that 40% to 50% of the monomer molecules are left in the resin, because one of the two methacrylate groups per dimethacrylate molecule could still be covalently bonded to the polymer structure, forming a pendant group.

Conversion of the monomer to a polymer depends on several factors, such as resin composition, the transmission of light through the material, and the concentrations of sensitizer, initiator, and inhibitor. As discussed earlier, transmission of light through the material is controlled by lamp intensity, absorption, and scattering of light by filler particles and opacifiers as well as by any tooth structure interposed between the light source and the composite.

The total DC within resins does not differ between chemically activated and light-activated composites containing the same monomer formulations as long as adequate light curing

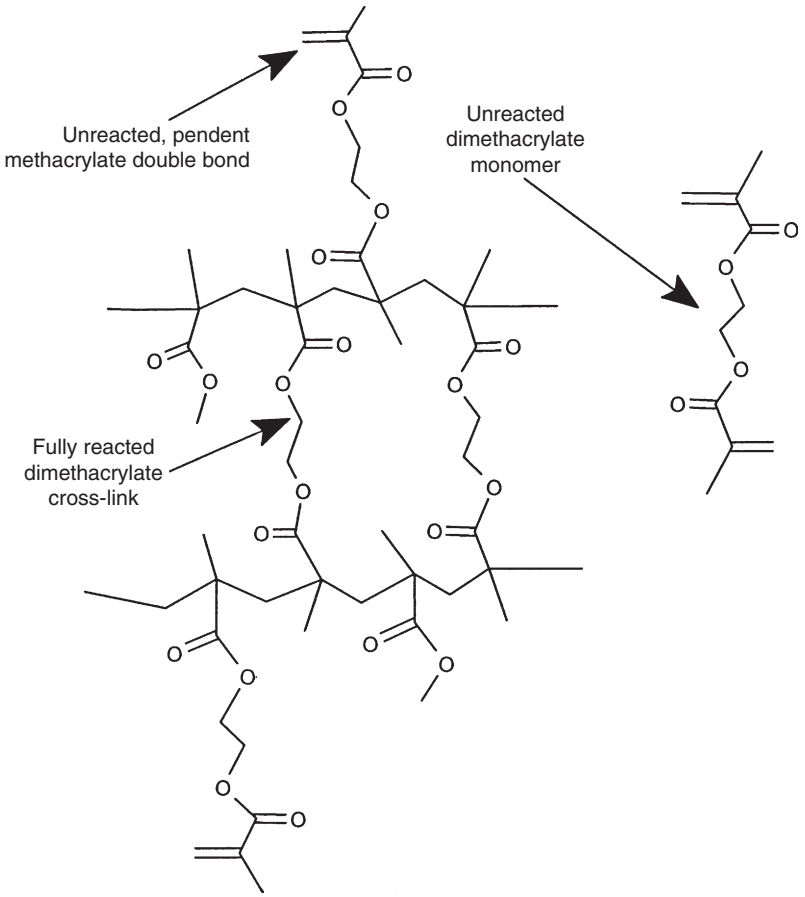


FIGURE 13-15 Degree of conversion (DC) reflects the percentage of methacrylate double bonds that are converted to single bonds during the curing reaction. This figure shows that a cured resin can contain dimethacrylates groups with zero, one, or two unreacted double bonds. If at least one double bond has reacted, the dimethacrylate group is bound to the polymer network as a "pendant" group with one double bond available for further reaction. Any completely unreacted monomers can migrate out of the cured resin. Cross-linked groups strengthen and make the resin rigid while pendant groups plasticize the resin (see Figure 6-14), and unreacted monomer softens and swells the resin structure, as explained in Chapter 6.

is employed. Conversion values of 50% to 70% are achieved at room temperature for both curing systems. Likewise, polymerization shrinkage of comparable light-activated and chemically activated resins is not significantly different. However, in light-cured materials, curing shrinkage leads to substantially greater stress buildup and leakage at the resin margins, in turn leading to staining, sensitivity, and secondary caries.

MATRIX CONSTRAINT

As mentioned above, the presence of filler particles bonded to the matrix via coupling agents reduces thermal expansion and contraction of the composite. When thermal stresses arise, the interfacial bond and the presence of a filler with a lower coefficient of thermal expansion (nearly zero in some cases) prevents or reduces the contraction or expansion of the matrix. Thus, during expansion, while the space occupied by the filler tries to increase, the filler with lower coefficient of expansion does not—and since the filler is chemically bonded to the matrix, it prevents the space from getting larger and hence prevents or reduces the expansion. Conversely, during cooling, the matrix contracts and decreases the space occupied by the filler, but since the filler occupies that space, contraction is prevented or reduced. Thus the filler particles not only lower thermal expansion and contraction by simply occupying space that polymers, which are susceptible to thermal expansion, would otherwise have occupied but also constrains the interfacial bond from expanding thermally.

This constraint does have its limits. During expansion, the composite can fracture within the matrix because of the added tension caused by the nonexpansion of the filler particle, within the filler particle, or at the interfacial bond, depending on whether the interfacial bond is stronger than the fracture toughness of the filler or the matrix. In contraction, the composite can fracture within the matrix or within the filler particle, depending on which is weaker.

TOUGHNESS

The strength of composites is highly dependent on the ability of the coupling agent to transfer stresses from the weak matrix to the strong filler particles. Without the coupling agent, the filler particles cannot absorb stresses in the matrix and act as if they were voids, thereby weakening instead of strengthening the matrix. Thus a crack traveling through the matrix simply bypasses the particles. The energy required to detour around noncoupled particles is low because the lack of coupling at the particle-matrix interface makes this interface behave the same as an already existing "crack." Consequently, in a true composite, the matrix and filler are chemically bonded. As the crack propagates to a bonded filler particle, the crack must pass around the particle, since it is stronger than the matrix and the interfacial bond. Thus the

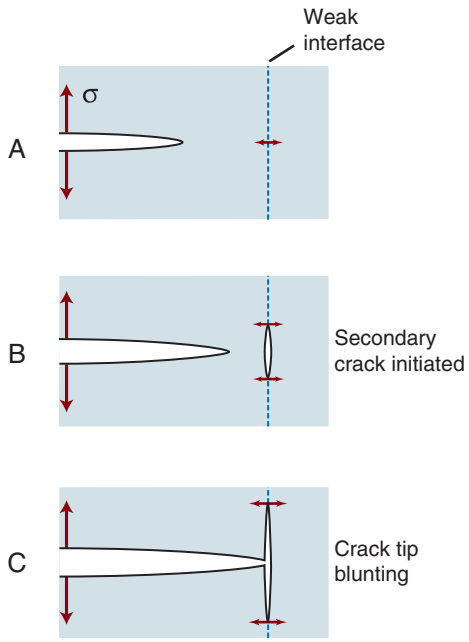


FIGURE 13-16 A crack propagates through the resin matrix under the influence of a tensile stress toward a weak interface (**A**), and initiates a secondary crack when the stress induced at the weak interface is greater than the interfacial bond strength (**B**). When the main crack reaches the extended secondary crack, its propagation is impeded by a process called crack blunting (**C**). (Adapted from Darvell BW: *Materials Science for Dentistry*, ed 9, Woodhead Publishing Ltd, Cambridge, UK, 2009.)

path the crack must take and the total new surface area that the crack must form is increased; therefore the energy needed for the crack to propagate is increased. This makes the composite tougher.

If the interfacial bond is weaker than the matrix, a process of crack blunting occurs (Figure 13-16). As the crack propagates to the weak interface, a void or tear opens up in front of the advancing crack because of the stresses that the weak bond experiences. However, this void is perpendicular to the propagating crack; thus when the crack arrives, the tip of the crack has been blunted and significantly more stress is required to propagate the crack.

Note that the use of a cross-linked polymer matrix also increases toughness, since it prevents the polymer chains from being drawn and separated as the crack propagates. However, the material then becomes brittle.

CURING SHRINKAGE AND SHRINKAGE STRESS

Curing shrinkage arises as the monomer is converted to polymer and the free space it occupies reduces (approximately 20% less than that among unreacted monomers). In turn, this polymerization shrinkage produces unrelieved stresses in the resin after it reaches the "**gelation**" point and begins to harden. The polymerization shrinkage and resultant stress can be affected by the (1) total volume of the composite material, (2) type of composite, (3) polymerization speed, and (4) ratio of bonded/nonbonded *surfaces* or the configuration of the tooth preparation (**C-factor**). These stresses tend to develop at the tissue/composite interface, weakening the bond, and eventually producing a gap at the restoration margins. Consequently the risk for marginal leakage and the ensuing problems of marginal staining and secondary caries are exacerbated. Undoubtedly this is one of the greatest problems of composites used for class II and class V restorations.

Traditionally this problem has been combated in two ways. First, larger monomers used to "dilute" the number of double bonds that need to be reacted. *Bis*-GMA and UDMA have five times or more the molecular weight of methyl methacrylate (MMA), so the density of methacrylate double-bond groups is approximately two-fifths as high in MMA. This reduces polymerization shrinkage proportionately.

Another method has been the addition of inorganic fillers that do not enter into the polymerization process, although they do bond to the polymer. Thus, because a percentage of the volume does not enter into the reaction, the amount of monomer necessary and the cure shrinkage are both reduced. When prepared correctly, commercial composites have done quite well, *but this shrinkage can still be excessive*. Thus elimination of cure shrinkage and shrinkage stress is still a major objective.

Reduction of Shrinkage Stresses

As discussed above, light-activated resins have overcome many of the deficiencies of chemically activated resins, including lack of control over working time, color shift (yellowing), and porosity from mixing the two-part system. However, the internal pores in chemically cured resins act to relax residual stresses that build up during curing (the pores enlarge during hardening and reduce the concentration of stresses at the margins). Also, the slower curing rate of chemical activation allows a larger portion of the shrinkage to be compensated by internal flow among the developing polymer chains before extensive cross-linking occurs (i.e., before gelation). After the gel point, stresses cannot be relieved but instead continue to increase and concentrate within the resin and the tooth structure adjacent to the bonded surfaces.

Two general approaches have been followed in seeking to overcome the problem of stress concentration and marginal failure experienced with light-activated resins: (1) reduction in volume contraction by altering the chemistry and/or composition of the resin system, and (2) clinical techniques designed to offset the effects of polymerization shrinkage. The former is the more desirable solution, and intensive research and development efforts are currently in progress to develop resins with low shrinkage and low thermal expansion. In the meantime, a variety of techniques have been investigated that can immediately be put into practice by the clinician. These techniques are associated with incremental buildup and control of the curing rate.

Incremental Buildup and Cavity Configuration

One technique attempts to reduce the C-factor, which is related to the geometry of the cavity preparation and

represented by the ratio of bonded to nonbonded surface areas. Residual polymerization stress increases directly with this ratio. During curing, shrinkage leaves the bonded cavity surfaces in a state of stress; the nonbonded, free surfaces (i.e., those that reproduce the original external tooth anatomy) relax some of the stress by contracting inward toward the bulk of the material. A layering technique (Figure 13-17) in which the restoration is built up in increments, curing one layer at a time, effectively reduces polymerization stress by minimizing the C-factor. That is, thinner layers reduce bonded surface area and maximize nonbonded surface area, thus minimizing the associated C-factor. In any case, as discussed previously, limitations on the depth of cure of photoinitiated resins dictate the use of incremental buildup of the composite. Thus, an incremental technique overcomes both limited depth of cure and residual stress concentration but adds to the time and difficulty of placing a restoration.

Soft-Start, Ramped Curing, and Delayed Curing

Another approach that is used to offset photopolymerization stress buildup is to follow the example of chemically initiated systems by providing an initial low rate of polymerization, thereby extending the time available for stress relaxation before reaching the gel point. This can be accomplished by using a soft-start technique, whereby curing begins at low light intensity and finishes with high intensity. This approach allows for a slow initial rate of polymerization and a high initial level of stress relaxation during the early stages and it ends at the maximum intensity once the gel point has been reached. This drives the curing reaction to the highest possible conversion only after much of the stress has been relieved. A number of studies have shown that varying levels of stress reduction in tooth-cavity walls can be achieved in this way while not increasing total exposure time or sacrificing either DC or depth of cure. Consequently, a variety of protocols have been developed and the necessary lamps made available that automatically provide one or more soft-start exposure sequences.

Variations of this technique include ramping and delayed cure. In ramping, the intensity is gradually increased or "ramped up" during the exposure. Such ramping employs stepwise, linear, or exponential modes. In delayed curing, the restoration is initially incompletely cured at low intensity. The clinician then sculpts and contours the resin to the correct occlusion and later applies a second exposure of light for the final cure. This delay allows substantial stress relaxation to take place. The longer the time available for relaxation, the lower is the residual stress. Delayed curing and exponential ramp curing appear to provide the greater reductions in curing stress but do require more time.

In response to this situation, care should be taken when high-intensity lamps are used. Increased lamp intensity allows for shorter exposure times for a given depth of cure in a particular shade and type of resin. Curing depths equivalent to that of a 500-mW/cm^2 QTH lamp (2 mm at 40 seconds) have been demonstrated using an exposure time of 10 seconds with certain PAC lights and 5 seconds with an argon laser. Thus, these high-intensity lamps should, in principle, provide substantial savings in chair time. However, a high-intensity short exposure time causes an accelerated rate of curing, which inevitably leads to substantial residual stress buildup due to inherently less time for stress relaxation mechanisms to take place. Because of these trade-offs, it would appear that little advantage is to be gained by ramped, delayed, or soft-start curing techniques. Numerous laboratory studies and some clinical evidence support this conclusion. Thus the clinician should carefully consider the tradeoffs before investing in these more expensive types of curing lamps.

? CRITICAL QUESTION

What are the problems that result from shrinkage and curing-induced marginal stress during polymerization of restorative resins?

How are polymerization stresses affected by the presence of reinforcing fillers in dental composites?

How can the composite clinical manipulation technique be used to improve the integrity of the marginal seal in a composite restoration?

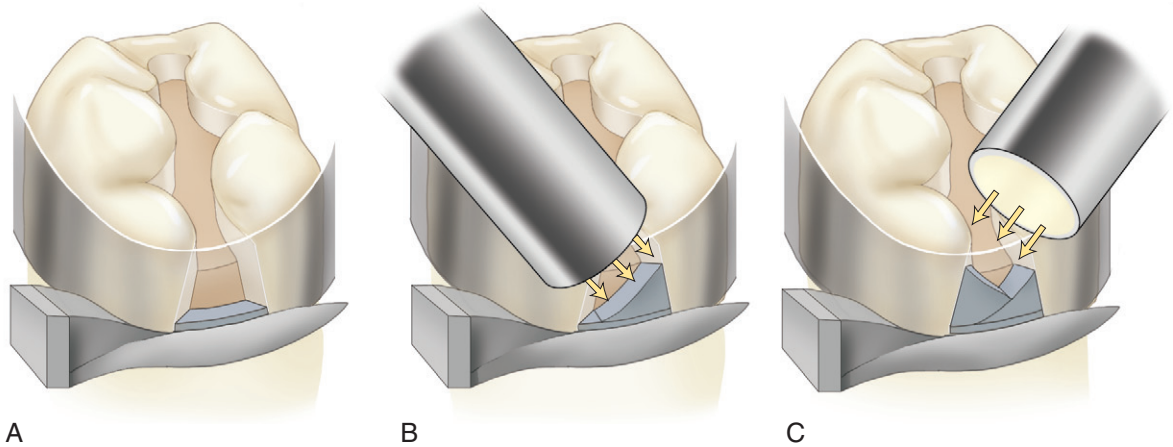


FIGURE 13-17 **A,** First incremental layer of resin composite (gray area) has been placed and cured. **B,** Second increment being cured with a light source. **C,** Third composite increment during curing.

WEAR (VOLUME LOSS BY ABRASION AND OTHER MECHANISMS)

In addition to polymerization shrinkage, other frequent clinical problems have been occlusal (Figure 13-18) and interproximal wear, especially in the case of posterior composites. The mechanism of occlusal wear is a complex problem that has been the subject of much research. Unfortunately, before clinical use, abrasion and wear resistance can be measured only by a laboratory test that simulates simplified environmental conditions. As yet no single test method has been agreed upon as a valid predictor of clinical performance. Although several laboratory test methods are useful to guide research and development efforts, controlled clinical evaluations are the only reliable means of evaluating the durability and useful lifetime of restorative materials. However, based on such studies, the best composites designed for posterior restorations still wear more than natural enamel under identical conditions. Although wear rate differences of 10 to 20 μm/year may seem small for posterior composites, this wear rate still amounts to 0.1 to 0.2 mm more than enamel over 10 years. Thus, it is important to be cautious in selecting the clinical cases to be treated with posterior composites.

Two principal mechanisms of composite wear have been proposed. The first mode is two-body wear, based on direct contact of the restoration with an opposing cusp or with adjacent proximal surfaces to mimic the high stresses developed in the small area of contact. This is related to the higher force levels exerted by the opposing cusp or forces transferred to proximal surfaces.

The second mode is three-body wear, which simulates loss of material in noncontacting areas, most probably owing to contact with food as it is forced across the occlusal surfaces. This type of wear is affected in a complex way by a number of composite properties such as toughness, porosity, stability of the silane coupling agent, degree of monomer conversion, filler loading, and the size and types of filler particles.

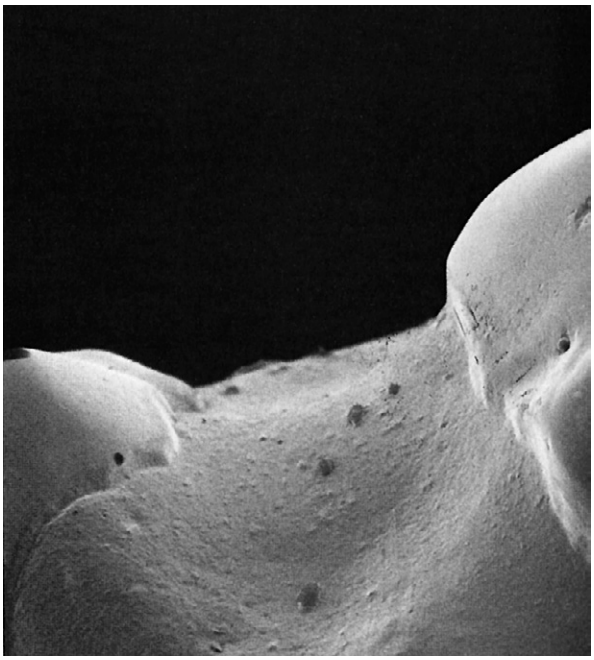


FIGURE 13-18 Scanning electron micrograph of a 9-year-old small-particle-filled composite, illustrating generalized, three-body wear. (Courtesy of Robert L. Erickson.)

Clinically, although direct tooth to restoration contact occurs infrequently during mastication, the loss of material caused by direct wear in areas of tooth-to-tooth contact appears to be greater than that of three-body abrasion by food in noncontact areas. Composites in which the filler particles are small (1 μm or less), high in concentration, and well bonded to the matrix are the most resistant to wear. Large restorations tend to wear more than do smaller ones, as do restorations in molars compared with those in premolars.

Variations among patients—such as differences in chewing habits, force levels, and variations in oral environments—also play a significant role in the wear process. A typical wear pattern for a composite is shown in Figure 13-18 for a 9-year-old, chemically activated, small-particle–filled composite restoration. Although the loss of material shown in this figure is more severe than that for current restorative materials, it illustrates the wear phenomenon. Notice the smoother anatomical contours and the exposed cavity walls where the composite has been worn away by abrasion.

The major indications for composites for class II restorations place emphasis on the demand for esthetics. A conservative preparation is preferred so that the tooth, rather than the composite, absorbs more of the stress. The dentist must also be familiar with the rigorous placement procedures essential for success, as described in textbooks on operative dentistry. However, there are obvious contraindications. A composite class II restoration is doomed to failure in the mouth of a patient who bruxes because of the greater potential for wear. Use of posterior composites in a caries-active mouth is also questionable because few current restorative materials have the ability to provide an anticariogenic effect or to resist leakage. If composites are used for such situations, the application of a hydrophilic sealing resin along the margins may be beneficial. Nonetheless, with the greater demand for esthetics and continual improvements in composite formulations, the use of these materials in stress-bearing situations continues to increase. In response, academic and industry research can be expected to continue to improve the clinical durability of composite materials (see below for a discussion of the longevity of composites).

The problem of wear in posterior resin applications has been considerably reduced by ongoing advances in composite technology. Nevertheless difficulties still exist in high-stress situations related to inherent problems with both the mechanical and chemical degradation of composites. However, polymerization shrinkage, technique sensitivity, and difficulty in obtaining a predictable, reliable bond to dentin or cementum margins are probably more important. These deficiencies remain a major concern regarding the potential leakage associated with class II restorations.

Indirect Posterior Composites

Indirect composites for fabrication of onlays and inlays are polymerized externally and then luted to the tooth with a compatible resin cement. Indirect composite inlays or onlays reduce wear and leakage and overcome some of the limitations of resin composites. Several different approaches to resin inlay construction have been proposed: (1) the use of both direct and indirect fabrication methods; (2) the application of light, heat, pressure, or a combination of these curing systems; and (3) the combined use of hybrid and microfilled composites.

The fabrication process for direct composite inlays first requires the application of a separating medium (e.g., agar solution or glycerin) to the prepared tooth. The restorative resin pattern is then formed, light-cured, and removed from the preparation. The rough inlay is then exposed to additional light for approximately 4 to 6 minutes or heat-activated at approximately 100 °C for 7 minutes, after which the preparation is etched, the inlay cemented into place with (typically) a dual-cure resin, and the inlay is then polished.

Composite systems are also available as indirect products. Indirect inlay resins require an impression and a dental laboratory technician to fabricate the inlay. In addition to conventional light- and heat-curing, laboratory processing may employ heat (e.g., 140 °C) and pressure (e.g., 0.6 MPa for 10 minutes). The potential advantage of these materials is that a significantly higher degree of polymerization is attained, which improves physical properties and resistance to wear. The polymerization shrinkage does not occur in the prepared teeth, so induced stresses and bond failures are reduced, which reduces the potential for leakage. Furthermore, these resins are repairable in the mouth and are not as abrasive to opposing tooth structure as ceramic inlays.

Laboratory studies support these expected advantages: for example, a recent review revealed that the annual clinical failure rates in class I and II posterior stress-bearing cavities are the same for composite inlays as for amalgam restorations (1.9%), somewhat superior to those for direct composites (3.6%), and only slightly (but not significantly) inferior to cast gold inlays and onlays (1.4%) (Manhart et al., 2004). However, technique sensitivity for indirect resin restoration systems remains high and their appropriateness as a substitute for amalgam or cast restorations in *all* posterior applications is not clear, even though the esthetics are appealing.

LONGEVITY OF COMPOSITES

The most commonly cited reasons for the failure of composites in clinical studies are secondary caries, fracture, marginal deficiencies, and wear. However, these reasons vary greatly depending on the type of study (randomized clinical trial versus private practice setting), type of composite used, period of observation, and other aspects of study design. Nonetheless, properly placed, composites can last many years even in posterior regions, where wear and bite forces are greatest.

Several studies report the clinical performance of posterior composite restorations over time. Opdam and colleagues (2007) published a retrospective study on the longevity of 1955 posterior composites placed in a private practice setting. Life tables calculated from the data reveal a survival rate for composite resin of 91.7% at 5 years and 82.2% at 10 years. There was a significant effect of the amount of restored surfaces on the survival of the restorations—that is, the more conservative the restoration, the longer it survived. A number of other studies published in the past 10 years report success rates ranging from 70% to 100% for posterior composites. These results are similar to those of a meta-analysis of studies conducted during the 1990s. Very few clinical studies with evaluation periods longer than 10 years are available. A study by Wilder and colleagues (1999) reported a 76% success rate for 85 UV-cured posterior composites after 17 years, whereas da Rosa Rodolpho and colleagues (2006) reported a 65% success rate for 282 hybrid visible light–cured composites after 17 years. These authors attributed the relatively low success rate reported in the latter study to the high number of large restorations that were placed.

The clinical performance of dental restorations is best judged on the basis of long-term clinical trials, preferably those based on randomized controlled experimental designs. Very few studies of this type exist in the dental literature. However, a recent evidence-based review of the longevity of amalgam and composite restorations was based on a critical review of clinical data over 10 years. The survival probability for restorations in permanent teeth is shown in Figure 13-19. Note that the most consistent survival levels are exhibited by amalgam restorations. The variability among studies is much larger for the composite restorations compared with amalgam restorations. The comparative survival probabilities for amalgam versus composite restorations in permanent teeth at 3, 4, 5, and 7 years are summarized in Table 13-6. Similar comparative data for restorations in primary teeth after 3 and 4 years are also listed in this table. The survival rate overall for composites in permanent teeth after 7 years was 67.4%, compared with 94.5% for amalgam restorations. More than 90% of amalgam restorations in permanent teeth survived longer than 9 years. In comparison, only 64% of glass ionomer restorations survived after 5 years. Only 41% of class V composites placed with dentin bonding agents survived longer than 5 years. Chadwick and associates (2001) concluded that the class II glass ionomer/composite restorations should be avoided because of a high percentage of failures at the gingival margin of the proximal box.

? CRITICAL QUESTIONS

How does the extent to which monomer is converted to polymer affect the longevity of composite restorations?

What factors related to the curing process affect the integrity of the seal between a photocured resin composite and the margins of a cavity preparation?

PLACEMENT TIME OF COMPOSITES

Although the performance of posterior composites has greatly improved during the past decade relative to amalgams, the placement time is significantly higher for composites, as shown in Figure 13-20. The placement time of ceramic and

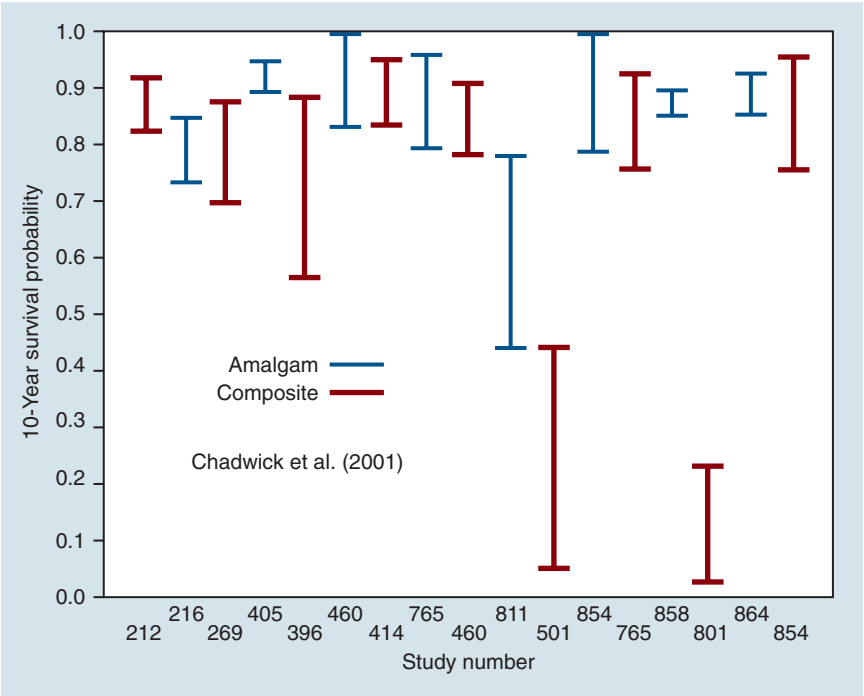


FIGURE 13-19 Ten-year survival probability for posterior composite and amalgam restorations. (Data from Chadwick BL, Dummer PMH, Dunstan F, et al: *The Longevity of Dental Restorations: A Systematic Review*. National Health Service Centre for Reviews and Dissemination, University of York, 2001.)

TABLE 13-6 Comparison of Survival Probabilities for Various Types of Restorations after 3, 4, 5, and 7 Years

RESTORATION	3 YEARS PRIMARY PERMANENT		4 YEARS PRIMARY PERMANENT		5 YEARS PRIMARY PERMANENT		7 YEARS PRIMARY PERMANENT	
Type	**Teeth**	**Teeth**	**Teeth**	**Teeth**	**Teeth**	**Teeth**	**Teeth**	**Teeth**
Amalgam	95.3	97.2	95.1	96.6	90.8	95.4	—	94.5
Composite	82.4	90.0	67.2	85.6	—	78.2	—	67.4
Glass Ionomer	51.5	73.8	51.5	73.8	31.2	64.9	—	—
DBA and Composite	—	83.7	—	47.7	—	41.5	—	—
Ceramic or Composite Inlay	—	93.3	—	90.1	—	85.3	—	

Modified from Chadwick BL, Dummer PMH, Dunstan F, et al: *The Longevity of Dental Restorations: A Systematic Review*. National Health Service Centre for Reviews and Dissemination, University of York, Heslington York, YO10 5DD, United Kingdom, 2001.
DBA, dentin bonding agent.

composite inlays is significantly higher than that for either amalgam or composite restorations. Obviously the cost of restorations for the patient is also proportionately higher for the inlay prostheses. In fact, the relative cost per tooth per year over a 5-year period for amalgam, composite, and ceramic or composite inlay restorations, in terms of multiples, is 1, 1.62, and 6.35, respectively. The relative cost per tooth per year of amalgam restorations is significantly less than that of composites after 10 years (1 versus 3.36, respectively). A comparative analysis of the placement times is summarized in Table 13-7 for class I, class II (two-surface), class II (three-surface, mesial-occlusal-distal), and pin-retained cusp replacement restorations.

BIOCOMPATIBILITY OF COMPOSITES

Concerns about the biocompatibility of restorative materials usually relate to the effects on the pulp from two aspects: (1) the inherent chemical toxicity of the material and (2) the marginal leakage of oral fluids.

A chemical insult to the pulp from composites is possible if components leach out or diffuse from the material and subsequently reach the pulp. Inadequately cured composite materials at the floor of a cavity can serve as a reservoir of diffusible components that can induce long-term pulp inflammation. This situation is of particular concern for light-activated materials. If a clinician attempts to polymerize too thick a layer of resin or if the exposure time to the light is inadequate (as discussed previously), the uncured or poorly cured material can release leachable constituents adjacent to the pulp. Nonetheless, adequately polymerized composites are relatively biocompatible because they exhibit minimal solubility, and unreacted species are leached in very small quantities. From a toxicological point of view, these amounts should be too small to cause toxic reactions. However, from

an immunological point of view, under extremely rare conditions, some patients and dental personnel can develop allergic responses to these materials.

The second concern is associated with polymerization shrinkage of the composite and the subsequent marginal leakage. The marginal leakage might allow bacterial ingrowth, and these microorganisms may cause secondary caries or pulp reactions. Therefore, the restorative procedure must be designed to minimize polymerization shrinkage and marginal leakage. A comprehensive review of biocompatibility is presented in Chapter 8.

Bisphenol A Toxicity

Bisphenol A (BPA), a precursor of *bis*-GMA, has been shown to be a xenoestrogen, a synthetic compound that mimics the effects of estrogen by having an affinity for estrogen receptors. BPA and other endocrine-disrupting chemicals (EDCs) have been shown to cause reproductive anomalies, especially in the developmental stages of fetal wildlife. Although the effects on humans are still unclear, testicular cancer, decreased sperm count, and hypospadias (displacement of the urethral meatus) have been seen as the result of exposure to EDCs.

BPA has recently also been shown to exhibit antiandrogenic activities, which may prove to be detrimental in organ development. Studies have shown that the **estrogenicity** of resin compounds is mainly associated with BPA and BPA dimethacrylate (*BPA-DM*), monomers found in the base paste of some dental sealants. *In vitro* reports have confirmed that BPA and BPA-DM applied to cancer cells significantly increase cell proliferation and DNA synthesis, similar to the effect of estrogen. *In vitro* studies with mammals have revealed numerous effects, such as delayed and sustained hyperprolactinemic changes in estrogen receptors in the hypothalamus and pituitary glands.

Controversy surrounds this issue because it is unclear how much BPA or BPA-DM is released to the oral cavity and what dosage is enough to affect human health. A clinical study (Olea et al., 1996) revealed that BPA was collected in saliva after 1 hour of sealant placement, leading the authors to conclude that sealant application led to xenoestrogen exposure in children. This led to a deluge of follow-up examinations to determine the validity of the results. More recent studies have shown that BPA-DM should be restricted to use in resin-based composites because of its very potent estrogenic effect and because of high levels found in the body; however, the effect of BPA is negligible. Further research should be conducted *in vivo* to show the chemical activity of these compounds and their effects on human development. Additional information on the biocompatibility of restorative materials is presented in Chapter 7.

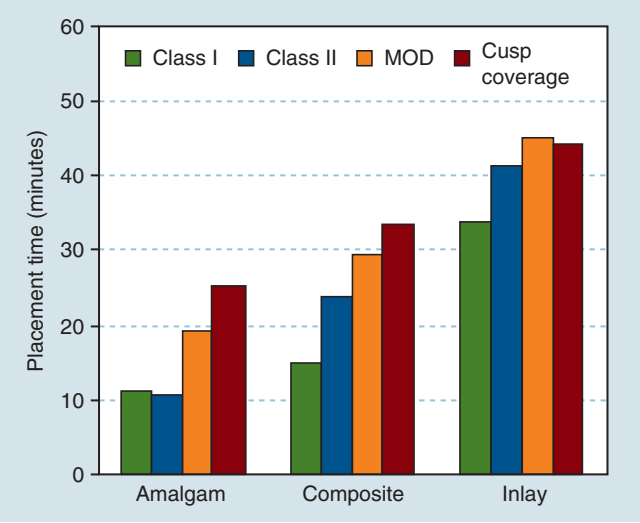


FIGURE 13-20 Placement time required for posterior amalgam, composite, and ceramic and composite inlay restorations. (Data from Chadwick BL, Dummer PMH, Dunstan F, et al: *The Longevity of Dental Restorations: A Systematic Review*. National Health Service Centre for Reviews and Dissemination, University of York, 2001)

FINISHING OF COMPOSITES

The term *finishing* usually refers to the process of adapting the restorative material to the tooth (e.g., removing overhangs and shaping occlusal surfaces), whereas *polishing* refers to removing surface irregularities to achieve the smoothest possible surface. Optimal finishing and polishing of resin-based composites is a very important step in the completion of a restoration. Residual surface roughness can encourage

TABLE 13-7 Comparison of Average Time (minutes) Required for Initial (I) and Replacement (R) Restorations

	AMALGAM		COMPOSITE		COMPOSITE AND CERAMIC INLAY	
Restoration Type	**I**	**R**	**I**	**R**	**I**	**R**
Class I	11	11	15	16	34	34
Class II	15	13	24	24	41	40
MOD: mesioocclusal-distal	19	19	29	31	45	45
Cusp replacement with pins	25	26	33	34	44	44

Adapted from from Chadwick BL, Dummer PMH, Dunstan F, et al: *The Longevity of Dental Restorations: A Systematic Review*. National Health Service Centre for Reviews and Dissemination, University of York, Heslington York, YO10 5DD, United Kingdom, 2001.
I: Initial restoration; R: replacement restoration.

bacterial growth, which can lead to a myriad of problems including secondary caries, gingival inflammation, and surface staining. Several methods for the finishing and polishing of resin-based composites have been advocated. The best possible finish is produced by not polishing surfaces at all, at least surfaces that have polymerized next to a smooth matrix strip. This minimizes porosities as well as the oxygen-inhibited layer. However, it is often difficult to achieve proper contours and margin adaptation without some amount of finishing because the plastic strip is often difficult to adapt to the convex and concave surfaces of the tooth. Therefore, different finishing and polishing systems are being marketed to achieve the best possible surface.

Research has been conducted to examine the effect of several significant factors on the finish and polish of a composite restoration: (1) environment, (2) delayed versus immediate finish, (3) the types of materials, and (4) surface coating and sealing.

ENVIRONMENT

Environment involves whether the process of finishing and polishing should be performed in a wet or dry field in the mouth. Some advocates say that finishing in a dry field with the finishing equipment mounted on a slow-speed handpiece allows for better visualization of the restoration margins. However, studies have shown that a dry polishing technique results in an increase in marginal leakage, possibly because of heat production, which can disturb the marginal sealing ability of the adhesive resins. Other studies have shown that structural and chemical changes occur on the surfaces of restorations as a result of a dry environment. However, still other research has confirmed that the dry polishing technique has no effect on the hardness or surface structure. As with many dental procedures, grinding and finishing are best accomplished in moderation. The clinician should finish the restoration in an environment where the margins are clearly discernible and where minimal heat is generated. Excessive heat results in smearing of the surface and depolymerization. Water-cooling during grinding and finishing should ensure a standard surface quality.

ELAPSED TIME BETWEEN CURING OF THE COMPOSITE AND FINISHING AND POLISHING

Elapsed time may also have an effect on surface characteristics and resistance to leakage that develops. Some advocate delaying the finishing of composite restorations for up to 24 hours because polymerization is incomplete at placement, although composite manufacturers recommend that finishing be accomplished shortly after placement. Studies have shown that delayed finishing can actually increase marginal leakage and has no effect on surface characteristics compared with immediate finishing. Also, delayed finishing has a minimal effect on hardness. Thus, for all practical purposes, almost all composite restorations should be finished and polished shortly after placement during the same appointment, although the finishing should be delayed for approximately 15 minutes after curing.

TYPES OF MATERIALS AND DEVICES

A variety of materials and devices can be used to finish and polish composite restorations. Use of a scalpel blade or any thin, sharp-edged instrument to remove flash on the proximal areas is recommended. However, this is a very risky procedure, especially if the trimming procedure involves shearing in a direction toward the composite and away from the gingival margin, which can lead to localized debonding and leakage. Trimming forces should be applied either parallel to the margin or toward the gingival tissue. Coarse to ultrafine aluminum oxide discs can be applied to areas with difficult access around the proximal surfaces or in embrasures (see Chapter 11). Tungsten carbide burs or fine diamond tips can be used to adjust occlusal surfaces and blend the composite to the surfaces of the teeth. Several studies in the literature have rated many of these systems as to their effect on surface smoothness and microleakage. Currently aluminum oxide discs produce the best surface while also inducing minimal trauma. Other systems include resin-finishing devices that use fine and extrafine polishing pastes, silicone-based systems, and silicon carbide–impregnated polishing brushes and points. Although high stresses may be associated with surface grinding and polishing, a recent study has shown that the type of polishing system used does not significantly affect the development of microleakage.

SURFACE COATING AND SEALING

An important step in finishing and polishing is the application of a bonding agent or a surface sealer. It has been widely documented that the finishing (and possibly polishing) process is detrimental to composite surfaces in that surface microcracks are introduced and the highly polymerized outer surface of the resin composite material is removed. Application of a penetrating surface sealer or a low-viscosity resin with little or no filler ensures that surface porosities are filled and microcracks sealed. Studies have shown that this "rebonding" technique also significantly decreases microleakage by improving the marginal seal of restorations. Additional information on the finishing and polishing of restorative materials is presented in Chapter 11.

REPAIR OF COMPOSITES

Composites can be repaired by replacing lost material. This is a useful procedure for correcting defects or altering contours on existing restorations. The procedures for adding new material differ depending on whether the restoration is freshly polymerized or an older restoration.

When a restoration has just been placed and polymerized, it may still have an oxygen-inhibited layer of resin on the surface. Additions of new composite can be made directly to this layer because this represents, in essence, an excellent bonding substrate. Even after the restoration has been polished, adding more material can still repair a defect. A restoration that has just been cured and polished may still have more than 50% of unreacted methacrylate groups to copolymerize with the newly added material.

As the restoration ages, fewer and fewer unreacted methacrylate groups remain and greater cross-linking reduces the ability of fresh monomer to penetrate the matrix. The strength of the bond between the original material and the new resin decreases in direct proportion to the time that has elapsed between polymerization and addition of the new resin. Furthermore, polished surfaces expose filler surfaces that are free from silane. Thus, the filler surface area does not chemically bond to the new composite layer. Even ideally—that is, with the addition of a silane-bonding agent to the surface before the addition of new composite—the strength of repaired composite is less than half the strength of the original material (Figure 13-21).

Even though repair is essential to the overall longevity of composite restorations, there are very few reports of formal investigations or long-term trials concerning composite repair. Recently, however, 2- to 3-year clinical results have been reported showing good outcomes for repairs or the resealing of marginal defects, and a recent 7-year recall reinforced the use of a conservative repair strategy. A survey of general practitioners found that half always repair defective composite margins adjacent to enamel but most replace a restoration if the defective margin is adjacent to dentin. Thus, it would appear that the repair of composite restorations with defective margins adjacent to enamel is becoming the standard of care.

ACID ETCHING

As described in Chapter 12, acid etching is used to aid and enhance the formation of a resin bond to the teeth. For example, when aqueous 30% to 50% phosphoric acid is applied to enamel, the enamel rods are attacked and dissolved to depths of 10 to 100 µm. The differential etching of the rods and interprismatic material results in etch pits about 4 µm in diameter. When a composite is applied, resin can readily wet the etched surfaces and flow into the pits, thus forming microscale mechanical bonds (micromechanical interlocking) and anchoring the resin to the enamel. Thus etching increases surface area, increases surface energy to enhance wetting, and creates porous enamel-rod ends for resin penetration.

Because some conventional restorative cavity walls are roughly parallel to the enamel rods, it may be necessary to overextend the restoration onto uncut enamel, or (better) to add chamfers or bevels to the enamel of the cavity preparation periphery to obtain bonding. More restorative tags are produced if an unfilled "bonding agent" resin is applied prior to application of the composite.

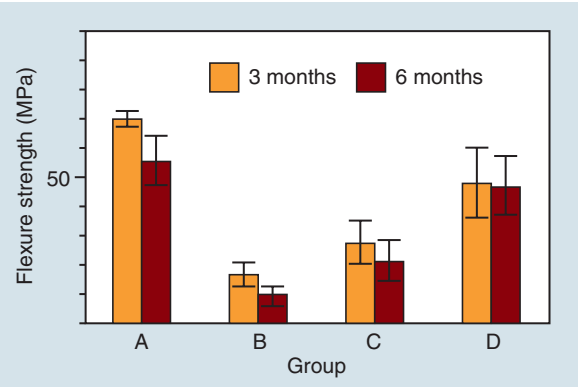


FIGURE 13-21 The influence of the method of composite repair on strength under in vitro conditions. Flexural strength after storage in distilled water at 37 °C for 3 and 6 months. **A,** Original, unbroken samples serving as a control. **B,** Repair without first acid-etching. **C,** Repair after acid-etching and the application of an unfilled resin. **D,** Repair after toluene/silane treatment to soften the broken surfaces and facilitate permeation by new monomer. (Data from K-JM Söderholm: Flexure strength of repaired dental composites. *European J Dent Oral Science* 94:364–369, 1986.)

USE OF COMPOSITES FOR RESIN VENEERS

Originally resin veneering materials were heat-polymerized polymethylmethacrylate, which were improved subsequently by the addition of fillers and cross-linking agents. Microfilled materials that use *bis*-GMA, UDMA, or other high-molecular-weight dimethacrylates—such as 4, 8-dimethacryloxymethylene-tricyclodecane (Figure 13-22)—as resin matrices have created renewed interest in resin-veneered metal restorations. These resins are polymerized using visible light or a combination of heat and pressure. In general, these new microfilled resins have physical properties superior to those of the original unfilled resin.

The first resin veneers were mechanically bonded to metal substrates using wire loops or retention beads. Recent improvements in bonding mechanisms have included micromechanical retention created by acid etching the base metal alloy and the use of chemical bonding systems such as 4-META, phosphorylated methacrylate, epoxy resin, or silicon dioxide flame-sprayed to the metal surface followed by the application of a silane coupling agent (silicoating).

Prosthetic resin-veneering materials have several advantages and disadvantages compared with ceramics. The advantages include ease of fabrication, predictable intraoral reparability, and less wear of opposing teeth or restorations. The drawbacks include low proportional limit and pronounced plastic deformation, which contribute to distortion on occlusal loading. Therefore, the resin should be protected with metal occlusal surfaces whenever feasible. Leakage of oral fluids and staining below the veneers, particularly those attached mechanically, are caused by dimensional changes from water sorption, heating, and cooling. Surface

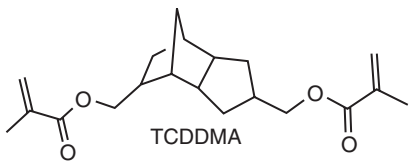


FIGURE 13-22 4,8-di(methacryloxymethylene)-tricyclodecane (TDC, TCDDMA), a bulky, space-filling urethane dimethacrylate monomer.

staining and intrinsic discoloration tend to occur with these resins.

Resins are also susceptible to wear during toothbrushing. Thus, it is necessary to instruct the patient on proper cleaning procedures using a soft toothbrush and mild abrasive toothpastes. Resin-veneered metal restorations are not suitable for use as removable partial denture abutment retainers where the clasp arm engages an undercut on the veneered surface because the resin is not as wear-resistant as porcelain.

Resin composites can also be used as a conservative alternative to conventional prosthodontic restorations, such as veneers for masking tooth discoloration or malformation. The resins are used as preformed laminate veneers, in which resin shells are adjusted by grinding and the contoured facing is bonded to tooth structure using the acid-etching technique with either chemically activated, visible light–activated, or dual-cure luting resin cements. Resins used to cement indirect restorations, veneers, and prosthetic devices are similar to flowable restorative resins but are adjusted to match the needs of luting applications. This type of resin material is discussed further in Chapter 14.

SELECTION CRITERIA FOR POSTERIOR COMPOSITES

Not all patients should be considered as candidates for these posterior restorations. The primary indication for using direct posterior composites in place of amalgam is esthetics. Unless the patient's esthetic demands are high, there are minimal advantages to using resin restorations in posterior regions. Often the disadvantages coupled with the difficulty in manipulation far outweigh the benefits. Other indications might include the need for conservative preparations along with conservation of tooth structure. Because composite restorations do not depend on mechanical undercuts for retention, the concepts of resistance form and retention form do not really apply to resin preparations. However, because of their inferior physical properties, composites should not be used for cuspal coverage or for large restorations exceeding one-third the buccolingual width of the tooth. If possible, occlusal load should always be borne by sound tooth structure and never by resin. Because wear is also an issue, posterior composites should not be placed in patients experiencing parafunctional habits. Another lesser indication is the use of composites to minimize thermal conduction. Because amalgam is metallic, it tends to conduct heat more rapidly, leading to tooth sensitivity and pain. Placement of composites or ceramics, which are good thermal insulators, often reduces this occurrence.

INNOVATIONS IN DENTAL COMPOSITES

Numerous variations have been introduced in order to improve composites beyond those obtainable with *bis*-GMA, TEGDMA, and UDMA dimethacrylates as the main monomer ingredients. Some of the more innovative new monomers are listed below. The products based on these monomers typically also include TEGDMA, *bis*-GMA, or UDMA in a formulated blend for such purposes as lowering viscosity and improving handling properties, reducing cure shrinkage and/or residual stress, increasing conversion, and improving esthetics.

Filler systems are trending toward ever smaller particle sizes. Accordingly, two types of systems in which a portion of the reinforcing component operates at molecular scale have recently been introduced.

Further, there have also been innovations in photocuring based on training aids and devices developed via a comprehensive approach to understanding the relationship between clinical technique and optimized performance properties of composites. These innovations are discussed below.

MONOMER SYSTEMS

Polycarbonate Dimethacrylate

"Alert" is a polycarbonate dimethacrylate product (Pentron Clinical Technologies, Wallingford, CT) (Figure 13-23). The cured polymer is a polyester using carbonate (-O-CO-O-) links, instead of the urethane links (-NH-CO-O-) found in UDMA, to connect the methacrylate ends to the central section of the monomer. The formulated composite has been reported to be packable like amalgam, photocurable in bulk segments, and readily curable without generating high residual shrinkage stress.

High-Molecular-Weight Urethane with a Rigid Central Section and Flexible End Groups

"Kalore," also known as "DX-511" (GC America, Alsip, IL) (Figure 13-24), has a high molecular weight and a long rigid central section with flexible methacrylate end groups; these provide rodlike shapes that facilitate self-assembly into compact molecular structures. This, together with dilution of the number of polymerizable end groups due to the high molecular weight (895, compared to with 512 for *bis*-GMA), reduces curing

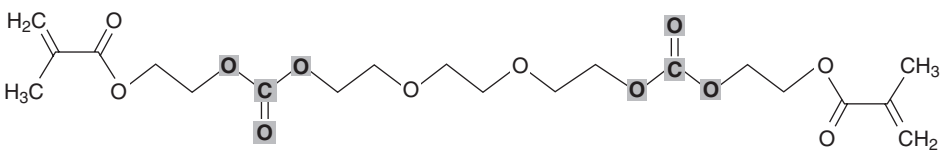


FIGURE 13-23 Polycarbonate dimethacrylate monomer (PCDMA; "Alert," Pentron Clinical Technologies, Wallingford, CT). PCDMA is similar to *bis*-GMA with two carbonate groups (–O-CO-O-, highlighted) in a central segment between two ethylmethacrylate end groups. (Courtesy of Barry K. Norling.)

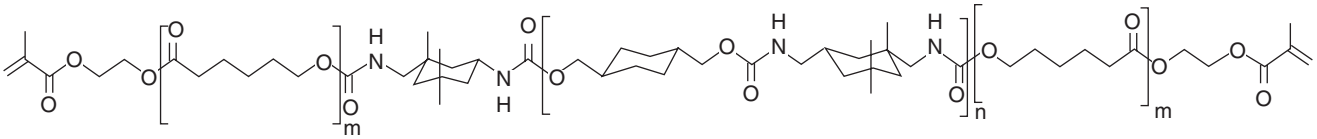


FIGURE 13-24 A high-molecular-weight polyurethane dimethacrylate monomer, DX-511, that contains a long, rigid central section between flexible methacrylate end groups ("Kalore," GC America, Alsip, IL). Like UDMA, DX-511 has urethane (–NH-CO-O-) groups that connect a central segment between two ethyl-methacrylate end groups. It also contains 2m +1 cyclohexane rings. (Courtesy of Barry K. Norling.)

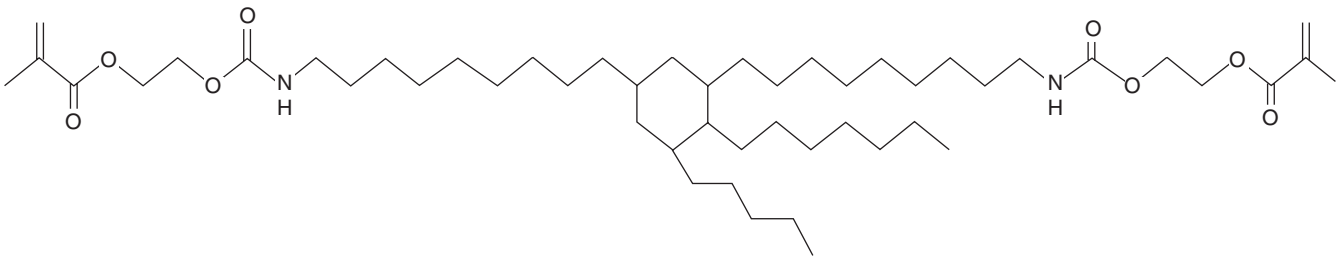


FIGURE 13-25 A phase-separating cycloaliphatic urethane dimethacrylate, DDCDMA (dimer dicarbamate dimethacrylate), with a bulky center is composed of a 6-carbon aliphatic ring with two long hydrocarbon side chains derived from a linoleic acid dimer. (Courtesy of Barry K. Norling.)

shrinkage, while the flexible end groups promote reactivity and enhance monomer-polymer conversion.

Dimethacrylate with a Bulky, Space-Filling Central Group

"Venus Diamond" (Heraeus Kulzer, South Bend, IN) is a resin product based on 4,8-di(methacryloxy methylene)-tricyclo-decane (TCDDMA), a bulky, space-filling dimethacrylate monomer (see Figure 13-22). The bulky three-ring central group provides steric hindrance, which holds the monomers apart and thus slows the rate of polymerization. This lengthens the time needed for the cross-linking reaction to reach the gel point and provides time for adjacent polymer chain segments to slip among themselves, rearrange to lower energy configurations, and relieve developing stresses before the gel point is reached, resulting in one of the lower curing-stress resins currently reported among commercial products.

High-Molecular-Weight Phase-Separating Dicarbamate with Hydrophobic Side Chains

"N'Durance" (Septodont USA, Confi-Dental Products, Louisville, CO) is a dimer dicarbamate dimethacrylate (DDCDMA) product that also contains a bulky central group, somewhat analogous to TDC-urethane dimethacrylate. The bulky center is made up of a 6-carbon aliphatic ring with two long hydrocarbon side chains derived from a linoleic acid dimer (Figure 13-25). The center section is connected to two methacrylate end groups via urethane groups (-NH-CO-O-, also referred to as *cabamate* groups). The chain length between reactive ends is very long (having a molecular weight of 843), similar to that of DX-511 (see Figure 13-24), which provides double-bond dilution and hence reduced shrinkage; the bulky center section allows greater conversion during copolymerization as well as greater stress relaxation prior to the gel point. A further advantage is the hydrophobic nature of the center group, which restricts water absorption and solubility with the other dimethacrylates in the formulation. This leads to the formation of two separate phases during polymerization and produces a small expansion which partially offsets the polymerization shrinkage.

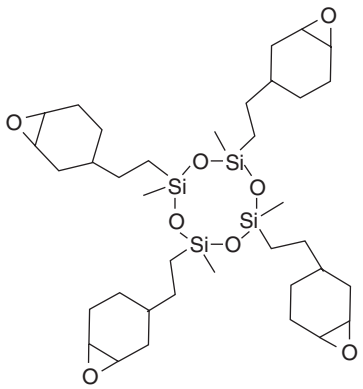


FIGURE 13-26 Tetrafunctional silorane monomer polymerizes via a cationic-initiated, epoxy ring-opening, cross-linking mechanism. When the rings open, the chains lengthen and occupy more space and partially offset the polymerization shrinkage. (From Weinmann, et al: Siloranes in dental composites. *Dent Mater* 21[1]: 2005.)

"Silorane" Ring-Opening Tetrafunctional Epoxy Siloxane

"Filtek LS" (3M ESPE, St. Paul, MN) involves an entirely different chemistry based on epoxy, rather than acrylic functionality. These tetra-functional "**silorane**" monomers (Figure 13-26) use ring-opening polymerization. Silorane chemistry utilizes a combination of epoxy functionality (three-unit ring with two carbons and an oxygen) combined with siloxane units (–O-Si-O–) that can be cured with low-shrinkage via a cationic cross-linking mechanism by means of ring-opening

polymerization. When the rings open, they lengthen and occupy more space; the resulting expansion offsets a substantial proportion of the polymerization shrinkage—thus, the "LS" (low shrinkage) designation for the commercial product. Previously, epoxy systems were not used for dental applications because a nontoxic curing initiator with hydrolytic stability could not be found.

MOLECULE-SIZED REINFORCING FILLER PHASES

Organically Modified Ceramic Oligomers

Ormocer is an acronym for *organically modified ceramics*. They are considered to be molecule-sized hybrid structures consisting of inorganic-organic copolymers. Organic, reactive monomers are bound to an inorganic -Si-O-Si- network. These molecular hybrids consist of, for example, methacrylate-terminated chains grafted onto a central cyclic polysiloxane 2- to 3-nm particle. These nanoparticles are dispersed on a molecular scale and do not produce separate phases the way DDCDMA does in the dimer dicarbamate dimethacrylates, discussed above. High-molecular-weight, flexible, relatively low-viscosity, cross-linkable molecules ("oligomers") result. The large spacing between cross-links resulting from curing produces a low level of polymerization shrinkage, while the inorganic network provides abrasion resistance through its glasslike structure and low water sorption due to its hydrophobicity.

Ormocers are used in the formulation of several commercial composites (e.g., "Definite" and "Admira," Voco GmbH; "Ceram-X," Dentsply International, York, PA). Whereas the molecule-sized silicate particles provide some reinforcement, ground glass and/or other fillers are typically required for sufficient reinforcement. Ormocer-type structures may also be formed as organic-inorganic hybrid particles, microparticles, and nanoparticles and can themselves be used as reinforcing dispersed-phase fillers.

Because of their unique composition, ormocer-based dental materials offer characteristic advantages in comparison to conventional composites. These are of particular note: limited cure shrinkage, very high biocompatibility, good manipulation properties, and excellent esthetics.

Polyhedral Oligomeric Silsesquioxane (POSS)

POSS molecules are 12-sided silicate cages produced from silane and functionalized to copolymerize with other monomers. A silsesquioxane is a chemical structure with the composition $R_nSi_nO_{1.5n}$, for example, $(CH_3)_8Si_8O_{12}$. For POSS materials used in dental applications, the R-group is typically a methacrylate (Figure 13-27).

POSS is a molecule-sized hybrid organic-inorganic oligomeric compound that can disperse homogeneously in compatible monomers and become covalently incorporated into cross-linked networks upon curing. Like the ormocer-type materials, the silicate cage structures provide a reinforcing function, but filler particles must also be included to achieve the balance of mechanical and other properties required for adequate performance as dental composites. Depending on the dispersed filler, POSS-based resins are characterized as being highly polishable and having excellent polish retention, mechanical properties, and wear resistance.

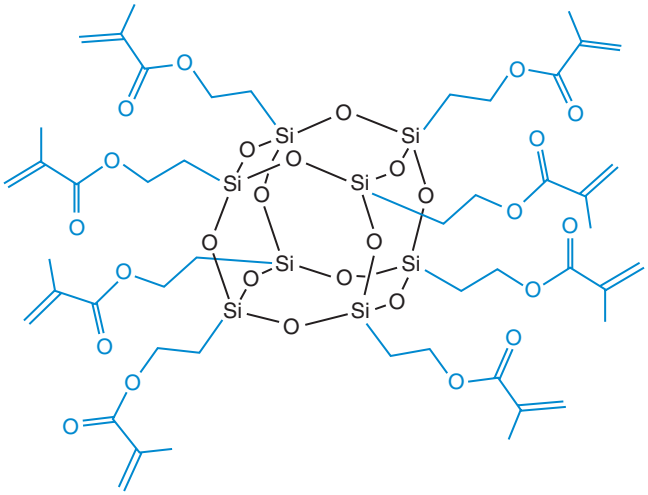


FIGURE 13-27 Methacryl polyhedral oligomeric silsesquioxane, a 12-sided silicate cage structure having polymerizable methacrylate pendent groups. (Courtesy of Hybrid Plastics, Inc. Hattiesburg, MS.)

Current commercial products based on silsesquioxane technology include "Artiste Nano-Hybrid Composite" (Pentron Clinical, Wallingford, CT).

PHOTOCURING TRAINING, EVALUATION, AND PROCESS MANAGEMENT

The MARC Device and Training System

The success of resin restorations depends on many factors, including the technical difficulty of the procedure, the degree of moisture control, the effects of shrinkage during polymerization, the type of resin, the porosity of the resin, and how well the resin is cured. Four variables affect the extent to which a resin is polymerized within the tooth: operator technique, type of curing light, location of the restoration, and type of resin used. A recently introduced device, "MARC" (an acronym for "managing accurate resin curing," BlueLight Analytics Inc., Halifax, NS), takes these four variables into by measuring both the irradiance and the energy received by simulated preparations in a mannequin head.

In order to reach a high degree of cure, photocured resins must receive sufficient energy at the appropriate wavelengths. Typically the top surface quickly hardens following even brief exposure to a curing lamp and delivery of a nominal amount of energy. Clinicians have inadequate means to determine if sufficient energy has been delivered to reach an adequate cure level and depth of cure. Recently there has been a paradigm shift away from measuring the average irradiance at the emitting tip of a curing light to measuring the irradiance, wavelengths, and energy that actually reach the resin being polymerized. This type of information cannot be collected with a conventional dental radiometer.

The MARC device combines precise, laboratory spectral technology with clinically relevant measuring conditions within prepared dentoform teeth in a mannequin head. Spectrum-corrected sensors inside the dentoform teeth are

attached to a laboratory-grade spectroradiometer embedded within the manikin's head to record the light received from curing units. Output from the spectrometer is fed into a laptop computer, where custom software provides real-time and accumulated comparison data: spectral irradiance, total energy delivered over a given exposure duration, and the estimated exposure duration needed to deliver a specified energy dosage. In addition to providing real-time feedback to judge when adequate photoenergy has been delivered, the MARC device can also be used as a training aid for performing optimal clinical photocuring. The effect of minor alterations in tip distance and angle and movement during exposure is displayed in real time, and the ultimate consequence in terms of altered energy delivered is determined. The device can also be used to determine the ability of various lamps to deliver adequate energy levels between different tooth locations.

ACKNOWLEDGEMENT

The authors would like to acknowledge Dr. Josephine Esquivel-Upshaw and Dr. Barry K. Norling, for their contribution to the previous edition of this chapter.

SELECTED READINGS

Useful Websites

Biomaterials Properties Database: http://www.lib.umich.edu/node/21860

The Biomaterials Network: http://www.biomat.net/

Dentistry Today, Advanced Resin Technologies: http://www.dentistrytoday.com/dental-materials/972

Dental products newsletters: http://www.dentaladvisor.com/, http://www.cliniciansreport.org/page/additonal-studies-archive, http://adeptinstitute.com/members/000_source/membership/list.php

Managing Accurate Resin Curing (MARC): http://curingresin.com/dental_clinicians.html

Ormocer technology: http://www.ormocer.de/EN/herstellungsverfahren/index.jsp

Polyhedral oligomeric silsesquioxane (POSS) technology, Hybrid Plastics: http://www.hybridplastics.com/docs/

Polymer Learning Center, acrylic polymers: http://www.pslc.ws/mactest/level3.htm

Virtual Textbook of Polymer Science: http://plc.case.edu/tutorial/enhanced/files/textbook.htm

Publications and Patents

Academy of Dental Materials: *International Congress on Dental Materials, Transactions*, Houston, TX, 1990, Academy of Dental Materials, Baylor College of Dentistry.
A host of review papers are presented on many aspects of dental composite chemistry, systems usage, dentin bonding agents, and microleakage.

Albers H: *Tooth-Colored Restoratives: Principles and Techniques*, ed 9, Hamilton, Ontario, Canada, 2002, BC Decker.
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Malhotra N, Mala K: Light-curing considerations for resin-based composite materials: a review. Part I. *Compend Contin Educ Dent* 31(7):498–505, 2010; ibid, Part II, 31(8):584–591, 2010.
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CHAPTER 14

Dental Cements

OUTLINE

Cements for Luting

Cements for Pulp Protection

Cements for Restoratives

Zinc Phosphate Cement

Zinc Polycarboxylate Cement

Glass Ionomer Cement (GIC)

Metal-Reinforced Glass Ionomer Cements

High-Viscosity Glass Ionomer Cement

Resin-Modified Glass Ionomer Cement (Hybrid Ionomer)

Calcium Aluminate Glass Ionomer Cements

Compomer

Resin Cements

Zinc Oxide–Eugenol Cement

Mineral Trioxide Aggregate Cements

Root Canal Sealers

Calcium Phosphate Cements

Fluoride-Releasing Materials

Solubility and Disintegration of Cements

KEY TERMS

Acid-base reaction—Chemical reaction between a compound with replaceable hydrogen ions (acid) and a substance with replaceable hydroxide ions (base) that yields a salt and water; for aqueous cements, the liquid is an acid and the powder is a base.

Anticariogenic—Capable of inhibiting or preventing dental caries.

Appliance—A dental device that is made extraorally and affixed intraorally, such as a crown, a fixed prosthesis, or an orthodontic bracket.

Atraumatic Restorative Treatment (ART)—A clinical procedure performed without dental burs, air/water spray, or anesthesia that consists of manual excavation of carious tissue in a cavitated lesion and restoration of the tooth cavity with a fluoride-releasing cement.

Base—A material that is used to protect the pulp in a prepared cavity by providing thermal insulation; a base may also serve as a medicament.

Calcium phosphate cement—A cement used for bone regeneration usually comprising a powder (di-, tri-, or tetra-calcium phosphate) that dissolves in an aqueous solution from which hydroxyapatite is precipitated.

Cavity liner—A material that coats the bottom of a prepared cavity to protect the pulp; it is applied in a thin layer and usually contains calcium hydroxide or mineral trioxide aggregate (MTA); also, includes certain glass ionomer cements used as intermediate layers between tooth structure and composite restorative material.

Cement—Substance that hardens from a viscous state to a solid state to join two surfaces; for dental applications, cements act as a base, liner, filling material, or adhesive to bind devices and prostheses to tooth structures or to each other.

Cement thickness—Distance between the abutment tooth and cemented prosthesis. This dimension is influenced by the design of the prosthesis and the viscosity of the cement during seating.

Cermet—A glass ionomer cement that is reinforced with filler particles prepared by fusing silver particles to glass.

Compomer—Resin-based composite consisting of a silicate glass filler phase and a methacrylate-based matrix with carboxylic acid functional groups; also known as polyacid-modified glass ionomer cement, a term derived from composite and ionomer; a secondary setting mechanism is related to acid-base reactions of the glass filler.

Craze—A network of fine cracks or craze lines that are formed in the surface of aqueous-based cements because of rapid dehydration.

Demineralization—The loss of mineral, typically calcium and phosphate ions, from tooth structure caused by exposure to organic acids produced by oral microorganisms.

Dew point—The temperature at which moisture in air begins to condense such as the temperature at which dew condenses on a cool glass mixing slab.

Di- and tricalcium silicate—The main phases present in MTA cement, which are hydraulically active (set with water). (Monocalcium silicate is not hydraulically active.)

Film thickness—Per ANSI/ADA Specification No. 96 (ISO 9917-1), the thickness in micrometers of set cement 10 minutes after a load of 150 N has been applied by a flat plate against another flat surface. The thickness should be less than 25 μm for luting cements.

Fluoride recharging—The process by which a restorative material, specifically glass ionomer cement, absorbs fluoride from a solution with a high fluoride concentration.

Formocresol—A compound consisting of formaldehyde, cresol, glycerin, and water.

Glass—A hard, stiff, amorphous material made by fusing silicates with one or more types of metal oxides, usually an alkali or alkaline earth oxide, boron oxide, or alumina. Radiopaque glass contains strontium oxide, barium oxide, or other high-atomic-mass metal oxides that are dissolved in the silicate glass. Fluoride or phosphate compounds may also be incorporated in a glass matrix.

Glass ionomer cement (conventional GIC)—A cement that hardens following an acid-base reaction between fluoroaluminosilicate glass powder and an aqueous-based polyacrylic acid solution.

Gutta-percha—A material composed of trans-polyisoprene rubber with various additives, usually including zinc oxide powder, barium sulfate, and modifiers to adjust the rheology for filling (obturating) a root canal after pulp extirpation and canal preparation; gutta-percha must be used with a root canal sealer to seal the canal from bacterial penetration.

HEMA—2-hydroxyethylmethacrylate.

High-viscosity glass ionomer cement—A conventional GIC that contains finer glass particles and a higher powder/liquid ratio for increased packability and strength.

Hybrid ionomer—Also called resin-modified glass ionomer.

Intermediate restoration—A tooth filling placed or prosthesis that is cemented for a limited time, from several days to months, which is designed to seal a tooth and maintain its position until a long-term restoration is produced; also called a temporary restoration.

Luting agent—A viscous cement-like material that fills a gap between bonded materials.

Maturation (cement)—The process of hardening a cement matrix through hydration with oral fluids to achieve greater mechanical strength.

Metal-reinforced glass ionomer cement—A glass ionomer cement that incorporates metal particles to improve certain mechanical properties.

Mineral trioxide aggregate (MTA)—A tri- and dicalcium silicate–based cement used for vital pulp therapy and endodontic indications including apexification, iatrogenic perforation repair, resorption repair, root-end filling, and sealing.

Permanent restoration—A long-lasting replacement or restoration for missing, damaged, or discolored teeth. Because of the tendency of materials to degrade or fracture over time, the term *permanent* does not signify an unlimited life expectancy.

P/L ratio—Powder-to-liquid ratio by weight or volume.

Polyacid-modified composite—See *compomer*.

Pulp capping—A procedure for treating a pulp that has been exposed through carious tissue removal by the application of a medicament; indirect pulp capping is the term used when the pulpal exposure is incipient, as when dentinal tubules are visible in a prepared tooth.

Remineralization—Process of restoring mineral content (calcium phosphate) in demineralized tooth structure.

Resin cement—A resin-based material containing fillers that are cured to form a composite material used for attaching orthodontic brackets and fixed prostheses. Such cements are applied following the application of an etchant and an enamel or a dentin bonding agent to bond to tooth structure. Generally, these cements are less viscous than resin-based composite restorative materials.

Resin-modified glass ionomer cement (hybrid ionomer cement)—A hybrid cement that combines a glass powder, such as used in glass ionomers, and a liquid that contains polymerizable groups attached to the polyacrylic acid, such as HEMA, and catalysts, such as diphenyliodonium chloride. This type of cement has a longer working time and is less sensitive to water contamination than conventional glass ionomer cement.

Root canal sealer—A material used in conjunction with an obturation material for root canal therapy such as gutta-percha, to prevent the ingress of fluid or bacteria within the tooth root.

Sandwich technique—Technique of placing glass ionomer cement as an intermediate layer between the tooth structure and a resin-based composite restorative material; this restoration design combines the adhesion and fluoride-releasing nature of a glass ionomer cement with the esthetic quality and durability of a resin-based composite.

Self-adhesive—Ability of a material to adhere to tooth structure without the aid of a dentin or enamel bonding agent.

Setting time—The elapsed time from the start of mixing to the time at which the setting reaction essentially stops as measured by reaching a desired hardness or consistency; setting time can be measured with a 1-mm-diameter needle indenter at a load of 400 g at a temperature of 37 °C and

a relative humidity greater than 90%. Setting time is the elapsed time from the start of mixing to the point at which the needle no longer makes a discernible circular indentation in the cement.

Silicate cement (silicophosphate)—Traditional restorative material made from the mixture of a liquid (phosphoric acid) and a fluoride-containing silicate glass powder.

Temporary restoration—Same as intermediate restoration.

Varnish—A material for application to the floor of a prepared cavity; a solution of natural gum, synthetic resins, or resins dissolved in volatile solvent, such as acetone, ether, or chloroform; not necessarily a cement.

Vital pulp therapy—The placement of a material in a prepared tooth over an injured pulp to induce the formation of secondary dentin. Pulp capping, cavity lining, and pulpotomies are all vital pulp therapy treatments. MTA and calcium hydroxide have been used for this therapy.

Working time—Elapsed time from the start of mixing to the time at which the consistency of a material is no longer suitable for its intended use or a rapid rise in viscosity occurs.

Zinc oxide–eugenol (ZOE) cement—A cement that is based on the reaction between zinc oxide and eugenol, formulated for use as a temporary material (type I), a long-term luting agent for fixed prostheses (type II), a base or a temporary filling (type III), or an intermediate restoration (type IV).

Zinc phosphate cement—A substance that is formed by the reaction between zinc oxide powder and phosphoric acid liquid, which can be used either as a base or as a luting agent.

Zinc polycarboxylate cement—A dental cement based on the reaction between zinc oxide powder and a liquid of polycarboxylic acid.

Dental **cements** are materials that set intraorally and that are commonly used to join a tooth and a prosthesis. They are classified according to their major chemical reacting components, as shown in Table 14-1. Every cement must be assessed for its biocompatibility, safety, and effectiveness. Ideally a cement does not cause damage to a tooth, has suitable physical properties for its intended use, and provides passive or active (bioactive) properties. Ultimately, the body should not recognize the cement as foreign, so that healing of affected tissues can begin as soon as possible.

? CRITICAL QUESTION

Dental cements are not as strong as composites or amalgams. Why do we use cement for restorations in certain situations?

Many types of dental cements are supplied as a powder and a liquid or as two pastes (Figure 14-1), so that mixing starts a chemical reaction. The liquids are usually acids (proton donors), and the powders are basic (alkaline) in nature, commonly composed of **glass** or metal oxides. The reaction between the powder and liquid is usually an **acid-base reaction,** although MTA undergoes a hydration reaction. **Resin cements** do not rely on an acid-base reaction but set through polymerization activated by light or a chemical. When mixed, cement hardens (or sets) within a reasonable time. Set cements are strong enough to be used as a **base** for pulp protection, as a restorative material for temporary or **permanent restorations,** or as a **luting agent.**

Many viscosities of cements are available in dentistry, ranging from a paste-like consistency to a highly flowable form. For cementing an **appliance,** a luting agent must exhibit a sufficiently low viscosity to flow readily along the interfaces between hard tissue and a fixed prosthesis, and they must be capable of wetting both surfaces to retain the prosthesis in place. For a pulp that may have been irritated or damaged from the caries process or prepared cavity, a protective layer may be needed, such as a cavity **varnish,** liner, or base material that flows and sets within the prepared cavity. For fixing a post in a root canal, a more viscous cement is needed. For a root-tip filling, a viscous paste that does not dissolve out of the root apex is necessary. In orthodontics, the cement must be adhesive and possess a viscosity that is low enough to seat a band and high enough to keep brackets from drifting before the cement is cured. This chapter is organized so that cements for luting are described first, followed by pulp protection and restorative cements, including some endodontic specialty applications.

Cements may have mechanical or chemical adhesion or by a combination of the two, as discussed below.

CEMENTS FOR LUTING

Some dental appliances are attached to the teeth by means of luting agents, which provide only mechanical adhesion, such as those used for (1) fixed prostheses made of metal, metal-ceramic, polymer, or ceramic materials; (2) **temporary restorations;** and (3) pins and posts used for retention of restorations. Microscopically the tooth and prosthesis surfaces are rough and the cement fills the irregular crevices between both surfaces to form a void-free continuum that microscopically locks one surface against another to

TABLE 14-1 Components and Reactions of Dental Cements

Materials	Formulation and Reacting Components	Reaction Type
Zinc phosphate	Powder: zinc oxide and magnesium oxide Liquid: phosphoric acid, water	Acid-base reaction
Zinc oxide–eugenol	Powder: zinc oxide Liquid: eugenol	Acid-base reaction
Zinc oxide–eugenol (EBA modified)	Powder: zinc oxide Liquid: eugenol and ethoxybenzoic acid	Acid-base reaction
Zinc polycarboxylate	Powder: zinc oxide and magnesium oxide Liquid: polyacrylic acid, water	Acid-base reaction
Glass ionomer	Powder: fluoroaluminosilicate glass Liquid: polyacrylic acid, polyprotic carboxylic acid, water	Acid-base reaction
Resin-modified glass ionomer	Powder: fluoroaluminosilicate glass, chemically and/or light-activated initiator(s) Liquid: polyacrylic acid, water-soluble methacrylate monomer, water, activator	Light- or chemically activated polymerization and acid-base reaction
	Powder: fluoroaluminosilicate glass, metallic oxides, sodium fluoride, chemically and/or light-activated initiator(s) Liquid: dimethacrylate/carboxylic monomers, multiple functional acrylate monomers water, activator (for chemical-cure)	Light- and chemically activated polymerization and acid-base reaction
	Paste A (nonaqueous): fluoroaluminosilicate glass, nonreactive filler reactive monomers Paste B (aqueous): nonreactive filler, methacrylate modified polyalkenoic acid, water-soluble methacrylate monomer, water	Light-activated polymerization and acid-base reaction
Calcium aluminate/glass ionomer hybrid	Powder: calcium aluminate, polyacrylic acid, tartaric acid, strontium-fluoro-alumino-glass and strontium fluoride Liquid: water	Acid-base reaction of glass ionomer and hydration of calcium aluminate cement
Compomer	One paste: methacrylate monomer, acidic monomer, fluoroaluminosilicate glass initiator	Light-activated polymerization
	Powder: fluoroaluminosilicate glass, metallic oxides, sodium fluoride, chemically and/or light-activated initiator(s) Liquid: dimethacrylate/carboxylic monomers, multiple functional acrylate monomers water, activator (for chemical cure)	Light- or chemically activated polymerization and acid-base reaction
Resin cement	One paste: methacrylate monomers, initiator	Light-activated polymerization
	Base paste: methacrylate monomers, fillers, chemically and/or light-activated initiator(s) Catalyst paste: methacrylate monomers, fillers, activator (for chemical-cure)	Light- and chemically activated polymerization, or chemically activated polymerization only
	Powder: polymethyl methacrylate beads (for thickening) Liquid 1: methacrylate monomers Liquid 2: catalyst	Chemically activated polymerization
Mineral trioxide aggregate (MTA)	Powder: tricalcium silicate, dicalcium silicate, radiopacifier (bismuth oxide, zirconia,or tantalum oxide), calcium aluminate, gypsum Liquid: water	Hydration of silicates

resist shear stresses that might dislodge the appliance (Figure 14-2). Mechanical retention may be insufficient. Chemical adhesion of the cement, tooth, and device improves retention.

Glass ionomer cements (GICs), based on polyacrylic acids, bond to teeth by chelating acrylic acids to both organic and inorganic tooth components, and continue to cure after the defined **setting time**. If glass ionomers are allowed to mature in an isolated environment (i.e., free of contamination from surrounding moisture and protected from loss of water through evaporation), the cements increase in strength and become more resistant to dissolution. Varnish coats applied at the margins of fresh GICs facilitate **maturation**; details are discussed later in this chapter.

Hydrophilic dentin bonding agents penetrate pores in dentin created by acid etching; these also have high bond strength through micromechanical retention. Resin cements based on NPG-GMA, polymerizable phosphates,

and 4-META (methacrylethyl trimellitic anhydride) bond to calcium within dentin.

Table 14-2 represents a compilation of the physical properties of various luting agents and the requirements for water-based dental cements from ISO 9917 (currently identical to ANSI/ADA Specification No. 96 requirements). All the materials in Table 14-2 set in less than 10 minutes and have a **film thickness** less than 25 μm. Although these values are typical, they were compiled from a variety of sources and a wide variation occurs among brands. To choose a cement for a specific task, one must consider (1) the cement's physical and biological properties, and (2) the cement's handling characteristics, such as **working time**, setting time, consistency, and ease of removing excess material.

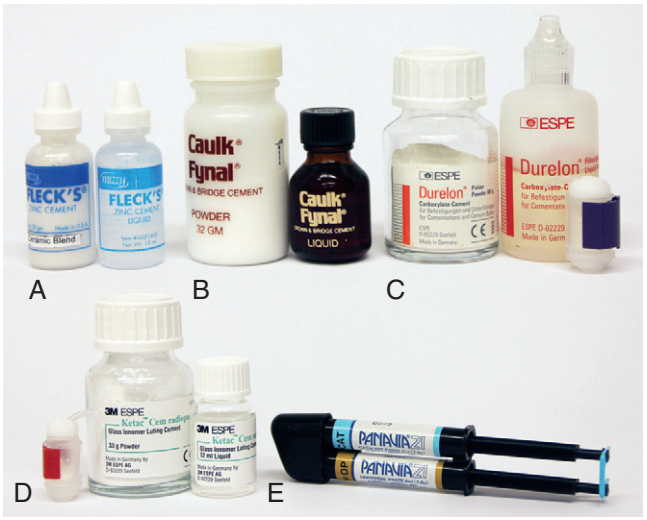


FIGURE 14-1 Dental cements as luting agents. **A,** Zinc phosphate. **B,** Reinforced zinc oxide–eugenol. **C,** Polycarboxylate with capsule. **D,** Glass ionomer with capsule. **E,** Resin cement. Each material system consists of two components: **A** to **D** are powder-liquid systems and **E** is a paste-paste system.

CRITICAL QUESTION

During the initial try-in of a three-unit fixed dental prosthesis (bridge), the prosthesis fits the prepared teeth perfectly and appears to be retained on the teeth so tenaciously that removal requires a great deal of force. Why is cement required for retention in this situation?

LUTING INTERFACE

Luting cements are designed to fill the microscopic gaps between a prosthesis and a prepared tooth. As shown in Figure 14-3, *A*, each surface is microscopically rough, having peaks and valleys, and only point contacts are made by the peaks (Figure 14-3, *B*). The areas that are not in contact must be filled by the cement to prevent oral fluid flow and bacterial invasion. One can seal the space by placing a soft adhesive between the two surfaces, which can conform under pressure to the roughened surface features.

The first dental luting cements were not adhesive to the tooth or prostheses, but they filled the microscopic space and

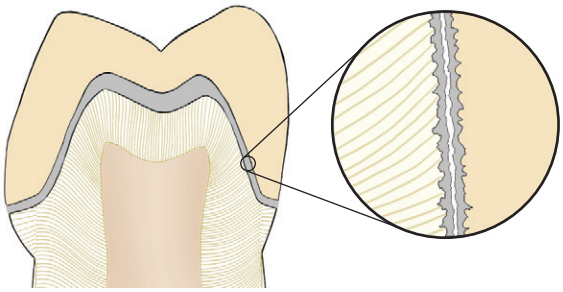


FIGURE 14-2 Diagram of the suggested mechanism through which a dental cement provides mechanical retention of a gold crown. The cement penetrates into irregularities in the tooth structure and the casting. Upon hardening, these retentive sites aid in retaining the cast crown in place. The enlargement shows a fracture through the cement, resulting in dislodgment of the crown.

TABLE 14-2 Typical Properties of Dental Cements Used for Luting Applications

Cement	Setting Time (min)	Film Thickness (μm)	24-hour Compressive Strength (MPa)	24-hour Diametral Tensile Strength (MPa)	Elastic Modulus (GPa)	Solubility in Water (wt%)	Pulp Response
Zinc phosphate	5.5	20	104	5.5	13.5	0.06	Moderate
ZOE*	4.0–10	25	6–28	–	–	0.04	Mild
Zinc polycarboxylate	6.0	21	55	6.2	5.1	0.06	Mild
Glass ionomer	7.0	24	86	6.2	7.3	1.25	Mild to moderate
Resin-modified glass ionomer	4.25	11–22	85–185	18–26	2.5–7.8	1.00	Mild to moderate
Compomer	4.0	36	165	–	3.6	0.69	Moderate
Resin	2.0–4.0	<25	70–172	40–77	2.1–3.1	0–0.01	Moderate
ISO 9917	2.5–8	25 (max)	50	N/A	N/A	0.20 (max)	See note†

*ZOE: zinc oxide–eugenol.
†Note: Response compared with the severe irritation of silicate cement.

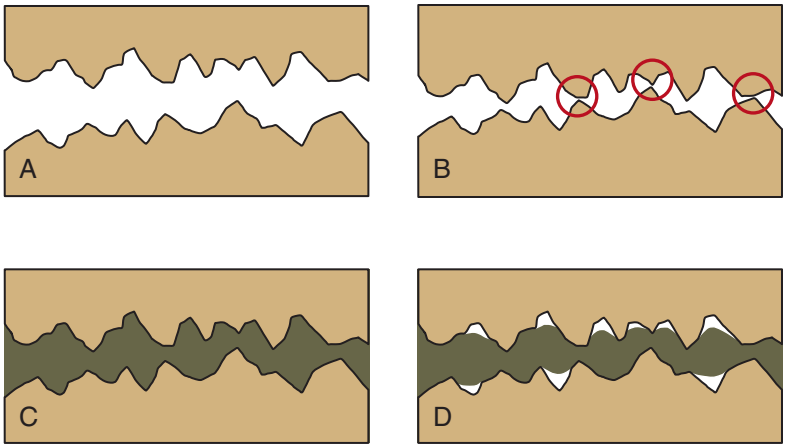


FIGURE 14-3 Schematic illustration of the abutment-prosthesis interfaces. **A,** Irregular surface morphology of the two surfaces to be bonded. **B,** Two surfaces pressed against each other without an intermediate layer. Note the small number of points of contact illustrated by the circles. **C,** Continuous interface when a third material, either cement or adhesive, is used as the intermediate layer. **D,** Voids generated as a result of the inability of the intermediate layer to wet the surfaces completely.

created a strong physical attraction to both substrates that prevented dislodgment. The current approach for cementing prostheses or appliances involves the use of an adhesive technique that forms a solid sealing layer within a few minutes (Figure 14-3, *C*) to improve retention of the prosthesis. The cement should flow under pressure and wet the surfaces. A luting agent must form a continuous film without forming voids (Figure 14-3, *D*), which are detrimental to retention and support of the prosthesis.

PROCEDURE FOR LUTING A SINGLE CROWN

Luting of a single crown is described as an example (Figure 14-4, *A*) in three steps: cement placement, seating of the crown, and excess cement removal.

Cement Placement

The cement should coat the entire inner surface of the crown and extend slightly over the margin to ensure that the space between the crown and tooth will be completely sealed. Cement should fill about half of the inner cavity volume of the crown (Figure 14-4, *B*) and must be free of bubbles. Air entrapment must be avoided in the critical occlusal region; otherwise masticatory forces may fracture any ceramic prosthesis. Do not fill the entire crown cavity because this increases the risk for bubble entrapment, the time and pressure required for seating, and the time and effort to remove excess cement.

Seating

Use moderate finger pressure to displace excess cement and seat the crown on the prepared tooth. Tapping or vibration of the crown or using an ultrasonic device may also help to achieve complete seating of the crown. Evaluate three points on the margin with an explorer to ensure that seating is adequate, and ask the patient to bite on a soft substance such as wood or a cotton roll to ensure complete seating; this will also expel excess cement (Figure 14-4, *C*). Complete seating is essential. Reevaluate at least three points of the margin and the occlusion before the cement has set.

Three characteristics make seating a crown easier: (1) lower-viscosity cements, (2) more taper of the prepared tooth (Figure 14-4, *D*), and (3) decreased height of the prepared tooth. Note that higher taper and lower tooth height compromise the retention.

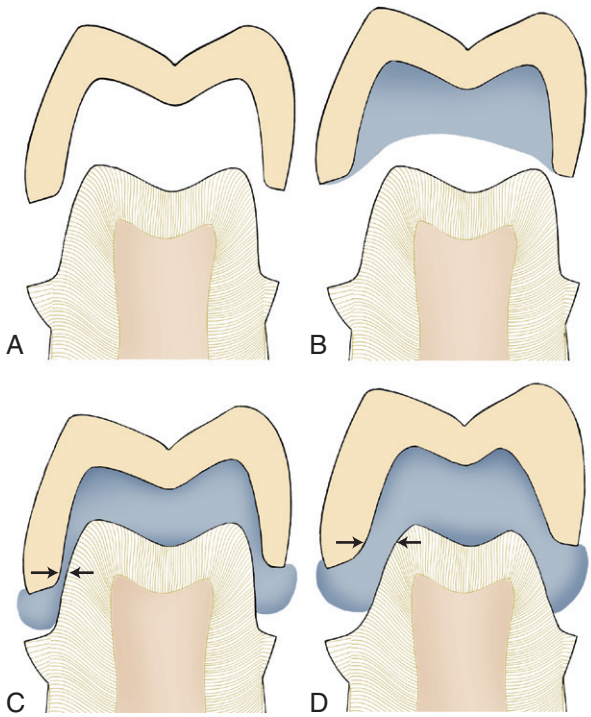


FIGURE 14-4 Mechanics of cementing a prosthesis. **A,** Assembly of a fixed prosthesis and respective tooth preparation. **B,** Luting agent placed in the prosthesis should cover the entire surface. **C,** Space for expelling excess cement decreases as the prosthesis reaches its final position. Arrows show the thickness of space for expelling excess cement. **D,** Higher degree of the abutment taper provides a greater space for expelling excess cement.

? CRITICAL QUESTION

Why does the technique of removing excess cement differ among types of cements?

Removal of Excess Cement

Excess cement should be present at the margin of a crown just after seating, but its removal depends on the properties of the cement used. Zinc phosphate and **zinc oxide–eugenol** (ZOE) cements do not adhere to the surrounding surfaces, the tooth, or the prosthesis, so the cement should set completely before the excess cement is removed. Glass ionomer, polycarboxylate, and resin cements adhere chemically and physically to the surrounding surfaces and should be removed as soon as the seating is completed to prevent adhesion to the exterior of the prostheses or to the surrounding teeth. A separating medium, such as petroleum jelly, can be applied carefully to external and surrounding surfaces to inhibit cement adherence, making cement removal easier when these cements are allowed to set completely.

Some GICs and dual-cure resin cements can be removed easily in about 1.5 to 3 minutes after mixing begins but before setting by an acid-base reaction or light curing is finished. At this point the cement has acquired some strength but is not strong enough to resist separation from the margin, which allows removal of larger pieces of the excess cement.

Zinc polycarboxylate cement transforms to a rubbery state before setting. At this stage, the cement is so thick that any attempt to remove the excess may inadvertently pull the cement away from the marginal area, or it may remove some of the cement from within the cemented prosthesis.

The technique of removing excess cement is usually described in the instructions for use provided by the manufacturer. Regardless of which cement the dentist may use, it is always advisable to run a knotted dental floss through the interproximal regions toward the margin immediately after complete seating of the prosthesis. The knot removes most of the excess cement and provides better access for cement removal required after the cement has set.

DISLODGMENT OF PROSTHESES

Debonding may be caused by cement fracture, dissolution or erosion, secondary caries, or excessive shear forces. The cement layer is the weakest link of a prosthetic/tooth assembly; therefore, cements with higher bond strengths are preferred. In the oral environment, luting agents may dissolve and erode, leaving a space (Figure 14-5) in which plaque may accumulate and caries may recur. Water-based cements mature after they have reached the defined setting time. If they are allowed to mature free of contamination from surrounding moisture and without loss of water, the cements increase in strength and become more resistant to dissolution. As a precaution, the clinician should apply a coat of varnish or a bonding agent along the accessible marginal area of cemented restorations before discharging the patient. Further details are discussed later in this chapter.

To maximize retention, the cement layer between the prosthesis and the abutment should be sufficiently thin to minimize pores in the cement. Thinner cement layers are created by applying a sufficient seating force such that excess cement is expressed out of the marginal space. The design of the prosthesis should allow the cement to flow and result in a uniform layer of cement between the prosthetic device and the tooth. Furthermore, when cement layers are thinner, plaque accumulation on the cement and microleakage are less likely. Cements should be insoluble in water and should not absorb water. Preferably the coefficient of thermal expansion between the tooth, the prosthesis, and the cement should be similar over the range of temperature associated with consumed foods and beverages. Cements having high compressive, shear, and flexural strengths are preferred. Dislodgment is minimized for cements with high shear bond strength (chemically bonded cements). When chemical bonding occurs, failure may occur cohesively through the cement (Figure 14-6, *A*). With a thin chemically bonded cement, the prosthesis may become dislodged when the luting cement fractures or dissolves. When a cement produces only mechanical retention, failure begins at the interfaces (Figure 14-6, *B*). A low setting contraction is preferred to minimize interfacial stresses.

? CRITICAL QUESTION

The terms *film thickness* and *cement thickness* are used to describe the properties of dental cements. What is the difference between these terms and what is their clinical significance of the terms?

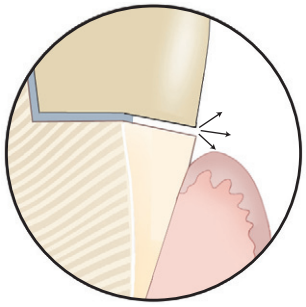


FIGURE 14-5 Loss of cement at the marginal area resulting from exposure to oral fluid.

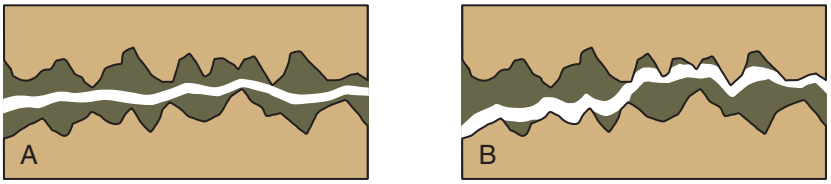


FIGURE 14-6 Failure modes of the interface. **A,** Cleavage through the cement layer. This is unlikely because of the small thickness of the cement involved. **B,** The most likely failure occurs at the luting agent/prosthesis interface. Remnants of the luting agent often remain on the opposing surface.

FILM THICKNESS

This property is often confused with **cement thickness**. *Film thickness* refers to the thickness of a continuous cement after setting under pressure, according to ANSI/ADA Specification No. 96 (ISO 9917-1). To determine film thickness, freshly mixed cement is placed between two optically flat surfaces and a 150-N vertical load is applied 10 seconds before the end of the measured working time. After 10 minutes have elapsed since application of the load, the thickness of the film between the two flat surfaces is measured as the film thickness. The cement film should be continuous and no voids should exist in the film. Thus, film thickness is an indication of the viscosity of the cement during seating. A lower film thickness implies lower viscosity. For luting applications, the maximum allowable film thickness is 25 μm for the ADA specification or ISO standard indicated above; a low film thickness is preferred, so that excess cement can be expressed more easily. The size of particles and the **P/L ratio** significantly affect the film thickness. For temporary and final restorations, the maximal acceptable film thickness is larger. However, there is no film thickness specification for base and liner and restorative applications. For root canal sealers, the maximal film thickness is 50 μm. For comparison, the diameter of flaxen human hair ranges between 17 and 50 μm.

Cement thickness refers to the thickness of the cement between the tooth structure and a cemented cast crown, inlay, onlay, or veneer. It plays a significant role in the retention of prostheses and varies with (1) the amount of force applied during seating of the prosthesis, (2) the direction in which the force is applied to the prosthesis during seating, (3) the design of the prosthesis relative to its potential to inhibit or facilitate the flow of cement, (4) the fit of the prosthesis on the prepared tooth, and (5) the inherent film thickness of the cement. An acceptable cement thickness in the literature ranges from 25 to 120 μm. However, cement thickness associated with resin cements can exceed 150 μm.

CEMENTS FOR PULP PROTECTION

Specialized materials are used in prepared cavity to protect the pulp from thermal or chemical irritation. For instance, metallic restorations are excellent thermal conductors, but they promote thermal sensitivity when hot and cold foods or beverages are consumed. Cements containing phosphoric acid, direct filling resins, and some glass ionomer cements (GICs) cause a chemical irritation. Generally, the inflammation caused by chemically irritating cements increases in the order of polycarboxylate cement, **zinc phosphate cement**, and GIC. The setting contraction of amalgam or composite can lead to marginal leakage as well as pulpal irritation.

Cavity varnishes, liners, and base materials have been used as adjuncts to restorative materials to protect the pulp from such injuries. Some of these agents may also provide caries prevention benefits, as described below. Most of materials used for this application are cements, although some are not. For example, copal varnish and calcium hydroxide are not cements, but they are discussed here because of the pulp protection they offer.

? CRITICAL QUESTION

What is the purpose of using cavity varnishes and why is copal varnish no longer used as often as it was between 1960 and 1990?

CAVITY VARNISHES

Varnishes are composed of natural gums—such as copal, rosins, or synthetic resins—dissolved in an organic solvent (acetone, chloroform, or ether). The varnish forms a thin coating on the tooth as the solvent evaporates. Varnishes have a high solvent content and at least two thin layers should be applied to produce a continuous coating; otherwise small pinholes may occur. A brush, or a small pledget of cotton may be used as an applicator, but it should be discarded after each application to the tooth to avoid introducing microorganisms into the varnish bottle.

In vitro studies suggest that varnish reduces the infiltration of irritating fluids through marginal crevices and lessens pulpal irritation. Clinical observations based on tooth sensitivity, as reported by patients, have yet to confirm these benefits in vivo. Varnish is also claimed to prevent the penetration of corrosion products of amalgams into the dentinal tubules, thereby reducing the unsightly tooth discoloration often associated with amalgam restorations. However, high-copper amalgam products, which are more corrosion-resistant than their predecessors, have diminished the need for varnish.

A varnish is not indicated when adhesive materials such as GICs or bonding agents for resin-based composite are used. Dentin bonding agents serve the same purpose as varnish.

CAVITY LINERS

Calcium hydroxide is the chief ingredient in many cavity-liners and cement-base materials because calcium hydroxide is antimicrobial, has an elevated pH (basic, alkaline), and stimulates the formation of secondary dentin over an injured pulp to protect it over the long term. As a **cavity liner**, the calcium hydroxide powder is suspended in a solvent carrier with a thickening agent. When it is placed on the pulpal floor, the solvent evaporates and leaves a thin film of calcium hydroxide. The liner does not possess significant mechanical strength or thermal insulation capability but it can neutralize acids that migrate toward the pulp and, in the process, it can induce the formation of secondary dentin. Eventually, the calcium hydroxide forms calcium carbonate and becomes inactive. Calcium hydroxide is soluble in water and must not be left on the margin of the prepared cavity or the margin will not be properly sealed.

Many formulas that are available for cavity lining materials are based on adding calcium hydroxide to low-viscosity ZOE, GI, or resin cements. Some of these liners adhere to the tooth-restoration interface; therefore, the function of liners has been expanded to include the sealing of dentin from the potential influx of microorganisms and irritants from restorative procedures.

Calcium hydroxide liners are commonly used for direct and indirect **pulp capping** and as a dressing after vital pulpotomy procedures on primary teeth. MTA is a newer cavity liner material that forms calcium hydroxide as it sets. Both MTA and calcium hydroxide undergo a transformation of hydroxide to calcium carbonate from exposure to carbon dioxide in the blood and oral fluids, causing their antimicrobial effectiveness to diminish.

Cyanoacrylate adhesives have been tested as liners for amalgams, but in vitro data show they are unsatisfactory for controlling microleakage. Formocresol has been used for vital pulp procedures in which calcium hydroxide has been used. However, the toxicity and carcinogenicity of its chief ingredient, formaldehyde, has rightfully led to its demise.

CRITICAL QUESTION

Why does the strength requirement of the cement base material depend on the type of restorative material to be placed?

CEMENT BASES

In contrast to liners, cement bases are applied in thicker layers (greater than 0.75 mm) beneath restorative materials to protect the pulp against thermal injury, galvanic shock, and chemical irritation. Clinical experience has shown that temperature changes have a more acute effect on the pulp when teeth containing large amalgam fillings are not insulated by a base. Zinc phosphate and ZOE cements are commonly used, as well as some polycarboxylate and fast-setting GICs. Table 14-3 shows that zinc phosphate and ZOE cements are better insulators (having lower thermal conductivity) than metals, although they have less insulating ability than portland cement, corkboard, or glass. The insulating abilities of polycarboxylate, glass ionomer, and calcium hydroxide materials also fall within this range. Their actual heat transfer is more complex and depends on the material's heat capacity, thickness, and density.

Zinc phosphate cement is an effective base for thermal insulation, but its low pH (acidity) may require a cavity liner under the cement to protect the pulp. However, the risk of low pH in contact with the pulp is minimized if the zinc phosphate cement is mixed to a thick, nontacky, putty-like consistency, which does not have excess acid. Calcium hydroxide, ZOE, polycarboxylate, and **glass ionomer cement** are effective barriers against the penetration of irritating constituents from restorative materials. When glass ionomer is used as a base, a calcium hydroxide liner should be applied first to protect the deep areas where pulp exposure is more likely to occur.

Cement bases should be strong enough to withstand forces during the placement of fillings and mastication forces during service. Restorative materials should be placed after the initial set of the base cement has occurred. Table 14-4 shows the compressive strength of representative dental cements over time. Their strength increases rapidly over the first 30 minutes and continues to increase over 24 hours.

The minimal strength required to resist masticatory forces has not been determined because of their complexity and the influence of the design of the prepared tooth cavity. However, a study of 350 amalgam restorations placed over a hard-setting calcium hydroxide base showed no evidence of fracture, even though its strength was only about 10 MPa after 24 hours. For a Class I tooth preparation where the base is supported on all sides by tooth structure, less strength is necessary than that required for Class II restorations.

A base cement should be selected after considering the design of the cavity, the direct restorative material, and the proximity of the pulp chamber relative to the cavity floor or wall. For amalgam restorations, calcium hydroxide and ZOE materials are effective base cements. For direct filling gold restorations, which are relatively ductile, a stronger base cement—such as zinc phosphate, polycarboxylate, or GIC—is indicated. In those cases where a liner of calcium hydroxide or ZOE cement on the cavity floor is desired the liner should be overlaid with a strong base cement.

Neither microleakage nor acid penetration is prevented by using a base cement in conjunction with amalgam or

TABLE 14-3 Thermal Conductivity of Cement Base Materials and Other Common Materials

Material	Thermal Conductivity (W/m·K)
Zinc phosphate cement (dry)	1.26
Zinc phosphate cement (wet)	1.63
Zinc oxide–eugenol	1.67
Corkboard	0.04
Gypsum plaster board	0.17
Portland cement	0.29
Glass	1.01
Zirconia ceramic	1.7
Ice	2.18
Stainless steel	15.9
Alumina	30
Pure gold	297

TABLE 14-4 Compressive Strength (MPa) of Cement Base Materials after Setting

Material	7 Minutes	30 Minutes	24 Hours
Zinc oxide–eugenol	2.8	3.5	5.2
	6.2	6.9	12.4
	15.9	20.7	24.1
Calcium hydroxide	3.8	4.8	10.3
	7.6	6.2	8.3
Zinc phosphate	6.9	86.9	119.3
MTA	–	–	28.0

direct-filling gold foil. When a cavity varnish or dentin bonding agent is indicated to seal a restoration, the base often governs the order of material application. If a zinc phosphate cement base is used, a sealing (varnish) material should be applied to the cavity walls before placement of the base. For the more biocompatible cement base materials (e.g., calcium hydroxide, ZOE, polycarboxylate, and GIC), the base cement is placed, followed by the cavity varnish after the base has hardened. For resin-based composites, calcium hydroxide and GIC are satisfactory base cements.

MTA is also used as a base because it is insulating, antimicrobial, and nonacidic. However, currently available products have slow setting characteristics. Thus, MTA is primarily a specialty material.

CEMENTS FOR RESTORATIVES

Cements can be employed for temporary or short-term periods (days to weeks), intermediate-term periods (weeks to months), or long-term periods (years) in the restoration of anterior teeth. The general procedure for using cements as restoratives is essentially the same as for the use of resin-based composites. In the early 1900s, ZOE, zinc phosphate, and **silicate cement** were the major material systems used for restoratives. Silicate cement, based on silicate glass particles and phosphoric acid, was a translucent restorative material and it was the primary esthetic material before resin composites were introduced. The mean survival time of silicate cement restorations was unimpressive—about 4 years—because of their high solubility rate, loss of anatomical contour, and margin degradation. In 1972, GICs, based on new silicate glass formulas and polyacrylic acid, were introduced. The use of silicate cement diminished markedly with the advent of resin composite, and silicate cement is rarely used today.

ZINC PHOSPHATE CEMENT

Zinc phosphate cement first appeared in the literature in 1879, and the chemistry of the modern-day cement was established in 1902. It is the oldest luting cement and its long clinical record of success serves as a standard by which newer cements are compared.

CHEMISTRY AND SETTING

Zinc phosphate cement consists of a powder and liquid which are mixed just before use. The powder contains more than 75% of zinc oxide and up to 13% of magnesium oxide; these powders are sintered above 1000 °C, then ground into a fine powder, and blended with radiopaque powders. The liquid contains phosphoric acid (38% to 59%), water (30% to 55%), aluminum phosphate (2% to 3%), and in some cases zinc phosphate (up to 10%). The liquid controls the pH and the rate of the liquid-powder (acid-base) reaction. Also, the finer the particle size, the faster the cement sets.

When mixed, phosphoric acid dissolves the zinc oxide, which reacts with the aluminum phosphate and forms zinc aluminophosphate gel on the remaining undissolved zinc oxide particles. The set cement contains unreacted zinc oxide particles encased in an amorphous matrix of zinc aluminophosphate. Loss of water from the liquid lengthens the setting reaction, while incorporation of additional water during mixing accelerates the reaction.

? CRITICAL QUESTION

Why does an extended spatulation prolong the setting time of zinc phosphate cement whereas it shortens the setting time of gypsum products?

CLINICAL MANIPULATION

The reaction between zinc oxide and phosphoric acid is exothermic and requires a careful mixing procedure to minimize the effect of heat generation. The zinc oxide cement powder should be dispensed on a glass slab and divided into several portions (Figure 14-7, *A*). The manufacturer's instructions should describe the amount of powder by including a measuring device, the number of liquid drops, the method for dividing powder increments, the mixing time for each increment, and the total mixing time. The liquid should not be dispensed onto the slab until the powder is dispensed and divided, and the cement is ready for use because the water from the liquid will evaporate, as shown in Figure 14-8.

Mixing of Zinc Phosphate Cement

Mixing of this cement should be initiated by incorporating the smallest portion of powder using a thin spatula and brisk spatulation. Most of the area of the mixing slab should be used to dissipate heat. A good rule to follow is to spatulate each increment of powder for 15 to 20 seconds before adding another increment, and all mixing should be completed within 1.5 to 2 minutes. After the powder is completely incorporated and a creamy mixture has been created, the cement is drawn across the slab and the flat blade of the mixing spatula contacts the mixture and is slowly drawn away. If a string of cement can be lifted 12 mm (½ inch) to 19 mm (~¾ inch) before separating from the spatula (Figure 14-7, *B*), the cement is considered fluid enough for cementing a prosthesis. If the string exceeds 19 mm, the cement is too viscous for proper seating of prostheses (Figure 14-7, *C*) and another mixture should be made. After the prosthesis is coated with the cement and is seated, it should be held under pressure until the cement sets. The field of operation should be kept dry during the entire seating procedure.

Removal of Excess Zinc Phosphate Cement

Excess cement must be removed from the interproximal area immediately with a knotted dental floss after complete seating and remaining excess cement should be allowed to set before removal. A layer of varnish or other impermeable coating should be applied to the margin after removal of excess cement to allow the cement more time to mature and to develop an increased resistance to dissolution in oral fluid.

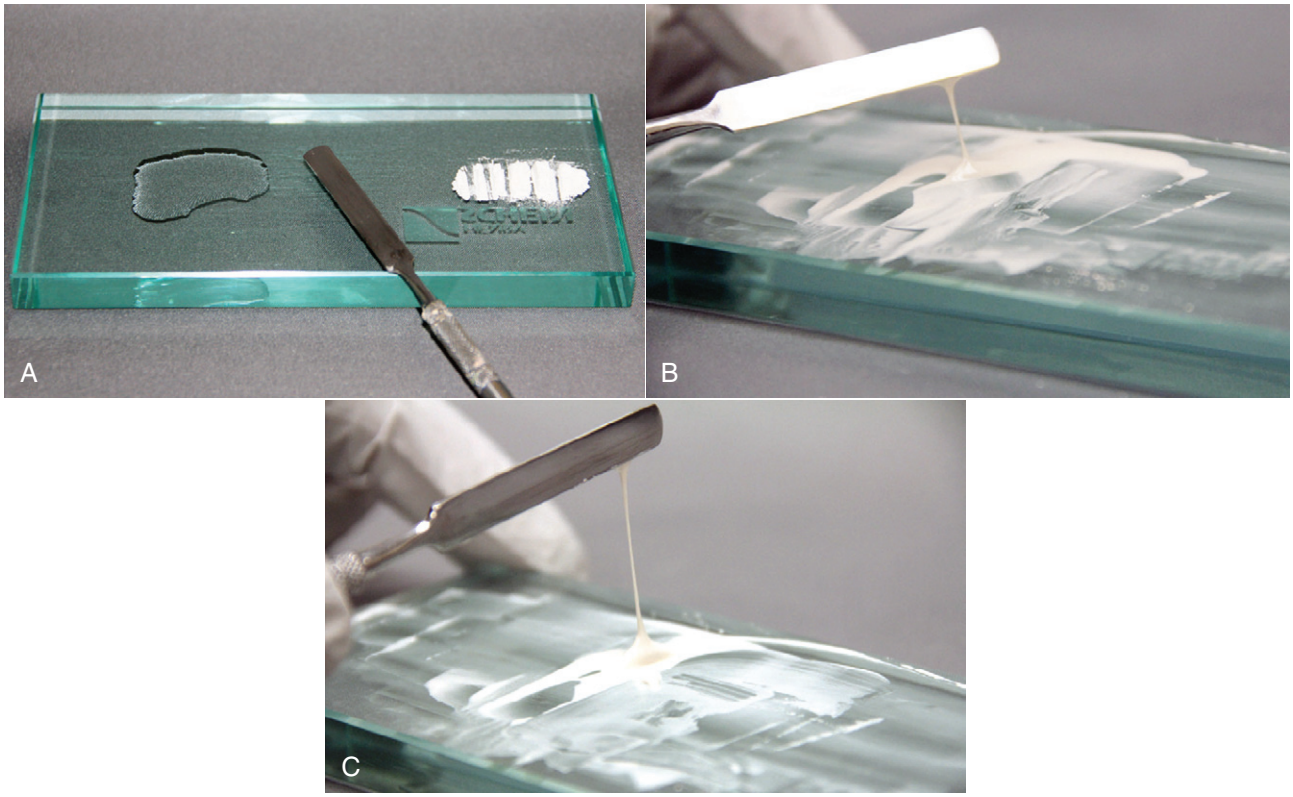


FIGURE 14-7 Manipulation of zinc phosphate cement. **A,** Powder and liquid dispensed on mixing slab; powder is divided into six increments: 1/16, 1/16, 1/8, 1/4, 1/4, and 1/4. **B,** Proper consistency for cementation; the mixture is strung up about 1/2 to 3/4 inch (~12 to 19 mm) at separation. **C,** The mixture is strung up more than 3/4 inch without separation; this indicates that the cement has become too thick for cementation.

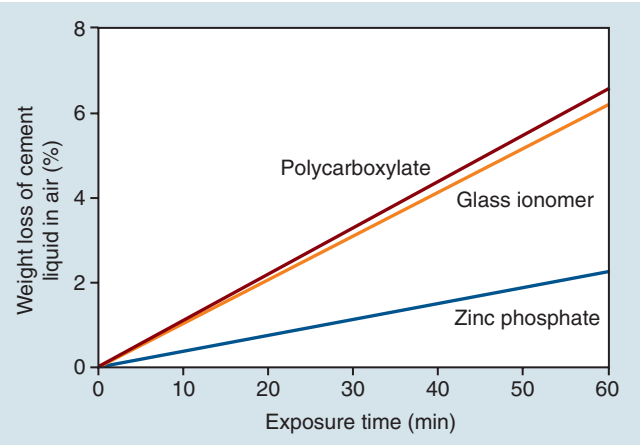


FIGURE 14-8 Loss of water from cement liquids when they are exposed to air.

Control of Working Time

The length of working time may be varied to some degree to fit the clinical situation. For example, a fixed dental prosthesis with multiple crowns requires more working time for cementation. Four techniques can extend the working time of zinc phosphate cement. First, the P/L ratio can be reduced to produce a thinner mixture. However, this change will result in a lower initial pH of the cement and it will adversely affect the mechanical properties of the cement (Figure 14-9).

Second, smaller portions of powder should be mixed for the first few increments. Initial small increments of powder dissolve in the liquid, which reduces the acidity of the liquid and retards the reaction rate with subsequent increments. Meanwhile, the heat generated from the reaction will be dissipated sufficiently during spatulation. If a large portion of powder is used initially, the quantity of heat generated cannot be dissipated fast enough to prevent it from accelerating the reaction.

Third, the operator can prolong the spatulation of the last increment of powder. The spatulation effectively destroys the matrix as it forms, which means that extra time is needed to rebuild the bulk of the matrix. This is not a preferred method for extending the working time.

Fourth, a colder mixing temperature will retard the chemical reaction between the powder and the liquid, thereby delaying formation of the matrix. However, the temperature of the slab should be above the **dew point**; otherwise, water condenses, dilutes the liquid, and reduces the compressive and tensile strength of the zinc phosphate cement. The use of a cool slab for mixing is the most viable method of extending the working time of zinc phosphate cement, and this should apply whenever multiple-unit prostheses are being cemented.

This procedure yields lower cement viscosity at the completion of mixing, as indicated by a much lower height of the cement at separation when lifted by the spatula. The lower viscosity cement facilitates the seating of multiple-unit cast restorations.

Retention

Zinc phosphate does not chemically bond to teeth or prostheses; its bond is simply mechanical. A cavity liner applied on the tooth surface for pulp protection before application of zinc phosphate cement will reduce retention by creating a smoother surface with less interlocking.

MECHANICAL AND BIOLOGICAL PROPERTIES

Zinc phosphate luting cements have a compressive strength as high as 104 MPa, a diametral tensile strength of 5.5 MPa, and an elastic modulus of 13 GPa (Table 14-2), making it relatively strong and stiff compared with other cements. Generally zinc phosphate cements have a relatively low solubility in water; however, in vivo disintegration occurs in the presence of lactic, acetic, and citric acids.

The phosphoric acid in the liquid makes the mixture quite acidic and therefore cytotoxic when a prosthesis is luted with this cement on a prepared tooth (Table 14-5). As setting occurs, the acidity is partially neutralized, but the cement remains acidic after 24 hours, with the pH rising from about 3 to about 6. For thin layers of dentin, a cavity liner (i.e., $Ca[OH]_2$) is recommended to prevent an adverse pulpal response from the pressure of luting, which forces acid into the pulp tissue. Younger patients are especially susceptible because they have a more open dentin tubule area, whereas older patients with sclerotic dentin will have a more tortuous path that restricts the penetration of acid toward the pulp.

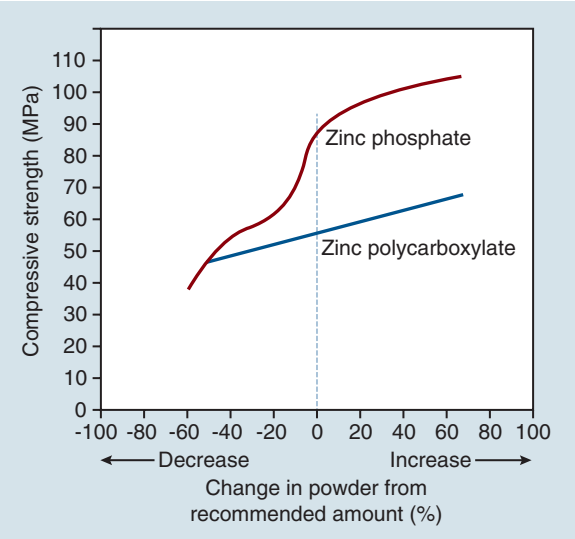


FIGURE 14-9 Effect of powder/liquid ratio on the strength of two cements. Cement specimens were prepared with greater and lesser amounts of powder (higher and lower powder/liquid ratios) than recommended by the manufacturers (represented by a zero percent change).

ZINC POLYCARBOXYLATE CEMENT

Zinc polycarboxylate cement was the first dental cement to exhibit chemical bonding to teeth, marking an improvement over the mechanical bonding of zinc phosphate cement. Zinc polycarboxylate cement is not used for restorative purposes because the cement is opaque.

CHEMISTRY AND SETTING

The polycarboxylate cements are powder-liquid systems that set by an acid-base reaction.

Composition

The liquid is a water solution of polyacrylic acid or a copolymer of acrylic acid with other carboxylic acids, such as itaconic acid. The molecular weight of the polyacids ranges from 30,000 to 50,000 and the acid concentration varies from 32% to 42% by weight. The powder contains mainly zinc oxide with some magnesia, tin oxide, bismuth oxide, and/or alumina. Small amounts of stannous fluoride are used in some brands to adjust the setting time, increase the strength, and enhance the manipulative properties. The amount of fluoride released from such cements is minor, i.e., only 15% to 20% of that released from GICs.

TABLE 14-5 pH of Cements for Luting Applications

			GLASS IONOMER	
Time (minutes)	Zinc Phosphate	Polycarboxylate	Polyacid Liquid	Water-Settable
2	2.1	3.4	2.3	1.8
5	2.6	3.9	3.0	2.0
10	3.1	4.4	3.8	3.4
15	3.3	4.8	3.9	3.9
20	3.6	4.9	4.0	4.2
30	3.7	5.0	4.2	4.5
60	4.3	5.1	4.6	4.8
1440	5.5	5.9	5.7	6.0

Setting Reaction

The reaction of zinc polycarboxylate cement is similar to that of zinc phosphate cement. Setting begins by dissolution of the powder particles by the acid, which releases zinc, magnesium, and tin ions; these bind and cross-link the carboxyl groups. The result is a cross-linked polycarboxylate matrix phase encapsulating the unreacted portion of the particles. The hardened zinc polycarboxylate cement is an amorphous gel matrix in which unreacted powder particles are dispersed, as occurs also with zinc phosphate cement. The pH of the cement liquid is initially slightly less acidic than that of zinc phosphate cements but it is still very low (about 1.7). The pH of the mix rises rapidly from 3 to 6 as the setting reaction proceeds (Table 14-5). The setting time ranges from 6 to 9 minutes, which is an acceptable range for luting cements.

Mechanism of Adhesion

The outstanding characteristic of zinc polycarboxylate cement is its chemical bond to tooth structure. The polyacrylic acid bonds to calcium ions on the surface of enamel or dentin. The bond to enamel is greater than that to dentin, because the enamel has a higher concentration of calcium. See Figure 14-10 for a comparison of its tensile bond strength with that of zinc phosphate cement. Thermal cycling of the cement reduces the bond strength of zinc phosphate cements to dentin or enamel to zero, unlike that of polycarboxylate cements.

CLINICAL MANIPULATION OF POLYCARBOXYLATE CEMENT

Despite the adhesion of the cement to tooth structure, polycarboxylate cements are not superior to zinc phosphate cement in the retention of cast noble metal prostheses. The likely cause is their surface contamination of the prostheses. The inner surface of a crown must be cleaned to improve wettability and the mechanical bond at the cement-metal interface. The surface can be carefully abraded with a stone or sandblasted with alumina abrasive. Note that long sandblasting times or excessive air pressure can deform metal margins and such procedures should be avoided. Crowns should be thoroughly rinsed to remove debris and dried. The outer surface of the prosthesis should be coated carefully with a separating medium, such as petroleum jelly, to prevent excess polycarboxylate cement from adhering to its surface.

A meticulously clean tooth surface is necessary to achieve adhesion and ensure intimate contact between the polycarboxylate cement and the tooth. A 10% polyacrylic or maleic acid solution should precede cement application and be applied to the tooth for 10 to 15 seconds, followed by rinsing with water. After cleansing, the prepared tooth should be isolated to prevent contamination by oral fluids and blotted dry. Drying with an air syringe is acceptable, although the patient may experience discomfort if a vital tooth is not anesthetized.

? CRITICAL QUESTION

Why should zinc polycarboxylate cement be applied on the prepared tooth before the cement loses its glossy appearance?

Mixing of Cement

The P/L ratio of polycarboxylate cements varies from product to product, but is about 1.5 by weight. This cement should be mixed on a nonabsorbent surface, such as a glass slab. The liquid component of polycarboxylate cement is viscous and should not be refrigerated. The liquid's viscosity depends on its molecular weight and the concentration of the polyacrylic acid in each brand. The liquid should be dispensed just before use because the water in the liquid evaporates quickly (Figure 14-8), which raises its viscosity. The powder should be rapidly incorporated into the liquid. A long mixing time can yield a cement that is too viscous for its intended application. The cement must be used before it loses its glossy appearance

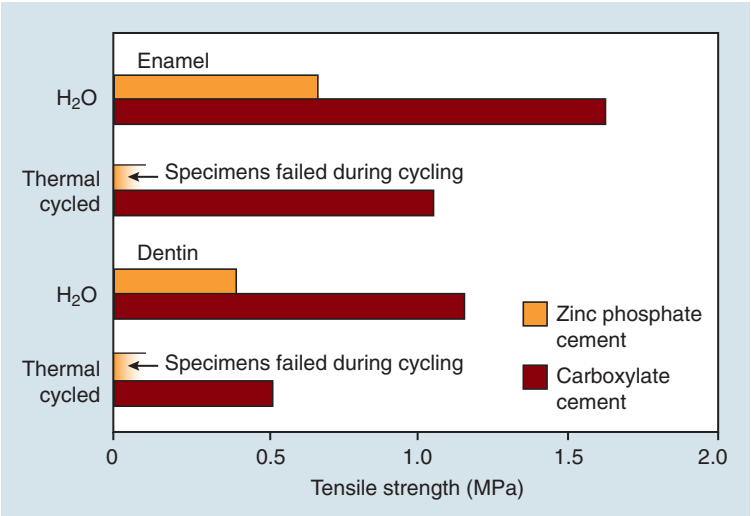


FIGURE 14-10 The tensile strength required to separate enamel and dentin surfaces luted with a polycarboxylate cement after storage in water for 1 week. Thermally stressed specimens were subjected to 2500 cycles between water baths maintained at 10 °C and 50 °C.

because the glossy surface indicates free carboxylic acid groups are still present for good bonding to the tooth. A dull-looking mixture means insufficient carboxyl groups are present for bonding to the calcium in the tooth.

Removal of Excess Cement

During setting, the polycarboxylate cement passes through a rubbery stage. Excess cement should not be removed while the cement is rubbery because some of the cement may be pulled out from beneath the margins, leaving a void. Excess cement can be removed as soon as the cementing process is completed, or when the cement becomes hard, provided that the outer surface of the prosthesis is coated with a separating medium.

Control of Working Time

The working time for polycarboxylate cement is much shorter than that for zinc phosphate cement, approximately 2.5 versus 5 minutes. Figure 14-11 shows the relative viscosities and working times of zinc phosphate, polycarboxylate, and GICs as they set. A cool slab lengthens the working time for zinc carboxylate cement, although it causes the polyacrylic acid to thicken, which hinders mixing. Refrigerating the powder is useful because it retards the reaction without raising the viscosity of the liquid.

Polycarboxylate cements are more viscous than a comparable mix of GIC; however, the polycarboxylate mix undergoes thinning at an increased shear rate. Clinically, this means that rapid spatulation and fast seating will reduce the viscosity of the polycarboxylate cement to ensure complete seating.

MECHANICAL AND BIOLOGICAL PROPERTIES

The compressive strength of polycarboxylate cement is approximately 55 MPa, which is lower than that of zinc phosphate cement. Zinc polycarboxylate cement is more elastic than zinc phosphate cement (Table 14-2), which makes it more difficult to remove excess polycarboxylate cement after setting. As with zinc phosphate cement, acids dissolve this cement, and lower P/L ratios increase solubility.

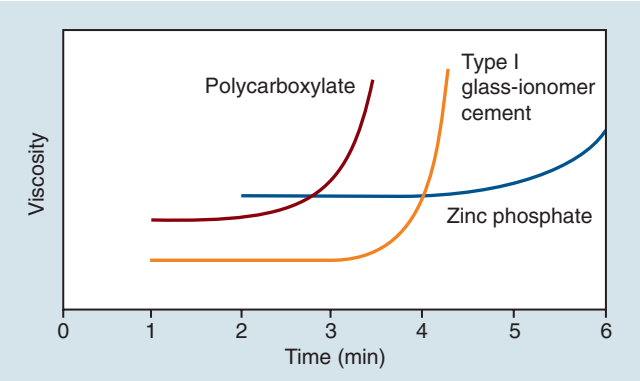


FIGURE 14-11 Viscosity of freshly mixed cements. The viscosity is related to the relative ability to allow complete seating of the prosthesis. Zinc phosphate cement is more viscous initially but provides a longer working time for seating compared with either polycarboxylate or GICs.

Polycarboxylate cements produce minimal irritation to the pulp. The larger size of the polyacrylic acid molecules compared with those of phosphoric acid limits acid penetration into the dentinal tubules, contributing to the excellent biocompatibility and lack of postoperative sensitivity of polycarboxylate cement.

GLASS IONOMER CEMENT (GIC)

GIC is the generic name for materials based on the reaction of glass powder and polyacrylic acid. The cements were developed in the 1970s to improve clinical performance compared with silicate cements and to reduce the risk of pulp damage.

The use of polyacrylic acid makes GIC capable of bonding to tooth structure. GIC is considered superior to many types of cements because it is adherent and translucent. Various formulas are available depending on the intended clinical application. Water-soluble polymers and polymerizable monomers have been replacing part of the liquid content. Particles of metal, metal-ceramic, and ceramic have been added to some products to enhance mechanical properties. Other new formulations are capable of being chemically cured, light-cured, or both.

GICs have been used for the esthetic restoration of anterior teeth, e.g., Class III and V sites, as luting cements, as adhesives for orthodontic appliance and **intermediate restorations**, as pit and fissure sealants, liners and bases, and as core buildup materials. The GICs are classified below:

Type I: Luting crowns, bridges, and orthodontic brackets
Type IIa: Esthetic restorative cements
Type IIb: Reinforced restorative cements
Type III: Lining cements, base

This section describes the original GIC formulation based on silicate glass particles and polyacrylic acid solution. Other variations of glass ionomers are discussed later in the chapter.

CHEMISTRY AND SETTING

The chemistry of GICs is essentially the same for all three types, with variations in powder composition and particle size to achieve the desired function. The consistency of the mixed GIC varies widely among manufacturers, from low to very high viscosity as influenced, by their use of various particle size distributions and the P/L ratio. Larger particles (about 50 µm) are used for the various restorative indications, and finer glass particles (about 15 µm) are used for cementing.

Glass Composition

The glass composition in GIC varies among manufacturers, but it always contains silica, calcia, alumina, and fluoride, as shown in Table 14-6. The ratio of alumina to silica is the key to their reactivity with polyacrylic acid. Barium, strontium, or other higher atomic number metal oxides are added to the glass to increase the radiopacity. The silica glass is melted at

TABLE 14-6 Composition of Three Glass Ionomer Cement Powders (weight percent)

Component	Composition A	Composition B	Composition C
SiO_2	41.9	35.2	20–30
Al_2O_3	28.6	20.1	10–20
AlF_3	1.6	2.4	–
CaF_2	15.7	20.1	–
NaF	9.3	3.6	–
$AlPO_4$	3.8	12.0	–
F	–	–	10–15
Na_2O	–	–	1–5
BaO	–	–	10–20
CaO	–	–	10–20
P_2O_5	–	–	1–5

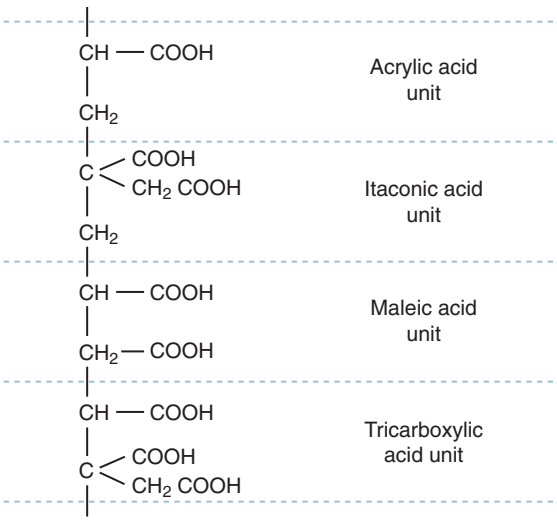


FIGURE 14-12 Structure of various types of alkenoic acids that make up polyacids of GICs.

temperatures between 1100 °C and 1500 °C, depending on the raw materials and the overall composition. The glass is ground into a powder with particles ranging from less than 15 µm to about 50 µm, depending on the indication.

Liquid Composition

Originally, aqueous solutions of polyacrylic acid (about 40% to 50%) were used, but such liquids were viscous and had a short shelf life because of gelation. Currently, the liquids are copolymers of itaconic, maleic, or tricarboxylic acids (Figure 14-12).

Tartaric acid is a rate-controlling additive in the GIC liquid that allows a wider range of glasses to be used, improves handling properties, decreases viscosity, lengthens shelf life before gelling of the liquid occurs, increases working time, and shortens the setting time (Figure 14-13).

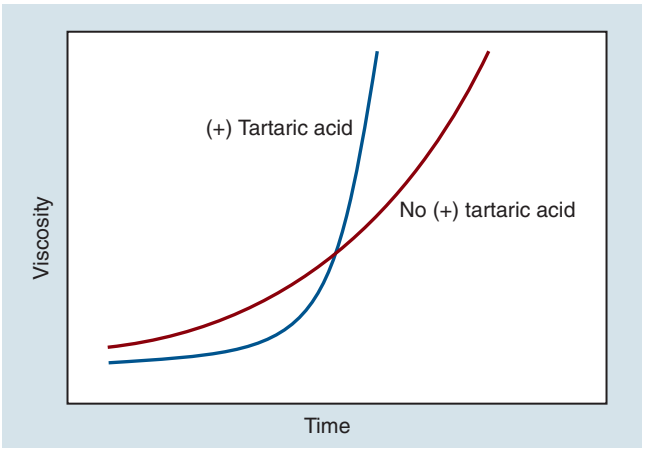


FIGURE 14-13 Effect of tartaric acid on the viscosity-time relationship for a GIC during setting.

? CRITICAL QUESTION

Water plays two critical roles in the setting of conventional GIC. What are they and how do they work?

A specialized GIC known as a water-settable glass ionomer is formulated with freeze-dried polyacrylic acid solid and glass powder, which is mixed with water or an aqueous solution containing tartaric acid. This type of GIC has an extended working time because additional time is needed to dissolve the dried polyacrylic acid in water and start the acid-base reaction.

Setting Reaction

When the powder and liquid are mixed for a GIC, the acid starts to dissolve the glass, releasing calcium, aluminum, sodium, and fluorine ions. Water serves as a reaction medium. The polyacrylic acid chains are then cross-linked by the calcium ions; however, over the next 24 hours, the calcium ions are replaced by aluminum ions. Sodium and fluorine ions from the glass do not participate in the cross-linking of the cement. Some of the sodium ions may replace the hydrogen ions of carboxylic groups, and fluorine ions are dispersed within the cross-linked (matrix) phase of the set cement. The cross-linked phase becomes hydrated over time as it matures. The undissolved portion of glass particles is sheathed by a silica-rich gel that is formed on the surface of the glass particles. Thus, the set cement consists of undissolved glass particles with a silica gel coating embedded in an amorphous matrix of hydrated calcium and aluminum polysalts containing fluoride. Figure 14-14 illustrates the structure of set GIC restoration, and Figure 14-15 is a photomicrograph of set GIC.

Mechanism of Adhesion

Glass ionomers bond to tooth structure by chelation of the carboxyl groups of the polyacrylic acids with the calcium in the apatite of the enamel and dentin (see Figure 14-14), in a manner similar to polycarboxylate cement.

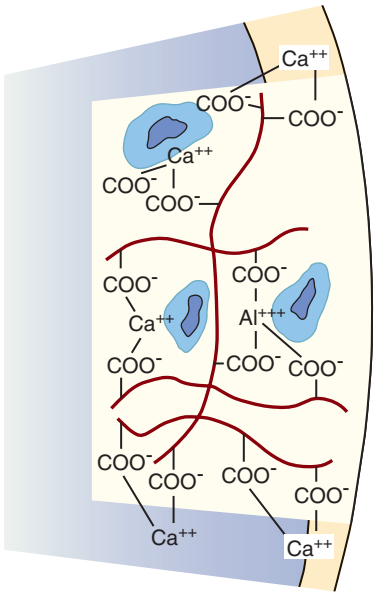


FIGURE 14-14 Diagram depicting the structure of GIC. The solid blue particles represent unreacted glass particles surrounded by the gel (*light blue shaded structure*) that form when Al^{3+} and Ca^{2+} ions are leached from the glass as a result of attack by the polyacrylic acid. The Ca^{2+} and Al^{3+} ions form polysalts with the COO^- groups of the polyacrylic acid to form a cross-linked structure. The carboxyl groups react with the calcium in enamel and dentin.

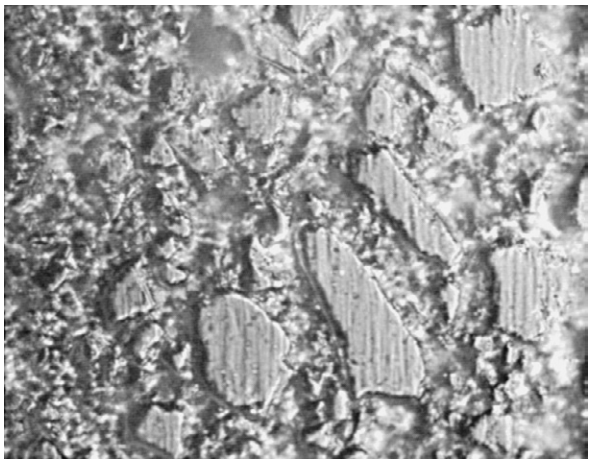


FIGURE 14-15 Photmicrograph of a set GIC showing unreacted particles surrounded by the continuous matrix.

? CRITICAL QUESTION

Under what condition might zinc phosphate cement be preferred over GIC for luting of ceramic crowns?

CLINICAL MANIPULATION

The following conditions for GIC must be satisfied for cementing fixed prostheses: (1) the surface of the prepared tooth must be clean and blotted dry, (2) the entire intaglio of the prosthesis must be coated with luting cement and seated completely, and (3) excess cement must be removed at the appropriate time. For restorative indications, the GIC surface must be protected to prevent dehydration or premature exposure to saliva. Surface finishing of GIC restorations must be carried out without excessive drying to ensure their survival.

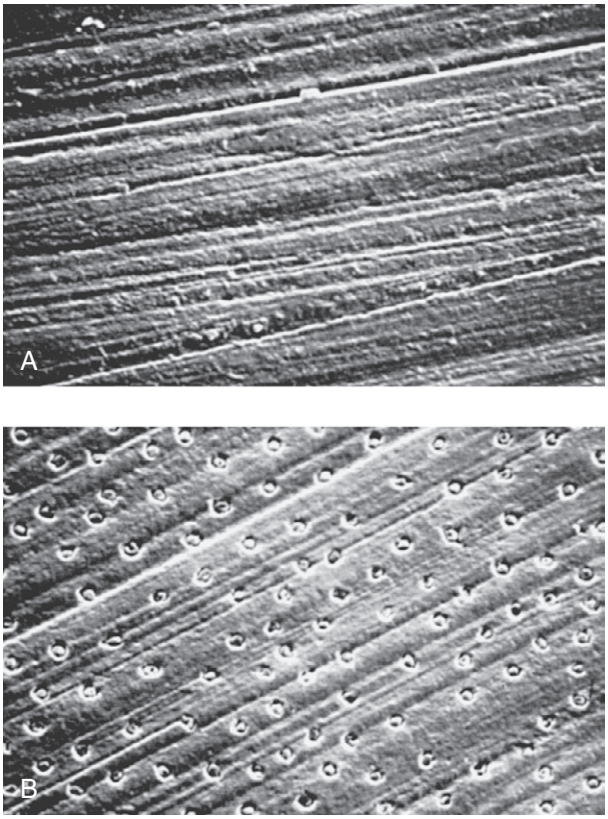


FIGURE 14-16 **A,** Prepared dentin surface showing the presence of the smear layer. **B,** After cleansing with polyacrylic acid, the smear layer is removed yet the tubules remain plugged.

Surface Preparation

Clean tooth surfaces are essential for sustained adhesion. A pumice slurry can be used to remove the smear layer produced by prepared cavity. Alternatively, the tooth may be etched (conditioned) with phosphoric acid (34% to 37%) or an organic acid like polyacrylic acid (10% to 20%) for 10 to 20 seconds, followed by a 20- to 30-second water rinse. Figure 14-16 shows the desired etching and smear layer removal on dentin after a 10-second swabbing action with a 10% polyacrylic acid solution. After conditioning and rinsing the preparation, the surface should be dried but not desiccated and it must remain uncontaminated by saliva or blood. For cases where the residual dentin thickness from the pulp is less than 0.5 mm, a calcium hydroxide liner is recommended.

Material Preparation

The P/L ratio recommended by the manufacturer should be followed. A paper pad or a cool, dry glass slab may be used for mixing. The latter serves to retard the reaction and extend

the working time. The slab should not be colder than the dew point. The powder and liquid should be dispensed just before mixing is begun; otherwise evaporation of water increases the acid/water ratio of the liquid. The powder should be incorporated rapidly into the liquid using a stiff spatula for restorative applications or a flexible metal or plastic spatula for luting applications. Normally half of the powder is mixed into the liquid for 5 to 15 seconds; the rest of the powder is then quickly added and mixed by folding the cement on itself until a uniform, glossy appearance is achieved. The mixing time should not exceed 45 seconds but may be less for certain products. A glossy appearance indicates the presence of unreacted polyacid, which is critical for bonding to the tooth. A dull appearance indicates that the acid has reacted too much with the glass particles for good bonding.

Glass ionomers are supplied in two bottles or capsules containing preproportioned powder and liquid (Figure 14-17). The capsules are convenient and offer a consistent P/L ratio with less variation than that for hand spatulation. A triturator is used to mix the powder and liquid after the seal between the powder and liquid has been broken. The trituration time and speed given by the manufacturer should be followed. The capsule contains a dispensation tip that facilitates direct injection of the mix into the prepared tooth cavity or onto a fixed prosthesis for bonding.

Placement of Material

A tooth cavity should be slightly overfilled with GIC restorative. A freshly prepared glass ionomer mixture is hygroscopic, which means that it absorbs water from the surrounding environment. After placement, the GIC surface should be covered with a plastic matrix for about 5 minutes to protect the material from gaining or losing water during the initial set. Water dilutes the matrix-forming cations and anions, destroying the ability to form the hydrated matrix. When the matrix is removed, the surface must immediately be protected with the varnish supplied with the GIC or with petrolatum while the excess GIC is removed from the margins. Finishing is improved if the cement sets while protected, which lowers the risk of dehydration and the tendency to **craze** the surface, which would make the restoration more opaque. Before the patient is dismissed, a type II GIC restoration should be coated with varnish, since the exposed cement is still vulnerable to dehydration until it has fully matured over a period of a few weeks. If these recommended procedures are not followed, the surface will inevitably become chalky or crazed (Figure 14-18).

For luting applications, the GIC is applied by a plastic instrument to the prosthetic device. The excess cement can be removed immediately upon seating or after a length of time as prescribed in the manufacturer's instructions. No matrix protection is needed during the initial setting. Coating of the margin of the cemented prosthesis with a varnish after complete removal of the excess will allow proper maturation of the GIC cement.

Release of Fluoride

After setting, glass ionomers release fluoride in amounts comparable to those released initially from silicate cement (Table 14-7). Whereas in vitro studies have shown the ability of the glass ionomer restorations to inhibit enamel and dentin **demineralization** produced by acidic gels or demineralizing buffer solutions, not all clinical studies confirm the ability of GIC to prevent secondary caries or the effectiveness of GIC over other nonfluoridated materials like composites. More information on fluoride release is presented later.

BIOLOGICAL AND MECHANICAL PROPERTIES

GICs elicit a greater pulpal reaction than ZOE cement but less than zinc phosphate cement. Glass ionomer luting agents pose a greater pulpal hazard than glass ionomer restorations



FIGURE 14-17 Two powder-liquid type II restorative GICs. **A,** Two-bottle system for hand mixing. **B,** Capsule for trituration (GC Fuji Triage capsule).



FIGURE 14-18 Crazed surface on glass ionomer restorations resulted from inadequate protection of the material during maturation. (Courtesy of Dr. S. Geradeli.)

when the GIC is mixed with a low P/L ratio because the pH remains acidic longer. With any GIC, a protective liner such as $Ca(OH)_2$ should be used if the preparation is closer than 0.5 mm to the pulp chamber.

Table 14-8 lists the properties of several restorative glass ionomers showing their compressive and tensile strengths. The compressive strength is similar to that of zinc phosphate, and its diametral tensile strength is slightly higher. The modulus of elasticity is only about half that of zinc phosphate cement (Table 14-2). Thus, the GIC is less stiff and more susceptible to elastic deformation. The higher elasticity (lower elastic modulus) makes GIC less desirable than zinc phosphate cement to support an all-ceramic crown, because greater tensile stress could develop in the crown that is supported by the GIC under occlusal loading.

GIC restoratives are more vulnerable to wear than are composites when subjected to in vitro toothbrush abrasion tests and simulated occlusal wear tests. Fracture toughness (Table 14-9), which is a measure of the energy required to cause crack propagation leading to fracture, is another property pertinent to restorative materials. Restorative GICs are less tough than resin-based composites.

METAL-REINFORCED GLASS IONOMER CEMENTS

Metallic fillers have been incorporated in GICs to improve their fracture toughness and stress-bearing capacity. The metallic fillers are derived from silver alloy powder or particles of silver sintered to glass that make the cement grayish and more radiopaque; these **metal-reinforced glass ionomer cements** are called alloy admixture and **cermet**, respectively. All of the concerns and procedures that apply to conventional GICs apply to metal-reinforced GICs.

These cement systems release appreciable amounts of fluoride, but the release rate decreases over time (Table 14-7). Less fluoride is released from the cermet cements because a portion of the glass particles were metal-coated. For the alloy admixed cement, the metal filler particles are not bonded to the glass; thus, all of the surface of the glass is available for fluoride leaching.

The adhesion and fluoride release from the metal-reinforced GICs are very useful for core buildups of teeth to be restored with cast crowns and for restoratives on occlusal surfaces of primary molars. However, metal-reinforced GICs are of limited in use as an alternative to amalgam or composite for posterior restorations. Studies show that these cements

TABLE 14-7 Cumulative Fluoride Release from Various Glass Ionomer Products

	FLUORIDE RELEASED (μG)	
Material	**14 Days**	**30 Days**
Type II	440	650
Cermet	200	300
Silver alloy admix	3350	4040
Type I	470	700
Liner (conventional)	1000	1300
Liner (hybrid)	1200	1600

TABLE 14-9 Fracture Toughness of Glass Ionomer Materials and Selected Other Materials

Type of Material	Fracture Toughness ($MPa \cdot m^{1/2}$)
Amalgam[1]	0.97–1.60
Hybrid composite[2]	1.75–1.92
Conventional GIC (luting)[3]	0.27–0.37
Conventional GIC (restoration)[4]	0.72
Metal-reinforced GIC (cermet)[5]	0.51
Metal-reinforced GIC (admixture)[5]	0.30
High-viscosity GIC[6]	0.45–0.72
Hybrid GIC (luting)[3]	0.79–1.08
Hybrid GIC (restoration)[5]	1.37
Compomer (restoration)[2]	0.97–1.23
Resin cement[3]	1.30

[1]Data from Lloyd CH, Adamson M: The fracture toughness (K_{IC}) of amalgam. *J Oral Rehab* 12:59–68, 1985.
[2]Data from Yap AU, Chung SM, Chow WS, et al: Fracture resistance of compomer and composite restoratives. *Oper Dent* 29:29–34, 2004.
[3]Data from Mitchell CA, Douglas WH, Cheng YS: Fracture toughness of conventional, resin-modified glass–ionomer and composite luting cements. *Dent Mater* 15:7–13, 1999.
[4]Data from Bonilla ED, Mardirossian G, Caputo AA: Fracture toughness of various core build-up materials. *J Prosthodont* 9:14, 2000.
[5]Data from Kovarik RE, Muncy MV. Fracture toughness of resin-modified glass ionomers. *Am J Dent* 8:145–148, 1995.
[6]Data from Yamazaki T, Schricker SR, Brantley WA, et al: Viscoelastic behavior and fracture toughness of six glass-ionomer cements. *J Prosthet Dent* 96:266–272, 2006.

TABLE 14-8 Properties of Restorative Glass Ionomer Cements

Materials	Compressive Strength (MPa)	Diametral Tensile Strength (MPa)	Hardness (KHN)
Type II	196–251	18–26	87–177
Cermet	176–212	19–22	30–45
High-viscosity	301	24	108
Hybrid	202–306	20–48	64–85

Data from Xie D, Brantley WA, Culbertson BM, Wang G: Mechanical properties and microstructures of glass-ionomer cements. *Dent Mater* 16:129, 2000.

fall short of expectations. For example, in vitro studies have shown that metal-reinforced GICs are weaker than resin-based composite cores; therefore, they should not be used if the cement represents greater than 40% of the total core buildup. The auxiliary use of pins or other retention forms is advisable in such cases. In addition, metallic fillers do not improve mechanical properties, including fracture toughness, compared with other restorative glass ionomers (Tables 14-8 and 14-9). Compared with conventional glass ionomers, the metal-reinforced GICs exhibit no improvement in clinical performance and life expectancy for Class II restorations in deciduous teeth. However, these cements harden rapidly, so they can be finished in a relatively short time, which is useful for pedodontic cases.

? CRITICAL QUESTION

For the atraumatic restorative treatment technique, why is a high-viscosity GIC the most appropriate material?

HIGH-VISCOSITY GLASS IONOMER CEMENT

Atraumatic restorative treatment (ART) is a preventive and restorative caries management concept developed for dentistry in regions of the world that do not have an infrastructure with electricity or piped water systems. ART relies on hand instruments for opening tooth cavities, removing carious dentin, and mixing the material. GIC, which releases fluoride and bonds chemically to tooth structure, is the natural choice of material for these situations. GIC may be superior to nonfluoridated materials, especially when the complete removal of carious tissue cannot be accomplished because of inadequate dental treatment facilities.

Initial results of using conventional GIC have proven the feasibility for ART, which has led to the development of **high viscosity glass ionomer cements** for general dental practices. These GICs contain smaller glass particle sizes and use a higher P/L ratio, yielding greater compressive strength (Table 14-8). They exhibit excellent packability for better handling characteristics. The high-viscosity GICs are also used for core buildups, primary tooth fillings, non-stress-bearing restorations, and intermediate restorations in general practices. Encapsulated packaging of the high-viscosity GICs (Figure 14-19) is convenient and increases their acceptance in developed countries.

CLINICAL MANIPULATION

The clinical steps in the ART procedure with high-viscosity GICs are as follows: (1) isolating the tooth with cotton rolls, (2) accessing the carious lesion with a hand instrument, (3) removing the soft tissue with an excavator, (4) using a weak acid to prepare the tooth and enhance chemical bonding, and (5) placing the high-viscosity GIC using finger pressure. Results of a study using the ART showed that the survival rate of partially and fully retained single-surface restorations on permanent teeth was 99% after 1 year and 88% after 3 years. The same study showed that the partial and full retention of

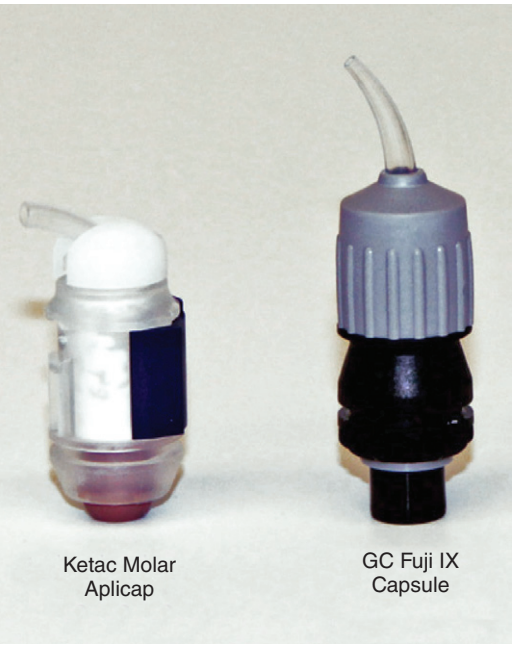


FIGURE 14-19 Two high-viscosity GICs. Ketac Molar Aplicap (*left*), GC Fuji IX Capsule (*right*).

sealants in the permanent dentition was 90% after 1 year and 71% after 3 years. A recent study followed two groups of children: one group received high-viscosity GIC by the ART procedure and one group received amalgam restorations. The cumulative survival rates after 6.3 years for ART and amalgam restorations were 66.1% and 57.0%.

In a general practice office, where electricity and water lines are available, the same procedures can be used, augmented by rotary instruments. Short-term clinical studies confirm that high-viscosity GICs are suitable alternatives to amalgam for Class I and II restorations in primary teeth. One 2-year study that compared the survival of high-viscosity GICs revealed no statistically significant differences between the ART procedure and the conventional procedure of preparing prepared cavities cavity using rotary instruments for Class I preparations. However, the use of conventional preparation techniques leads to a higher survival rate for Class II preparations. A retrospective clinical study of Class II restorations made of a high-viscosity GIC showed 100%, 93%, and 60% survival rates after 1.5, 3.5, and 6 years based on conventional techniques.

? CRITICAL QUESTION

What are the advantages of incorporating polymerizing resin in GICs?

RESIN-MODIFIED GLASS IONOMER CEMENT (HYBRID IONOMER)

Water-soluble methacrylate-based monomers have been used to replace part of liquid component of conventional GIC results in a group of materials called **resin-modified glass**

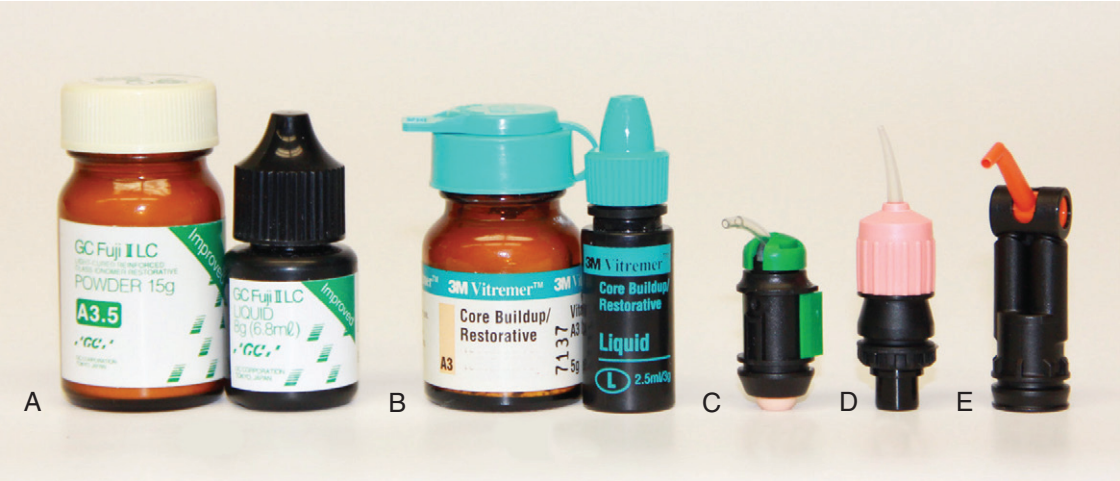


FIGURE 14-20 Representative resin-modified GICs. **A** and **B,** Two-bottle powder liquid system. **C,** Photac Fil Quick Aplicap. **D,** GC Fuji Plus Capsule. **E,** Ketac Nano; a paste-paste system using static mixing.

ionomer cements (Figure 14-20), also known as **hybrid ionomer** cement. The monomers can be polymerized by a chemical or light activation or both, and the GIC acid-base reaction will occur along with polymerization. Some hybrid ionomer cements also contain nonreactive filler particles, which lengthens the working time, improves early strength, and makes the cement less sensitive to moisture during setting.

CHEMISTRY AND SETTING

The liquid component of hybrid ionomer cements usually contains a water solution of polyacrylic acid, **HEMA**, and polyacrylic acid modified with methacrylate. The powder component contains fluoroaluminosilicate glass particles of a conventional GIC plus initiators, such as camphorquinone, for light curing and/or chemical curing. The acid-base reaction begins upon mixing and continues after polymerization at a much slower rate than for conventional GICs because less water is present and the reaction is much slower in the solid phase than in the liquid phase.

Some hybrid ionomers are designed for restorative purposes and contain nonreactive fillers normally found in the resin composite, replacing some silicate glass; the quantity of carboxylic acid groups is also decreased. These changes do not affect the setting mechanism but impart changes in the characteristics of the material, such as bonding and strength.

Mechanism of Bonding

The bonding mechanism for hybrid ionomer cements to tooth structure is the same as that for conventional GICs. However, the use of polymerizable monomers in hybrid ionomers leads one to speculate that the bonding mechanism should also include the "hybrid layer" of the cement that infiltrates the tubules. Currently no conclusive evidence exists of hybrid layer formation with hybrid ionomer cements. Studies have reported the presence of an "indistinct" or "structureless" layer at the ionomer-dentin interface, although other studies show no evidence of resin infiltration into the etched dentin. Higher bond strengths to teeth and resin-based composites have been reported for hybrid ionomer cements than for conventional glass ionomers, which is probably associated with enhanced micromechanical interlocking to the roughened tooth surface.

Unfortunately, the methacrylate polymerization of resin-based composites causes more shrinkage of hybrid ionomers during setting as compared with a conventional GIC. The lower water and carboxylic acid contents also reduce the ability of the cement to wet tooth substrates, causing more microleakage than with conventional glass ionomers.

CLINICAL MANIPULATION

Clinical applications of hybrid ionomers include liners, fissure sealants, base materials, core buildups, restoratives, adhesives for orthodontic brackets, repair materials for damaged amalgam cores or cusps, and retrograde root filling materials. For any indication, surface conditioning of the tooth structure with a mild acid is essential for bond formation. For the hybrid ionomer containing nonreactive filler particles, less carboxylic acid is available for bonding to tooth structure and a dentin bonding system is needed.

A few reports of adverse effects have been attributed to hybrid ionomers, which release HEMA, a monomer that can cause pulpal inflammation and allergic contact dermatitis. Therefore, hybrid ionomers are not as biocompatible as conventional glass ionomers. Dental personnel may be at risk from adverse effects such as contact dermatitis and other immunological responses. The temperature increase associated with the polymerization process can also be considered as a drawback of hybrid ionomer cements.

Fissure Sealant

Low-viscosity hybrid ionomers or conventional GICs may be used for fissure/sealant indications. One clinical study shows that the retention rate of glass ionomer sealant is poor after

1 year, but patches of GIC were retained within the fissures and no signs of carious lesions were observed.

Liner and Base

As a liner or base material, hybrid ionomer serves as an intermediate bonding material between the teeth and composite restorations. Hybrid ionomer is not indicated for direct pulp capping. If the situation warrants a direct pulp capping procedure, a calcium hydroxide liner should be used prior to the application of a hybrid ionomer. The adhesion of GIC to dentin reduces the probability of gap formation at gingival margins located in dentin or cementum, compensating for the polymerization shrinkage of the overlying resin-based composite restoration on the hybrid ionomer base. Furthermore, a hybrid ionomer base or liner reduces the technique sensitivity of resin bonding agents and provides the **anticariogenic** effect from fluoride (Table 14-7). This procedure is often referred to as the sandwich technique, which combines the desirable qualities of the glass ionomer and the esthetics of the composite restoration. This **sandwich technique** is recommended for Class II and V composite restorations when individual patients are at a moderate to high risk for caries.

Restorations

The monomers in hybrid GICs make the cements more translucent. Fluoride release is unchanged from that of conventional GICs, and the diametral tensile strengths of hybrid glass ionomers are higher than those of GICs (Table 14-8). This increase in tensile strength (but not compressive strength) is attributed to their lower elastic modulus and the greater amount of plastic deformation that can be sustained before fracture occurs.

Water Uptake

The presence of HEMA in hybrid ionomers increases water absorption and causes expansion of up to about 8% by volume. This expansion has been linked to the fracture of all-ceramic crown restorations when used for core buildups or as luting cements. However, recent in vitro studies show that all-ceramic crowns cemented on natural teeth or titanium abutments with hybrid ionomer luting agents did not crack after 12 months of storage in water.

Delivery System

Porosity in cement is the result of air incorporation during mixing of powder and liquid. One study of luting agents showed that the method of mixing had no influence on the formation of small pores but that hand mixing yielded more large pores than triturator mixing of capsules. A later study showed that hand mixing yielded significantly greater compressive strength with the luting cement whereas capsule mixing resulted in a stronger restorative cement, although the difference was small. Porosity measurements in four types of hand-mixed cements showed that polycarboxylate cement had the highest porosity and **resin cement** (discussed later) had the least. Zinc phosphate and GICs had intermediate amounts of porosity. This study and others suggest that the viscosity of the cement play a significant role in the formation of porosity.

The most recent mixing method is the static mixing used in preparing impression materials (Figure 8-9), where dual cartridges of pastes are blended as they are expressed through a mixing tip. Complete mixing with a static mixer depends on the paste's properties, inner diameter of the dispensing cylinder, number of mixing elements, and mixer design. The benefit of static mixing is that it does not mix air into the cement and it takes less time to complete mixing. A low-porosity cement is expected with static mixing, although little information on this matter is available.

? CRITICAL QUESTION

What is the setting mechanism of calcium aluminate GIC?

CALCIUM ALUMINATE GLASS IONOMER CEMENTS

A hybrid product with a composition between that of calcium aluminate and GIC, designed for luting fixed prostheses, is a new addition to the family of GICs. The calcium aluminate component is made by sintering a mixture of high-purity Al_2O_3 and CaO (approximately 1:1 molar ratio) to create monocalcium aluminate. The material is crushed and milled to a specified particle size distribution. When mixed with water, the calcium-aluminate powder starts to dissolve Ca^{2+}, $Al(OH)_4^-$, and OH^- ions and a weak acid-base reaction begins. The powder acts as the base and water as the weak acid. At low water-to-cement volume ratios, the reaction is followed by an immediate precipitation of hydrates, caused by saturation of the solution, which grow and harden over time. This type of cement is also known as a hydraulic cement and has been advocated as a restorative material. This reaction has been paired with glass ionomer ingredients to create the hybrid calcium aluminate GIC.

The main ingredients in the powder of this hybrid cement are calcium aluminate, polyacrylic acid, tartaric acid, strontium-fluoro-alumino-glass, and strontium fluoride. The liquid component contains 99.6% water and 0.4% additives for controlling setting. The glass ionomer components of the cement are responsible for the early properties (i.e., viscosity, setting time, and strength). The calcium aluminate contributes to a basic pH during curing, reduction in microleakage, excellent biocompatibility, and long-term stability and strength. The polyacrylic acid has a dual function in this hybrid material. As in a conventional GIC, the polyacrylic acid is cross-linked by Ca^{2+} ions leached from both the soluble glass and the calcium aluminate. The polyacrylic acid also acts as a dispersing agent for the calcium aluminate. The resulting material is a composite of hydrated ceramic material and a cross-linked polyacrylate polymer. The cement is packaged in capsules for mechanical mixing (Figure 14-21).

In vitro retention and shear bond test strength are excellent, as is compressive strength for the hybrid calcium



FIGURE 14-21 A calcium aluminate GIC.

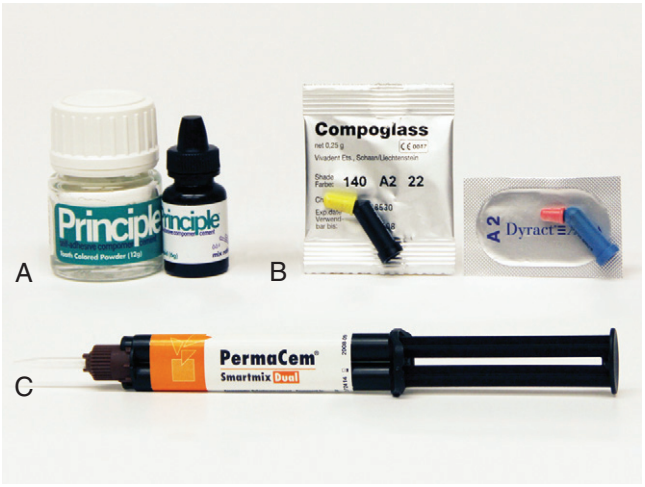


FIGURE 14-22 Typical compomer materials. **A,** A powder-liquid system. **B,** Two single-component systems. **C,** A paste-paste dual cartridge using static mixing. All systems are light-curable.

aluminate cement. The working and setting times are reported to be 2 and 5 minutes, respectively. The film thickness is 15 ± 4 μm. Setting expansion of 0.4% in vitro has been reported. A study of cement set inside glass tubes showed no fracture of the glass; therefore, this amount of expansion was considered acceptable. A microstructure study showed formation of hydroxyapatite in a phosphate buffer solution on the surface of the luting cement. Results of a 2-year clinical study revealed a favorable performance of this cement.

? CRITICAL QUESTION

How does **compomer** differ from resin-based composite?

COMPOMER

Compomer is a polyacid-modified composite made by incorporating glass particles of GIC in water-free polyacid liquid monomer with appropriate initiator. The rationale for using this material is the integration of the fluoride-releasing capability of glass ionomers with the durability of resin composites. Compomers possess properties distinctly different from those of resin composites and glass ionomers.

CHEMISTRY AND SETTING

Compomers are usually a one-paste, light-cure materials for restorative applications, although powder-liquid systems for luting applications are available (Figure 14-22). These water-free materials contain nonreactive inorganic filler particles, reactive silicate glass particles, sodium fluoride, and polyacid-modified monomers, such as a diester of 2-hydroxyl methacrylate with butane carboxylic acid and photoactivators. Setting of these one-component compomers is initiated by photopolymerization of the acidic monomer. Compomer cements are sensitive to moisture and are packaged to protect against moisture absorption, even though their acid-base reaction is slow. Like resin composites, compomers are functionally hydrophobic but to a lesser extent, and intraorally they absorb water from the saliva that begins the slow acid-base reaction of GIC between the acidic functional groups and silicate glass particles, which leads to fluoride release.

For the powder-liquid compomer products, the powder contains strontia-alumina-fluorosilicate glass, metallic oxides, and initiators. The liquid contains polymerizable methacrylate/carboxylic monomers, multifunctional acrylate monomers and water. Depending on the initiators, the material can be chemically cured, light-cured, or dual-cured to augment the slower acid-base reaction.

Bonding Mechanism

Compomer restorative materials require a dentin-bonding agent prior to their placement because they do not contain water, which could make them **self-adhesive,** like conventional GIC or hybrid ionomer. Bond strength of one-paste compomers to tooth structure using a dentin-bonding agent is similar to or higher than that of hybrid ionomers. The powder-liquid compomer cements for luting are self-adhesive, because water in the liquid makes the mixture acidic, like hybrid ionomers.

CLINICAL MANIPULATION

The restorative compomer materials are mainly used in low-stress-bearing areas such as Class III and V prepared cavity, or as an alternative to glass ionomer restoratives or resin-based composites. The tooth structure should be etched prior to application of the dentin bonding agent and the compomer. Compomers are finished just like resin composites.

Compomer luting systems are indicated for cementing prostheses with a metallic substrate. The cement mixture is placed only on the prosthesis, which is seated with finger pressure. The margin should be light-cured immediately to stabilize the prosthesis. The chemical-cure compomers

complete their setting reaction in approximately 3 minutes in the oral environment, although they may take 10 minutes or more to set on the bench top. Ninety seconds from the end of mixing, the material will reach a gel state, at which point the excess cement may be removed.

Water Uptake

Water absorption by restorative compomers, which is as high as 3.5% by weight, is a desired process to complete the acid-base reaction and subsequent fluoride release. As expected, restorative compomer releases less fluoride than that from conventional GICs and hybrid ionomers. Studies have shown that the compressive strength and flexural strength of compomers decrease on storage in saline solution, a phenomenon not observed in resin composites. The decrease in strength is associated with the water uptake and the acid-base reaction. However, the surface hardness and microtensile strength appear to be unchanged. When manufacturers treat the reactive glass with silane, water uptake is reduced and strengths are higher.

Clinical Performance

Not all compomers exhibit acceptable clinical performance in Class V restorations, and the color stability of compomer cements is a problem. The change in refractive index on the surface by water absorption and staining by food are the likely causes. A 24-month clinical study shows that, except for marginal integrity, they perform as well as resin-based composite sealants when used to seal fissures. Compomers perform as well as resin composites for Class I and II restorations and acceptably as luting agents for orthodontic bands.

RESIN CEMENTS

The success of attaching unfilled resin to etched enamel gave rise to the concept of using resins to bond fixed prostheses to abutments. Numerous resin cements are now available for bonding fixed prostheses.

CHEMISTRY AND SETTING

Resin cements are low-viscosity versions of restorative composites. These cements are virtually insoluble in oral fluids, but the brands vary widely in physical properties because of the variety and proportions of resins and fillers in the formulas. Organosilanes are used to ensure that the filler materials bond to the resins and create a durable, wear-resistant material. A dentin bonding agent is needed to promote the adhesion of resin cements to dentin. The adhesive monomers incorporated in the bonding agent and the resin cements include HEMA, 4-META, carboxylic acids, and an organophosphate, such as MDP (10-methacryloyloxydecamethylene phosphoric acid). For systems that require a bonding agent, the resin primers partially infiltrate the collagen fibrils that have been demineralized by acid etching. The resin tags reduce adverse pulpal responses.

Not all resin cement systems require a bonding agent. The 4-META–containing cements do not need a separate bonding agent. One system uses only liquid monomers and catalysts without any traditional inorganic fillers, and it relies on mixing with various amount of polymer beads to adjust the viscosity of the cement for intended applications. Recent developments have aimed at eliminating the steps of etching, priming, and bonding that allow the clinician to bond prostheses directly to clean abutments with only one-component material. These cement systems rely on modified dimethacrylate monomers with acid-containing side chains—such as phosphoric acid—attached as pendant groups. Upon contact with the tooth surface, the acidic group bonds to calcium ions in the tooth structure, making the cement a so-called self-adhesive resin cement.

Polymerization of the resin cement occurs by chemical-, light-, or dual-cure mechanisms. The majority of resin cements today are of the dual-cure variety. Light-cured resin cement is less common because of the potential for incomplete polymerization of the cement under a prosthesis; it is used for cementing porcelain veneers. They are supplied in various delivery systems, as are hybrid ionomers (Figure 14-23).



FIGURE 14-23 Commercial resin cements. **A,** A hand-mixing paste-paste dual-cure system for temporary prostheses. **B,** A single-component light-cure system for porcelain veneers. **C,** A paste-paste dual-cartridge dispensing system that requires hand mixing. **D,** A powder-liquid capsule system that is triturated. **E,** Two paste-paste dual-cartridge systems that requires static mixing; the top one requires a bonding agent and the bottom one is self-adhesive. **F,** A liquid-liquid system.

CLINICAL MANIPULATION

The monomeric component of the resin cements is irritating to the pulp. To prevent the infiltration of irritants, pulp protection with a liner is important when the thickness of the remaining dentin is less than 0.5 mm.

Chemically cured resin cements are suitable for all types of restorations. They are supplied as powder and liquid or two pastes, which are mixed on a paper pad for 20 to 30 seconds. Chemical activation is very slow and provides extended working time, and the strength increases as the chemical

process continues. However, excess cement should be removed immediately after the restoration is seated.

Dual-cure cements require mixing similar to that for the chemical-cure systems. Static mixing and trituration of capsules have largely replaced the need for hand mixing. Curing proceeds slowly until the cement is exposed to the curing light, at which point the cement hardens rapidly. These dual-cure cements should not be used with light-transmitting prostheses thicker than 2.5 mm; anything thicker than 2.5 mm should be bonded with chemical-cure cement. Removal of excess cement may be performed after seating or after waiting for a specific period as indicated in the manufacturer's directions for use.

? CRITICAL QUESTION

Why are different types of resin cements used in the treatment of prosthesis surfaces?

The procedure for preparing tooth surfaces remains the same for each system, but the treatment of the prosthesis differs depending on the composition of the prosthesis, as described below.

Metallic Prostheses

The bondable surface of base metal prostheses should be roughened by electrochemical etching or by grit blasting with 30- to 50-µm alumina particles at an air pressure of 0.4 to 0.7 MPa. Some bonding systems include a metal primer containing an adhesion promoter. Oxide formation on the base metal surfaces contributes to the bond strength when resin cement containing MDP or a 4-META-based resin is used. To enhance bonding to noble alloys, which lack a stable oxide at room temperature, one can electrochemically deposit a thin (about 0.5 µm) layer of tin on noble metal and heat it to an appropriate temperature to form a tin oxide surface. Silica deposition on noble and base alloy surfaces can be achieved by blasting silica-coated Al_2O_3 particles on these surfaces. Subsequent silanization improves metal surface bonding to resin cements, although the bond-strength is similar to that measured for grit blasting and electrochemical etching.

Polymeric Prostheses

Resin-based veneers, inlays, onlays, crowns, and fixed dental prostheses are cemented with resin cements. The polymer's surface should be grit-blasted to increase the roughness for mechanical adhesion. Some polymer prosthesis systems have a special adhesive based on the same monomer that is used to fabricate the prosthesis. Sufficient time, as much as 30 minutes, must be allowed for adequate penetration and diffusion of the adhesive into the cross-linked polymer prosthesis to occur before curing.

Ceramic Prostheses

Some dental ceramic restorations are translucent and the shade of the luting cement can affect the esthetics of the ceramic restoration. Resin cements are the luting agents of choice for all-ceramic inlays, crowns, and bridges because of their ability to reduce fracture of the ceramic structures and the range of shades available to produce an optimal esthetic appearance. If the ceramic prostheses are silica based, like feldspathic porcelain, the inner surfaces of the prostheses are etched with hydrofluoric acid, and a silane coating is applied prior to cementation, either by the dental laboratory or chairside. Etching and silanization are not effective with ceramics that do not contain silica, such as alumina and zirconia-based ceramics.

Light-cure resin cements are indicated for the cementation of thin ceramic prostheses, resin-based prostheses, and direct bonding of ceramic or plastic orthodontic brackets. Seat the prosthesis with light pressure to expel excess cement, secure the prosthesis in place by spot curing part of the prosthesis without irradiating the excess cement, clean of the excess cement from the margin and then light cure the remaining area for the specific duration recommended by the manufacturer.

To match the resin cement with the ceramic prosthesis, some systems provide water-soluble try-in materials with the same shades as the cements. The try-in gels are applied in the same way as a cement, and the prosthesis is seated and examined in situ for its esthetic appearance. This process can be repeated with various try-in gel shades until the clinician is satisfied with the esthetic appearance. After the proper cement shade has been selected, the residual try-in paste must be rinsed off the tooth and the prosthesis is thoroughly rinsed with a water spray. The cementation process is then completed using a cement of the same shade as the selected try-in gel.

Orthodontic Brackets

Orthodontic bonding is a specialized use of cement that must be strong enough to withstand the forces exerted on the device for about 2 years, but then the bond must be broken for removal with minimal effect on the tooth. The bonding of orthodontic brackets requires proper isolation and etching of the enamel surface to secure the bond between the tooth and the bracket. The tooth-facing side of the bracket requires some means of mechanical retention, such as the metal mesh of a metal bracket or retentive dimples or ridges on ceramic or polymer brackets. Ceramic bracket bases are commonly precoated with an organosilane, like that used to bond the inorganic fillers to the resin matrix of resin-based composites. Polycarbonate brackets are primed with a solvent containing methylmethacrylate monomer.

Mechanical and chemical adhesion to the bracket and tooth are important for the prevention of premature debonding. Because of cement exposure to the oral cavity, the bond strength decreases over the course of treatment and bracket removal can be uneventful. Debonding of brackets at the tooth/cement interface, or less preferably at the cement/bracket interface, is desirable, but not within the tooth enamel.

Orthodontic bands are commonly cemented with GIC. Their removal is facilitated by using air to desiccate and weaken the cement.

ZINC OXIDE–EUGENOL CEMENT

ZOE cement is commonly used for luting and intermediate restorations because of its medicament quality and neutral pH.

CHEMISTRY AND SETTING

ZOE cement is formulated as a powder-liquid or two-paste system. The powder contains zinc oxide particles and the liquid is eugenol (Figure 14-1). For the two-paste system, the base paste contains zinc oxide powder and the eugenol is contained in the accelerator (or catalyst) (Figure 14-24). The setting reaction starts with water in the eugenol solution that hydrolyzes the zinc oxide to form zinc hydroxide. The zinc hydroxide and eugenol chelate and solidify. The setting reaction is slow but proceeds more rapidly in a warm, humid environment. A wide variety of ZOE cements are available, with compressive strengths ranging from 3 to 55 MPa, which makes the ZOE formulations best suited for provisional applications. Finer powders increase the strength of the resulting cement.

Residual free eugenol interferes with the proper setting of resin-based composites or resin cements; therefore, various types of carboxylic acids have been used to replace eugenol and produce a ZOE-like material. These products are called zinc oxide-noneugenol cements.

Other modifications have been made to improve the strength and abrasion resistance of ZOE cement for long-term luting. One system substitutes orthoethoxybenzoic acid (EBA) for part of the eugenol liquid, and includes alumina in the powder. Another system (ZOE plus polymer) consists of eugenol liquid and a special powder containing of 20% to 40% by weight of fine polymer particles and zinc oxide particles that have been surface treated with carboxylic acid. The compressive strength of these improved ZOE cements (Table 14-4) is acceptable but their strength values are inferior to those of zinc phosphate, glass ionomer, and resin cements (Table 14-2).

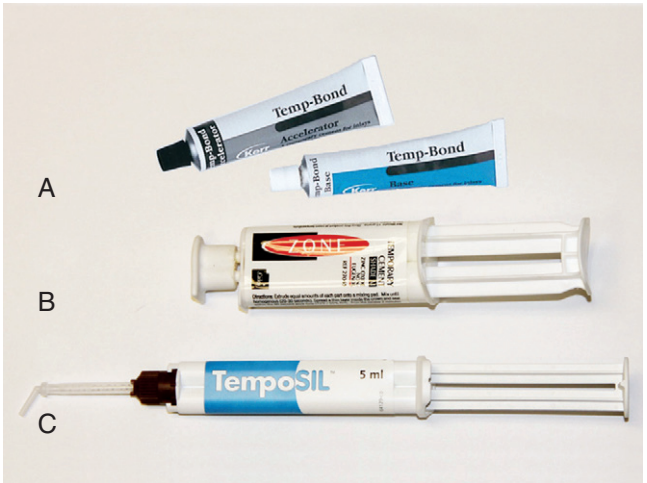


FIGURE 14-24 Zinc oxide–based paste-paste temporary cements. **A,** A two-tube system for hand mixing. **B,** A dual-cartridge system for hand mixing. **C,** A dual-cartridge system with static mixing.

CLINICAL MANIPULATION

The versatile uses of ZOE are reflected in ANSI/ADA Specification No. 30 or ISO 3107; Dentistry—Zinc oxide/eugenol cements and zinc oxide/non-eugenol cements, which lists four types of ZOE cements by clinical application: (I) temporary cementation; (II) long-term cementation of fixed prostheses; (III) temporary fillings and thermal insulating bases; and (IV) intermediate fillings. ZOE cement is also used as a **root canal sealer** and periodontal dressings. Its antimicrobial attribute is a benefit compared with glass ionomer cements or resin-based composites.

Temporary ZOE cements, including eugenol-free cement, are excellent for luting provisional acrylic crowns and fixed partial dentures. Temporary ZOE restorations are expected to last a few weeks at most. They seal the dentinal tubules surprisingly well against the ingress of oral fluids and have a sedative effect on the pulp. Hence, irritation caused by microleakage is minimized and these cements are suitable for temporary restorative treatment while the pulp heals or until a longer-lasting restoration can be fabricated and cemented. The ZOE cements can cause pulp-necrosis and should not be used directly on a pulp. ZOE cements should never be used for temporary cementation of final fixed prostheses since the cement can be difficult to remove and removal can risk the integrity of the prepared teeth.

When ZOE cement is mixed to a stiff puttylike consistency, it serves effectively as an intermediate restorative material for at least a year. Mixing on a cool glass slab slows the setting to enable the formation of a thick consistency, but the slab should not be colder than the dew point; otherwise water will condense onto the cement and accelerate the reaction.

ZOE luting cements used for long-term applications are somewhat difficult to manipulate because of their high film thicknesses. Figure 14-24 shows three delivery systems for zinc-oxide–based temporary cement.

ZOE cement is one of the several cements of choice for implant superstructure cementation. One of the disadvantages of restoring dental implants with a cement-retained prosthesis is the lack of easy retrievability of the cemented superstructure. Retentive cement can damage the supporting implant if the prosthesis is removed with aggressive removal techniques; on the other hand, less retentive cement causes frequent loosening of the prosthesis. As a result, practitioners who desire retrievability have generally gravitated toward using cements with lower retentive properties. ZOE cement is one of the several cements of choice for implant superstructure cementation. Mechanical factors—such as resistance/retention form, height, distribution, number of abutments, accuracy of superstructure fit, as well as maxillary versus mandibular arch—strongly influence the degree of cement retentiveness required for a given restoration. Knowledge of the relative retentiveness of cements improves the clinician's success in choosing a cement. In vitro studies have ranked the retentive nature of commercial products, but the clinical literature does not provide accurate information about the

ideal type of cement for stability and retrievability of cement-retained prostheses.

CRITICAL QUESTION

Why is MTA cement biocompatible and considered bioactive?

MINERAL TRIOXIDE AGGREGATE CEMENTS

A new category of cement, based on some of same compounds found in Portland cement, has gained popularity for endodontic applications (Figure 14-25, *A*). This material is beneficial because of its sealing ability and biocompatibility. In 1878, Witte published a case report in Germany on using Portland cement to fill root canals; however, Portland cement–type materials were not used in common practice until the 1990s. The first product, called **mineral trioxide aggregate (MTA)**, is made of a hydraulically active powder that combines calcium oxide (calcia, CaO), aluminum oxide (alumina, Al_2O_3), and silicon dioxide (silica, SiO_2) into hydraulically active ceramic compound.

CHEMISTRY AND SETTING

The essential phases of MTA cement powder are tricalcium silicate, dicalcium silicate, and radiopaque filler. Usually minor phases of tricalcium aluminate and calcium sulfate (Table 14-10) are present. Some MTA-type products contain calcium carbonate or tetracalcium aluminoferrite. MTA has been denigrated in the literature as expensive Portland cement because the same phases are present in both materials; however, MTA-type products contain a radiopaque agent—usually bismuth oxide, zirconia, or tantalum oxide—without which MTA would not be distinguishable on a radiograph. The term *MTA* is used here to denote all of the tricalcium- and dicalcium-silicate products.

MTA sets by reaction with water (Figure 14-25, *B*) and forms a highly alkaline (pH about 12) cement composed of a rigid matrix of calcium silicate hydrate and calcium hydroxide. These hydrates form on the surface of the original calcium silicate particles and hydration gradually progresses inward. The setting time for MTA is lengthy, about 165 minutes for the initial set and less than 6 hours for the final set, which is a major drawback to using this cement. When MTA sets, it expands less than 0.1%, which helps to create a barrier that is especially important for endodontics.

After mixing with water, the pH of MTA cement rises rapidly by the release of calcium hydroxide. The remarkable success of MTA as a biocompatible material has been attributed to the calcium hydroxide in the set MTA, which makes the material antibacterial and antifungal. For example, MTA cement is less cytotoxic than GIC, and hydroxyapatite crystals form on the surface of MTA in vitro with a phosphate-buffered saline, making this cement uniquely bioactive. Cementum-like layers have formed over root ends where MTA has been used for endodontic surgeries.

New formulations are being introduced that include polymers, salts (especially calcium chloride), and water-reducing agents to improve handling and to shorten the setting time for MTA products. Such products will expand the indications and utility of these calcium-silicate powders.

CLINICAL MANIPULATION

MTA was first used for root-apex filling in endodontic surgeries, but its indications have expanded to include procedures for **vital pulp therapy** (pulp capping and pulpotomy dressing) and procedures that contact the periradicular tissues, such as root-end filling, apexification, perforation repair, root resorption repair, obturation, and root canal sealing. Because it is caustic, MTA should not be allowed to stay in contact with the mucosa because the high pH can cause a superficial lesion. Excess material should be removed from the oral cavity.

MTA will set over a wide range of P/L ratios, roughly between 4 to 1 and 2 to 1, although most products employ a

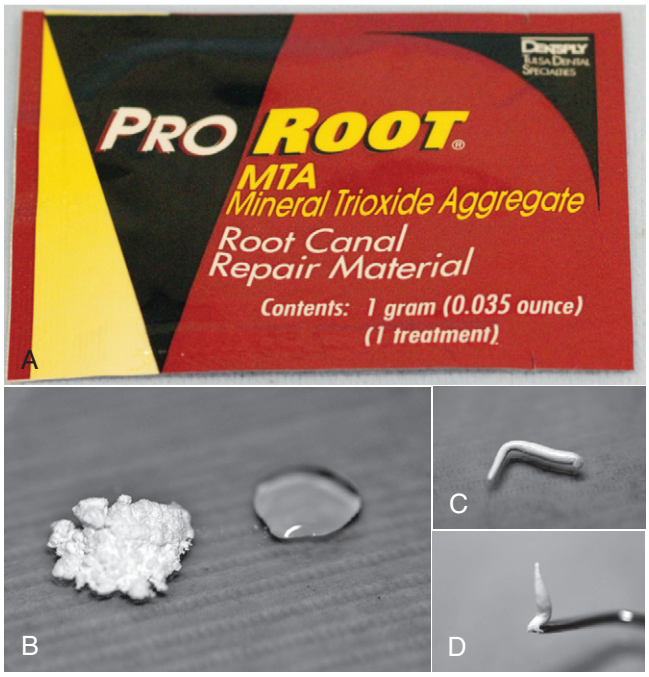


FIGURE 14-25 Manipulation of MTA. **A,** A package of MTA powder. **B,** Powder and water on a glass slab ready for hand mixing. **C,** The mixture should exhibit a puttylike consistency as it is rolled into a log. **D,** The log can be cut into suitable pieces for placement.

TABLE 14-10 Phases in MTA-Type Powders before Hydration

Ceramic Phases	Wt%
Tricalcium silicate: $(CaO)_3 \cdot SiO_2$	45–75
Dicalcium silicate: $(CaO)_2 \cdot SiO_2$	7–32
Radiopaque filler: Bi_2O_3 or Ta_2O_5	20–35
Tricalcium aluminate: $(CaO)_3 \cdot Al_2O_3$	0–13
Tetracalcium aluminoferrite: $(CaO)_4 \cdot Al_2O_3 \cdot Fe_2O_3$	0–18
Gypsum: $CaSO_4 \cdot 2H_2O$	2–10

P/L ratio of 3 to 1. To mix MTA, the powder should be dispensed onto a glass slab, with a drop of the liquid from the kit next to the powder. A stiff metal spatula should be used to incorporate the powder gradually into the liquid until a puttylike consistency is reached (Figure 14-25, *C*). Thorough mixing and repeated spatulation should be performed. The mixed material can be formed and rolled into a "log" with gloved fingers (Figure 14-25, *D*); then the spatula can be used to cut off small sections for insertion in a root-end filling or a perforation site. A spatula, a small amalgam carrier, or a condenser is commonly used to transport the MTA delicately into the surgical location. If mixed MTA is not used immediately, a moist gauze "tent" can be placed over the material to prevent dehydration. If drying occurs, the material can be reconstituted with water within the first hour because its setting time is so long. If hemorrhage is not controlled before placement, MTA may be discolored by blood seeping into the MTA material via capillary action as it gradually sets. Inhomogeneity of the radiopaque phases has been noted in some MTA products, and other MTA products have coarse powders. The products are evolving in the marketplace and improving.

Thorough flushing of root canal irrigants should be performed before placing an MTA mixture. Common canal irrigants and debridement preparations often contain ethylenediaminetetraacetic acid (EDTA) or other organic acids that partially dissolve and impair the seal of MTA by the chelation of EDTA to the calcium in MTA.

Endodontic Applications

MTA cement is starting to replace the use of calcium hydroxide as an endodontic dressing. For instance, calcium hydroxide powder has been used as a disinfectant material for apexification when the tooth necrosed before the root was completely formed. In these cases, the dressing is used to allow the tooth to remain in place and encourage normal root development. The apexification procedure removes the pulp, cleans and shapes the root canal, removes the smear layer, disinfects the canal, and concludes by placing calcium hydroxide to promote osteocementum at the apex. The calcium hydroxide powder can plug the tubules and neutralize acid, minimize adverse pulpal responses, help dissolve residual tissue after debridement, and induce a calcified apical tissue barrier that allows a deciduous tooth to remain in place and the apex to finish development. Calcium hydroxide is also used as a dressing after vital pulpotomy procedures in primary teeth and as a temporary intracanal medicament during root canal therapy. MTA and tricalcium phosphate (TCP) slurries have also been used for these indications. Usually calcium hydroxide dressings are left in place or changed every 3 months, but MTA cement does not need to be replaced because it sets to an insoluble solid.

Pulp Capping

For treating pulp exposures, the consistency of MTA can be more fluid. Hemorrhage should be controlled by pressure on the exposure site with a cotton pellet moistened with saline, a dilute solution of sodium hypochlorite (0.5% to 1.0%), or a commercially available mild hemostatic agent. The material can be applied with a Dycal instrument or other similar instrument to access the area. A hybrid ionomer liner or flowable compomer may be placed and light-cured over MTA and the immediately surrounding dentin. The remaining preparation can be acid-etched, followed by placing an adhesive and a resin-based composite. Resin-based composite or an interim glass ionomer can be placed directly over MTA; however, etchant should not be applied on the MTA because acid destroys the integrity of the material and prevents MTA from setting. The pulp should be periodically assessed for its responsiveness, as indicated by a dentinal barrier forming adjacent to the MTA cement.

Compatibility with Restorative Materials

Research has shown that GIC placed over the setting MTA does not affect the setting of the MTA even though a calcium salt formed at the interface. No change was observed in the setting time, susceptibility to crazing of the GIC, or the shear bond strength between glass ionomer and MTA. A study of the bonding of resin-based composite and compomer to MTA, which had set for 48 hours in a moist condition, shows that the use of total-etch single-bottle bonding agent yields a higher bond strength. The results may differ from one brand of material to another; more studies are needed to confirm these effects.

Mechanical Properties

The hydration reactions of MTA continue for about 28 days, while the strength increases over this period to about 50 MPa. Its 24-hour compressive strength is significantly less than that of amalgam, ZOE intermediate-type restorations, and ZOE-EBA materials. However, after 3 weeks, no significant differences were measured in compressive strength between ZOE, calcium hydroxide, and MTA cements. Flexural strength is not usually measured for such ceramic materials and is low for MTA compared with metals or resin composites. The bond strength of MTA to endodontic post materials is not high and MTA should not be used for post retention. Set MTA is quite insoluble and has low setting expansion, a property required by ISO 6876 for root canal sealers (<3% solubility and < 0.01% expansion after 30 days).

ROOT CANAL SEALERS

Root canal sealers (Figure 14-26) are specialized versions of cement used with **gutta-percha** to fill and seal debrided root canals. The most popular root canal sealers are ZOE-based, although the materials are cytotoxic when extruded past the apex. Epoxy-based sealers and polyvinylsiloxane sealers are available as powder-liquid and two paste systems. Canal sealers based on calcium hydroxide, glass ionomer, and polyketones are also available. The gold standard (control) root canal sealer as determined from endodontic histology studies is a ZOE-based sealer, but the standard is shifting to epoxy-based root canal sealers because of their improved



FIGURE 14-26 Root canal sealers. The two materials in the back are powder-liquid systems. The dual cartridge syringe in the foreground is a paste-paste system with static mixing tip.

biocompatibility. MTA-based root canal sealers are also being developed. Additional discussion is presented in Chapter 12.

CALCIUM PHOSPHATE CEMENTS

Calcium phosphate cements are potentially useful water-setting cements because of their osteoconductive and osteoinductive properties. This type of cement consists of a powder (e.g., di-, tri-, or tetra-calcium phosphate) that is mixed with an aqueous medium saturated with calcium phosphate to form a paste. They are low in strength and often dissolve; their primary application has been for bone regeneration because the gradual setting process yields hydroxyapatite. The potential of this material for pulp capping has been examined and found to be as effective as calcium hydroxide.

An experimental formulation base and liner formula has been made with polymerizable resins and additives in the liquid phase and water-settable calcium phosphate powders. The resins are polymers that allow water diffusion, thus facilitating the conversion of calcium phosphate to hydroxyapatite. Research shows that after 3 months, the caries-infected dentin beneath this cement exhibited significantly more calcium and phosphorus to a depth of 30 µm and the mineral content was in the range of healthy dentin.

FLUORIDE-RELEASING MATERIALS

The anticariogenic potential of silicate cement confirms the ability of F^- to inhibit demineralization, leading to the development of several fluoride-containing restorative materials and cements: conventional glass ionomers, resin-modified glass ionomers, polyacid-modified composites (compomers), composites, and even amalgams. For the fluorosilicate glass–based materials, fluoride is first released to the matrix from the glass during the acid-base reaction and then to the oral cavity over time. For composite and amalgam, the fillers—such as inorganic salts, leachable glasses, and organic fluoride compounds—incorporated in the material dissolve partially upon contact with water and diffuses into the material to provide the fluoride for release. The rate of fluoride release depends on the cement matrix, porosity, and nature of the fluoridated filler (i.e., type, amount, particle size, and silane treatment). Figure 14-27 illustrates the typical behavior of fluoride release from dental materials.

FACTORS AFFECTING FLUORIDE RELEASE IN VITRO

Fluoride release studies are usually conducted in vitro, where the experimental conditions can be controlled and the fluoride is easier to measure. Also, intrinsic characteristics of the material—such as formulas, filler compositions, ratios of component mixing , mixing procedure, and curing time—can be studied more easily. For such in vitro tests the protocols have varied in terms of the composition and pH of storage media, frequency of the storage solution change, and plaque and pellicle formation.

The kinetics of fluoride release are similar among all materials, although composite and amalgam have much lower release levels than those from glass ionomer–based materials. When the demineralization-**remineralization** cycle was used, a higher fluoride release in an acidic medium was observed. Ion-enriched (ions other than F^-) storage media, such as artificial saliva, reduced the release. The presence of esterase or hydrolases in the storage media or on the surface of the material can increase the release further. Removal of the outer layer of compomers by air-polishing or finishing was found to restore fluoride release near their initial release rates resulting form exposure of new surfaces. However, simulated toothbrushing with non-fluoridated dentifrice showed no changes in fluoride release, indicating insignificant change of the surface by toothbrushing.

FLUORIDE RECHARGING

In vitro data have shown that fluoride release from glass ionomer remains detectable for years, although the rate of release is reduced by a factor of 10 within the first few months (see Figure 14-27, *A*). To boost fluoride release from existing restoratives, recharging with fluoride has been suggested. The most common recharging method is to expose the restorative to a concentrated fluoride agent in the range of 0.02% for a NaF solution (90 ppm) to 1.23% acidulated phosphate fluoride (APF, 12,300 ppm) for 4 to 5 minutes. The ability of a restorative material to be recharged and serve as a fluoride reservoir depends on the type and permeability of the material, the frequency of fluoride exposure, and the concentration of the fluoridating agent. For example, recharging is more effective by acidic fluoridating agents such as APF. However, the extensive use of APF is known to cause surface damage of restoratives and is not recommended for frequent application on conventional glass ionomers. Glass ionomers and compomers are significantly better for recharging than resin-based composite materials, but this depends on the composition of the materials. Hybrid ionomers are often reported to have the highest capacity for recharging. It has also been reported that as the specimens age, their efficiencies of fluoride recharging decrease.

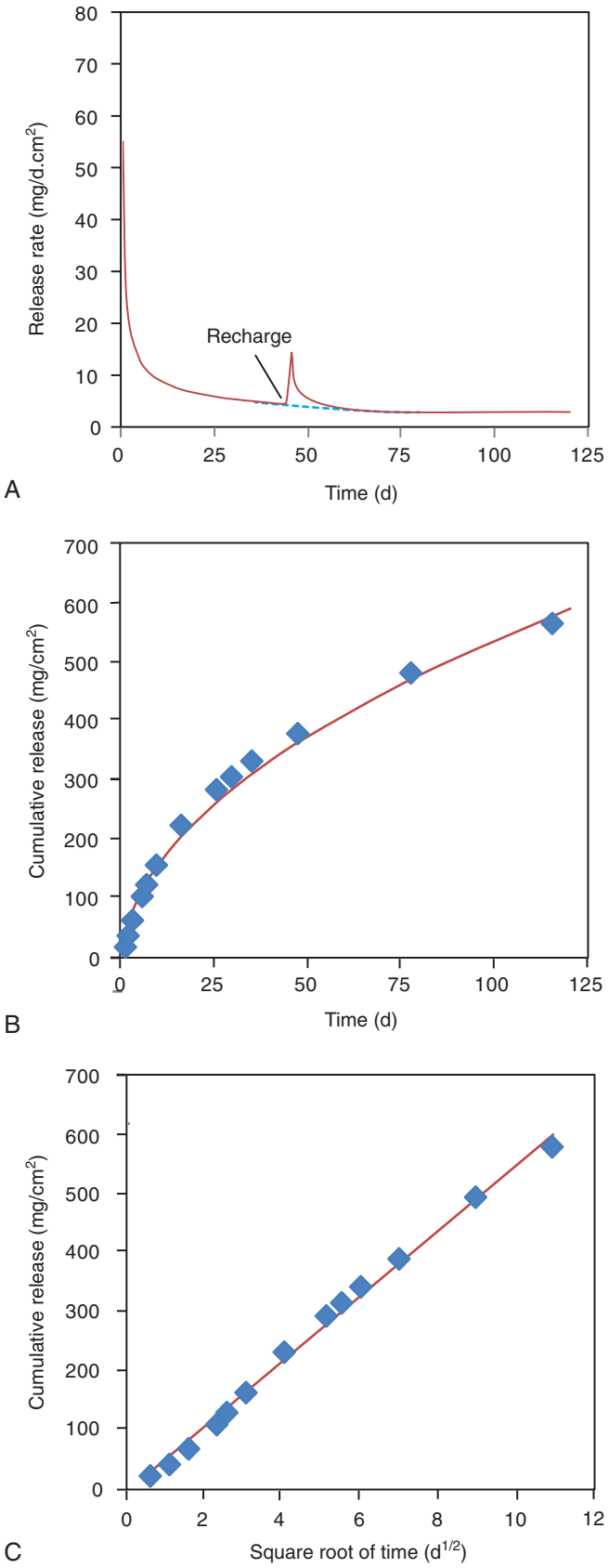


FIGURE 14-27 Typical fluoride-release profiles. **A,** Release rate versus time; the spike reflects fluoride recharging and the blue dotted line represents the fluoride release where no recharging has occurred. **B,** Cumulative release over time; the diamonds are experimental data of (**A**) without recharging, and the curve is the best-fit curve of Y (total release) = a + b•(time)$^{1/2}$. **C,** The same data in (**B**) plotted against square root of time; it reveals a linear relationship. The effect of recharging is not shown in **B** or **C**.

In vivo **fluoride recharging** in the oral environment and subsequent release are influenced by saliva and plaque. The higher viscosity of saliva reduces the diffusion of ions in and out of the material, and a surface pellicle can act as barrier to the recharging process. The release data for recharged materials was significantly higher in the first 24 hours but decreased within several days to its pre-exposure level (see Figure 14-27, *A*), suggesting that the elevated release occurs partly by the washout of fluoride retained on the surface or in the pores of the restorative. The level of release after recharging also depends on the concentration of the recharging medium and the duration of treatment.

In the oral environment, dental restoratives are frequently exposed to exogenous sources of fluoride, such as fluoridated dentifrices, mouth rinses, fluoride gels, and varnishes. Clinically, fluoride recharging of restorations can be achieved through toothbrushing with fluoridated dentifrices and the application of neutral fluoride gels.

CLINICAL SIGNIFICANCE

Fluoride release varies between categories of material and brands. The rate of release from a material is influenced by the matrices, setting mechanisms, fluoride content, and testing conditions. Clinical studies have not clearly shown whether the initial burst or long-term release of F^- ions is clinically more important to prevent caries. Nonetheless, fluoride-releasing materials can act as reservoirs by absorbing fluorides from topical fluoride treatment or toothbrushing with a fluoridated dentifrice, leading to an elevation of fluoride in plaque or saliva in the immediate vicinity of the restorative. Despite the proven effects from in vitro studies, clinical studies conflict as to whether or not these materials sufficiently prevent or inhibit secondary caries compared with nonfluoridated restoratives. Thus clinical studies, preferably of a split-mouth design, are needed to evaluate the impact of fluoride-releasing restoratives on the secondary development and progression of caries, especially in patient groups with limited access to fluoride or who exhibit low compliance with prophylactic measures.

SOLUBILITY AND DISINTEGRATION OF CEMENTS

Cements in the oral environment are continually exposed to a variety of acids produced by microorganisms or consumed in foods and drinks. A number of procedures have been used to assess the relative resistance of various cements to degradation in the mouth. ANSI/ADA Specification No. 96 (ISO

9917-1) describes the use of 0.1 M lactic acid/sodium lactate (pH 2.74) to test the erosion rate of glass ionomer, zinc polycarboxylate, and zinc phosphate cements. The depth at the center of each sample after 24 hours of immersion is measured and the value of eroded depth in millimeters per hour is calculated. The procedure described in ISO 4049 measures the weight (mg) and volume (mm^3) of the specimen before immersion in water and the weight of the specimen after 5 days of immersion and desiccation. The solubility is calculated by dividing the weight changes by the volume. A third method used in ANSI/ADA Specification No. 30 and No. 57 (ISO 6876) specifies measurement of specimen weight before 24 hours of immersion in water and weight of the residue after the water in the eluted solution has evaporated. The weight percentage is then reported.

To make the solubility results clinically relevant, various testing conditions—such as varying the pH of storage media between 3 and 10, the concentration of electrolytes of the storage media, the powder-liquid ratio of the material, and extended observation period 30 days or longer—have been used and each condition was found to have a statistically significant influence on solubility. Because of water sorption, some specimens have shown a negative solubility (weight gain) within the duration of the test. Several studies have reported that there is no correlation between solubility data from acidic erosion and weight loss. The vast amount of in vitro data shows that cement solubility differs among categories of materials and may be product-specific. Therefore, the clinical relevance of in vitro solubility data is not clear.

Calcium hydroxide, ZOE, and early formulations of glass ionomer–based endodontic sealer often exhibited solubility near the maximum specified in the standards. However, despite their high solubility in laboratory tests, ZOE-based root canal sealers have been used successfully for decades in endodontics. Other sealers based on epoxy, polyvinylsiloxane, new GIC and polyketone all show significantly lower solubility than ZOE. A resin-based, calcium-hydroxide-containing cavity liner was found to be less soluble than its conventional counterparts. These results show that the cement's matrix phases derived from acid-base reactions exhibited higher solubility than those resulting from resin polymerization.

For the aqueous-based cements, the solubility increases in order as follows: conventional GIC, zinc phosphate cement, and polycarboxylate cement, although some studies reported no difference between zinc phosphate and polycarboxylate cements. The presence of polymerizing monomers reduces the solubility of hybrid glass ionomer relative to that of conventional GIC. Fully set RMGI cements have higher strength and lower early solubility than those of conventional glass ionomer. Acid impingement studies showed that erosion after 24 hours in 0.1 M lactic acid decreased in the following order: zinc phosphate, conventional GIC, and hybrid GIC to compomer.

Resin cements are the least soluble of all dental cements. It appears that the solubility is inversely proportional to the resin content, especially for hydrophobic resins. As for glass-ionomer, the tooth preparation should be well isolated and saliva must not contact the cement for 7 to 10 minutes to minimize the loss by solubility of the cement at the margins.

In addition to the in vitro tests described earlier, the durability of cementing agents has been obtained in situ by placing small specimens of the cements in intraoral appliances that can be removed from the mouth to measure the loss of material. In one study cements were inserted in tiny wells placed in the proximal surfaces of cast crown restorations. These crowns were cemented with temporary ZOE cement. After 1 year, the crowns were removed and the cement loss was measured. GIC exhibited the least degradation, followed by zinc polycarboxylate cement, zinc phosphate cement, and zinc polycarboxylate cement mixed in a lower P/L ratio. The relative disintegration rates of the cements apparently bear no relationship to the solubility data presented in Table 14-2. The solubility of zinc polycarboxylate cement mixed at the recommended P/L ratio and zinc phosphate cement were not significantly different. However, a reduction of powder in the zinc polycarboxylate mixture produced a cement that disintegrated rapidly.

SUMMARY

No single type of cement satisfies all of the ideal characteristics or is best suited for all indications in dentistry. It is prudent for the dentist to have several types of cements available. Each situation should be evaluated based on the pertinent environmental, biological, and mechanical factors. This chapter provides a framework for making appropriate clinical choices of cement systems for each case. Manufacturers' formulas and manufacturing processes dictate most of cement characteristics, but the clinician has some control over the handling, setting, and biocompatibility by the mixing technique. Overall, for prosthesis retention and pulpal health, it is important to use thin layers of cement and cavity liners over thin layers of remaining dentin.

Zinc phosphate has long served as the universal luting cement, having good handling characteristics and proven longevity in the oral cavity for cementation of well-designed and well-fitting restorations. Its disadvantages include pulp irritation, lack of adhesiveness to tooth structure, lack of anticariogenic properties, and poor mechanical retention. However, clinically these do not pose a problem or explain most failures. In fact, lack of adhesiveness facilitates the removal of old crowns. Zinc phosphate is not suitable when the esthetic demand is high, as for anterior ceramic veneers.

ZOE cements are biocompatible as luting cements and temporary restorations, but the ZOE properties and handling characteristics are inferior to those of other long-term luting cements, such as zinc phosphate, glass ionomer, and resin cements. However, ZOE cements have been useful for retaining fixed prostheses on implant-supported abutments, which facilitates retrievability of the prostheses.

Polycarboxylate cements are non-injurious to the pulp and adhesive to tooth structure. These cements are often used when patients have a history of postoperative sensitivity, but

their short working time limits their use to single- or three-unit fixed dental prostheses.

Glass ionomer luting cements bond to tooth structure, release fluoride, show greater resistance than zinc phosphate cements to disintegration, and have mechanical properties similar to those of zinc phosphate with the exception of a lower modulus of elasticity. Glass ionomers can often be used where zinc phosphate is used, and they are useful for cementing some ceramic prostheses because of their translucency. However, their low stiffness makes them unsuitable for weaker, thinner ceramic prostheses. These cements work well for orthodontic bands. The fluoride-releasing capability makes GIC the material of choice for the replacement of restorations that have failed because of secondary caries and for patients living in areas where fluoridated drinking water is not available. A primary disadvantage of GICs is their slow maturing process, which is required to develop their highest strength.

Hybrid ionomer and compomer cements combine some of the best characteristics of GIC and resin cements. Hybrid ionomer cements are used as liners, fissure sealants, base material, for core buildup, and for orthodontic band cementation. Compomers are used for cementing metallic prostheses and for some other restorative applications in low-stress bearing areas.

Resin cements are virtually insoluble in oral fluids, and their fracture toughness is higher than that of other cements. Early resin cements bonded to dentin and formed a strong attachment to enamel through the use of bonding agents. Self-adhesive resin cements are now available. Resin cements can be used for all types of cementation, most notably for prostheses with poor retention and for all-ceramic prostheses where the esthetic demand is very high. It is critical to remove excess cement immediately after seating of the restoration or an orthodontic attachment device, and prior to the initial set or by light-curing. Although the elastic modulus of resin cements is generally lower than that of zinc phosphate cement, this deficiency does not appear to affect the fracture resistance of ceramic prostheses luted with resin cements.

Calcium hydroxide and MTA products are suitable for pulp capping. The role of hydraulic cement in dental applications has increased with the introduction of MTA and calcium aluminate GICs. MTA cement has the healing attributes of calcium hydroxide but greater strength; it is suitable for vital pulp therapy and endodontic treatments. Calcium aluminate GIC relies on GIC to establish early strength and the hydration of calcium aluminate to improve its final properties.

Specialty areas of dentistry such as orthodontics and endodontics use variations of the cements described here to meet the special needs for their procedures. Hydraulic cements have been especially useful for endodontics, and orthodontists have benefited from specialized versions and combinations of resin and GIC cements that optimize their procedures.

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CHAPTER
15

Dental Amalgams

OUTLINE

Amalgam alloys

Amalgamation

Clinical Manipulation of Amalgam for Restorations

Properties of Amalgam

Clinical Performance of Amalgam Restorations

Safety of Amalgam Fillings

KEY TERMS

Amalgam—An alloy containing mercury.

Amalgamation—The process of mixing liquid mercury with one or more metals or alloys to form an amalgam.

Creep—The time-dependent strain or deformation that is produced by a stress. The creep process can cause an amalgam restoration to extend out of the restoration site, thereby increasing its susceptibility to marginal breakdown.

Delayed expansion—The gradual expansion of a zinc-containing amalgam over a period of weeks to months. This expansion is associated with the development of hydrogen gas, which is caused by the incorporation of moisture in the plastic mass during its manipulation in a cavity preparation.

Dental amalgam—An alloy that is formed by reacting mercury with silver, copper, and tin, and which may also contain palladium, zinc, and other elements to improve handling characteristics and clinical performance.

Dental amalgam alloy (alloy for dental amalgam)—An alloy of silver, copper, tin, and other elements that is processed in the form of powder particles or as a compressed pellet.

Marginal breakdown—The gradual fracture of the perimeter or margin of a dental amalgam filling, which leads to the formation of gaps between the amalgam and the tooth.

Trituration—The mixing of amalgam alloy particles with mercury in a device called a triturator; the term is also used to describe the reduction of a solid to fine particles by grinding or friction.

CRITICAL QUESTION

After reacting an alloy for dental amalgam with liquid mercury, how do the original powder particles become structural components of a set dental amalgam?

By definition, an amalgam is an alloy that contains mercury. Mercury, a liquid at room temperature, can dissolve and react to form an alloy with numerous metals. When metal particles are mixed with mercury, the outer portion of the particles dissolves into mercury. At the same time, mercury diffuses into the metal particles. When the solubility of the metal in mercury is exceeded, crystals of mercury-containing compounds start to precipitate within the mercury. During this period of reaction the metal particles coexist with the liquid mercury, giving the mix a plastic consistency. This means that the mixture can be adapted to any shape with a light pressure. As the content of liquid mercury in the mixture decreases by the formation of precipitates, the mixture hardens. This process is called **amalgamation** and the material has been used for restoring tooth structure. The first use of amalgam for tooth filling was recorded in the Chinese medical literature in 659 A.D. In this chapter the term restoration refers to the amalgam filling and the adjacent tooth structure.

The amalgams used today are largely based on the formulation published by G.V. Black in 1895, although the amalgam concept was introduced in the United States in

1833 by the Crawcours brothers, who were from France. Since then, major modifications of G.V. Black's formulation included the incorporation of a higher copper content and spherical particles, both of which were introduced in the early 1960s. Despite its long history of success as a restorative material, there have been periodic concerns regarding the potential adverse health effects arising from exposure to mercury released from dental amalgam. Because of advances in resin-based composites and adhesive technology in dentistry, the use of amalgam has declined substantially. Its use may be limited in the near future and it may eventually disappear from the clinician's armamentarium.

As is true for other materials discussed in this book, practical skill and sound scientific familiarity with the material are needed for making high-quality restorations. Even when no new amalgams are being placed in patients, there will still be billions of amalgam restorations remaining in patients' mouths. These restorations require periodic examinations to decide whether defective fillings should be replaced, repaired, or refinished. However, these clinical decisions require an understanding of several key terms commonly used by the dental profession. In this chapter, amalgam structure, properties, and manipulation characteristics are discussed.

AMALGAM ALLOYS

Before these alloys are reacted with mercury, they are known as **dental amalgam alloys** or alloys for dental amalgam**.** They are usually provided as (1) irregularly shaped particles (Figure 15-1) produced by milling or lathe-cutting a cast ingot of the amalgam alloy, (2) as spherical particles (Figure 15-2) produced by atomizing the liquid alloy in a chamber filled with inert gas, or (3) as a mixture of both lathe-cut and spherical particles (Figure 15-3).

Originally, the dentist dispensed alloy powder and mercury in a mortar and mixed them together with a pestle by hand. The process of mixing is called **trituration**. Later, the powder was compacted in the form of pellets, which were dispensed along with mercury in a reusable capsule with a pestle (Figure 15-4, *A*) and triturated by a power-driven triturator or amalgamator (Figure 15-5). Today, disposable amalgam capsules are widely available (Figure 15-4, *B & C*). Each capsule contains a predetermined amount of alloy powder and mercury in a sealed pouch, and the capsule is sealed to prevent evaporation of the mercury.

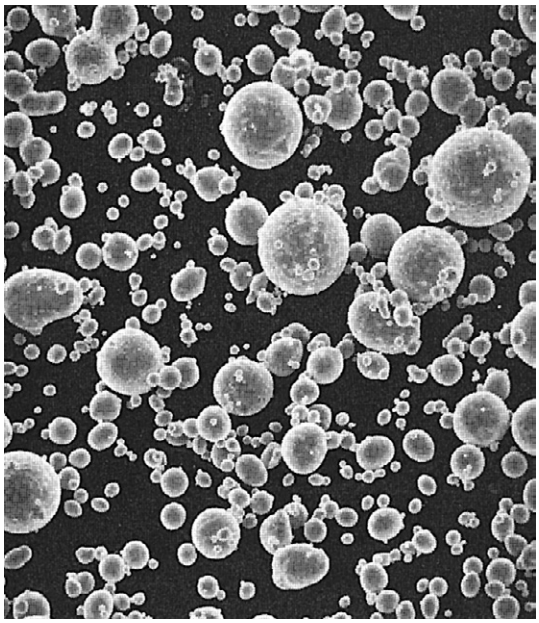


FIGURE 15-2 Particles of spherical alloy for dental amalgam (×500).



FIGURE 15-1 Particles of conventional lathe-cut alloy for dental amalgam (×100).

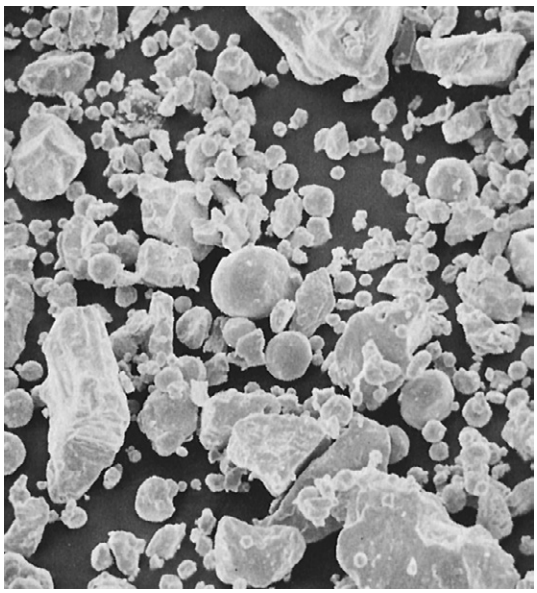


FIGURE 15-3 Typical admix high-copper alloy powder showing the lathe-cut silver-tin particles and silver-copper spherical particles (×500).

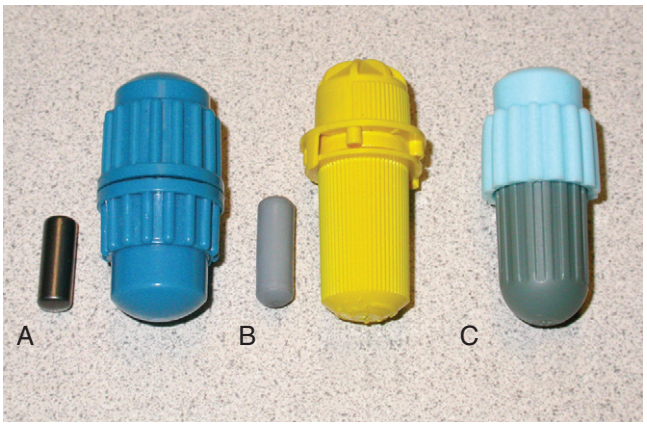


FIGURE 15-4 Types of capsules. **A,** Reusable capsules with pestle. **B,** Preproportioned capsule with pestle. **C,** Preproportioned capsule without pestle.



FIGURE 15-5 A programmable triturator.

TABLE 15-1 Composition of Some Typical Commercial Amalgam Alloys

	COMPOSITION (MASS %)			
Amalgam	**Ag**	**Sn**	**Cu**	**Zn**
Low copper (lathe-cut)	70.3	25.9	2.8	0.9
Low copper (spherical)	72.0	25.0	3.0	-
High copper (admix)	69.5	17.7	11.8	1.0
High copper (spherical)	61.0	26.0	13.0	-

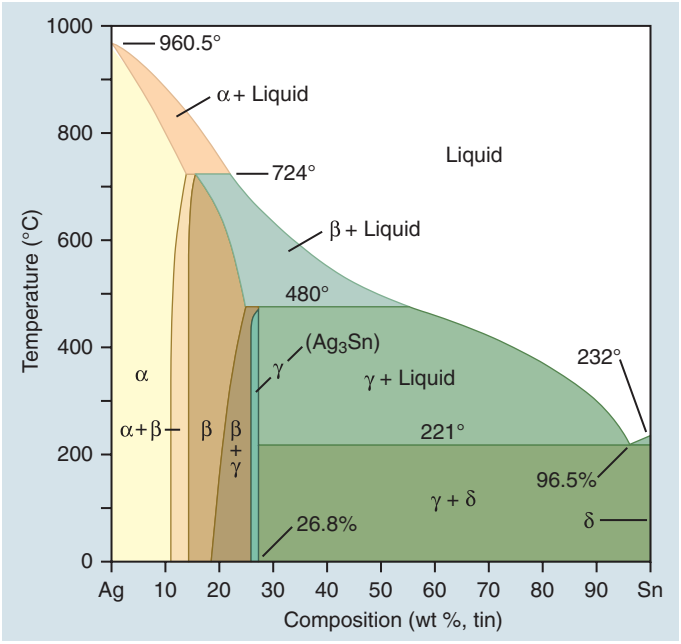


FIGURE 15-6 Equilibrium-phase diagram of silver-tin system.

COMPOSITION

The introduction of a higher copper content in amalgam alloys marked a significant change in the properties of amalgams. It is now customary to classify amalgam alloys as either low-copper (conventional) or high-copper alloys (Table 15-1). In both types, the major components of the alloys are silver and tin.

The Silver-Tin System

Figure 15-6 is an equilibrium-phase diagram of the silver-tin alloy system. Conventionally, starting from the left of the phase diagram, each phase is designated with a Greek letter in alphabetical order from 0% Sn to 100% Sn. The ratio of silver to tin in Table 15-1 shows that amalgam alloys have a narrow range of compositions, falling within the β + γ and the γ phases of the diagram shown in Figure 15-6.

? CRITICAL QUESTION

How can zinc be a beneficial additive to alloy for dental amalgam but also a component that can potentially cause significant postoperative discomfort to the patient?

Low-Copper Alloys

Silver-tin alloys are quite brittle and difficult to blend uniformly unless a small amount of copper is substituted for silver. Within the limited range of copper solubility, an increased copper content hardens and strengthens the silver-tin alloy. The chief function of zinc in an amalgam alloy is to act as a deoxidizer, which is an oxygen scavenger that minimizes the formation of oxides of other elements in the amalgam alloys during melting. Alloys without zinc are more brittle, and their amalgams tend to be less plastic during condensation and carving. The American Dental Association (ADA) Specification No. 1 for amalgam alloys allows some mercury in the alloy powder.

The ranges of conventional alloy composition by weight in the early 1980s were 66.7% to 71.5% silver, 24.3% to 27.6% tin, 1.2% to 5.5% copper, 0% to 1.5% zinc, and 0% to 4.7% mercury. The structure of these conventional alloys was dominated by Ag_3Sn (γ phase) with some Cu_3Sn (ε phase).

High-Copper Alloys

The first high-copper alloy was formulated by mixing one part of silver-copper, spherical eutectic (Ag-Cu; 71.9% silver

and 28.1% copper by weight) particles to two parts of Ag_3Sn, provided as lathe-cut particles. This modification raises the copper content to 11.8% by weight. This is often called "dispersed-phase alloy" or "admixed high-copper alloy."

A second type of high-copper alloy was made by melting all components of the dispersed phase alloy. This process yields a single composition system. The presence of the higher copper content makes mechanical cutting of ingots into particles difficult. Thus, they are often provided in a spherical form that is produced by an atomization process. The copper content of this group of alloys can be as high as 30% by weight. Various amounts of indium or palladium have been included in some commercial systems.

Gallium-Based Alloys

In an attempt to eliminate mercury from direct metallic restorative materials, gallium, which is also a liquid when alloyed with indium and tin at room temperature, has been considered as a substitute. Like mercury, this metal element can be triturated with alloys for high-copper amalgam.

POWDER CONFIGURATION

Dental amalgams are made by mixing alloy powders with mercury. The reaction begins at the particle/mercury interface. Therefore, the physical configuration and condition of the particles will have a significant influence on the setting process.

Lathe-Cut Powder

To produce this powder, an as-cast ingot is first annealed to retain a uniform phase and then it is placed in a milling machine or in a lathe to be fragmented by a cutting tool or bit. The powders obtained from cutting are acid-washed to produce a more reactive surface. Since the stresses induced into the particle during cutting are not uniform and can slowly be self-relieved over time, they will cause the performance of the amalgam to be inconsistent. However, a stress-relief process can be performed by annealing the powder particles at a moderate temperature.

Atomized Powder

The liquid metal is atomized into fine spherical droplets of metal in a chamber of inert gas. If the droplets solidify before hitting a surface, the spherical shape is preserved as spherical powders. Like the lathe-cut powders, spherical powders are given an annealing heat treatment and surface washing.

Particle Size

The average particle sizes of modern powders range between 15 µm and 35 µm. Smaller particles greatly increase the surface area per unit volume of the powder. A powder containing tiny particles requires a greater amount of mercury to form an acceptable amalgam. It is critical to maintain an optimal particle size and size distribution.

The particle size distribution can affect the character of the finished surface. When the amalgam has partially hardened, the tooth anatomy is carved in the amalgam with a sharp instrument. During carving, the larger particles may be pulled out of the matrix, producing a rough surface. Such a surface is probably more susceptible to corrosion than a smooth surface. A smaller average particle size tends to produce a more rapid hardening of the amalgam with greater early strength.

Lathe-Cut Powder versus Spherical Powder

Amalgams made from lathe-cut powders or admixed powders tend to resist condensation better than amalgams made entirely from spherical powders. Since freshly triturated amalgams from spherical powders are very plastic, one cannot rely on the pressure of condensation to establish a proximal contour for a class II restoration. Spherical alloys require less mercury than typical lathe-cut alloys because spherical alloy powder has a smaller surface area per volume ratio than does the lathe-cut powder. Amalgams with low mercury content generally have better properties.

? CRITICAL QUESTION

Through what mechanism does the addition of 65% or more of copper by weight prevent the formation of the undesirable γ_2 phase?

AMALGAMATION

As discussed earlier, modern dental amalgam alloys are based on the intermetallic compound Ag_3Sn; therefore, the main reaction after trituration occurs between Ag_3Sn and mercury. Other elements in the alloy, especially copper, also play a significant role in the final microstructures of set amalgams.

LOW-COPPER ALLOYS

The main reactions of low-copper alloy produce alloy phases including the body-centered cubic Ag_2Hg_3 (γ_1) phase and the hexagonal $Sn_{7\text{-}8}Hg$ (γ_2) phase (Figure 15-7). Both phases are designated as the γ phase because they happen to be the third phase of the respective Ag-Hg and Sn-Hg systems. Since the solubility of silver in mercury is much lower than that of tin, the Ag_2Hg_3 phase precipitates first and is designated as γ_1, whereas the $Sn_{7\text{-}8}Hg$ phase precipitates later and is designated as γ_2. There is evidence from x-ray diffraction and thermal analyses of set amalgam that a δ phase, which is richer in mercury than γ_2, is present in low-copper alloy instead of γ_2. The existence of γ_2 or δ phases in low-copper amalgams remains an unresolved question. For the purpose of this discussion the Sn-Hg phase is designated as γ_2 in this chapter.

The low-copper alloy is usually mixed with mercury in a ratio of about 1:1. This is an insufficient amount of mercury to consume the original alloy particles completely; consequently, unconsumed particles are present in the set amalgam. Thus, a typical low-copper amalgam is a composite in which the unconsumed particles are embedded within γ_1 and γ_2 phases. The sequence of amalgamation of the silver-tin alloy is shown schematically in Figure 15-8.

Low-copper alloy

$Ag_3Sn + Hg \longrightarrow Ag_2Hg_3 + Sn_{7\text{-}8}Hg + \text{unreacted } Ag_3Sn$

High-copper admix alloy

$Ag_3Sn + Ag\text{-}Cu + Hg \longrightarrow Ag_2Hg_3 + Sn_{7\text{-}8}Hg + \text{unreacted Ag-Cu} + \text{unreacted } Ag_3Sn$

Secondary solid-state reaction: $Sn_{7\text{-}8}Hg + \text{unreacted Ag-Cu} \longrightarrow Cu_6Sn_5 + Ag_2Hg_3 + \text{unreacted Ag-Cu}$

High-copper spherical alloy

$[Ag_3Sn + Cu_3Sn] + Hg \longrightarrow Ag_2Hg_3 + Cu_6Sn_5 + \text{unreacted } [Ag_3Sn + Cu_3Sn]$

Symbols and stoichiometry of phases	
Phase Symbols	Composition
γ	Ag_3Sn
γ_1	Ag_2Hg_3
γ_2	$Sn_{7\text{-}8}Hg$
ϵ	Cu_3Sn
η (η')	Cu_6Sn_5

FIGURE 15-7 Reactions of low-copper and high-copper amalgams, and symbols of phases involved in the setting of dental amalgams.

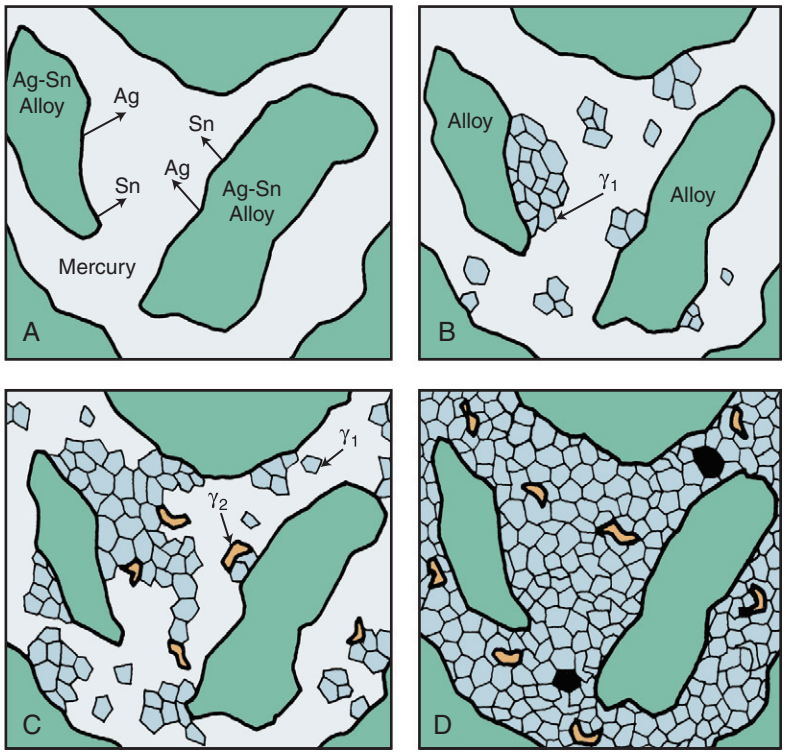


FIGURE 15-8 Schematic drawings that illustrate the development sequence of the amalgam microstructure when lathe-cut low-copper alloy particles are mixed with mercury. **A,** Dissolution of silver and tin into mercury. **B,** Precipitation of γ_1 crystals in the mercury. **C,** Consumption of the remaining mercury by growth of γ_1 and γ_2 grains. **D,** The final set amalgam.

The physical properties of the hardened amalgam depend on the relative percentages of each of the microstructural phases. The greater the number of unconsumed Ag-Sn particles retained in the final structure, the stronger the amalgam will be. The γ_2 phase is the weakest and least stable in a corrosive environment and may suffer corrosion attack especially in crevices of the restorations.

A reaction between Cu_3Sn (ε phase) and γ_2 also occurs and yields Cu_6Sn_5 (η' phase). Because of the low copper content, a majority of γ_2 remains. Figure 15-9 illustrates the features found in a typical microstructure of amalgam made from a lathe-cut, low-copper alloy. As described later, the addition of more than 6% of copper by weight can reduce or eliminate the γ_2 phase by formation of the Cu-Sn phase.

According to the phase diagram of Cu-Sn, the Cu_6Sn_5 phase exhibits a solid state transformation at 186 °C to 189 °C. The new phase is different structurally from the previous phase with no change in composition. The high-temperature phase is designated as η and the lower temperature phase is η'. Since the formation of the Cu_6Sn_5 phase in amalgam occurs at room temperature, η' is used throughout the following discussion.

? CRITICAL QUESTION

Compared with amalgams made from admixed high-copper alloys, what are the benefits and risks of the amalgams made from high-copper single-composition spherical particles?

HIGH-COPPER ALLOYS

Two different types of high-copper alloy powders are available. The first is a two-phase admixed powder and the second is a single-composition single-phase powder. Both types contain more than 6% of copper by weight.

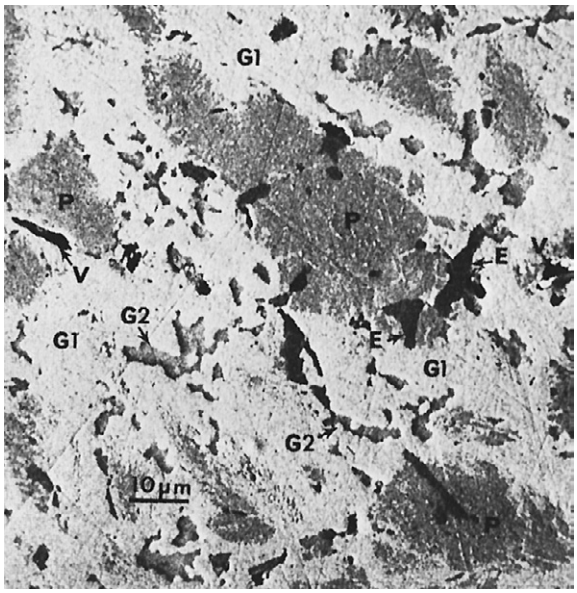


FIGURE 15-9 A scanning electron micrograph of a low-copper amalgam (×1000). The micrograph features remaining β and γ Ag-Sn phases (the large dark areas labeled P), ε phase (small dark patches labeled E), γ_1 phase (light background labeled G1), γ_2 phase (small grains labeled G2), and voids (left center and right center areas labeled V).

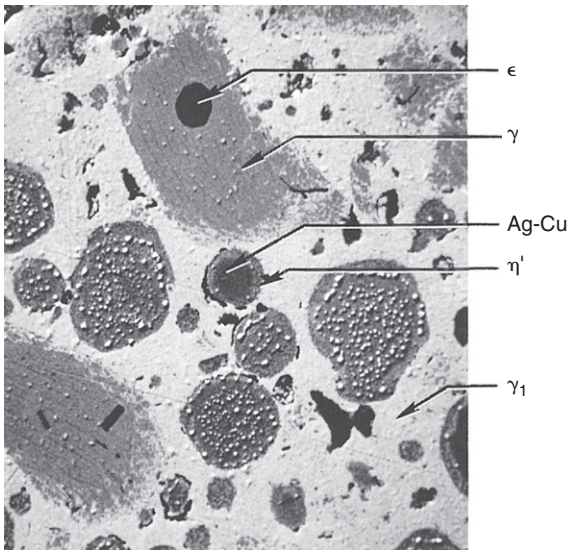


FIGURE 15-10 Scanning electron micrograph of an admixed high-copper amalgam. The various phases and reaction layer are labeled. ε phase is part of lathe-cut particle. The small, very light drop-shaped areas on particle phase are high in mercury owing to the freshly polished specimen (×1000).

Admixed Alloys

When mercury reacts with an admixed powder, silver in Ag-Cu spheres and silver and tin from Ag-Sn particles dissolve into the mercury. Whereas both γ_1 and γ_2 crystals form, as in lathe-cut alloys, the tin in mercury diffuses to the surfaces of the Ag-Cu alloy particles and reacts with the copper to form a layer of η′ phase crystals on the surface. The η′ layer on the surface of Ag-Cu alloy particles also contains γ_1 crystals, since γ_1 and η′ phases form simultaneously. As in the low-copper amalgams, γ_1 is the matrix phase (i.e., the phase that binds the unconsumed alloy particles together). In this reaction, the γ_2 phase does form along with the η′ phase but later reacts with copper from Ag-Cu particles, yielding additional η′ phase (the secondary solid-state reaction in Figure 15-7). The γ_2 phase can be eliminated with at least 11.8% of copper by weight in the alloy powder.

Figure 15-10 illustrates the microstructure of an admixed amalgam. Included in this structure are the γ phase particles, Ag-Cu particles, ε particles, the γ_1 matrix, and η′ reaction layers. In some admixed amalgams, a small number of the η′ crystals are also found amid the γ_1 matrix.

Single-Composition Alloys

The major components of single-composition particles are usually silver, copper, and tin. The copper content of various single-composition alloys ranges from 13% to 30% by weight. In addition, small amounts of indium or palladium are included in some of the single-composition alloys. A number of phases are found in each single-composition alloy particle, including the β phase (Ag-Sn), γ phase (Ag_3Sn), and ε phase (Cu_3Sn). Some of the alloys may also contain some η′ phase.

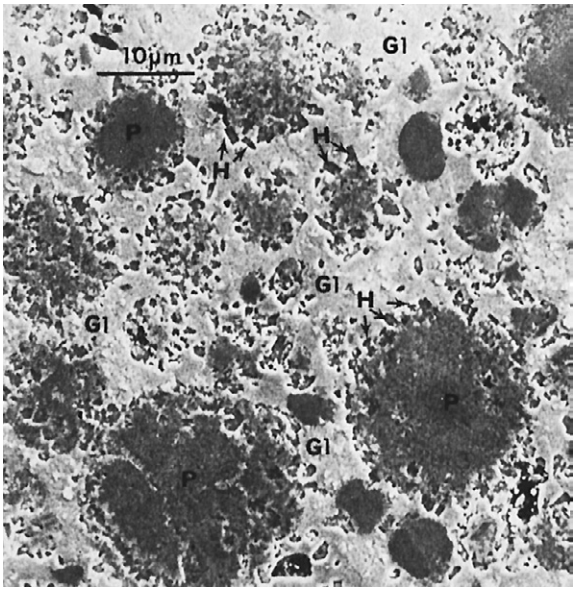


FIGURE 15-11 A scanning electron micrograph of a high-copper single-composition amalgam (×560). The micrograph features unconsumed alloy particles (labeled P), γ_1 matrix phase (labeled G1), and η′ crystals (labeled H).

When triturated with mercury, silver and tin from the Ag-Sn phases dissolve in mercury. Very little copper dissolves in mercury. The γ_1 crystals grow, forming a matrix that binds together the partially dissolved alloy particles. The η′ crystals are found as meshes of rodlike crystals at the surfaces of alloy particles, dispersed in the matrix. In most single-composition amalgams, little or no γ_2 forms (Figure 15-7). Figure 15-11 shows the microstructure of a typical single-composition

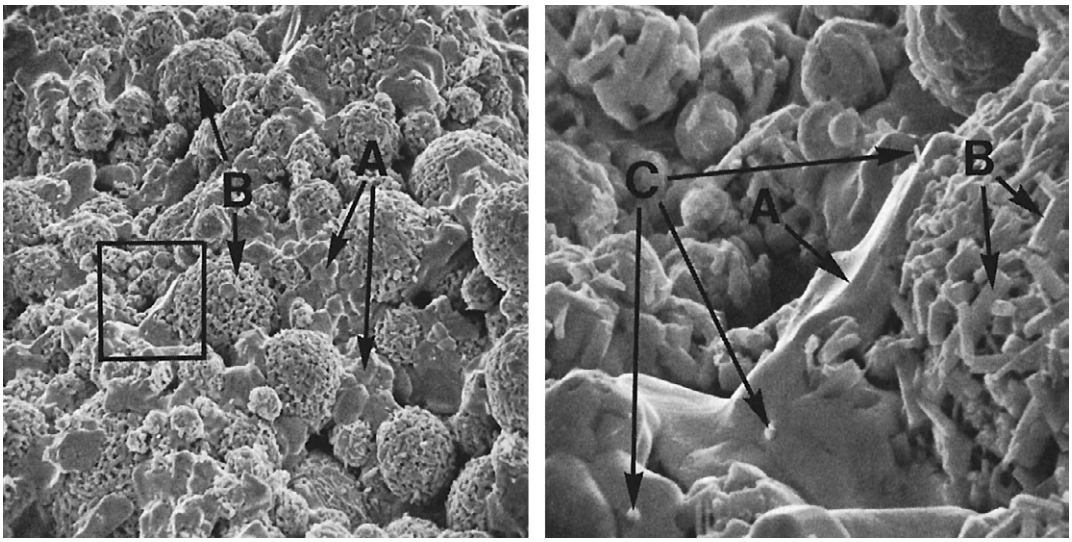


FIGURE 15-12 **A,** Scanning electron micrograph of a high-copper single-composition amalgam fractured shortly after condensation, showing reaction products being formed: γ_1 (*arrow A*), and mesh of η' phase (*arrow B*) covering unreacted spherical particles. **B,** Higher magnification of marked area in (A). η' rods (*arrow C*) embedded in γ_1 crystals (*arrow A*) can be identified (×5000).

amalgam. This structure includes unconsumed alloy particles (P), γ_1 grains (G1), and η' crystals (H).

Figure 15-12, *A*, shows a scanning electron micrograph of a high-copper single-composition amalgam fractured a few minutes after condensation when the amalgamation reaction was still taking place. Two kinds of crystals are seen on the surface: polyhedral crystals (γ_1), shown by arrow *A*, between the unconsumed alloy particles, and meshes of η' rod crystals, shown by arrow *B*, for the unconsumed alloy particles.

Figure 15-12, *B*, shows details of the marked areas in Figure 15-11, *A*. In addition to a mesh of η' crystals (*arrow B*), which formed on an unconsumed particle, η' rods (*arrow C*) are seen embedded in a γ_1 crystal (*A*). Meshed η' crystals on unconsumed alloy particles may strengthen bonding between the alloy particles and γ_1 grains, and η' crystals dispersed between γ_1 grains may interlock γ_1 grains. This interlocking is believed to improve the amalgam's resistance to deformation.

CRITICAL QUESTIONS

What is the ideal mercury/alloy ratio for an admixed amalgam and a spherical particle amalgam? What are the consequences of insufficient and excess amounts of mercury for amalgam restorations?

CLINICAL MANIPULATION OF AMALGAM FOR RESTORATIONS

A good modern dental amalgam alloy can be manipulated so that the restoration lasts, on average, 15 years. The cavity preparation must be designed correctly and the amalgam must be manipulated properly so that the set amalgam restoration is not placed under excessive tensile stress.

Obviously the selection of one type of amalgam over others should be based on clinical performance; lacking such information, it should be based on the physical and mechanical properties. However, the initial analysis of properties should be compared with clinical performance as such data become available. Another criterion is that the alloy should meet the requirements of the ADA's Specification No. 1 or ISO 1559. However, it is the operator who controls the performance of a restoration. Thus, it is essential that the alloy selected be one with which the dentist and the assistant feel comfortable. Use of alloys and techniques that are technique insensitive relative to the manipulation and placement of the amalgam will enhance the quality and durability of the restoration.

MERCURY/ALLOY RATIO

The amount of alloy and mercury to be used can be described as the mercury/alloy ratio, which signifies the number of parts by weight of mercury divided by the number of parts of alloy to be used for the particular technique. Sufficient mercury must be present in the original mix to provide a coherent and plastic mass after trituration, but it must be low enough that the mercury content of the restoration is at an acceptable level without the need to remove an appreciable amount of mercury during condensation. The mercury content of the lathe-cut alloy is about 50% by weight and that for spherical alloys is 42% by weight.

When mortar and pestle were used for mixing amalgam, it was necessary to use an excess amount of mercury to achieve a smooth and plastic amalgam. Removal of excess

mercury was accomplished by squeezing or wringing the mixed amalgam in a squeeze cloth prior to insertion of the increments into the prepared cavity. However, the amount of mercury removed by the squeeze cloth process and during condensation varied. Thus, there was a considerable chance for error.

Proportioning of Mercury and Alloy

A wide variety of mercury and alloy dispensers are available. The most common is the dispenser based on volumetric proportioning. Preweighed pellets or tablets are first placed in a capsule. In mechanical mixing, the capsule serves as a mortar. As a liquid, mercury can be measured by volume without appreciable loss of accuracy. The dispenser should be held vertically to ensure consistent dispensing of mercury. The dispenser should be at least half full when it is used. If it is not, the weight of mercury dispensed may be erratic. Probably the most common cause of inaccurate delivery of mercury is the entrapment of contaminants in the reservoir and orifice of the device. This variable could decrease the amount of mercury by 3% or 4% and this may lead to an unusable mix. Regardless of the alloy or triturator used, no more than two pellets of alloy should be mixed in a capsule at one time.

Disposable capsules containing preproportioned aliquots of mercury and alloy are now widely used. To prevent any amalgamation from occurring during storage, the mercury and alloy are physically separated from each other. The older types of preproportioned capsules require activation before trituration to allow the mercury to enter the compartment with the alloy. Some alloys are now available in *self-activating capsules*, which bring the alloy and mercury together automatically during the first few oscillations of the triturator. Although the preproportioned material is more expensive, it is more convenient, it eliminates the chance of mercury spills during proportioning, and it should result in a reliable mercury/alloy ratio. However, these capsules do not provide an opportunity to make minor adjustments in the mercury/alloy ratio to accommodate personal preferences.

Regardless of the method used, the proper amount of mercury and alloy always must be proportioned before the start of trituration. The addition of mercury after trituration is contraindicated.

? CRITICAL QUESTION

How should the optimal trituration time be determined for a given dental amalgam product?

MECHANICAL TRITURATION

The objective of trituration is to provide proper amalgamation of the mercury and alloy. There is always an oxide layer of the alloy surface that hinders diffusion of mercury into the alloy. This film must be disrupted so that a clean surface of alloy can make intimate contact with the mercury. The oxide layer is removed by abrasion when the alloy particles and mercury are triturated.

Triturators

The main mixing mechanism of a mechanical triturator is a reciprocating arm that holds the capsule under a protective hood. The purpose of the hood is to confine mercury that might escape into the room or to prevent a capsule from being accidentally ejected from the triturator during trituration. A commonly used older model is a single-speed device with an automatic timer for controlling the length of the mixing time. Later models have multiple speed settings. A modern triturator is often microprocessor controlled (Figure 15-5) and contains preset trituration programs for a number of materials. It can also be programmed by the operator to include other materials. A cylindrical metal or plastic piston of smaller diameter than the capsule is inserted into the capsule, and this serves as the pestle (Figure 15-4, *A & B*). Spherical alloys often do not need a pestle (Figure 15-4, *C*).

A triturator should be used at the speed recommended by the alloy manufacturer. Older triturators do not operate at a sufficient rate of speed to amalgamate high-copper alloys properly with minimal mercury. Self-activating capsules are usually very sensitive to trituration speed.

Manufacturers often provide a list of recommended time schedules and speed settings for their alloys and various types of triturators. Because of the speed variations in triturators, the schedule should serve only as a rough guide. Dentists and assistants can adjust the amalgamation time required to attain a mix of correct consistency. For a given alloy and mercury/alloy ratio, increased trituration time and/or speed shorten the working and setting times. In addition, alloys differ in their sensitivity to trituration time (Figure 15-13).

A reusable capsule should be clean and free of previously mixed, hardened alloy. At the end of each trituration procedure, one should quickly remove the pestle from the capsule, replace the lid, reinsert the capsule in the triturator, turn it on for a second or two, and then remove the amalgam. This mulling process generally causes the mix to cohere so that it can be readily removed from the capsule with minimal residue in the capsule. It minimizes the need of scraping out partially hardened alloy, which usually produces scratches in the capsule.

Consistency of the Mix

The proper time of mixing can be determined by observing the consistency of the mix. For example, the very grainy mix (Figure 15-14, *A*) indicates undertrituration. Not only will the amalgam restoration made from this mix be weak, but also the rough surface left after carving of the granular amalgam will increase its susceptibility to tarnish. If the trituration has produced an amalgam of the general appearance shown in Figure 15-14, *B*, the strength will be optimal and the smooth carved surface will retain its luster long after polishing.

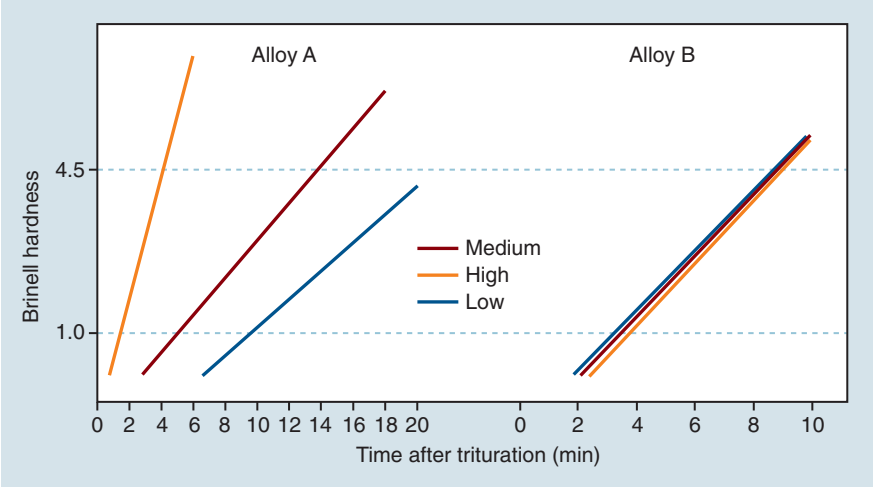


FIGURE 15-13 Hardening data for two alloys mixed at low, medium, and high settings of trituration speed. Broken lines at 1.0 and 4.5 represent desirable working and carving consistencies, respectively.

Because of the friction between particles during trituration, such an amalgam mix should be warm (not hot) when it is removed from the capsule. This will have no effect on the physical properties of the amalgam other than to shorten the working time somewhat. Overtrituration that results from a higher speed or a longer mixing time results in a softer (mushy) mixture that often sticks to the wall of the capsule. Compared with the properly mixed amalgam, the surface of overtriturated amalgam is shinier, the shape of the mass is flatter (Figure 15-14, *C*), and the working time is shorter with a slightly higher setting contraction.

? CRITICAL QUESTION

During the condensation of an amalgam, at what point in time should the triturated mixture be discarded and replaced by a new mixture?

CONDENSATION

The goal of condensation is to compact the alloy into the prepared cavity so that the greatest possible density is attained, with sufficient mercury present to ensure continuity of the matrix phase (Ag_2Hg_3) between the remaining alloy particles. This results from a reduction of excess mercury and porosity within the set amalgam.

After the mixture is made, the increments of alloy should be carried to, and inserted in, the prepared cavity by means of instruments such as small forceps or an amalgam carrier designed for this purpose. Condensation of the amalgam should then be promptly initiated. The field of operation must be kept absolutely dry during condensation. Because of the nature of the operation, condensation is usually accomplished within four walls and a floor. One or more walls may be a thin sheet of stainless steel, called a *matrix*. Sufficient pressure should be used to remove voids and to adapt the material to the walls.

Condensation Procedure

The condenser tip, or face, is forced into the amalgam mass under hand pressure. Condensation is usually started at the center, and then the condenser point is stepped incrementally toward the cavity walls. The force requirements depend on the shape of the alloy particle.

After condensation of each increment, the surface should be shiny in appearance. This indicates that there is sufficient mercury present at the surface to diffuse into the next increment so that each increment is added, it will bond to the preceding one. It is important to remove some of the soft or mushy material brought to the surface of each increment.

The procedure of adding an increment, condensing it, adding another increment, and so forth is continued until the cavity is overfilled. Any mercury-rich material at the surface of the last increment will be removed when the filling is carved. If the cavity is a large one or if for some reason undue time is taken to complete condensation, another mix should be made just before the original one is used up or when it starts to lose its plasticity.

A well-condensed amalgam restoration can be achieved only if the mixture has a proper consistency. A dry, grainy mix (Figure 15-14, *A*) lacks a uniform distribution of mercury and plasticity, as described previously, and a mix that is hard and hot to the touch has probably been mixed too long. In either case, a new mix should be prepared. The longer the time that elapses between mixing and condensation, the weaker the amalgam will be (Figure 15-15). Condensation of partially set material fractures and breaks up the matrix that has already formed. In addition, when the alloy has lost a certain amount of plasticity, it is difficult to condense without producing internal voids and layering.

Condensation Pressure

The area of the condenser tip and the force exerted on it by the operator govern the condensation pressure (force per unit area). When a given force is applied, the smaller the condenser, the greater is the pressure exerted on the amalgam. If

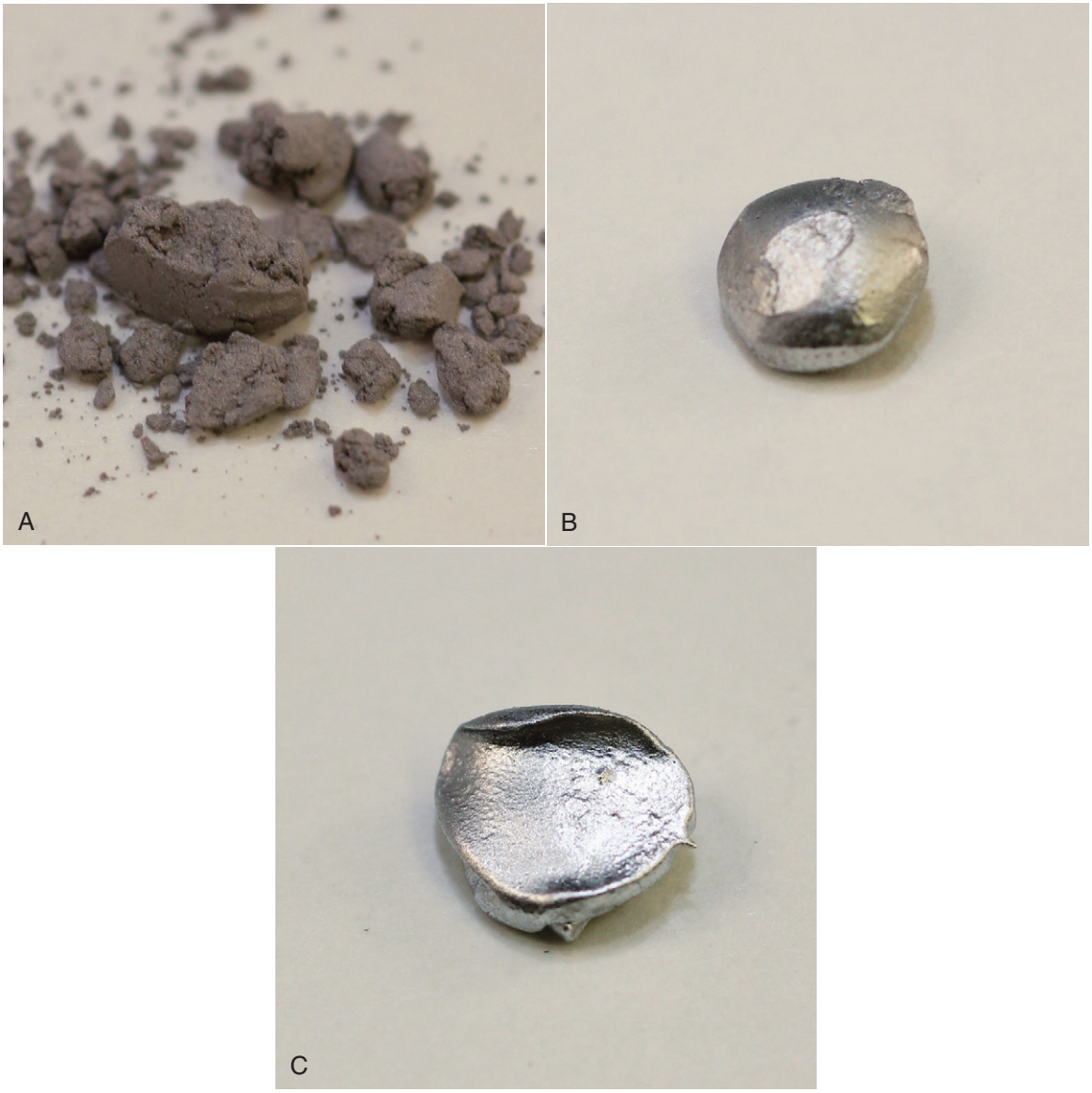


FIGURE 15-14 Appearance of freshly triturated amalgam mixture. **A,** A grainy undertriturated mixture; restoration made of such a mixture has low strength and poor resistance to corrosion. The mixture may appear in solid mass, but the surface remains without luster as shown. **B,** A properly triturated amalgam that appears rounded with a smooth shiny surface. **C,** An overtriturated amalgam mixture, which is shinier than that of the properly triturated one, and because of more fluid consistency the mass appears flattened by the force of trituration.

the condenser point is too large, the operator cannot generate sufficient pressure to condense the amalgam adequately and force it into retentive areas.

A study of 30 practitioners showed that condensation forces average between 13.3 and 17.8 N (3 to 4 lb) employed. To ensure maximum density and adaptation to the cavity walls, the condensation force should be as great as the alloy will allow, and consistent with patient comfort. Many of the spherical alloys have little "body" and offer only minimal resistance to the condensation force. Therefore, the strength properties of spherical amalgam alloys tend to be less sensitive to condensation pressure. In many instances, condensation becomes a matter of attaining good adaptation. The potential disadvantages of a spherical alloy compared with an admixed alloy (lathe-cut and spherical particles) are the tendency for overhangs in proximal areas and weak proximal contacts.

The shape of the condenser tips should conform to the area under condensation. For example, a round condenser tip is ineffective adjacent to a corner or angle of a prepared cavity; a triangular or square tip is indicated in such an area. Tips of various shapes are available to provide effective condensation.

CARVING AND FINISHING

After the amalgam has been condensed into the prepared cavity, it is carved to reproduce the proper tooth anatomy. The objective of carving is to simulate the anatomy rather than to

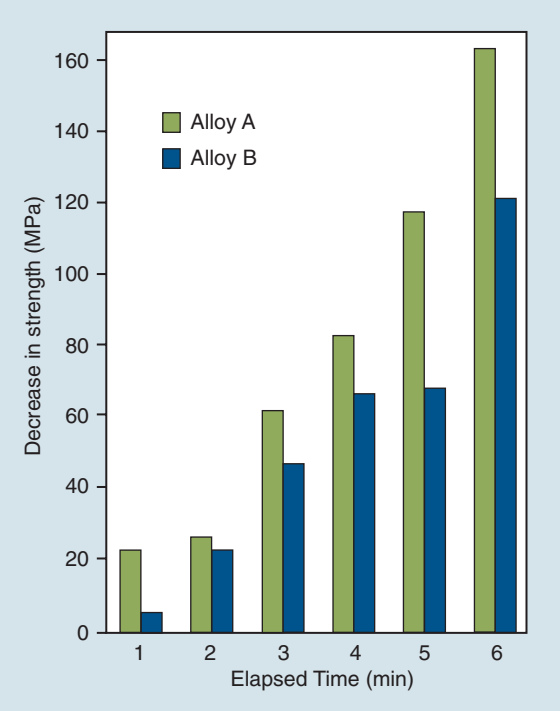


FIGURE 15-15 Effect of elapsed time between trituration and condensation on the strength of the hardened amalgam. The greater the elapsed time, the lower is the strength.



FIGURE 15-16 A, Amalgam restorations as they appear after carving. **B,** The same restorations after final finishing. (Courtesy of S. Geraldeli.)

reproduce extremely fine details. If the carving is too deep, the bulk of amalgam may become too thin and it may fracture under direct occlusal loading.

Carving should not be started until the amalgam is hard enough to offer resistance to the carving instrument. A scraping or "ringing" sound should be heard when it is carved. If the carving is started too soon, the amalgam may be so plastic that it may be pulled away from the margins, even by the sharpest carving instrument. When a matrix band is used to facilitate condensation, it should be removed during the final carving procedure. It is important to check that excess amalgam has not been forced gingivally beyond the matrix during condensation.

After carving is completed, the surface of the restoration should be smoothed. This may be accomplished by judiciously burnishing the surface and margins of the restoration. Burnishing of the occlusal anatomy can be accomplished with a ball burnisher. Alternatively, a rigid flat-bladed instrument is best used on smooth surfaces. Smoothing can be concluded by gently rubbing the surface with a moist cotton pellet or by lightly smoothing the surface with a rubber polishing cup and an extremely fine polishing or prophylaxis paste. Clinical data on performance of restorations support the desirability of burnishing the fast setting, high-copper systems. Burnishing slow-setting alloys can damage the margins of the restoration. Undue pressure should not be exerted in burnishing, and heat generation should be avoided. Temperatures above 60 °C (140 °F) cause a significant release of mercury. The mercury-rich condition created at the margins results in accelerated corrosion, fracture, or both.

Regardless of alloy, trituration method, or condensation technique, the carved surface of the filling is rough, as demonstrated by the dull surface of the restorations in Figure 15-16, *A*. The surfaces are covered with scratches, pits, and irregularities, which can result in concentration cell corrosion over time. The smooth surface on the restorations shown in Figure 15-16, *B*, is produced by the final finishing procedure. The final finishing of the restoration should be delayed until the amalgam develops sufficient strength to resist the pressure of polishing. Generally, the recommendation is to wait for at least 24 h or until the next appointment. However, the trend has been to forego the previously recommended final finishing procedure after 24 h. The need for extremely high luster is questionable, but the metal surface should be smooth and uniform. The use of dry polishing powders and disks can easily raise the surface temperature to cause vaporization of mercury. Thus, a wet abrasive powder in a paste form is necessary.

PROPERTIES OF AMALGAM

ADA Specification No. 1 (ISO 1559) for amalgam alloys lists dimensional change, compressive strength, and creep as the measures of amalgam quality. The controlling variables and significance of these properties are described later.

CRITICAL QUESTION

How does the mercury content and condensation method affect the expansion or contraction that may occur during setting of an amalgam filling?

DIMENSIONAL STABILITY

Amalgam can expand or contract, depending on its manipulation. Severe contraction can lead to microleakage, plaque accumulation, and secondary caries. Excessive expansion can produce pressure on the pulp and postoperative sensitivity. Protrusion of a filling can also result from excessive expansion. ADA Specification No. 1 requires that the dimensional change of amalgam be in the range of 15 to 20 μm/cm measured at 37 °C between 5 min and 24 h after the beginning of trituration.

Mechanism of Dimensional Change

When the alloy and mercury are mixed, contraction results as the particles dissolve (and hence become smaller). Since the final volume of the γ_1 phase is less than the sum of the silver and liquid mercury volume needed to produce the γ_1 phase, contraction continues as long as the γ_1 phase keeps growing. As γ_1 crystals grow, they will impinge against one another. When there is sufficient liquid mercury present to provide a plastic matrix, expansion will occur when γ_1 crystals impinge on each other. After a rigid γ_1 matrix has formed, growth of γ_1 crystals cannot force the matrix to expand further. The reaction continues with γ_1 crystals growing into interstices containing mercury.

This model implies that expansion will occur if sufficient mercury is present in the mix when the dimensional change begins. Therefore, manipulation with less mercury in the mix, as occurs for lower mercury/alloy ratios and higher condensation pressures, will favor contraction. In addition, manipulative procedures that accelerate setting and consumption of mercury also favor contraction, including longer trituration times and use of smaller alloy particles.

Many modern amalgams exhibit a net contraction on setting, whereas in the past, measurements invariably indicated that an expansion occurred (Figure 15-17). Two reasons for the difference are that older amalgams contained larger alloy particles and were mixed at higher mercury/alloy ratios than present-day amalgams. Likewise, hand trituration was used to prepare the specimens. Now high-speed mechanical triturators are employed.

Effect of Moisture Contamination

When a zinc-containing, low-copper or high-copper amalgam is contaminated by moisture during trituration or condensation, a large expansion, such as that shown in Figure 15-18, can take place. This expansion usually starts 3 to 5 days after placement and may continue for months, reaching values greater than 400 μm/cm (4%). This type of expansion is known as **delayed expansion** or secondary expansion. The effect is caused by the hydrogen produced by electrolytic action involving zinc and water. The hydrogen does not combine with the amalgam but, rather, collects within the filling, increasing the internal pressure to levels high enough to cause the amalgam to creep, thus producing the observed expansion. The main source of contamination is saliva from poor isolation of the operative field. It should be noted that water must be incorporated into the bulk of amalgam during trituration or condensation to cause delayed expansion.

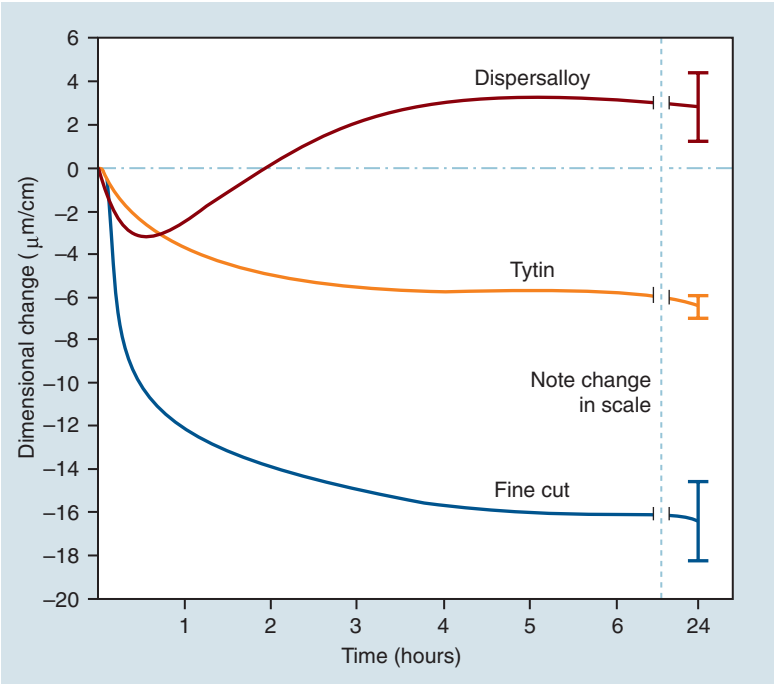


FIGURE 15-17 Dimensional change of three amalgam products over a 24-hour period. **A,** A high-copper admixed amalgam (Dispersalloy). **B,** A high-copper single-composition amalgam (Tytin). **C,** A lathe-cut low-copper amalgam (Fine-Cut).

CRITICAL QUESTIONS

What is the mechanism of **marginal breakdown**? What are the steps that can be taken to reduce the risk or extent of this process?

STRENGTH

A lack of adequate strength to resist masticatory forces is one of the inherent weaknesses of amalgam restorations. In properly designed restorations, such failures are relatively rare. More common are defects at the margins of amalgams.

Traditionally, the strength of dental amalgam has been measured under compressive stress using specimens of dimensions comparable to the volume of typical amalgam fillings. When strength is measured in this manner, the compressive strength of a satisfactory amalgam probably should be at least 310 MPa. Table 15-2 shows typical compressive and tensile strengths at 1 hour and 7 days after preparation for a low-copper amalgam and two high-copper amalgams.

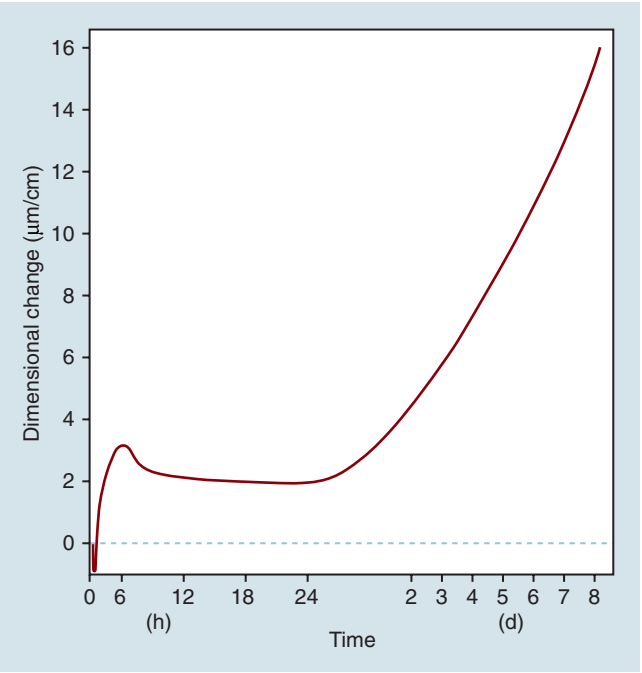


FIGURE 15-18 Delayed expansion of an amalgam.

The significance of the 7-day compressive strength to clinical performance has been questioned. The strength of amalgam is more than adequate under compressive loads. However, amalgam is much weaker in tension than in compression (Table 15-2). For example, a compressive stress on a restored cusp introduces complex stresses that result in tensile stresses in the area. Since dentin has a relatively low elastic modulus, as much tooth structure as possible should be preserved to prevent the dentin from bending, which allows amalgam to bend and for tensile stresses to develop. Since amalgam cannot withstand high tensile or bending strength, the design of the restoration should include a stiff supporting structure whenever there is danger that it will be flexed in tension.

Effect of Trituration

The effect of trituration depends on the type of amalgam alloy, the trituration time, and the speed of the triturator. Either undertrituration or overtrituration will decrease the strength for both conventional and high-copper amalgams.

Effect of Mercury Content

The strength of an amalgam is a function of the volume fractions of unconsumed alloy particles and mercury-containing phases, and the inherent flaw density and depth of flaws. Insufficient mercury between particles yields a dry, granular mix. Such a mix results in a rough, pitted surface that promotes corrosion. Increasing the final mercury content increases the volume fraction of the matrix phases at the expense of the alloy particles. A higher mercury content promotes the formation of γ_2 phase, even in a high-copper amalgam. As a result of the higher the mercury content, the incidence and severity of fracture increase as the amalgam restorations age. The effect of the mercury content upon the compressive strength of amalgam is shown in Figure 15-19.

Mercury analysis of a large number of restorations reveals that the mercury content of the marginal areas averages between 2% to 3% higher than the bulk of the restoration. This is true regardless of the condensation method or the "dryness" of the increments used to build the restoration.

Effect of Condensation

Good condensation techniques will express mercury and result in a smaller volume fraction of matrix phase. Higher

TABLE 15-2 Compressive Strength, Creep, and Tensile Strength of Low-Copper and High-Copper Amalgams

	COMPRESSIVE STRENGTH (MPa)			
	1 Hour	7 Days	Creep (%)	Tensile Strength at 24 Hours (MPa)
Low copper*	145	343	2.0	60
Admix (high copper)†	137	431	0.4	48
Single composition (high copper)‡	262	510	0.13	64

*Fine Cut; †Dispersalloy; ‡Tytin

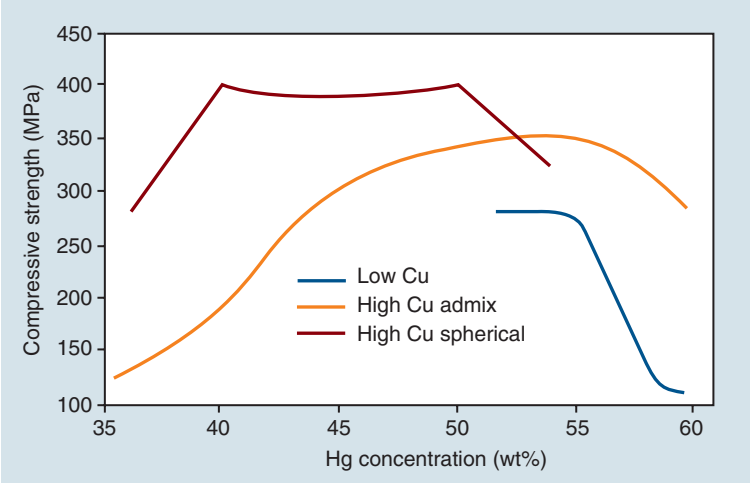


FIGURE 15-19 Effect of mercury content (percent by weight) on the compressive strength of amalgam prepared with representative low-copper, high-copper admix, and high-copper single-composition spherical alloys.

condensation pressures are required to minimize porosity and express mercury from lathe-cut amalgams. On the other hand, spherical amalgams condensed with lighter pressures produce adequate strength. Greater condenser pressure will simply punch through the amalgam.

Effect of Porosity

Voids and porosity are factors that may reduce the compressive strength of set amalgams. The lack of plasticity of amalgam mixes caused by delayed condensation or undertrituration leads to porosity in set amalgams. Insufficient condensation pressure on lathe-cut alloys results in more porosity.

Effect of Amalgam Hardening Rate

Since a patient may be dismissed from the dental chair within 20 minutes after trituration of the amalgam, a vital question is whether the amalgam has gained sufficient strength to prevent fracture caused by a prematurely high occlusal force imposed by the patient. Amalgams do not gain strength as rapidly as might be desired. When the patient is dismissed, the compressive strength of the amalgam may be only 6% of the 1-week strength. Thus, it is likely that a high percentage of fractures in amalgam restorations occur within the first few hours after insertion.

ADA Specification No. 1 requires a minimal compressive strength of 80 MPa at 1 hour. The 1-hour compressive strength of high-copper single-composition amalgams is exceptionally high (Table 15-2). This strength will make fracture less probable if the patient accidentally bites on the restoration soon after leaving the dental office. In addition, these amalgams may be strong enough shortly after placement to permit amalgam buildups to be prepared for crowns and allow earlier impressions of crown preparations to be made. Nonetheless, patients should be warned not to subject the restoration to high biting stresses for at least 8 hours after placement. By that time a typical amalgam will have reached at least 70% of its strength.



FIGURE 15-20 Two-surface amalgam restorations from (left) a low-copper amalgam with severe marginal breakdown and (right) minimal marginal discrepancy of a higher-quality amalgam restoration produced from a high-copper admix alloy. Both amalgams were placed at the same time. (Adapted from Quality Evaluation of Dental Restorations: Criteria for Placement and Replacement. Chicago, Quintessence,1989.)

CREEP

Creep occurs when a solid material slowly deforms plastically under the influence of stresses. Creep of amalgam is determined by placing a cylinder of set amalgam (4 mm in diameter and 6 mm long) under a 36 MPa compressive stress. The specimen is prepared and stored at 37 °C for 7 days before testing. The change of length between 1 and 4 hours as a percentage of the original length is the creep value reported in Table 15-2.

Creep rate has been found to correlate with marginal breakdown of conventional low-copper amalgams; that is, the higher the amount of creep, the greater is the degree of marginal deterioration. Creep causes the amalgam to flow over time such that unsupported amalgam protrudes at the margin of the restoration. Because of low tensile strength and the onset of corrosion, the protruded segment of amalgam fractures and leaves a ditch around the margin (left restoration in figure 15-20). Figure 15-20 shows marginal breakdown in

a class 2 amalgam (left side) filling that was produced with a high-creep amalgam.

When an amalgam creeps, it is the γ_1 phase that deforms plastically. Higher creep rates should be expected for low-copper amalgam with higher γ_1 volume fractions and vice versa. The presence of the γ_2 phase increases the creep rate. In addition to the absence of the γ_2 phase, the very low creep rates in single-composition high-copper amalgams may be associated with η' phase rods, which act as barriers to deformation of the γ_1 phase. Therefore, the manipulative factors discussed previously that maximize strength also minimize creep for any given type of amalgam.

? CRITICAL QUESTION

How can corrosion of an amalgam restoration lead to both positive and negative outcomes?

TARNISH AND CORROSION RESISTANCE

Amalgam restorations often tarnish and corrode in the oral environment. A tendency toward tarnish, which is the result of silver sulfide forming on the surface, does not affect or change the mechanical properties of the amalgam. Corrosion, on the other hand, has a negative effect on the properties.

The most common corrosion products found with conventional amalgam alloys are oxides and chlorides of tin. These are found at the tooth-amalgam interface and within the bulk of amalgam restorations (Figure 15-21). In the case of high-copper amalgams, many of the same products are found (Figure 15-22).

There is indirect evidence that the γ_2 phase is implicated in both marginal failure and active corrosion in conventional alloys, but such a correlation is not possible for high-copper alloys. Corrosion products containing copper can also be found in high-copper amalgams. However, the corrosion process is more limited, since the η' phase is less susceptible to corrosion than the γ_2 phase of conventional amalgams. Every effort should be made to produce a smooth, homogeneous surface on a restoration in order to minimize tarnish and corrosion, regardless of the alloy system used.

Whenever a gold restoration is placed in contact with an amalgam, corrosion of the amalgam can be expected as a result of the large differences in electromotive force (EMF) of the two materials. The corrosion process can liberate free mercury, which can contaminate and weaken the gold restoration. Biological effects such as galvanism can also result.

A high-copper amalgam is cathodic with respect to a conventional amalgam. Thus concern has been expressed that if high-copper amalgam restorations were placed in the same mouth with existing restorations of conventional amalgam, corrosion and failure could be accelerated in the latter. Clinical observations do not indicate accelerated corrosion in such situations. Laboratory models designed to monitor corrosion in adjacent restorations suggest that the current flow paths are such that the electrochemical interaction between restorations is minimal.

CLINICAL PERFORMANCE OF AMALGAM RESTORATIONS

Amalgam does not adhere to the tooth structure. At best it affords only a reasonably close adaptation to the walls of the prepared cavity. For this reason cavity varnishes are used to

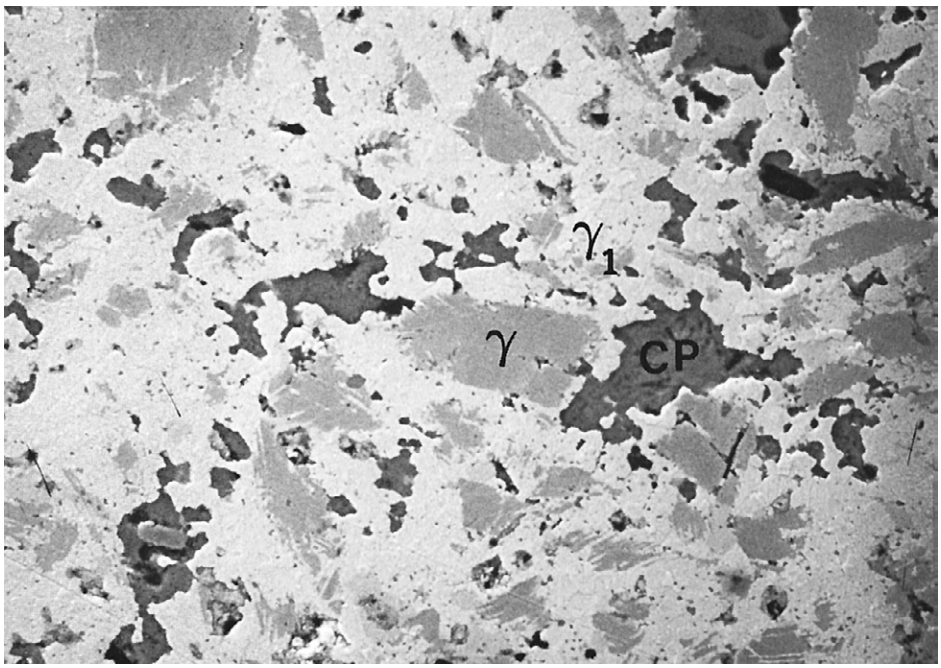


FIGURE 15-21 Microstructure of 7-year-old conventional amalgam alloy filling. The various phases are marked. Note extensive porosity and that the γ_2 area has been replaced by a Sn-Cl corrosion product (CP). (Courtesy of G. W. and S. J. Marshall.)

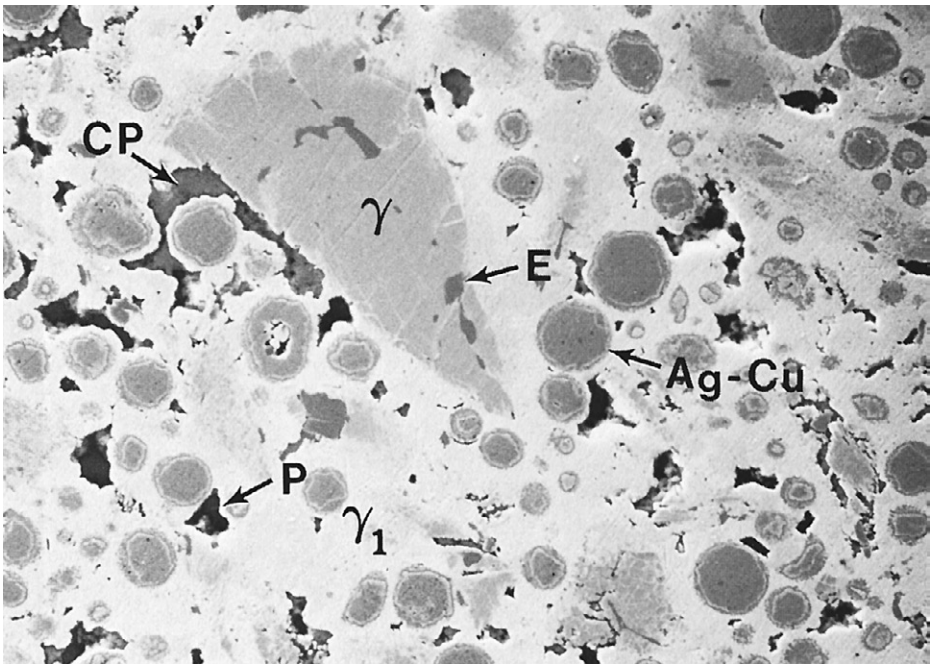


FIGURE 15-22 Microstructure of an 8-year-old high-copper amalgam restoration. The gamma and gamma 1 phases are labeled. Although some porosity (P) is seen, it is less than that in the microstructure the conventional alloy restoration seen in Figure 15-21. The high-copper amalgam shown here also has less corrosion product (CP). (Courtesy of G. W. and S. J. Marshall.)

reduce the gross leakage that occurs around a new filling. The use of dentin bonding agents with amalgam is another relatively new method to reduce microleakage. Clinical trials using the bonded-amalgam technique continue to show promise. Results after 2 to 5 years appear to be equivalent to those from conventional amalgams. The long-term promise of this method is that it may allow more conservative cavity preparations with reduced mechanical retentive features.

If the amalgam is properly inserted, leakage decreases as the restoration ages in the mouth. This may be caused by corrosion products that form in the interface between the tooth and the filling, sealing the interface, thereby preventing leakage. The presence of calcium and phosphorus and the demineralization of tooth structures adjacent to the amalgam filling also strongly suggest a possible biological interaction in this corrosion process. The ability to seal against microleakage is exhibited by both the older low-copper amalgams and the newer high-copper amalgams. However, the accumulation of corrosion products is slower for the high-copper alloys.

After the amalgam is placed, a variety of changes occur at both the microstructural and the visual levels. At the visual level, many amalgam restorations must be replaced because of problems, including secondary caries, gross fracture of the amalgam, "ditched" or fractured margins, excessive tarnish and corrosion, or a variety of other factors. At the microstructural level, changes occur as a result of corrosion and stresses associated with mastication forces. All of these factors are probably interrelated, and the precise contribution of each to a specific case of failure is uncertain.

The ultimate lifetime of an amalgam restoration is determined by a number of factors: (1) the material, (2) the dentist and the assistant, and (3) the patient's environment. The first two parameters are the dominant factors controlling the amalgam performance during the early life of the restoration. A study based on insurance claim data collected between 1993 and 2000 (Bogacki et al., 2002) showed that changing dentists reduced the longevity of amalgam and composite restorations by up to 33%. As time proceeds, differences in the dynamics of the oral environment among patients contribute significantly to the variability in deterioration of the process, particularly marginal ditching. Changes in the amalgam structure during clinical use and survival of amalgam restorations of various types are discussed below.

CLINICAL SIGNIFICANCE OF DIMENSIONAL CHANGE

There are several causes for excessive expansion of amalgam. One is insufficient trituration and condensation; the other is delayed expansion brought about by the contamination of the Zn-containing amalgam with moisture during trituration or condensation. At 20 weeks, amalgam specimens prepared from both types of alloys (alloy A, low copper, and alloy B, high copper) when contaminated by moisture, expanded far more than the same uncontaminated amalgams (Figure 15-23). The expansion of the alloys at 20 weeks was also accompanied by a substantial reduction in compressive strength (Figure 15-24).

Delayed expansion of amalgam often causes intense pain. It is presumed that when an expansion of this magnitude occurs, the filling may become wedged so tightly against the cavity walls that pressure develops in the pulp chamber. Such

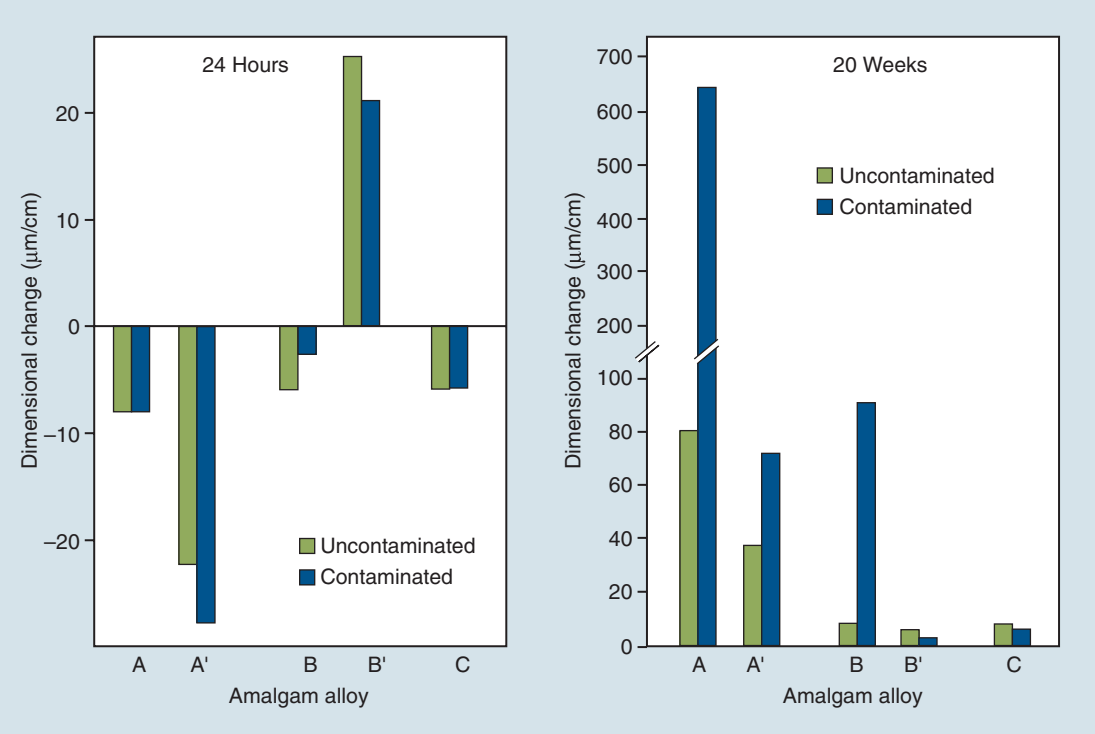


FIGURE 15-23 Effect of moisture contamination on the dimensional change of various types of amalgam alloys. **A,** Zinc-containing low-copper lathe-cut alloy. **A′,** Zinc-free low-copper lathe-cut alloy. **B,** Zinc-containing high-copper lathe-cut alloy. **B′,** Zinc-free high-copper lathe-cut alloy. **C,** Zinc-free high-copper spherical alloy.

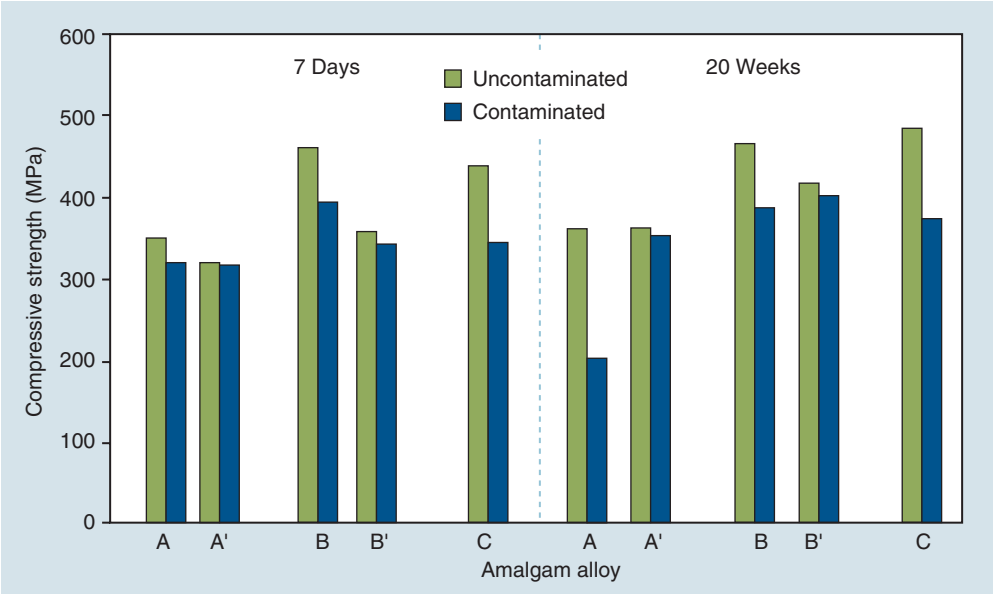


FIGURE 15-24 Effect of moisture contamination on the compressive strength of various types of amalgam alloys. **A,** Zinc-containing low-copper lathe-cut alloy. **A′,** Zinc-free low-copper lathe-cut alloy. **B,** Zinc-containing high-copper lathe-cut alloy. **B′,** Zinc-free high-copper lathe-cut alloy. **C,** Zinc-free high-copper spherical alloy.

pain may be experienced 10 to 12 days after the amalgam is inserted. If it is not removed, a contaminated amalgam continues to expand, and the final result may be a protruding filling. Because the brittle amalgam margins are unsupported, they are susceptible to fracture, and marginal defects result. Leakage at the amalgam/enamel interface can produce marginal discoloration, with further corrosion and pitting by the concentration cells (Chapter 3). Pitting and corrosion, regardless of the cause, reduce the strength of amalgam restorations.

CRITICAL QUESTION

A patient reports pain during chewing one day after an amalgam restoration has been placed. What are most likely causes of this condition and what are the best solutions?

A patient who complains of pain one day after an amalgam restoration is placed cannot be suffering the effects of delayed expansion caused by moisture contamination. One should examine the surface of the restoration for shiny abrasion marks indicating the possibility of hyperocclusion. If this condition exists, the pain will disappear soon after the occlusion is properly adjusted. Another possibility is the development of cracks in the tooth because of excessive tooth reduction and weakened cusps. This situation may require replacement of the amalgam and hooding of the weakened cusp or cusps, as is done with a cast onlay restoration. It is also possible that the cracks are minor and do not threaten the integrity of the cusps or the vitality of the tooth. In this case, etching of the crack walls and bonding of the fissure may provide a sufficient interim solution. The last resort is to restore the tooth with an onlay or full crown to minimize the risk of fracture.

If a zinc-containing alloy is used where moisture contamination is expected, as in the posterior teeth of a child, the dentist must sacrifice normal condensation procedures for the sake of speed. The condensation should be accomplished by filling the prepared cavity with one or two large increments rather than several small increments.

Laboratory tests indicate that there is no difference in the sealing properties of expanding and contracting alloys. Clinical studies of restorations placed with amalgams that contract 2 to 40 µm/cm failed to reveal a marginal contraction gap after several years. It is virtually impossible to detect margins that may be open by a few micrometers, either with the eye or with a dental instrument such as an explorer. It is for these reasons that the ADA's specification has been broadened in terms of the permissible dimensional change on hardening as measured on an unrestricted specimen.

These observations should not be construed as a recommendation for a contracting amalgam. They merely emphasize that small contractions during hardening are not clinically significant.

CRITICAL QUESTIONS

Which variables affect the marginal breakdown of amalgam restorations? Which of these factors are under the control of the dentist?

MARGINAL BREAKDOWN

Although the ditching of a margin (Figure 15-25) may not have progressed to the point where secondary caries may have developed, the restoration is unsightly and further deterioration may be anticipated. Examination of clinical restorations has associated secondary caries with marginal discrepancies that exceed 400 µm. Many such restorations are replaced as a preventive measure. Recent studies have shown that for a population with good oral hygiene, the incidence of secondary caries is quite low even in the presence of severe marginal deterioration. Thus, a more conservative approach, such as repair or recontouring, has been suggested.

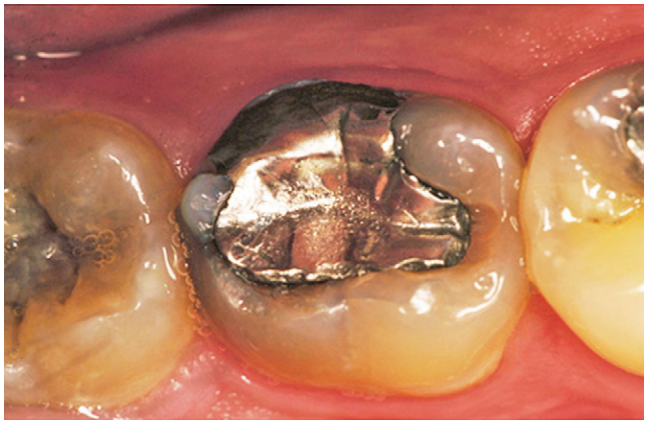


FIGURE 15-25 A "ditched" amalgam restoration with severe marginal breakdown. (Courtesy of S. Geraldeli.)

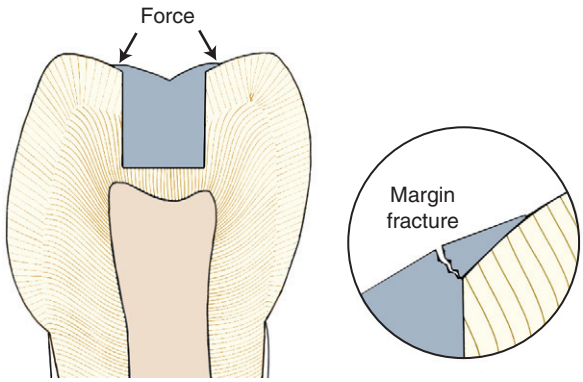


FIGURE 15-26 Marginal ditching of an amalgam restoration. If a feather edge of the amalgam is left overlapping the enamel at the margin or if a mercury-rich surface layer is not properly removed, the marginal extension may fracture under masticatory stress.

IMPROPER CAVITY PREPARATION OR FINISHING

If unsupported enamel is left at the marginal areas of the cavity preparation, the tooth structure may fracture over time. Thus, the ditched amalgam may involve fracture of adjacent enamel as well as the amalgam.

Improper carving and finishing of the filling and/or failure to remove a mercury-rich surface layer may leave a thin, weak ledge of amalgam extending over the enamel that will eventually fracture, leaving a ditched margin (Figure 15-26). Such thin extensions beyond the finish line of the tooth preparation are often difficult to detect and remove. One method is to finish the margins lightly with a soft, unribbed, prophylactic polishing cup and a fine, slightly moist prophylaxis paste. However, the cup should be tilted such that the edge rotates from amalgam to tooth, as shown in Figure 15-27.

CREEP

There appears to be little correlation between creep and marginal breakdown with alloys having creep values below 1%. However, when creep values are above this level, restorations made from higher-creep alloys generally experience greater marginal breakdown than do restorations of lower-creep alloys.

The absence of the corrosion-susceptible γ_2 phase in the microstructure of high-copper amalgams is assumed to be the principal factor responsible for the superior resistance of these alloys to marginal breakdown. If this assumption is correct, the property of creep is not an important property for the prediction of marginal breakdown in high-copper amalgams. Expansion of the amalgam from moisture contamination of a zinc-containing alloy can also cause this type of failure.

Thus, several mechanisms, separately or working synergistically, may be responsible for marginal breakdown. The precise mechanism of marginal breakdown and these specific properties are not completely understood. However, it is advisable to select alloys that inherently have low creep and possess excellent resistance to corrosion.

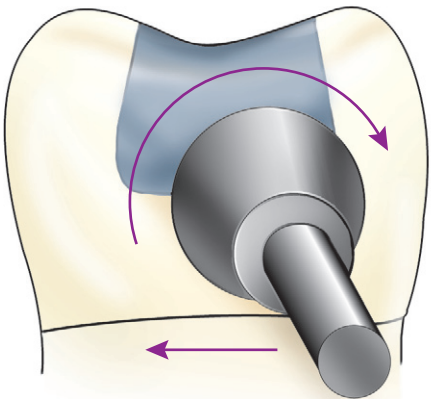


FIGURE 15-27 Final finishing of an amalgam margin with a soft, unribbed prophylaxis cup and fine prophylaxis paste. The cup should be used with very light pressure to avoid flattening of anatomic contours.

SURVIVAL OF AMALGAM RESTORATIONS

Although many factors may contribute to the deterioration of dental amalgams, as noted in the prior sections, the ultimate test is the long-term survival of the well-placed dental amalgam restoration. The longevity of amalgam restorations depends on whether they were placed in general practices or in controlled clinical studies. The median survival times for posterior amalgam restorations were 7 to 15 years in general practices. Larger, more complex restorations fall within the lower end of this range. Based on controlled clinical studies, calibrated dentists working under few time constraints for placement of restorations in motivated patients projected median survival times of 55 to 70 years.

Figure 15-28 is based on 14 independent controlled clinical studies initiated between 1974 and 1983, in which the survival of amalgam restorations was rated in terms of their copper and zinc contents. Modern high-copper amalgams with Zn have the best overall survival of nearly 90% after 12 years. High-copper amalgams without Zn performed the next best with survival rates of approximately 80%. The survival curves for these two groups of amalgams could be distinguished only after approximately 6 years, when the better survival of the high-copper systems containing a small quantity of Zn became apparent. The next group comprised conventional low-copper amalgams with Zn. The worst performance was exhibited by low-copper amalgams that were Zn-free. These systems exhibited failures in 50% of the restorations after only 10 years. The reasons for the differences seen in this study are not completely clear. However, the combined and perhaps synergistic effects of the additional Cu and Zn contents probably offered increased corrosion protection to the restorations.

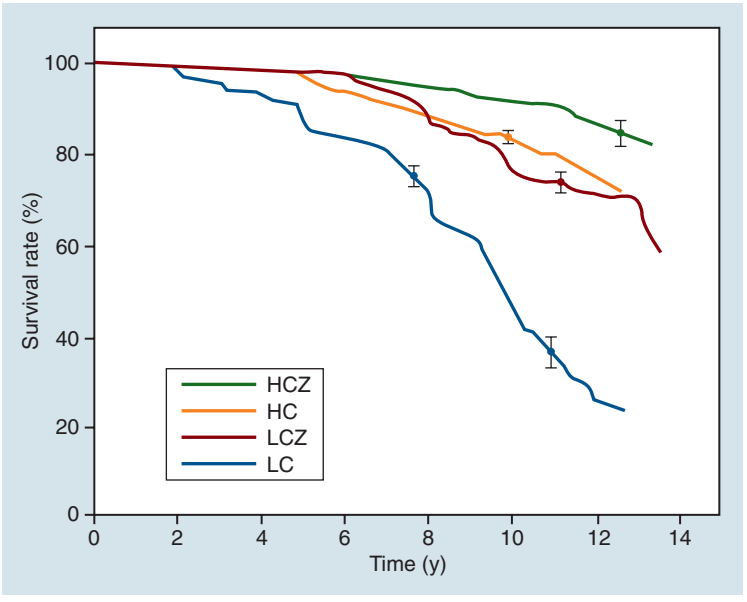


FIGURE 15-28 Survival curves for amalgam restorations classified according to copper and zinc content. Both copper and zinc appear to provide protection to restorations. Thus, in these clinical trials, many more high-copper restorations containing zinc survived than low-copper restorations without zinc. HCZ: high-copper amalgam with zinc; HC: high-copper amalgam without zinc; LCZ: low-copper amalgam with zinc; and LC: low-copper amalgam without zinc.

REPAIRED AMALGAM RESTORATIONS

Occasionally when part of an amalgam restoration fails, as from marginal fracture, it is repaired. A new mix of amalgam is condensed against the remaining part of the existing restoration. The important factor related to the quality of the amalgam repair is the interfacial bond between the new and the existing amalgam. Surface treatment of the aged amalgam appears to be a major factor in achieving a high-quality bond. The surface of an old amalgam to be bonded should be roughened to remove corrosion and saliva contaminants and freed of loose debris. When a freshly triturated amalgam is condensed directly onto the roughened surface of an existing amalgam, the flexural strength of the repaired structure can reach 50% of that of unrepaired amalgam. The repair should be attempted only if the area involved is one that will not be subjected to high stresses or one in which the two restoration parts are adequately supported and retained. It is worthwhile to note that rubbing mercury on the repair site before condensing new amalgam or increasing mercury content in the new amalgam can further improve the repair strength. Both approaches are discouraged as they increase the patient's exposure to mercury.

Making a slot on the existing amalgam to establish mechanical interlocking between the two materials also improves the quality of the repair joint. In vitro studies show that resin bonding agents appear to be effective when no mechanical roughening of the surface was performed, but yielding no benefit if adequate surface roughening of the existing amalgam had been carried out. Therefore, the use of resin bonding agents for amalgam repair is discouraged. It is important to point out that it is the reaction between the unreacted amalgam alloy in the old amalgam and the mercury in the new amalgam that provides the bonding. One may consider mercury as a bonding agent for amalgam repair.

Another repair option for areas that exhibit minor marginal breakdown—gaps that are 250 μm or less in width—is to etch the enamel adjacent to the restoration and, after rinsing and drying the marginal gap area, sealing the gap with a dentin bonding adhesive. There is evidence from a 10-year study (Mertz-Fairhurst, 1998) that bonded and sealed composite restorations placed directly over frank cavitated lesions extending into dentin arrested the clinical progress of these lesions for the duration of the study. Both sealed composite and conservative amalgam restorations exhibited superior clinical performance and longevity compared with unsealed amalgam restorations. This repair option is promising but needs more scientific evidence to prove that it can prevent secondary caries.

The clinical diagnosis of secondary (recurrent) caries is the main reason for replacing amalgam restorations; fracture is the second most common reason for failure of amalgam restorations. When secondary caries is diagnosed, it inevitably requires the replacement of the restoration, but an alternative treatment is to remove part of the restoration to the full depth at the site of the defect. This is a recognized procedure to make a definitive diagnosis of the extent of the caries. Provided the main part of the restoration is satisfactory, the removed part of the restoration can then be filled with amalgam. The repair of an existing restoration is now considered a viable and cost-effective alternative to complete replacement.

? CRITICAL QUESTION

A patient is concerned about the safety of amalgam fillings after hearing a news report on the toxicity of mercury. What quantifiable information can you provide to assure him that the levels of mercury vapor released from amalgam restorations are well below known threshold levels for mercury toxicity?

SAFETY OF AMALGAM FILLINGS

The use of mercury in the oral environment has raised concerns ever since it was introduced in North America in 1833. Information on the biocompatibility of mercury and amalgam is presented in Chapter 7. The side effects of mercury and reduction of mercury hazard in dental offices is discussed here to place the issue in perspective relative to the safety of amalgam. To understand the possible side effects of dental amalgam, the differences between allergy and toxicity must be discussed.

ALLERGY

Typically, allergic responses represent an antigen-antibody reaction marked by itching, rashes, sneezing, and difficulty in breathing, with swelling or other symptoms. Contact dermatitis or Coombs' type IV *hypersensitivity* reactions represent the most likely physiologic side effects to dental amalgam, but these reactions are experienced by less than 1% of the treated population. To confirm suspicions of true hypersensitivity, especially when a reaction has been sustained for 2 weeks or more, the patient should be evaluated by an allergist. A small percentage of people are allergic to mercury, just as a certain number of people are allergic to many other metallic elements. When such a reaction has been documented by an allergist, an alternative material, such as a composite or ceramic material, must be used. However, none of these materials has yet been proven to be *safer*, in all respects, than dental amalgam.

TOXICITY

As defined in Chapter 7, toxicity is the relative ability of a material to cause injury to biological tissues, ranging from improper biochemical function, organ damage, and cell destruction to death. It is still sometimes conjectured that mercury toxicity from dental fillings is the cause of certain undiagnosed illnesses and that a real hazard may exist for the dentist or dental assistant when mercury vapor is inhaled during mixing, placement, and removal. In fact, fewer than 100 documented reports of mercury toxicity and allergy attributable to dental amalgam have been published over the past 70 years in the scientific literature. Of these cases, most of the affected individuals were dentists or assistants (nurses) in a dental clinic. Few such cases have been reported during the past several decades, presumably because of

improvements in encapsulation technology, capsule design, scrap storage methods, and the elimination of carpets and other mercury retention sites. The matter has again come to the fore with recent concern over mercury pollution of the environment.

The patient's encounter with mercury vapor during insertion of the restoration is brief, and the total amount of mercury vapor released during occluding on amalgam restorations is far below the "no effect" level. The most reliable estimates suggest that mercury from dental amalgam does not contribute a significant amount to the total exposure of patients. Studies have shown that the magnitude of vapor exposure for a patient with 8 to 10 amalgam restorations is in the range of 1.1 to 4.4 μg per day. The threshold value for workers in the mercury industry is 350 to 500 μg per day. Thus, the toxicity threshold for patients receiving several amalgam restorations is far below the range of values established by the U.S. government for occupational environments.

Mercury blood levels as measured in one study indicated that the average level in patients with amalgam was 0.7 ng/mL, compared with a value of 0.3 ng/mL for subjects with no amalgam. This difference was found to be statistically significant ($P < 0.01$). However, one should be aware of a study in Sweden demonstrating that one saltwater seafood meal per week raised average blood levels of mercury of the subjects from 2.3 to 5.1 ng/mL, a sevenfold increase (2.8 ng/mL) compared with the increase (0.4 ng/mL) associated with amalgam fillings. In fact, the normal daily intake of mercury is 15 μg from food, 1 μg from air, and 0.4 μg from water.

Undoubtedly small amounts of mercury are released during mastication. However, toxic reactions in the patient from these traces of mercury penetrating the tooth or sensitization from mercury salts dissolving from the surface of the amalgam are extremely rare.

MERCURY HYGIENE IN DENTAL OFFICES

The potential hazards of mercury can be greatly reduced by attention to a few precautionary measures. The operatory should be well ventilated. All excess mercury—including waste, disposable capsules, and amalgam removed during condensation—should be collected and stored in well-sealed containers. Debris of amalgam from cutting and grinding can be trapped by installing amalgam particle separators in the dental wastewater stream. Proper disposal through reputable dental vendors is mandatory to prevent environment pollution. Increasing attention is being focused on correct disposal of potentially hazardous waste materials, including dental amalgams and mercury. Amalgam scrap and materials contaminated with mercury or amalgam should not be incinerated or subjected to heat sterilization. If mercury is spilled, it must be cleaned up as soon as possible. It is extremely difficult to remove mercury from carpets. Ordinary vacuum cleaners merely disperse the mercury further through the exhaust system. Mercury suppressant powders are helpful, but should be considered as temporary measures. If mercury comes in contact with the skin, the skin should be washed with soap and water.

As noted earlier, the reusable capsule utilized with a mechanical triturator should have a tightly fitting cap to avoid mercury leakage. When amalgam is being ground, a water spray and suction should be used. Eye protection, a disposable mask, and gloves are now standard requirements for dental practices.

The use of an ultrasonic amalgam condenser is not recommended. A spray of small mercury droplets has been observed surrounding the condenser tip during condensation. More detailed recommendations can be obtained by consulting the most recent reports of the ADA's Council on Scientific Affairs.

An important part of a program for handling toxic materials is periodic monitoring of actual exposure levels. Current recommendations suggest that this procedure be conducted annually. Several techniques are available. Instruments can be used that yield a time-weighted average for mercury exposure to sample the air in the operatory. Film badges are also available that can be worn by office personnel in a manner similar to radiation exposure badges. Biological determinations can be performed on office staff to measure mercury levels in blood or urine. The risk from mercury exposure to dental personnel cannot be ignored, but close adherence to simple hygiene procedures will help to ensure a safe working environment.

REGULATION OF AMALGAM USE BY GOVERNMENTS

Currently several countries are phasing out the use of dental amalgam because of environmental concerns as well as alleged side effects that may be sustained by the patients who receive amalgam restorations. An important aspect of all of these actions is the conclusion that, from a medical point of view, there is no clinical evidence to suggest that amalgam is causing illness in the general population.

Denmark published draft orders in 1989 proposing to discontinue the sale of all mercury-containing products, including dental amalgam, by 1999. In 1992, the Swedish parliament approved a general plan to phase out mercury from all sources, including amalgam in children's primary teeth. The Swedish national health system stopped reimbursing patients for amalgam restorations in 1999. This decision greatly reduced the use of amalgam before the general ban in 2009. In 2008, Norway announced a general ban on the use of mercury in products, which includes dental amalgam with a 3 year phase-out period. Sweden and Denmark announced similar bans in the same year.

In 1996, Health Canada recommended that the use of amalgam should be avoided in the primary teeth of children, pregnant women, and patients with renal impairment. In addition, clinicians should use safe handling practices with mercury and provide information to patients on the benefits and risks of amalgam treatment. Austria, Germany, and Japan have similar restrictions on the use of dental amalgams. In Japan, the demand for mercury used in amalgam decreased from 5200 kg in 1970 to 100 kg in 2006. The annual emission of mercury into air from amalgam in 2005 was estimated at about 3 kg as the country stopped manufacturing dental

amalgam and dental schools no longer teach the subject. In 2009, the FDA issued a final rule (FDA-2008-N-0163) classifying dental amalgam as a class II device. Class II devices are those for which general controls alone are insufficient to ensure safety and effectiveness and for which other methods are available to provide such assurances.

While the policy of dental amalgam use is being revised in several countries, a global discussion led by the United Nations Environmental Programme (UNEP) on limiting the use of mercury products including dental amalgam will continue between June 2010 and 2013. The UNEP will hold five sessions to facilitate expert consultations and negotiations and assist partners in the implementation of initiatives to reduce mercury use. Following consultations with stakeholders and partners, a new global, legally binding instrument on mercury will be developed, taking into account the challenges faced by both developed and developing countries.

The United States is strongly aligned against any rash decisions on phasing out dental amalgam from a dental standpoint because if composite were the only choice available for long-term cost-effective treatment, it could put urgent dental care out of reach for the poor in developed countries and the general population in developing countries. Regardless of the outcomes of these sessions, the emphasis should remain on the need to educate patients and health providers about the benefits and risks of dental amalgam and to improve the care and consideration of patients who might benefit from treatment with amalgam fillings.

ACKNOWLEDGEMENTS

The authors wish to acknowledge Drs. G.W. Marshall, Jr., and S.J. Marshall for their previous contribution to this chapter.

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PART 4

INDIRECT RESTORATIVE MATERIALS

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CHAPTER 16

Dental Casting Alloys and Metal Joining

OUTLINE

Historical Perspective on Dental Casting Alloys

Classification of Dental Casting Alloys

Desirable Properties of Dental Casting Alloys

Functional Mechanical Properties of Casting Alloys

Alloys for All-Metal Prostheses

Alloys for Metal-Ceramic Prostheses

Alloys for Removable Partial Dentures

Alternative Technologies for Fabricating Prostheses

Biological Hazards of Base Metal Alloys

Joining of Dental Alloys

KEY TERMS

Age hardening—Process of hardening certain alloys by controlled heating and cooling, which usually is associated with a phase change.

Antiflux—A substance such as graphite that prevents flow of molten solder on areas coated by the substance.

Base metal—A metal that readily oxidizes or corrodes.

Coping—Metal substructure for a cast-metal or veneered-metal prosthesis.

Copy milling—Process of cutting or grinding a desired shape to the same dimensions as a master pattern in a manner similar to that used for cutting a key blank from a master key.

Flux—Compound applied to metal surfaces that dissolves or prevents the formation of oxides and other undesirable substances that may reduce the quality or strength of a soldered or brazed area.

Lost wax technique—Process in which a wax pattern, prepared in the shape of missing tooth structure, is embedded in a casting investment and burned out to produce a mold cavity into which molten metal is cast.

Noble metal—Gold and platinum group metals (platinum, palladium, rhodium, ruthenium, iridium, and osmium), which are highly resistant to oxidation and dissolution in inorganic acids. Gold and platinum do not oxidize at any temperature, rhodium has excellent oxidation resistance at all temperatures, osmium and ruthenium form volatile oxides, and palladium and iridium form oxides in the temperature ranges of 400 °C to 800 °C and 600 °C to 1000 °C, respectively.

Postsoldering—Process of brazing or soldering two or more metal components of a prosthesis after the metal substructure has been veneered with a ceramic.

Presoldering—Process of brazing or soldering two or more metal components of a prosthesis before a ceramic veneer is fired or hot-pressed on the metal structure.

Soldering—Process of building up a localized metal area with a molten filler metal or joining two or more metal components by heating them to a temperature below their solidus temperature and filling the gap between them using a molten metal with a liquidus temperature below 450 °C. In comparison with welding, fusion of the joined alloy part(s) does not usually occur during this process. Bonding of the molten solder to the metal parts results from flow by capillary action between the parts without appreciably affecting the dimensions of the joined structure. In dentistry, many metals are joined by brazing, although the term *soldering* is commonly used. If the process is conducted above 450 °C, it is called brazing.

Welding—Process of fusing two or more metal parts through the application of heat, pressure, or both, with or without a filler metal, to produce a localized union across an interface between the workpieces.

The twentieth century has generated substantial changes in dental prosthetic materials. The major factors driving new development are (1) economy—the new material performs the same function as the old but at a lower cost; (2) performance—the new material performs better than the old in some desirable way, as in the processing method, handling characteristics, or delivery system; and (3) esthetics—the new material provides a more esthetic result. A brief description of the evolution of the currently

marketed alloys is presented below in order to clarify the rationale for the development of the wide variety of alloy formulations.

HISTORICAL PERSPECTIVE ON DENTAL CASTING ALLOYS

1907: THE LOST WAX PROCESS

In his 1907 US Patent #865823, Taggart described a method of making gold inlays using the **lost wax technique**. It led to the casting of onlays, crowns, multiple-unit fixed dental prostheses (FDPs), and frameworks for removable partial dentures.

1932: CLASSIFICATION OF GOLD-BASED CASTING ALLOYS

The dental materials group at the National Bureau of Standards (now National Institute of Standards and Technology) evaluated the properties of alloys being used and classified them by their Vickers hardness number (VHN): type I (soft, VHN, 50 to 90), type II (medium, VHN, 90 to 120), type III (hard, VHN, 120 to 150), and type IV (extra hard, VHN 150 and above).

1933: COBALT-CHROMIUM AND NICKEL-CHROMIUM ALLOYS

The advantages of cobalt-chromium and nickel-chromium alloys are their lighter weight, greater stiffness (elastic modulus), greater strength, and reduced cost. For these reasons, they have largely replaced gold-based alloys for making removable partial dentures. The rapidly fluctuating escalating price of gold between 1980 and 2012 has made them logical alternatives to gold alloys for FDPs.

1959: PORCELAIN-FUSED-TO-METAL PROSTHESES

It is possible to attain a bond between porcelain and gold alloys containing both platinum and palladium. This type of prosthesis is also called a metal-ceramic prosthesis; the mechanism of bonding is discussed in Chapter 18, "Dental Ceramics."

1971: THE END OF THE BRETTON WOODS SYSTEM

The Bretton Woods system, implemented after World War II, was an international monetary framework of fixed exchange rates between gold and currency. The system ended on August 15, 1971, a step that completely abandoned the gold standard. Gold then became a commodity freely traded on the open market. As a result, the price of gold rose steadily over the next 9 years. The price of gold skyrocketed again between 2006 and 2011, approaching $1900 per ounce in August 2011.

In response to the ever-increasing price of gold, new dental alloys were introduced by replacing gold partially or entirely with a less expensive **noble metal** or adapting removable partial denture alloys for crown and bridge casting applications.

1976: THE MEDICAL AND DENTAL DEVICES ACT

This law placed the U.S. dental industry under the auspices of the U.S. Food and Drug Administration (FDA). Dental alloys for prosthetics were classified as passive implants. All materials on the market prior to 1976 were automatically "grandfathered" as acceptable for market distribution. Manufacturers were required to have a quality system in place, but no product standards were established.

1996: THE EUROPEAN MEDICAL DEVICES DIRECTIVE

The European Union (EU) established that any imports of dental devices required a CE (Certification-Expert) mark. To sell products in the EU, a company must be compliant with an International Organization for Standardization (ISO) standard (ISO 9000) and meet the requirements of the European Medical Device Directive. This performance standard extended beyond the FDA requirements, since no existing products were grandfathered and safety had to be demonstrated. Information and data on the development process were also required. Again, no specific product standards were established.

1998: THE CLEAN AIR ACTS

The price of palladium increased to a record high of $1000 per troy ounce in 2000 because of the increased demand for palladium-containing catalytic converters. At the same time during that decade, the price of gold was trading below $300 per troy ounce and gold-based dental alloys were less expensive than palladium-containing alloys. The poor economy of 2001 decreased the demand for palladium and its price fell to a level comparable to that of gold, in the range of $300 to $350 in 2002. In 2012, the price of palladium was less than half that of gold.

CLASSIFICATION OF DENTAL CASTING ALLOYS

Traditionally, dental gold alloys have been specified by the gold content based on carat or fineness. The carat system specifies the gold content of an alloy based on parts of gold per 24 parts of the alloy. Fineness is the unit that describes the gold content in noble metal alloys by the number of parts of gold per 1000 parts of alloy. For example, pure gold is 24-carat or 1000 fine, whereas an 18-carat alloy contains 75% pure gold and is 750 fine. The terms *carat* and *fineness* are rarely used to describe the gold content of current dental alloys. However, *fineness* is often used to identify gold alloy solders.

Since the classification of gold alloys was established in 1932 by the National Bureau of Standards, the number of alloy compositions has increased astronomically. Dental alloys currently available for dental castings can be classified according to their composition, their intended usage, or their mechanical properties.

ALLOY CLASSIFICATION BY NOBLE METAL CONTENT

In 1984, the American Dental Association (ADA) proposed a simple classification for dental casting alloys based on the content of noble metals. Three categories were described: high noble (HN), noble (N), and predominantly **base metal** (PB). This classification is presented in Table 16-1. Noble

metals comprise a group of seven metals that are resistant to corrosion and tarnish in the mouth. In order of increasing melting temperature, they include gold, palladium, platinum, rhodium, ruthenium, iridium, and osmium. Only gold, palladium, and platinum, which have the lowest melting temperatures of the seven noble metals, are currently of major importance in dental casting alloys. The noble metals and silver are sometimes called precious metals, referring to their high economic values, but the term *precious* is not synonymous with *noble*. Silver is reactive in the oral cavity and is not considered a noble metal.

As described in Chapter 5, the IdentAlloy program was established by manufacturers to provide documentation of certified alloys. Under the program, each alloy has a certificate that lists its manufacturer, alloy name, composition, and ADA classification. Some insurance companies use it as well to determine the cost of crown and bridge treatment. This system lacks the potential to discriminate among alloys within a given category, which may have quite different mechanical properties.

ALLOY CLASSIFICATION BY MECHANICAL PROPERTIES

Over the past few decades base metal alloys have been developed to the point where they are superior to high noble and noble alloys in several respects, such as low cost and low density, excellent strength, high stiffness, and stable oxide formation (which is required for bonding to porcelain). The classification described in ADA specifications and ISO standards has changed over time.

ADA Specification No. 5 formerly classified gold alloys as types 1 through 4, depending on the content of gold, palladium, and platinum. The content of noble metals by weight ranges from 83% (type 1) to 75% (type 4). Both the current ADA Specification No. 5 (1997) and ISO Standard 1562 (2004) have classified four types of casting alloys using similar minimal yield strength and percent elongation values for each type of alloy. The only difference is that the ISO standard is specific for casting gold alloys whereas ADA Specification No. 5 covers all alloys that pass the tests for toxicity and tarnish. Table 16-2 lists the classification and mechanical properties described in ISO 1562.

The more recent ISO 22674 standard classifies metallic materials for fixed and removable restorations and appliances into six types according to their mechanical properties without referring to the composition of the alloys (Table 16-3). Although the properties for heat-treated specimens are not given in the table, it is assumed that the specimens are bench-cooled.

TABLE 16-1 **Alloy Classification by Noble Metal Content—American Dental Association (1984)**

Alloy Type	Total Noble Metal Content
High noble (HN)	Must contain ≥40% Au and ≥60% by weight of noble metal elements*
Noble (N)	Must contain ≥25% by weight of noble metal elements
Predominantly base metal (PB)	Contains <25% by weight of noble metal elements

*Noble metal elements include Au, Pd, Pt, Rh, Ru, Ir, and Os.

ALLOY CLASSIFICATION BY PRINCIPAL ELEMENTS

Alloys may be classified based on the principal or most abundant element (e.g., a palladium-based alloy), or they may be named based on the two or three most important elements (e.g., Pd-Ag, Co-Cr, or Ni-Cr-Be alloys). When an alloy is identified according to the elements it contains, the components are listed in declining order of composition, with the largest constituent first followed by the second largest constituent. An exception to this rule is the identification of certain alloys by elements that significantly affect physical properties, which represent potential biocompatibility concerns, or both. For example, Ni-Cr-Mo-Be alloys are often designated as Ni-Cr-Be alloys because of the contributions of beryllium to the control of castability and surface oxidation at high temperatures and the relative toxicity potential of beryllium compared with other metals. Alloy groups shown in Table 16-4 are identified by principal elements.

ALLOY CLASSIFICATION BY DENTAL APPLICATIONS

There are three categories of dental alloys designated by their applications, including all-metal fixed prostheses, metal-ceramic prostheses, or removable partial dentures. Alloys for all-metal prostheses are also used as substrates for resin-veneered metal prostheses. As shown in Table 16-4, each type of alloy by noble metal content (HN, N, and PB) is available in all three categories. High noble and noble alloys for metal-ceramic prostheses can be used for all-metal prostheses, whereas those for all-metal restorations are rarely used for metal-ceramic restorations. The reasons are as follows: (1) the

TABLE 16-2 **Mechanical Property Requirements Proposed in ISO Draft International Standard 1562 for Casting Gold Alloys (2002)**

Type	Descriptor	Yield Strength (MPa)	Elongation (%)	Examples of Applications
1	Low	80	18	Inlays
2	Medium	180	10	Inlays and onlays
3	Hard	270	5	Onlays, thin cast backings, pontics, full crowns, saddles
4	Extra hard	360	3	Saddles, bars, claps, crowns, bridges, and partial denture frameworks

TABLE 16-3 Classification of Metallic Material for Dental Applications—ISO 22674 (2006)*

Type	Yield Strength (MPa)	Elongation (%)	Examples of Applications
0*	-	-	Single-tooth fixed restorations—e.g., small veneered one-surface inlays, veneered crowns
1	80	18	Single-tooth fixed restorations, veneered or nonveneered one-surface inlays, veneered crowns
2	180	10	For single-tooth fixed restorations—e.g., crowns or inlays without restriction on the number of surfaces
3	270	5	For multiple-unit fixed restorations—e.g., bridges
4	360	2	For appliances with thin cross sections that are subjected to very high forces—e.g., removable partial dentures, clasps, thin veneered crowns, wide-span bridges or bridges with small cross sections, bars, attachments, implant retained superstructures
5	500	2	For thin removable partial dentures, parts with tin cross sections, clasps

*Metallic materials for metal-ceramic crowns produced by electroforming or sintering belong to type 0.

TABLE 16-4 Classification of Casting Metals for Full-Metal and Metal-Ceramic Prostheses and Partial Dentures

Metal Type	All-Metal Prostheses	Metal-Ceramic Prostheses*	Partial Denture Frameworks
High noble (HN)	Au-Ag-Pd	Au-Pt-Pd	Au-Ag-Cu-Pd
	Au-Pd-Cu-Ag	Au-Pd-Ag (5–12 wt% Ag)	
		Au-Pd-Ag (>12 wt% Ag	
		Au-Pd	
Noble (N)	Ag-Pd-Au-Cu	Pd-Au	
	Ag-Pd	Pd-Au-Ag	
		Pd-Ag	
		Pd-Cu-Ga	
		Pd-Ga-Ag	
Predominantly base metal (PB)	CP Ti	CP Ti	CP Ti
	Ti-Al-V	Ti-Al-V	Ti-Al-V
	Ti-Al-Nb	Ti-Al-Nb	Ti-Al-Nb
	Ni-Cr-Mo-Be	Ni-Cr-Mo-Be	Ni-Cr-Mo-Be
	Ni-Cr-Mo	Ni-Cr-Mo	Ni-Cr-Mo
	Co-Cr-Mo	Co-Cr-Mo	Co-Cr-Mo
	Co-Cr-W	Co-Cr-W	Co-Cr-W
	Cu-Al		

*Alloys for metal-ceramic prostheses can be used for all metal prostheses, but not vice versa.

alloys may not form thin, stable oxides required for porcelain bonding; (2) their melting range may be too low to resist deformation or melting at porcelain-firing temperatures; and (3) their thermal contraction coefficients may not be close enough to those of commercial porcelains. The introduction of ultralow-fusion high-expansion porcelains, which sinter below 850 °C, has led to the use of some yellow-colored, high gold alloys that can be veneered with porcelain. There is a group of high gold-containing alloys that are designated for both all-metal and metal-ceramic applications.

Base metal alloys, on the other hand, are often marketed for both all-metal and metal-ceramic prostheses because of their oxide formation at room temperature. In this chapter, dental alloys are discussed by their applications.

DESIRABLE PROPERTIES OF DENTAL CASTING ALLOYS

Depending on the primary purpose of the prosthesis, the choice of casting alloy or metal is made by the dentist in collaboration with a qualified dental laboratory technician or technologist. From the standpoint of patient safety and the risk of medico-legal issues, it is highly important to understand the following clinically important requirements and properties of dental casting alloys.

BIOCOMPATIBILITY

The alloy must tolerate oral fluids and not release any harmful products into the oral environment. When components of the

alloy are released in the oral environment, they can cause a toxic or allergic reaction. Toxic materials are eliminated by national or international regulations as well as sound business practices. Allergic reactions, however, are peculiar to the individual patient, and the practicing dentist has an obligation, morally and legally, to minimize this risk.

TARNISH AND CORROSION RESISTANCE

As previously discussed in Chapter 3, corrosion is the physical dissolution of a material in the oral environment and tarnish is a thin film of a surface deposit that is adherent to the metal surface. Corrosion resistance is derived from the use of noble metals that do not react in the oral environment (e.g., gold and palladium) or by the ability of one or more of the metallic elements to form an adherent passivating surface film, which inhibits any subsurface reaction (e.g., chromium and titanium).

THERMAL PROPERTIES

The melting range of the casting alloys must be low enough to form smooth surfaces with the mold wall of the casting investment (Chapter 10). To achieve an accurate fit of cast prostheses, oversized dies for waxing and controlled mold expansion are needed to compensate for casting shrinkage of the alloy and provide space for the luting cement. For metal-ceramic prostheses, the alloys must have closely matching thermal expansion coefficients to be compatible with given porcelains, and they must tolerate high processing temperatures without deforming via a creep process.

STRENGTH REQUIREMENTS

The alloy must have sufficient strength for the intended application. Alloys for bridgework require higher strength than alloys for single crowns. Alloys for metal-ceramic prostheses are finished in thin sections and require sufficient stiffness to prevent excessive elastic deflection from functional forces, especially when they are used for long-span frameworks.

FABRICATION OF CAST PROSTHESES AND FRAMEWORKS

The molten alloy should flow freely into the most intricate regions of the investment mold, without any appreciable interaction with the investment material, and wet the mold surface without forming porosity within the surface or subsurface regions of the alloy. This property is also termed *castability*, which is measured by percent completion of a cast mesh screen pattern or other castability patterns. The selection of an investment material suitable for the metal to be cast is critical.

Cutting, grinding, finishing, and polishing are necessary steps in obtaining a prosthesis with a satisfactory surface finish. The hardness of an alloy is a good primary indicator of the likely difficulty of cutting and grinding it.

PORCELAIN BONDING

To achieve a sound chemical bond to ceramic veneering materials, the alloy must be able to form a thin adherent oxide, preferably one that is light in color so that it does not interfere with the esthetic potential of the ceramic.

ECONOMIC CONSIDERATIONS

For the dental laboratory owner who must guarantee the cost of prosthetic work for a certain period of time, the cost of fabricating prostheses must be adjusted periodically to reflect the fluctuating prices of casting metals, mostly those of high noble and noble metal alloys.

FUNCTIONAL MECHANICAL PROPERTIES OF CASTING ALLOYS

The strength of an alloy is an important factor in ensuring that the prosthesis for which it is used will serve its intended functions effectively, safely, and for a reasonable time (Chapter 4). In a general sense, mechanical properties are the measured responses of materials under an applied force or distribution of forces, such as elastic deformation, plastic deformation, or a combination of both. The level of strength needed depends on the intended categories of application and types of prostheses to be made. The following are important functional characteristics of casting alloys.

? CRITICAL QUESTIONS

What are two clinical disadvantages of cast metals that have lower elastic moduli?

? CRITICAL QUESTION

Why does a long-span bridge require alloys of high elastic modulus?

ELASTIC MODULUS

This property represents a proportional constant between stress and strain during the elastic deformation of a material. One characteristic of a material with high elastic modulus is its rigidity or stiffness. For a dental prosthesis, it is equivalent to its flexure resistance. For long-span FDPs, resistantce to flexure is important. When such a prosthesis flexes during loading of the pontic, the mesiodistal bending moment exerted on the abutment teeth can act as a dislodging force, lifting the mesial and distal aspects of the prosthesis. Furthermore, a flexing bridge can induce lateral forces on the abutment teeth, resulting in the loosening of teeth. For a metal-ceramic prosthesis, the overlying brittle porcelain will fail catastrophically when the metal substructure flexes beyond the flexural strength limit of the ceramic. Elastic modulus is also important for the major connectors of removable partial dentures, which must have enough rigidity to prevent flexure during placement and function of the prosthesis. Resistance to flexure also allows clasps to fit into areas of minimal undercuts and still provide adequate retention.

The elastic moduli of base metal alloys, excluding titanium alloys, are up to twice as high as those for some popular noble metal alloys. This is not considered a major disadvantage for noble metal alloys if proper geometries are employed for the framework connectors. The deflection of a cantilever beam is inversely proportional to t^3E, where t is the beam thickness in the plane of bending and E is the elastic modulus.

Calculations show that increasing the thickness of the gold alloy connector by 26% yields the same resistance to bending stress as a base metal alloy connector. For a circular cross section, the diameter must increase by 19% to achieve the same degree of stiffness.

CRITICAL QUESTION

Why is it that a cast metal prosthesis that is subjected to tensile stress above its yield strength will not necessarily fracture?

YIELD STRENGTH

The yield strength, proportional limit, and elastic limit all are essentially measures of the same property under tension (Chapter 4). It is important to note the difference between these three properties. Yield strength is defined as the amount of stress needed to cause 0.2% plastic deformation of the material, which is why it is also called 0.2% offset yield strength. Proportional limit is the elastic stress above which the linear relationship between stress and strain no longer exists on the stress-strain plot. The elastic limit is the greatest stress to which the alloy can be subjected, such that it will return to its original dimensions when the forces are removed. Both yield strength and proportional limit can easily be located on the stress-strain curve, but elastic limit cannot be identified precisely.

Yield strength reflects the capacity of a cast prosthesis to withstand mechanical stresses without permanent deformation. Ideally, the alloys should have a high yield strength, so that a great deal of stress must be applied before a permanent change in dimensions occurs. Generally, alloys with tensile yield strengths above 300 MPa function satisfactorily in the mouth.

CRITICAL QUESTION

How does the ductility of a metal increase the fracture resistance of a margin of a cast metal crown or a clasp arm on a partial denture?

DUCTILITY

This mechanical property represents the amount of plastic deformation under tensile stress that an alloy can undergo before it fractures. When this tensile strain is converted to a percent of the original length of the specimen, the property is called percent elongation. If the force applied is in compressive mode, the property is called malleability. A reasonable amount of ductility and malleability are essential if the clinical application requires some plastic deformation of the as-cast structure, as is needed for clasp and margin adjustment and for burnishing. Some base metal alloys have a ductility higher than that of age-hardened Au-Cu noble metal alloys. High ductility means that the amount of deformation that one can produce by adjusting a prosthesis or by burnishing a cast metal margin plastically is higher for the alloy. In order to burnish an alloy, one must exert a high enough stress that is sufficient to exceed its yield strength. Therefore, if the alloy with high ductility also has a high yield strength, the alloy may not achieve the full benefit of high ductility.

CRITICAL QUESTION

Why is a harder metal more resistant to wear than a softer metal?

HARDNESS

Hardness is a measure of the resistance of the surface to indentation by an object in the shape of a spherical or a diamond-shaped point. Hardness of the metal should be high enough to resist scratching and abrasion and also to maintain the smoothness of the prosthesis in the oral environment. A hard restoration surface can also cause excessive wear of the opposing dentition or restoration(s) and requires more energy in grinding and polishing of the restorations.

An important requirement of inlay and crown and bridge alloys is that they must be easily burnished by the dentist. One measure of burnishability is the percent elongation divided by the hardness or yield strength. Some researchers believe that the burnishability of alloys can be compared by dividing the elongation (ductility) by the product of yield strength and hardness. This would indicate that the gold alloy would be easier to burnish. The extremely high hardness of most base metal alloys renders them difficult to cut, grind, and polish. From a clinician's point of view, the lower hardness and greater ductility of most noble alloys are major advantages compared with those of base metal alloys.

FATIGUE RESISTANCE

This phenomenon occurs when a material is subjected to repeated loading and unloading below its elastic limit. Most fractures of prostheses and restorations develop progressively over many stress cycles. When the load is above a certain threshold, it initiates cracks from surface flaws of the material. Eventually a crack propagates to a critical size, and sudden fracture occurs.

Fatigue behavior is often determined experimentally by subjecting a material to a cyclic stress between two values and determining the number of cycles required to produce failure. When a removable partial denture is inserted and removed daily, the clasps are strained elastically as they slide over the undercuts of abutment teeth. A comparison of number of constant-deflection cycles that caused fracture of cast clasps made of cobalt-chromium alloy, commercially pure CP Ti, Ti-6Al-4V alloy, and type 4 gold alloy after a number of constant-deflection cycles that caused fracture of cast clasps has shown that cobalt-chromium alloys exhibit the highest fatigue resistance, followed by the type 4 gold alloy, Ti-6Al-4V alloy, and CP Ti. Any casting procedure that produces porosity or that produces carbides in the microstructure of a clasp arm will reduce fatigue resistance because the former represents internal flaws and the latter reduces the elongation of the casting.

Other expressions of fatigue fracture resistance include fatigue strength and endurance limit. Fatigue strength (S_{Nf}) is defined as the stress at which failure occurs after N_f cycles.

Endurance limit is the maximum stress that can be maintained without failure over an infinite number of cycles.

ALLOYS FOR ALL-METAL PROSTHESES

These alloys are discussed in three main categories: noble (includes high noble), predominantly base metal, and CP Ti and titanium alloys. Titanium alloys are discussed separately, as they possess properties that are different from those of other base metal alloys.

HIGH NOBLE AND NOBLE ALLOYS

For prosthetic dental applications, it is necessary to incorporate various elements in gold to produce alloys with suitable properties. Platinum increases the hardness and elasticity of gold and raises the melting temperature of the alloy. When palladium became expensive in the late 1990s, platinum was used in place of palladium. Copper in a sufficient quantity relative to the gold content renders the alloy heat-treatable (Chapter 5). Silver forms solid solutions with gold and palladium and is a common component in this group of alloys. In gold-copper (Au-Cu) alloys, silver is effective in neutralizing the reddish color of copper. In the case of palladium-based alloys, silver is needed to develop the white color of the alloys. Palladium has a good range of solubility with several metals, such as gold, silver, and copper, and an ability to impart good mechanical properties. It has excellent tarnish/corrosion resistance and is relatively biocompatible. It has also been incorporated in small quantities (about 1.5% by weight) in gold alloys to improve resistance to tarnish and corrosion without a significant loss of gold color. Zinc acts as an oxygen scavenger during melting and casting of noble and high noble alloys. Indium can be used in place of zinc and, when added in greater amounts (18% to 30% by weight), it can promote a gold-like color in Pd-Ag-based alloys. Iridium or ruthenium is added in small quantities as a grain refiner, since smaller grains improve yield strength.

The compositions of selected high noble and noble alloys are given in Table 16-5. Their physical and mechanical properties are shown in Table 16-6. Since some noble metals contain no gold and rely on palladium for corrosion resistance, these alloys are discussed in two categories: Au-based alloys and Ag-Pd alloys.

Gold-Based Alloys

These alloys are generally yellow in color (see Table 16-5). Type 1 gold alloys are soft and designed for inlays supported by teeth and not subjected to significant mastication forces. Type 2 alloys are widely used for inlays because of their superior mechanical properties, but they have less ductility than type 1 alloys. Type 3 alloys are used for constructing crowns and onlays for high-stress areas. Increasing the Pt or Pd content raises the melting temperature, which is beneficial when components are to be joined by **soldering** (or brazing). Type 4 gold alloys are used in high-stress areas such as bridges and partial denture frameworks. The cast alloy must be rigid to resist flexure, possess high yield strength to prevent permanent distortion, and be ductile enough for adjustment if the clasp of a framework has been distorted or needs adjustment.

Changes of alloy color caused by the reduction in gold content are compensated for by an increase in copper, silver, and palladium. Higher silver and copper content reduces the corrosion resistance of these alloys. These reduced gold alloys have moderate moduli of elasticity but a higher hardness and yield strength than their high noble counterparts.

? CRITICAL QUESTIONS

Why must Type 3 and Type 4 gold-copper alloys be softened by a heat treatment before they are hardened by another heat treatment? What effects can the cooling rate of a heat treated Type 3 gold-copper alloy have on its hardness and ductility?

TABLE 16-5 Typical Compositions of High Noble and Noble Alloys for All-Metal Prostheses

		ELEMENTAL COMPOSITION (PERCENT BY WEIGHT)						
Alloy Type	**Color**	**Au**	**Pd**	**Ag**	**Cu**	**Pt**	**In**	**Balance***
1	Yellow	83	0.5	10	6	-	-	Zn; Ir
2	Yellow	82	-	-	-	18	-	Ir
	Yellow	77	1	13	8.5	-	-	Zn; Ir
3	Yellow	74.5	3.5	11	10.5	-	-	Zn; Ir
	Yellow	50	4	35	10	-	-	Zn; Ir
	Yellow	2	34.9	30	-	-	30	Zn:3; Ir
	White	-	25	71.5	-	-	2.5	Zn; Ru
4	Yellow	60	4	20.5	15	-	-	Zn; Ir
	Yellow	50	3	26	11.5	-	3	Zn:1; Ir
	Pale yellow	20	20	36	-	-	18	Zn:6; Ir
	White	4	30.3	45.7	18.5	-	-	Zn:1.5; Ir

*Elements without value are less than 1 percent by weight.

TABLE 16-6 Physical and Mechanical Properties of Some Modern High Noble and Noble Metal Dental Alloys for Full-Metal Prostheses

Alloy Type	ADA Classification	Density (g/cm^3)	Yield Strength (soft/hard) (MPa)	Hardness (soft/hard) (VHN)	Elastic Modulus (GPa)	Percent Elongation (soft/hard)
1	High noble	16.6	126	85	70	51
2	High noble	19.2	146	95	50	23
	High noble	15.4	221	120	109	54
3	High noble	15.5	207/276	121/182	76	39/19
	Noble	13.2	309/648	138/225	104	28/15
	Noble	10.5	297	180	51	5-6
	Noble	10.5	248/310	145/155	55	10/8
4	High noble	14.5	350/607	165/235	88	35/4
	Noble	13.2	428/683	180/255	86	28/16
	Noble	11.3	420/530	165/220	103	10/2
	Noble	10.6	460/700	195/265	116	10/3

CRITICAL QUESTION

What happens within gold-copper alloys when subjected to a prescribed heating-cooling cycle?

Heat Treatment of Gold-Copper Alloys

To soften the alloy, the casting is placed in a furnace for 10 minutes at 700 °C and then quenched in water. All intermediate phases in the alloy are changed to a disordered solid solution at 700 °C, and the rapid quenching prevents ordering from occurring during cooling. The tensile strength, proportional limit, and hardness are reduced by such a treatment, and the ductility is increased. To harden the alloy, the temperature of the furnace is set between 200 °C and 450 °C and the casting is heated for 15 to 30 minutes before it is quenched in water. Ideally, before the alloy is age-hardened, it should be subjected to a softening heat treatment to relieve all residual strain hardening (Chapter 17) before the alloy is hardened again by heat treatment to produce a disordered solid solution. Otherwise the amount of solid-state transformation will not be properly controlled. In metallurgical terminology, the softening heat treatment is referred to as a *solution heat treatment* and the hardening heat treatment is termed ***age hardening***. Mechanical properties of both the softened and age-hardened states are shown in Table 16-6.

The softening heat treatment is indicated for structures that are ground or reshaped plastically to a different form, either in or out of the mouth. Because the proportional limit is increased during age hardening, a considerable increase in the modulus of resilience can be expected. The hardening heat treatment is indicated for metallic partial dentures, saddles, FDPs, and other similar structures where rigidity of the prosthesis is needed. For small structures, such as inlays, a hardening treatment is not usually required. Age hardening reduces the ductility of gold alloys. A reasonable amount of ductility is essential if the clinical application requires some permanent deformation of the as-cast structure, as is needed for clasp and margin adjustment and for burnishing.

CRITICAL QUESTION

What characteristics of palladium make it a natural choice of element to replace gold for dental alloys?

Silver-Palladium Alloys

These alloys are white and predominantly silver in composition, but they contain at least 25% of palladium to provide nobility and increase the tarnish resistance of the alloy. They may also contain copper and a small amount of gold. Casting temperatures are in the range of those for yellow gold alloys. The copper-free Ag-Pd alloys may have physical properties similar to those of a type 3 gold alloy. With 15% or more copper, the alloy may have properties more like those of a type 4 gold alloy. Despite reports of poor castability because of the lower density and propensity of dissolving oxygen in the molten-state, Ag-Pd alloys can produce acceptable castings when close attention is paid to precise control of the casting and mold temperatures. The major limitation of Ag-Pd alloys in general and in the Ag-Pd-Cu alloys in particular is their greater potential for tarnish and corrosion. The amount of corrosion expected during service is negligible if the palladium content is greater than 25%.

By melting palladium and indium at the composition of 50% In and 50% Pd in atomic percent (52% In and 48% Pd by weight), the alloy is copper colored but increasing the palladium content causes the alloy to lose its reddish color and acquire a gold color. A minimum of 15% by weight of Pd-In intermetallic compound is needed to maintain the yellowish color. A much higher proportion of Pd-In intermetallic compound is used in commercial dental alloys (see Table 16-5). The tarnish resistance of the alloys is especially dependent upon the composition and the integrity of the casting. The colored phase of the Pd-In binary alloy system is hard and brittle and is not a strenghener. Silver, copper, and/or gold

TABLE 16-7 Typical Compositions of Base Metal Alloys for Crown, FDP, and Metal-Ceramic Applications

	ELEMENTAL COMPOSITION (PERCENT BY WEIGHT)					MECHANICAL PROPERTIES			
Alloy (supplier)	Ni	Co	Cr	Mo	Balance*	Yield Strength (MPa)	Hardness (VHN)	Elastic Modulus (GPa)	Elongation (%)
IPS d.Sign 15 (Ivoclar)	58.7	1	25	12.1	Fe:1.9; Si:1.7; Ce	340	230	200	13
Rexalloy (Pentron Alloys)	67	-	14	8	Ga:8; Al; Fe; Si; Mn; Zr; Cu	300	177	191	27
Heraenium S (Heraeus Kulzer)	62.9	-	23	10	Si:2; Fe:15.5; Ce:0.5	310	220	120	29
NPX-III (CMP Industries)	76.5	x†	14	4.5	Al:2.5; Be:1.6; Ti	784	350	200	9
Argeloy Bond (Argen)	77	-	14	4.7	Mn; Fe; Si; C	630	370	207	10
Norex (Pentron)	-	55	25	-	W:10; Ru:5; Al, Nb, Y, Zr	621	350	204	7
Heraenium P (Heraeus Kulzer)	-	59	25	4	W:10; Si:1; Mn:0.8; N	650	330	200	8
Jelbond Supreme (Jelenko)	-	61	27	6	W:5; Mn; Si; Fe; C	475	365	223	8

*Elements wihtout value are less than 1 percent by weight.
†"x" indicates trace amount.

can be added to increase the ductility and improve the castability of the alloy for dental applications.

CRITICAL QUESTIONS

What is the role of chromium in predominantly base metal alloys? How does beryllium improve the properties of nickel-based metal alloys?

PREDOMINANTLY BASE METALS

Base metal alloys generally comprise the group of cast metals that rely on chromium for corrosion resistance. Chromium on the surface of the alloy rapidly oxidizes to form a thin layer of chromium oxide, which prevents the diffusion of oxygen into the underlying metals and improves its corrosion resistance. Chromium also strengthens the alloy by solution hardening. Since the introduction of cobalt-chromium alloys as cast dental appliances in 1928 and subsequent development of nickel-chromium and cobalt-nickel-chromium alloys, base metal alloys have gained widespread acceptance as the predominant choice for the fabrication of removable partial denture frameworks. Because of the high cost of noble metals, these base metals have been adapted also for dual applications such as the production of all-metal and metal-ceramic prostheses.

Currently there are two main groups of base metal dental alloys: nickel-chromium (Ni-Cr) and cobalt-chromium (Co-Cr). The Ni-Cr alloys can be further divided into those with and without beryllium, which improves castability and promotes the formation of a stable metal oxide for porcelain bonding. The majority of Ni-Cr alloys are for small castings such as crowns and FDPs, and Co-Cr alloys are primarily used for casting removable partial dentures in which high elastic modulus and yield strength are needed. Some Ni-Cr alloys, which are used for partial denture frameworks, are formulated for their relative ease of finishing and polishing compared with Co-Cr alloys, which are used for crowns and FDPs in spite of their low ductility. Table 16-7 lists compositions and properties of selected base alloys for all metal and metal–ceramic applications. Molybdenum increases corrosion resistance and strength and decreases the thermal expansion coefficient of base metal alloys. The latter is beneficial for porcelain bonding and minimizes the risk of porcelain cracking or fracture. Base metal alloys for partial frameworks are discussed later.

Their corrosion resistance and high strength make base metal alloys desirable for dental applications. In addition to the four major elements (Ni, Co, Cr, and Mo), base metal alloys may contain one or more of the following elements: aluminum, beryllium, carbon, copper, cerium, gallium, iron, manganese, niobium, nitrogen, ruthenium, silicon, titanium, tungsten, yttrium, and zirconium. These elements are added to improve manipulation and mechanical properties. Beryllium refines grain size, which increases strength, and lowers the fusion temperature of the alloys, which improves castability. Manganese and silicon also improve the castability of the alloys. Carbon forms carbides with any of the components in the alloy that increase the hardness and yield strength of the alloy but these carbides decrease its ductility. This strengthening mechanism is required primarily for removable partial dentures. Aluminum in Ni-Cr alloys forms a nickel and aluminum compound, Ni_3Al, which increases both tensile and yield strength. Nitrogen, which is incorporated in the alloy during casting in ambient air, also improves the overall qualities of the casting.

The manipulation and mechanical properties of base metal alloys are described in more detail in the section titled "Alloys for Metal-Ceramic Prostheses," below, and in the section on partial dentures, since base metals are used to a lesser extent for all-metal prostheses.

TITANIUM AND TITANIUM ALLOYS

The use of commercially pure titanium (CP Ti) and titanium alloys for dental applications has increased significantly since a description of its applications was first reported in 1977. These metals can be used for all-metal and metal-ceramic prostheses as well as for implants and removable partial denture frameworks. Titanium derives its corrosion protection from a thin passivating oxide film (approximately 10 nm thick), which forms spontaneously with surrounding oxygen. Titanium is considered the most biocompatible metal used for dental restorations produced with prostheses.

Titanium has a high melting point (1668 °C) and high rate of oxidation above 900 °C. It requires a special casting machine with arc-melting capability and an argon atmosphere along with a casting investment consisting of oxides, such as MgO, ZrO_2, or Y_2O_3, which are more stable than titanium oxide, to ensure acceptable castability. Because of reactions with the investment, the very hard so-called α case, with a thickness of approximately 150 μm, forms at the surface of cast dental titanium alloys. The Vickers hardness of cast CP Ti increases from a bulk value of nearly 200 to approximately 650 at a depth of 25 μm below the surface. Special tools are required in the dental laboratory for finishing and adjusting CP Ti castings.

For metal-ceramic prostheses, a porcelain sintering temperature below 800 °C is desirable to minimize oxidation and to avoid the conversion of the alpha phase to the higher-temperature beta phase, discussed below. The high melting temperature of titanium alloys makes them highly resistant to sag deformation when used as metal frameworks at porcelain sintering temperatures, and the accompanying relatively low thermal expansion coefficient demands special low-expansion dental porcelains for bonding to titanium. Because the α case, special surface modifications to cast titanium must be made. Caustic NaOH-based solutions or silicon nitride coatings have been employed to improve the bond between cast CP Ti and dental porcelain.

Commercially Pure Titanium

According to the American Society for Testing and Materials (ASTM F-67), there are four unalloyed grades of CP Ti based on the concentration of impurities (Table 16-8). The elastic modulus of CP Ti is comparable to that of tooth enamel and noble alloys, but it is lower than that of other base metals (see Table 16-7). CP Ti is often selected for its excellent corrosion resistance, especially in applications for which high strength is not required. Increasing its oxygen content not only increases its flexural strength but also its fatigue strength.

? CRITICAL QUESTIONS

Why is a Ti-Al-V alloy with high strength not always preferred to the commercially-pure titanium metal for dental prostheses? How do alloying elements affect the properties of titanium dental alloys?

Titanium Alloys

CP Ti undergoes an allotropic transformation from a hexagonal close-packed crystal structure (α phase) at 882 °C to a stronger and more ductile body-centered crystal structure (β phase). By incorporating α and/or β microstructural stabilizers, four possible types of titanium alloys can be produced: α, near-α, α-β, and β. Alpha-phase stabilizers, such as aluminum, carbon, nitrogen, and gallium, cause the transformation from α to β phase to occur at a higher temperature on heating. Beta-phase stabilizers, such as molybdenum, cobalt, nickel, niobium, copper, palladium, tantalum, and vanadium, cause the transformation from β to α phase to occur at lower temperatures on cooling. Alpha alloys will form no beta phase on cooling and may contain α stabilizers. Near-alpha alloys will form a limited amount of beta phase on cooling by alloying with a small percentage of β stabilizers. Alpha-beta alloys are metastable and contain some combination of α and β stabilizers. This group of alloys is heat-treatable and will contain α phase at room temperature; they may contain retained β phase and/or transformed β phase. Thermal treatment dictates the relative amount of α and β phases and their contributions to mechanical properties. Beta alloys contain sufficient beta stabilizers to retain the beta phase on cooling; they can be solution-treated and aged to improve strength.

The most widely used titanium alloy in dentistry and for general commercial applications is Ti-6Al-4V (Ti-10.2Al-3.6V in atomic percent), which is an α-β alloy. Although this alloy has greater strength than that of CP Ti, it is not as attractive because of some concerns about health hazards from the slow release of aluminum and vanadium. Vanadium is highly

TABLE 16-8 Tensile Properties and Impurity Limits for ASTM F 67 Unalloyed Titanium*

	PHYSICAL PROPERTIES (MINIMUM)				IMPURITY LIMITS (MAX), PERCENT BY WEIGHT				
Designation	Tensile Strength (MPa)	Yield Strength (MPa)	Hardness (VHN)	Elongation (%)	N	C	H	Fe	O
Grade 1	240	170	126	24	0.03	0.08	0.015	0.20	0.18
Grade 2	340	280	178	20	0.03	0.08	0.015	0.30	0.25
Grade 3	450	380	221	18	0.05	0.08	0.015	0.30	0.35
Grade 4	550	480	263	15	0.05	0.08	0.015	0.50	0.40

*Elastic modulus is approximately 110 GPa for each type.

TABLE 16-9 Properties of Two α-β Titanium Alloys for Dental Prostheses

Alloy	Elastic Modulus (GPa)	Yield Strength (MPa)	Hardness (VHN)	Elongation (%)
Ti-6Al-4V	117	860	320	10–15
Ti-6Al-7Nb	105	795	330	10

toxic both in the elemental state and in oxide forms, and aluminum has been reported to cause potential neurological disorders. Niobium has not been associated with any known toxic or adverse reactions in the body. Both vanadium and niobium belong to group VA in the periodic table, and they show similar common characteristics, especially as β stabilizers. Hence, replacing vanadium with the same atomic percentage of niobium yields Ti-6Al-7Nb (Ti-10.5Al-3.6Nb in atomic percent). Both materials are acceptable for biomedical applications. The mechanical properties of the two alloys are similar (Table 16-9) and their corrosion resistance is similar to that of CP Ti. Their elastic moduli are similar to those of type 4 gold alloys and their yield strengths range from those of type 2 to type 5 metallic materials, as described in ISO 22674 (see Table 16-3).

CRITICAL QUESTIONS

Which properties of CP Ti make it difficult to machine?

CRITICAL QUESTIONS

Why does the manipulation of titanium alloy differ so much from that for C-Cr and Ni-Cr alloys?

Manipulation of Titanium Alloys

An argon/arc with a nonconsumable tungsten electrode or high-frequency induction is used for melting titanium alloys in an argon or helium atmosphere. Crucibles are made of copper, magnesia, or carbon. Centrifugal force, casting pressure difference, and gas pressure have been used to force the molten-metal flow into the mold. Castability indices for CP Ti, when cast with centrifugal force, are comparable to those of traditionally cast Ni-Cr and gold alloys. Radiographic examination of the castings reveals that there are much larger pores in castings made by the pressure-difference casting method.

The surface of titanium castings after divestment must be ground and polished to remove surface porosity and the alpha case for optimal functionality of the final prosthesis. The machinability of titanium and its alloys is generally considered poor because of several inherent properties of titanium, such as high chemical reactivity, relatively low thermal conductivity, high strength at high temperature, and low modulus of elasticity.

To eliminate the effect of oxygen during fabrication of titanium prostheses, computer-aided design/computer-aided manufacturing (CAD/CAM) has been used to produce fixed prosthesis frameworks.

CRITICAL QUESTION

How do alloys for all-metal prostheses differ from those required for metal-ceramic prostheses?

ALLOYS FOR METAL-CERAMIC PROSTHESES

The chief objections to the use of dental porcelain as a restorative material are its low tensile strength and relatively low shear strength (Chapter 18). A method of minimizing this disadvantage is to support the porcelain with a cast alloy substructure made to fit the prepared teeth provided that a strong bond is attained between the porcelain veneer and the metal. This system is referred to as the porcelain-fused-to-metal (PFM) design, even though it involves sintering rather than fusing of porcelain. The metal used is often called a PFM alloy or a metal-ceramic. The preferred descriptive term of this composite system is metal-ceramic rather than ceramometal or metaloceramic. The mechanism and procedures for bonding porcelain to metal are presented in Chapter 18. In this section, the requirements of metals, some representative alloy systems, and issues associated with these alloys are discussed.

REQUIREMENTS OF ALLOYS FOR METAL-CERAMIC APPLICATIONS

Because there was no evidence of chemical bonding between early high-gold-content alloys and dental porcelain, mechanical retention and undercuts were used to prevent debonding of the ceramic veneer. It was found later that by adding less than 1% of oxide-forming elements, such as iron, indium, and tin to these alloys, the porcelain-to-metal bond strength was improved by a factor of three. Iron also increases the proportional limit and strength of the alloy by forming a $FePt_3$ precipitate with platinum, as noted in Chapter 5.

Regardless of their chemical composition, the alloys discussed in this section share at least three common features: (1) they have the potential to bond to dental porcelain, (2) they exhibit coefficients of thermal contraction compatible with those of dental porcelain, and (3) their solidus temperature is sufficiently high to resist softening during the sintering of porcelain.

Porcelain Bonding to Metals

The addition of a small quantity of base metal to noble and high noble alloys promotes oxide formation on the surface, which promotes chemical bonding between the alloy and the porcelain. For base metal alloys, some oxides may be poorly adherent oxide to the metal substructure, which can result in porcelain delaminating from the metal substrate. The bond strength of base metal alloys to porcelain as determined in

vitro have not generally been shown to be superior or inferior to those of noble metal alloys. Furthermore, clinical studies have not demonstrated a difference in the failure incidence between metal-ceramic restorations made from base metal alloys and those fabricated from high noble or noble metal alloys. However, some research indicates that frequency of porcelain firing may adversely affect the bond strength of porcelain to metal substrate. For the laboratory technician to produce the optimal metal oxide characteristics, the manufacturer's instructions must be followed precisely. The use of more economical, lower-purity aluminum oxide abrasives by dental technicians can contaminate the metal surface and subsequently affect the integrity of the metal-ceramic adherence zone. The ability of a laboratory technician to discriminate light from moderate grit blasting to remove these surface oxides is one example of the technique-sensitivity of base metal alloys.

Coefficient of Thermal Contraction

The thermal expansion and contraction values of base metal alloys are generally similar to those of noble metal alloys. The thermal contraction differential between metal alloys and dental porcelains may, under certain conditions, contribute to high levels of stress in porcelain, which can induce cracking of porcelain or delayed fracture.

Solidus Temperature

When an alloy is heated close to its solidus temperature, it may become susceptible to flow under its own mass (creep). The degree of creep can be enhanced by the size of the prosthesis and the number of firings that are required for porcelain veneering. Figure 16-1 is a schematic illustration of sag deformation in a framework for an FDP. All metal-ceramic alloys should have a solidus temperature that is significantly higher than the sintering temperature of the porcelain so as to minimize creep deformation.

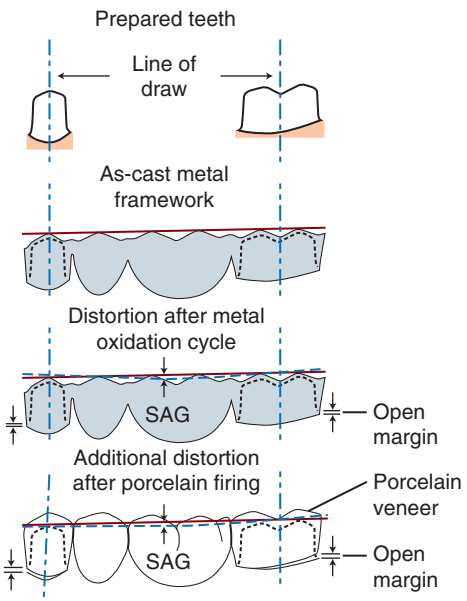


FIGURE 16-1 Sag deformation in a fixed dental prosthesis (FDP) framework.

CRITICAL QUESTION

How can certain differences in thermal contraction between a metal and its veneering ceramic either increase or decrease the resistance to cracking or fracture of the veneer? Why must a metal for metal-ceramic prostheses have its thermal contraction coefficient slightly higher than that of its veneering ceramic?

THERMAL COMPATIBILITY OF METAL-CERAMIC SYSTEMS

When a metal-ceramic prosthesis is cooled from the sintering temperature, the metal and its veneering ceramic contract at different rates because of differences in their thermal contraction coefficients. Meanwhile, the chemical bond between the metal and the porcelain prevents the two components from separating; this condition forces the two components to adjust their respective dimensions in response to stresses that develop during the cooling cycle. Thus, the component that contracts more will be stretched by the adjacent component, which contracts less; at the same time, the material that contracts less will be compressed by the other. Such changes in dimension are controlled by certain stresses (Chapters 4 and 18) that act on each of the two components. The instantaneous stress at a given temperature during the cooling cycle is termed *transient stress*, and the stress distribution, which exists at room temperature, is called the *residual stress*. When the prosthesis is cooled, the tensile stress that develops in the porcelain is of concern. If the transient tensile stresses that develop during cooling are insufficient to cause immediate cracking of the porcelain or delayed cracking after cooling to room temperature, the combination of a metal-porcelain system is considered thermally compatible.

Effect of Metal-Ceramic Contraction Mismatch

A slight thermal contraction mismatch (produced with a higher contraction of the metal) is recommended to develop residual compressive hoop and axial stresses in porcelain, which are protective in nature. When the porcelain shown in Figure 16-2 is under compression in hoop and axial (tangential) directions, the porcelain in the radial direction (oriented toward the center of the crown and perpendicular to the facial surface) is pulled outward by tensile stress in the radial direction. Shown in Figure 16-3, *A*, is a two-dimensional (tangential/axial and radial axes) illustration of the additive effects of tangential tensile stress (+20 MPa) induced in the porcelain veneer by intraoral forces and residual tangential compressive stress (−40 MPa) produced by thermal contraction differences for the case in which α_m is greater than α_p. Thus, the result is −20 MPa of tangential compressive stress. Note that the residual compressive stress in the tangential direction actually increases the "effective" tensile strength of porcelain, since this net compressive stress (−20 MPa) must first be overcome before tensile stress can develop by the applied intraoral force on the facial surface of porcelain. The residual circumferential (hoop) stress (not shown in Figure 16-3) and the residual tangential stress adjacent to the

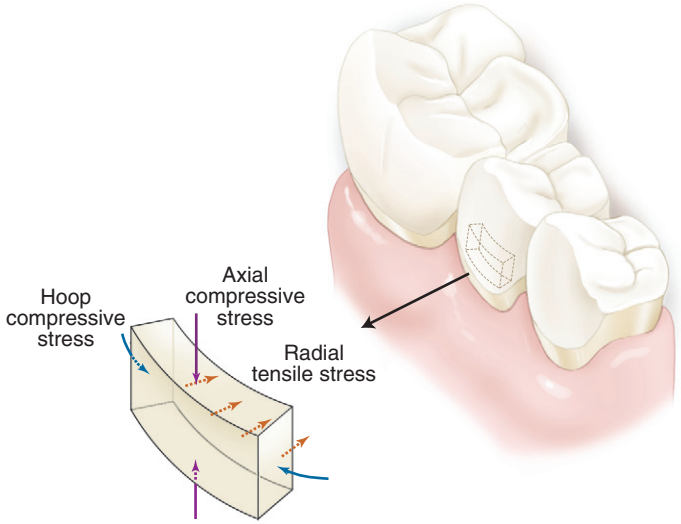


FIGURE 16-2 Residual stress in the porcelain veneer of a metal-ceramic crown for a case in which the coefficient of thermal contraction for the porcelain is less than that for the metal. The arrow pointing from the tooth to the cutout slab does not represent a stress but the projection of the area from within the prosthesis.

metal-porcelain interface are both compressive in nature, and each one tends to increase the fracture resistance of the metal-ceramic bond.

Conversely, a thermal contraction mismatch that results from a higher coefficient of contraction of porcelain (α_p is greater than α_m) will introduce residual tangential and hoop tensile stresses. The additive effect of tangential tensile stress induced in the porcelain by the intraoral force can exceed the tensile strength of the porcelain and causes crack propagation in the porcelain veneer (Figure 16-3, *B*). When the contraction coefficient of the porcelain is much lower than that of the metal (α_P much lower than α_M), porcelain cracking or metal-ceramic bond failure can occur near the metal–porcelain interface. This incompatibility failure is likely caused by the development of radial tensile stresses that exceed the tensile strength of porcelain.

Other Causes of Premature Failures

The percentage of clinical failures attributable to poor adherence of porcelain to the metal substrate, which is fabricated with gold-based alloys, is believed to be low. Of greater concern are the development and progression of delayed cracks in porcelain caused by the interaction of moisture and the relatively high residual tensile stresses within porcelain at the conclusion of the glazing cycle. Delayed failure of this type

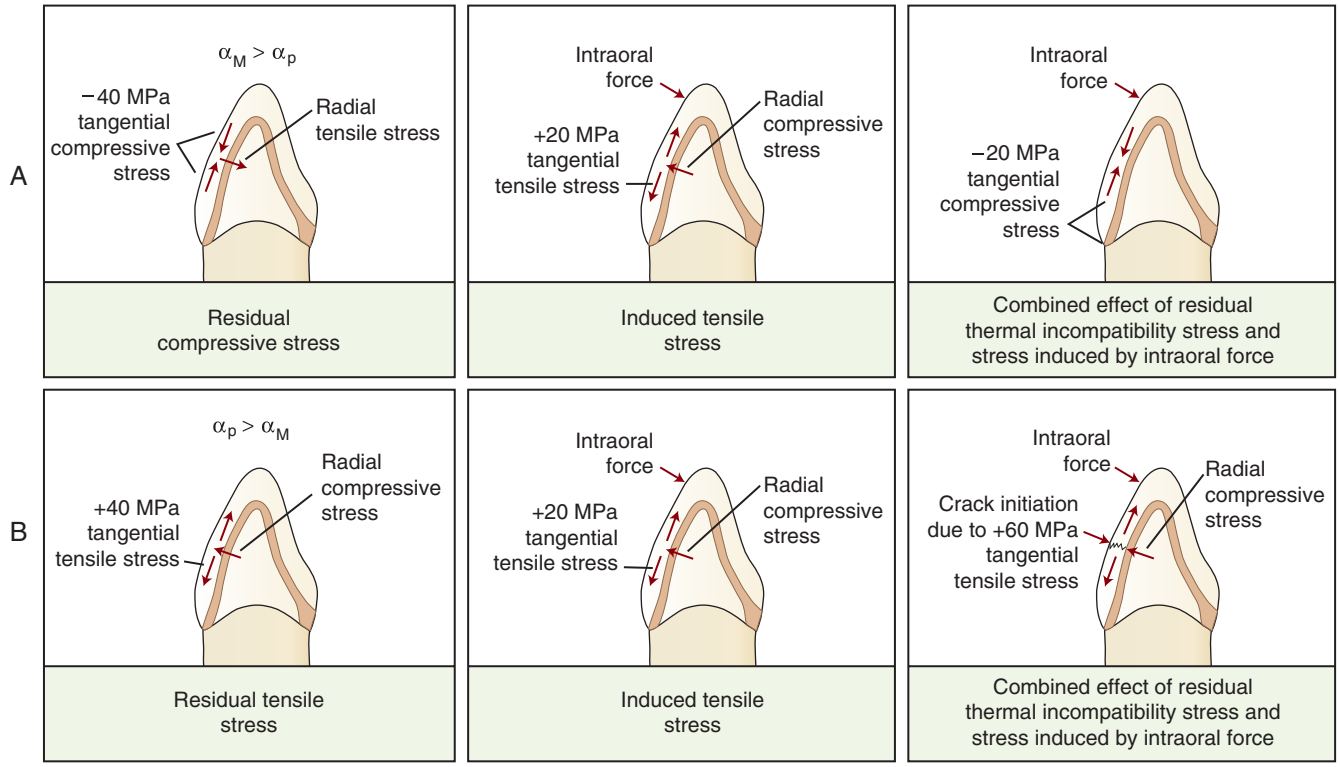


FIGURE 16-3 Combined effect of residual metal/ceramic incompatibility stress and intraorally induced stresses. Negative values represent compressive stress and positive values represent tensile stress. **A**, Thermally compatible metal-ceramic system $\alpha_M > \alpha_p$, in which a residual compressive tangential stress of –40 MPa results in the ceramic veneer. An induced intraoral tensile stress of +20 MPa results in a combined stress of –20 MPa. **B**, Thermally incompatible metal-ceramic system $\alpha_p > \alpha_M$, in which a residual incompatibility tensile stress of +40 MPa is produced in the ceramic veneer. An induced intraoral tensile stress of +20 MPa results in a combined stress of +60 MPa and the formation of a crack within the ceramic.

is attributed to "stress corrosion." To minimize subsequent clinical failures caused by stress corrosion or residual stress combined with stresses induced by intraoral forces, only compatible systems should be used. Since there is no known laboratory test that can adequately predict the residual stress compatibility of metal-ceramic systems, one must rely on feedback from dental alloy or porcelain manufacturers who obtain case report information on failed prostheses, which are prepared under a wide variety of laboratory conditions.

A significant number of prostheses may be fabricated under less than ideal conditions including atypical cooling rates, excessive porcelain-metal thickness ratios, improper framework or **coping** geometries, or an excessive number of firing cycles. Excessive firing is known to cause an increase in the contraction coefficient of some porcelains because of microstructural changes of leucite, the principal crystal present in the glassy matrix (Chapter 18). In addition, the presence of small acute external angles on the incisal edges of metal copings may act as stress raisers which amplify the magnitude of tensile stresses in these areas even though the average residual tensile stress in low. In addition, the temperature distribution in the furnaces may be different from one type to another and they may yield variable heating and cooling cycles.

One of the more controversial issues regarding the compatibility of metal-ceramic systems is whether marginal opening of single-unit copings or generalized distortion of frameworks can result from the generation of high transient stresses in the alloy. Several studies have provided evidence that the marginal gap change is greatest after the oxidation cycle, as previously noted for the high-palladium alloys. The results of these studies indicate that metal-ceramic thermal incompatibility stresses are not the primary cause of marginal or generalized distortion of castings. In fact, sandblasting the internal surface of the metal coping to remove the oxide layer is an equally probable cause of such metal distortion. Care should be taken to limit the time of sandblasting and to apply a minimal sandblasting pressure to minimize distortion of metal margins.

DISCOLORATION OF PORCELAIN BY SILVER

This adverse effect has been overcome recently by the compositional modification of some veneering porcelains. Discoloration of the porcelain near the cervical region of the metal-ceramic prosthesis has been reported to occur when a silver-containing alloy is used as the substrate. Color changes included green, yellow-green, yellow-orange, orange, and brown hues. This discoloration phenomenon has generally been called "greening." It was likely caused by the colloidal dispersion of silver atoms entering body and incisal porcelain or the glazed surface from vapor transport or surface diffusion. The extent of porcelain discoloration was most severe for higher-silver-content alloys, lighter shades, multiple firing procedures, higher temperatures, body porcelain in direct contact with the alloy, vacuum firing cycles, and with certain porcelains containing lower opacifier and higher sodium contents.

"Greening" has occurred even when porcelains were fired on silver-free alloys. This is attributed to vaporization of silver from the walls of contaminated furnaces that was deposited during prior firing with silver-containing alloys. Placing a graphite block in a contaminated furnace and operating the furnace through a complete firing cycle has been used to purge the furnace of silver in preparation for subsequent firing. This process relied on the ability of the graphite to absorb vaporized silver in the furnace.

? CRITICAL QUESTION

What are the benefits and drawbacks of the different types of alloys used for metal-ceramic prostheses?

HIGH NOBLE AND NOBLE ALLOYS

Table 16-10 shows some typical metal-ceramic alloys. Most alloys contain palladium, whose high melting point improves sag resistance during firing, and whose thermal contraction coefficient is lower than that of silver, gold, and platinum, which is helpful in developing lightweight metal-ceramic alloys that are compatible with currently used dental ceramics. The physical and mechanical properties of representative alloys are given in Table 16-11.

Gold-Platinum-Palladium Alloys

This group of alloys produced the first successful metal-ceramic restorations. Platinum increased their melting temperature. Rhenium (Re) is added to some alloys as a grain refiner to increase hardness. Iron, which is added to form a bonding oxide, also increases the proportional limit and strength of the alloy by forming a $FePt_3$ precipitate with platinum. These alloys have adequate elastic modulus, strength, hardness, and elongation but are low in sag resistance. Therefore, they should be limited to crowns and three-unit FDPs. Their use has decreased over time, since more economical alloys have been developed with significantly better mechanical properties and sag resistance.

Gold-Palladium-Silver Alloys

These alloys are economical alternatives to the Au-Pt-Pd or Au-Pd-Pt alloys. Their excellent tarnish and corrosion resistance and relative freedom from technique sensitivity—associated with porcelain bonding and thermal contraction compatibility with several types of alloys—have contributed to their long-term success.

Because of the higher palladium concentrations in Au-Pd-Ag alloys, the melting ranges are raised above those of the Au-Pt-Pd alloys. Thus, one would expect an improved resistance to creep deformation (sag) at elevated temperatures.

Gold-Palladium Alloys

This silver-free alloy has a lower thermal contraction coefficient than that of either the Au-Pd-Ag or Pd-Ag alloys. The latter two types of alloys have thermal expansion or contraction coefficients that are considered too high for use with lower expansion porcelains.

TABLE 16-10 Compositions of Representative High Noble (HN) and Noble (N) Alloys for Metal-Ceramic Prostheses

		PRINCIPAL ELEMENTS (PERCENT BY WEIGHT)						
Alloys	**Typical Products (supplier)**	**Au**	**Pt**	**Pd**	**Ag**	**Cu**	**Ga**	**Balance***
Au-Pt-Pd/ Au-Pt-Ag	SMG-3 (Dentsply Ceramco)	81	6	11	-	-	-	Re; Sn; Fe
	Jelenko "O" (Jelenko)	87	4.5	6	1	-	-	Ir; In; Sn; Fe
	Argedent Y86 (Argen)	86	10	2	-	-	-	In:2
	Degunorm (Dentsply Ceramco)	74	9	-	9	4.4	-	Zn; In; Ir
Au-Pd-Ag	PenCeram 75YA (Pentron Alloys)	75	-	13	10	-	-	In; Sn; Ir
	Argedent 62 (Argen)	62	-	24	9	-	-	Sn:2.3
	Aspire (Dentsply Ceramco)	52	-	26	17	-	-	Zn; In; Sn; Re
	Herabond (Heraeus-Kulzer)	52	-	27	18	0.2	-	Sn:2.7; In
Au-Pd	Olympia (Jelenko)	52	-	38	-	-	1.5	In:8.5; Ru
	Lodestar (Ivoclar Vivadent)	52	-	39	-	-	1.5	In:8.5; Re; Ru
	Argedent 65SF (Argen)	65	-	26	-	-	-	In:8.7
Pd-Au	Olympia II (Jelenko)	35	-	57	-	-	4.8	Sn:3; Zn; Ru
Pd-Au-Ag/ Pd-Ag-Au	Argedent 30 (Argen)	30	-	44	18	-	3	Sn:4.4; Ir
	Aspen (Pentron Alloys)	5.5	1	75	6.5	-	-	In:6; Ga:6; Ru
Pd-Ag	Albabond A (Heraeus-Kulzer)	-	-	57	33	-	-	Sn:6.8; In:3.4; Zn; Ir; Ru
	W-1 (Ivoclar Vivadent)	-	-	53	38	-	-	Sn:8.5; In; Ru
Pd-Cu-Ga	Spartan Plus (Ivoclar Vivadent)	2	-	78.8	-	10	9	Ir; Ge; Li
Pd-Ga-Ag	Argebond 80 (Argen)	-	-	80	5	-	6.3	In:6.5; Sn; Ru
	Argelite 85 (Argen)	2	-	85	1.2	-	10	In:1.2; Ru

*Elements without value are less than 1 percent by weight.

TABLE 16-11 Physical and Mechanical Properties of Some Noble Metal-Ceramic Dental Alloys

Alloy Type	Density (g/cm^3)	Yield Strength (soft/hard) (MPa)	Hardness (soft/ hard) (VHN)	Elastic Modulus (GPa)	Elongation (soft/hard) (%)
Au-Pt-Ag	18.4	405/469	160/195	76	12/9
Au-Pd-Ag	16.0	434	145	100	7
Au-Pd	14.4	550	210	124	30
Pd-Au	13.9	510/572	220/224	124	25/20
Pd-Au-Ag	11.0	450	240	114	11
Pd-Ag	11.0	552	200	124	21
Pd-Cu-Ga	10.7	795	310	97	20
Pd-Ga-Ag	11.2	585/630	230/245	130	35/28

When used with compatible low-expansion and -contraction porcelains, Au-Pd alloys are considered nearly ideal compared with other noble metal alloys, since these alloys contain no silver and their surface oxide is virtually indiscernible. Thus, the esthetic quality of metal-ceramic prostheses made with Au-Pd alloys is comparable to that obtained with Au-Pt-Pd alloys. The sag resistance of these alloys is somewhat better than that of Au-Pt-Pd alloys. All of these alloys are white in color.

Palladium-Gold Alloys

The physical properties of these alloys are generally similar to those of the Au-Pd alloys, although this effect seems to have been resolved by changes in the porcelain composition. Few data are available on their laboratory and clinical performance.

Palladium-Gold-Silver Alloys

These alloys are similar to the Au-Pd-Ag alloys in their potential for porcelain discoloration. They have a range of thermal contraction coefficients that increase with an increase in silver content.

Palladium-Silver Alloys

This alloy type was the first gold-free noble alloy available for metal-ceramic restorations. The replacement of gold by palladium raises the melting range but lowers the thermal expansion coefficient of the alloy. Silver, on the other hand, lowers the melting range but increases the thermal expansion coefficient. A proper balance of the two elements maintains a reasonably low casting temperature and a compatible thermal expansion coefficient. The thermal compatibility of these alloys is generally good except with certain

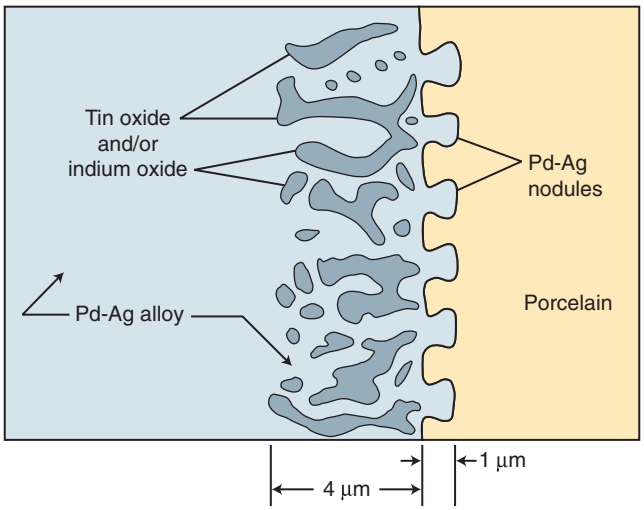


FIGURE 16-4 Internal oxide formation and creep-induced nodule formation in a Pd-Ag alloy for metal-ceramic restorations.

low-expansion porcelains. The addition of tin and indium promotes oxide formation for porcelain bonding and yields precipitates for improving mechanical properties.

Adherence to porcelain is considered acceptable for most of the Pd-Ag alloys. However, one study has indicated that one of these alloy products formed an internal oxide rather than the preferred external oxide. Instead of the formation of the desired external oxide, Pd-Ag nodules developed on the surface (Figure 16-4), enhancing the retention of porcelain by mechanical rather than chemical bonding. However, this condition has not apparently produced clinical bond failures to warrant concern.

Because of their high silver content compared with that of gold-based alloys, the potential silver discoloration effect is most severe for these alloys. One should proceed with caution when light shades (higher values) of ceramic are desired.

Palladium-Copper-Gallium Alloys

Compositional differences for the Pd-Cu-Ga alloys result in a wide range of mechanical properties: yield strengths ranging from 520 MPa to over 1200 MPa, percent elongation ranging from 7% to 30%, and VHN ranging from approximately 265 to over 400. Careful composition control by manufacturers has resulted in Pd-Cu-Ga alloys with VHN substantially less than 300.

The dark brown or black oxide formed during oxidation and subsequent porcelain sintering cycles make it difficult for a technician to mask the color. Sometimes a thicker opaque porcelain layer is required to avoid excessive darkness (i.e., low value) with certain porcelains. The increase in oxide layer thickness occurs during the initial oxidation step for these alloys. To reduce the discoloration effect, the surface can be sandblasted prior to application of opaque porcelain.

Palladium-Gallium-Silver Alloys

The oxide on this type of alloy is relatively dark but somewhat lighter than that of the Pd-Cu-Ga alloys. Pd-Ga-Ag alloys generally tend to have relatively low thermal expansion coefficients, which make the alloys more compatible with lower-expansion porcelains. The silver content is generally low (less than 5% by weight in most cases) and is not sufficient to cause significant porcelain "greening."

The effects of several dental laboratory variables (recasting old alloy, alternative oxidation cycle, stripping and rebonding porcelain) on porcelain adherence were investigated for one Pd-Ga-Ag alloy, three Pd-Cu-Ga alloys, and one Au-Pd alloy. One finding was that remelting two and three times degraded porcelain adherence to the Pd-Ga-Ag alloy and one Pd-Cu-Ga alloy but not to the two other Pd-Cu-Ga alloys or the Au-Pd alloy. Stripping of the original porcelain did not cause a significant decrease in adherence of the subsequent. An alternate oxidation procedure from the one recommended by the manufacturer significantly affected porcelain adherence to one Pd-Cu-Ga alloy and the Au-Pd alloy but not to the other alloys. However, where there is doubt, the manufacturer should be asked to provide precise instructions to ensure sound bonding.

? CRITICAL QUESTION

What are the benefits and drawbacks of using base metal casting alloy versus a noble metal casting alloy for a metal-ceramic restoration?

BASE METAL ALLOYS

Compared with other alloys for metal-ceramic prostheses, base metal alloys generally have a higher hardness and elastic modulus (stiffness) (see Tables 16-6 and 16-7); this enables the coping to be 0.1 to 0.2 mm thick without risking significant deformation under mastication stress or sagging of the metal framework at the porcelain firing temperature. The same properties also make the alloys more difficult to cast and presolder than Au-Pd or Pd-Ag alloys. Some claims have been made that base metal alloys are, in general, more technique-sensitive than well-established noble metal alloys.

Manipulation of Base Metal Alloys

Since the fusion temperatures of Ni-Cr and Co-Cr alloys are in the range of 1150 °C to 1500 °C, an acetylene-oxygen flame or an electrical induction heating source is required for melting these alloys. The investment mold should be made of either phosphate- or silicate-bonded investment material, which maintains its surface integrity at the casting temperature of base metal alloys (Chapter 10). The density of a base metal alloy is about half that of a gold-based alloy. Lower density is important in reducing the force of gravity of bulky maxillary appliances on the supporting teeth. Because of its lighter weight, the thrust generated by the casting unit may not be adequate to force the molten metal to fill the mold. This deficiency can be addressed by the use of a vent and a larger sprue size than that used for gold-based alloys.

Castability studies of metal-ceramic alloys—including Ni-Cr-Be, Ni-Cr, Co-Cr, noble, and high noble metals—by percent completion of the cast mesh screen patterns often show Ni-Cr-Be to have the best castability of all alloys tested.

The castability of Co-Cr is in the same range as that of Ni-Cr without beryllium. Some of noble and high noble metals were found to exhibit lower castability than those of Co-Cr. In contrast, a study of the marginal accuracy of a high noble alloy, four noble alloys, and an Ni-Cr-Be alloy revealed that for all alloys, marginal completeness was adequate and marginal openings were considerably less than 50 μm. In addition, some researchers claim that all alloys will theoretically produce complete castings under optimal burnout, melting, and casting conditions. However, generalized statements on the superiority of beryllium-containing or non-beryllium-containing alloys should not be made without appropriate supporting data and statistical analyses.

In general, the high hardness and high strength of these base metal alloys contribute to certain difficulties in clinical practice. After casting, it is useful to sandblast the prosthesis to remove investment materials as well as oxides. Grinding and polishing of fixed restorations to achieve proper occlusion occasionally require more time at chairside. Removal of defective restorations may also require more time. In addition, the potential hazard of dust generated from the procedure is a concern and is discussed with the biological hazards of base metal alloys (Chapter 7).

The solidification shrinkages of base metal alloys are greater than those of gold base alloys, which represents a challenge for technicians to obtain acceptable-fitting base metal castings. Using type V die stone for dies and enhancing the expansion of the investment mold during setting of the investment are the most common practices to improve the fit of prostheses (Chapter 10). One advantage of the greater hardness of base metal alloys is that the margins are unlikely to be damaged or destroyed during polishing.

The thickness of the oxide layer and wetting of the oxide layer by porcelain are important factors in establishing the bonding of porcelain to the metal substrate. An oxide layer that is nonadherent or poorly adherent to the alloy substrate is susceptible to result in porcelain delamination under relatively low stresses. The bond strength of porcelain to Ni-Cr or Co-Cr has not generally been shown to be superior or inferior to those for noble metal alloys. Furthermore, clinical studies have not demonstrated a difference in the failure incidence between metal-ceramic restorations made from base metal alloys and those fabricated from noble metal alloys.

For the laboratory technician to produce optimal metal oxide characteristics, the manufacturer's instructions must be followed precisely. However, some instructions are relatively imprecise. For example, some alloys require a "light" sandblasting of the oxide layer formed during the initial oxidation step. The size of aluminum oxide abrasive is generally recommended, but neither the quality of abrasive nor the grit-blasting pressure is usually specified. Contamination of the oxide layer with lower-purity abrasives could degrade the integrity of the interface between metal oxide and opaque porcelain. The ability of a laboratory technician to discriminate light from moderate grit blasting to reduce these surface oxides is one example of the technique sensitivity of base metal alloys.

The thermal contraction differential between base metal alloys and dental porcelains may, under certain conditions, contribute to high levels of residual tensile stress in porcelain and induce transient cracking of porcelain or delayed failure. Although the thermal expansion and contraction coefficients of base metal alloys generally fall within the range of noble metal alloys, cracks in porcelain occasionally result when the thermal expansion and contraction differences between metal and porcelain are excessive.

Mechanical Properties

Perhaps the greatest disadvantage of nickel-based alloys is the variability in quality and strength of presoldered connectors of fixed prostheses. Flexure tests of presoldered specimens reveal relatively brittle fracture patterns and porosity, which are distributed typically across the soldered metal interface. Tensile tests of soldered prostheses have demonstrated both intrasolder and interfacial types of failures. The principal defects within the solder alloy are voids, localized shrinkage porosity, and **flux** inclusions. Beryllium-containing alloys are generally more difficult to solder, and specimens of these alloys may contain relatively high concentrations of pores within the solder joint.

The elastic modulus of base metal alloys is as much as two times greater than the moduli for some of the more popular noble metal alloys. This property allows the technician to reduce the cross-sectional area of cast interproximal connectors. Although the rigidity of the prosthesis is proportional to the elastic modulus, the connector width (buccal-lingual dimension) and the cube of the connector thickness (occlusal-gingival dimension), a doubling of the elastic modulus does not mean the thickness of the connector can be reduced by 50%. Calculation shows that the connector thickness can be reduced by only 20.4% when the elastic modulus is doubled. By the same token, a reduction of the coping thickness from 0.3 mm to 0.1 mm may increase the risk of porcelain fracture because of the increased coping flexibility. However, a recent study based on finite element stress analysis of stresses induced in anterior PFM crowns under intraoral forces indicates that a reduction of base metal coping thickness (in veneered areas) from 0.3 to 0.1 mm has only a slight effect on porcelain stresses when anterior maxillary crowns are subjected to vertical forces.

It is a common practice to design the occlusal surface of metal-ceramic prostheses to be made from cast metal to avoid excessive wear of the opposing natural dentition. Compared with the same prostheses made of high noble or noble alloys, the hardness of the base metal alloys makes the occlusal adjustment slightly more difficult to perform, and the resulting roughness can cause greater wear of the opposing tooth enamel. Repair of crowns with fractured porcelain veneers, which may be simply performed on noble metal substrates using pin-retained facings or metal-ceramic onlays, is more difficult to accomplish when the failed restoration has a framework cast with nickel- or cobalt-based alloys. Such difficulties may partially offset the economic advantage of these alloys.

TABLE 16-12 Comparative Properties of High Noble Alloys and Base Metals for Metal-Ceramic Prostheses

Property	High Noble Alloy	Co-Cr	Ni-Cr-Be	CP Ti
Biocompatibility	Excellent	Excellent	Fair	Excellent
Density	14 g/cm^3	7.5 g/cm^3	8.7 g/cm^3	4.5 g/cm^3
Elastic modulus (stiffness)	90 GPa	145–220 GPa	207 GPa	103 GPa
Sag resistance	Poor to excellent	Excellent	Excellent	Good
Technique sensitivity	Minimal	Moderately high	Moderately high	Extremely high
Bond to porcelain	Excellent	Fair	Good to excellent	Fair
Metal cost	High	Low	Low	Low*

*The dental laboratory costs for fabricating metal-ceramic prostheses are high for CP Ti, and few dental laboratories have the capability of producing Ti prostheses.

? CRITICAL QUESTION

What three questions concerning metal-ceramic prostheses should be asked when using a commercial dental laboratory for the first time?

There are three vital groups of information you should obtain from your laboratory technician to ensure that you are approaching the selection of metal-ceramic systems from a conservative point of view. These include:

1. The brand name of the alloy, the alloy type, and the porcelain. The response allows you to determine if the alloy has been tested and accepted according to the standards of national or international standards organizations (ADA, ISO, British Standards Institute [BSI] etc.). The porcelain brand name must be known to determine if a compatible system is being used.
2. The number of years of experience with the material systems and main problems encountered. If the system has been used for less than 3 years, limited information will be available on its clinical performance. If porcelain debonding or crack formation is the major problem, find another laboratory or a more reliable product.
3. If there is difficulty in soldering the alloy or bonding porcelain to it, the laboratory should provide evidence of at least 3 years of proven success of the system used in all aspects of use for the indicated purposes.

TITANIUM-BASED ALLOYS

Commercially pure titanium undergoes a phase transformation at 882 °C. For the CP Ti metal and α-β titanium alloys, the firing temperature for porcelain sintering must be performed well below that temperature to prevent any phase transformation that may alter metal properties upon cooling. In addition, high temperature accelerates the formation of the oxide layer, which can be thick, and increases the risk of failure within the oxide after porcelain firing. Therefore, the recommended type of low-fusing ceramic should be used.

In general, in vitro bonding tests show that conventional metal-ceramics exhibit higher bond strength than those of low-fusing porcelain to titanium. However, a small number of studies show that the bond strengths are not statistically significantly different between the two groups. Differences in porcelain composition often require different firing temperatures, which may result in bond strength changes. However, there is no difference in bond strength between CP Ti and titanium alloys. Studies also show that surface treatment of the alloy before porcelain application can improve the bond strength. The treatments include silica deposition by magnetron sputtering, deposition of an intermediate metallic layer by silver plating, admixture of titanium particles and porcelain as a bonding agent, an intermediate ceramic layer, nitridation of the titanium surface, and a surface roughening by a caustic bath, hydrochloric acid, or sandblasting. Although multiple firing has no effect on bond strength, firing in an argon atmosphere, which reduces oxide formation, improves bond strength. It is believed that controlling the thickness and adherence of the oxide are keys to higher bond strength.

Properties of high noble and base metals for metal-ceramic prostheses are listed in Table 16-12.

? CRITICAL QUESTION

Which factors must be considered by the dental laboratory and dentist for the preparation and adjustment of partial denture frameworks that are cast from base metal alloys?

ALLOYS FOR REMOVABLE PARTIAL DENTURES

Removable partial dentures (RPD) have four major metal components: connectors, rests, clasps, and mesh bases. Except for clasps, each component should be rigid and resist plastic deformation, which suggests a material of high elastic modulus and yield strength. Table 16-13 lists the compositions and mechanical properties of selected base metal alloys. The density of these alloys ranges from 7.6 to 8.3 g/cm^3. For clasps, the material must be resistant to plastic deformation, with a lower modulus of elasticity to engage undercuts and ductility to facilitate adjustment without fracture. Ideally, the clasps should be made of type 4 gold because of its lower elastic modulus and adequate yield strength (see Table 16-6) and then soldered (discussed later) to the remaining framework made of a base metal alloy. This arrangement, however, inevitably promotes corrosion at the soldered (brazed) joint (Chapter 3). Although it is possible to embed gold base clasps in the polymeric denture base resin to avoid corrosion at the

TABLE 16-13 Composition and Mechanical Properties of Selected Base Metal Alloys for Removable Partial Frameworks*

	ELEMENTAL COMPOSITION (PERCENT BY WEIGHT)					MECHANICAL PROPERTIES			
Alloy Type (Supplier)	Ni	Co	Cr	Mo	Balance*	Yield Strength (MPa)	Hardness (VHN)	Elastic Modulus (GPa)	Elongation (%)
Nobilstar (CMP Industries)	-	65	27.5	5.5	Si; Fe; Mn; C	640	430	193	9
Vitallium (Dentsply)	-	63.1	28.5	6	Mn; Si; C; N	600	410	200	9
JD (Jelenko)	-	63	28.5	6	Si; C; Mn; Fe; W	620	290	207	5
Heraenium EH (Heraeus Kulzer)	-	63.5	28	6.5	Si:1; Mn; C; N	620	310	228	7
Suprachrome+ (Argent)	-	63	30	5	Mn; Si; C; N	745	390	200	13
Supercast (Pentron Alloys)	-	64	30	4	Mn; Si; C; N	655	340	228	3.5
Ticonium 100 (CMP Industries)	71.6	x†	16	5	Al: 2.9; Mn: 3.7 Be: 0.8; Ti	790	360	186	7

*Elements wihtout value are less than 1 percent by weight.
†"x" indicates trace amount.

solder joint, in practice removable partial dentures are cast in one piece using the same alloy. The effect of high elastic modulus of base metal on the flexure and retention of the clasp can be adequately addressed by altering the thickness of the clasps. The situation is similar to that discussed for FDPs.

BASE METAL ALLOYS

Cobalt-chromium-molybdenum alloy has been the primary metal for partial denture prostheses. Cobalt increases the elastic modulus and strength. Inclusion of greater than 30% of chromium by weight makes the alloy difficult to cast and forms the brittle σ phase. Molybdenum and manganese improve the alloy's corrosion resistance. Carbide formation is essential for high yield strength and hardness in the alloy, but it lowers ductility. Particular concerns are the higher hardness of some alloys compared to that of tooth enamel, which can cause in vivo wear, as well as the need for special finishing in the dental laboratory and the tendency of these alloys to undergo rapid work hardening.

Co-Cr clasps are reported to be too retentive initially and that they slowly lose this retention because of plastic deformation (also known as work hardening) of the clasp from repeated seating and removal of the appliance. This rapid work hardening is associated with the complex microstructure of these alloys, which arises from their complex elemental compositions. Caution is called for on the part of the dental laboratory technician or the clinician in adjusting clasps on the cast framework to avoid fracture, even for partial denture alloys that exhibit higher values of percent elongation. Heat treatment is generally ineffective for improving the mechanical properties of these alloys. Thus, these alloys are recommended for clinical use in the as-cast condition.

It is important to select a technician who is highly experienced in fabricating partial denture frameworks. Because of their high melting temperatures, these alloys are induction-melted and cast using phosphate- or silicate-bonded investments, as recommended by the manufacturer, to compensate for their high casting shrinkage and to minimize the potential for casting defects. Some Ni-Cr alloys exhibit higher mean values of percent elongation than the Co-Cr alloys, but it is unclear whether the former alloy types would show better long-term clinical performance.

CRITICAL QUESTIONS

Which two types of surface quality defects in a cast CP Ti framework must be managed during fabrication of a prosthesis? Since titanium alloy has a low elastic modulus that is comparable to that of gold, how can the stiffness of removable partial denture (RPD) made from a titanium alloy be increased to the same level of a cobalt-chromium RPD?

TITANIUM-BASED ALLOYS

Commercially pure titanium and titanium alloys have occasionally been used to make removable denture frameworks because of their excellent biocompatibility, outstanding corrosion resistance, and mechanical properties. Because of the connector's low elastic modulus, its rigidity is often improved by increasing its thickness or changing its design. Increasing the rigidity is beneficial in reducing debonding between resin and the metal framework. On the other hand, the lower yield strength and tensile strength and higher percent elongation of CP Ti suggest that cast clasps may be more easily adjusted.

Laboratory casting of titanium remains a challenge, since internal porosity within the clasp assemblies can lead to clasp fracture. The reaction layer on the surface must be removed chemically with hydrofluorosilicic acid or mechanically by grit blasting and rotary instruments.

The high electrostatic binding capacity of the titanium surface oxides results in higher plaque adherence to titanium frameworks compared with other base metal frameworks. A clinical survey of RPDs revealed gradual discoloration of titanium alloy frameworks, while those made with CP Ti and other base metal alloys do not discolor. It is hypothesized that aluminum segregates from the titanium alloy during casting and corrodes during service. An in vitro study has also revealed that exposing titanium alloys to alkaline denture cleansers (pH greater than 11) causes discoloration. Laser **welding** of titanium has facilitated repair of titanium frameworks because of the low thermal conductivity of titanium and localized heating during laser welding. This is also true for Co-Cr and Ni-Cr alloys.

? CRITICAL QUESTION

What are merits and concerns of using alternative techniques for the casting of dental alloys?

ALTERNATIVE TECHNOLOGIES FOR FABRICATING PROSTHESES

All metals and alloys of practical dental interest shrink when they change from the liquid to the solid state and cool from the casting temperature to room temperature. The shrinkage of dental casting alloy in an investment occurs in three stages: (1) the thermal contraction of the liquid metal cooling from its casting temperature to its liquidus temperature, (2) the phase change from the liquid to the solid state, and (3) the thermal contraction of the solid metal from the solidus temperature to room temperature.

The first-stage contraction is of no consequence to the final dimension of the cast because the design of the investment mold allows molten metal to flow freely. For the second–stage contraction, the metal starts to solidify at the walls of the mold and the first layer of metal tends to adhere to the mold while the liquid metal continues to be fed from the reservoir, which results in no contraction of the casting relative to the investment mold. As the casting cools, it gains sufficient strength to contract independently of the mold. Any contraction of the casting from this point will affect the fit of the prosthesis. Finally, the casting shrinks thermally until it reaches room temperature. Since the thermal contraction coefficient of the metal casting is higher than that of the investment mold, the final casting will be too small if the investment mold is an accurate reproduction of the missing tooth structure. This shrinkage normally is compensated for by the setting and thermal expansion of the investment used (Chapter 10). Table 16-14 lists the linear solidification shrinkage of various alloys cast as smooth cylinders. Because the contraction of the alloy as it cools to room temperature dominates the casting shrinkage, the higher-melting alloys tend to exhibit greater shrinkage.

Technologies are currently available for fabricating metallic prostheses without the challenges of casting procedures and casting shrinkage. Except for removable partial denture frameworks, most metal prostheses can be made by one or more of the following methods: (1) sintering (or diffusion bonding) of burnished metal foil, (2) CAD-CAM processing of metal blocks, (3) **copy milling** of metal blocks, (4) electroforming of metal copings, and (5) three-dimensional printing with metal powder followed by sintering.

TABLE 16-14 Linear Solidification Shrinkage of Casting Alloys

Alloy Type	Casting Shrinkage (%)
Type 1 (Au-based)	1.56
Type 2 (Au-based)	1.37
Type 3 (Au-based)	1.42
Type 4 (Ni-Cr–based)	2.30
Type 4 (Co-Cr–based)	2.30

SINTERING OF BURNISHED FOIL

The most commonly used commercial foil system, Captek (Leach & Dillon, North Attleboro, MA), is used for making copings or frameworks for metal-ceramic prostheses. The system requires three pairs of materials to form composite metal structures: (1) Captek P and Captek G, which are used to fabricate crown copings and fixed dental prosthesis abutments; (2) Capcon and Capfil, which are used to connect copings; and (3) Captek Repair paste and Capfil, which are used to add material to Captek structures. Captek copings contain, by weight, 88.2% Au, 9.0% platinum-group metals (including 4% Pt), and 2.8% Ag. The copings are made with a thickness of 0.25 mm for anterior crowns and 0.35 mm for posterior crowns. The inner and outer gold-rich layers are approximately 25 μm in thickness, and the middle layer is made of a Au-Pt metal. The Captek P layer is adapted first to the die and fired at a temperature of 1075 °C. During this firing cycle, the adhesive and binders are eliminated, and the Pd and Pt particles become interconnected by sintering to form a three-dimensional network of capillary channels. Captek G, which contains 97% gold by weight plus binders, which is applied over the Captek P coping. The Captek G metal is drawn by capillary action into the network structure of the Captek P coping. Captek G is provided in two thicknesses, one for anterior copings and one for posterior copings. A 0.35-mm-thick layer of porcelain is applied to the coping, which may or may not require the Capbond bonding agent.

The main advantage of Captek crowns is their very low thickness, which ensures minimal tooth reduction or improved esthetics compared with conventional metal-ceramic crowns made with cast metal copings. For example, the metal margin of a Captek coping can be ground to a thickness of 50 μm, and the total thickness of metal and porcelain can be as low as 0.3 mm, although optimal esthetics dictates an anterior crown thickness of 0.7 to 1.0 mm. Posterior crowns should be at least 1.2 mm thick to resist fracture.

For construction of multiple-unit fixed prostheses, a connector for the two abutment copings is waxed and cast with

a recommended gold alloy. The copings are then joined with the connector using furnace soldering, electrical welding, or laser welding before the porcelain application procedure.

CAD-CAM PROCESSING

Indirect prostheses can be made of cast alloys, sintered ceramics, or polymerized resins. Each material that is used for making a prosthesis requires a process that often takes two or more patient appointments to complete. CAD/CAM (computer-aided design and computer-aided machining) systems offer an alternative method that can produce metal, ceramic, or composite restorations in one appointment. In addition, CAD/CAM technology allows a technician or dentist to use higher quality ceramics, which are produced under nearly ideal conditions. Such materials exhibit several improved properties compared with conventional sintered or hot-pressed ceramics.

The dental application of CAD/CAM became available in the early 1980s to produce ceramic inlays and crowns during one chairside appointment. This technology has since been improved and expanded as an alternative to the metal-casting and ceramic sintering processes, since computer-aided milling or grinding of a metal or a ceramic block can be performed by a CAD-CAM process or by electrolytic or electrical discharge removal of metal.

The following description focuses on the CAD-CAM option, since it is the most widely used technology. A CAD-CAM system electronically or digitally records surface coordinates of the prepared teeth and stores these data in the memory of a computer. The image data can be retrieved immediately to mill or grind a metal, ceramic, or composite prosthesis by computer control from a solid block of the chosen material. Within minutes, the prosthesis can be fabricated and placed on prepared teeth and bonded or cemented in the mouth of the patient in a time ranging from 10 minutes to 1 hour.

The optical scanning procedure eliminates the need for an impression. An advantage of ceramics is that homogeneous, high-quality materials with minimal porosity and few other defects are used for CAD/CAM applications. The computer-controlled milling machine can then perform the milling or grinding for fabrication of a ceramic prosthesis within a few minutes. Note that all-ceramic prostheses suffer from some degree of near-surface damage that is directly related to material selection and machining parameters with CAD/CAM fabrication. Any surface damage increases the probability of catastrophic failure. Understanding and managing the damage phenomena are critical to the success of ceramic prostheses made by CAD/CAM.

The CAD/CAM technique can also be used to prepare prostheses from CP Ti or titanium alloy, which do not contain bulk casting defects or the hard α case found near the surface of cast titanium prostheses.

COPY MILLING

This process is based on the principle of tracing the surface of a resin prosthesis pattern, which is then replicated on a blank of ceramic, composite, or metal that is ground, cut, or milled by a rotating wheel whose motion is controlled by a link through the tracing device. The process is similar to that associated with cutting a key blank using a tracing of a master key. One commercial system of this type (Celay, Mikrona Technologies, Spreitenbach, Switzerland) has been in use since 1991. The pattern to be traced is made from a blue-colored resin-based composite (Celay-Tech, ESPE, Seefeld/Oberbay, Germany).

ELECTROFORMING

A master cast of the prepared tooth (teeth) is prepared and coated with a special die spacer to facilitate separation of the duplicating material. The dies are duplicated with a gypsum product that has a setting expansion of 0.1% to 0.2%. After a conductive silver layer is applied to its surface, the die is connected to a plating head and then to a power source and placed in a plating solution. After a sufficiently thick layer of gold or other metal is deposited, the gypsum is removed and the coping is sandblasted. The coping is then coated with a bonding agent during the wash bake and subsequent ceramic layers are condensed and sintered in a conventional way.

As is true for the burnished foil system, a cast pontic is needed for joining electroformed copings to construct multiple-unit prostheses.

THREE-DIMENSIONAL PRINTING

This process is a form of additive manufacturing technology where a three-dimensional object is created by depositing successive layers of material. The first commercial three-dimensional printer was based on a technique called stereolithography. This technology has been in use to generate wax patterns for casting and provisional prostheses from CAD data as well as models fabricated from intraoral or impression scans. These three-dimensional objects are made using liquid resins curable by ultraviolet or laser irradiation.

Metal powders can be used in place of liquid resins. The metal powder is first spread across the working platform. A laser traces the outline of each part being printed, and metal powder is fused to the layer below it. As the platform is lowered, a new layer of material is spread across the platform and the process is repeated until the printing process is completed. This process is called direct laser metal sintering (DLMS). For dental applications, the metal powder can be titanium, Co-Cr, or a noble metal. A high-energy electron beam has also been used to fuse the metal powder; this process is called electron beam melting (EBM). Other emerging technologies are described in Chapter 21.

One study reported the marginal and internal fit among three-unit Co-Cr-based FDPs using four fabrication techniques: (1) the traditional lost wax casting method, (2) CAD/CAM milling of a wax pattern followed by the lost wax casting method, (3) the CAD/CAM milling method, and (4) the direct laser metal sintering method. Initial results indicate that the best fit was exhibited by group 4, followed by groups 2, 1, and 3.

CRITICAL QUESTIONS

Who is at the greatest risk of adverse effects resulting from the use of base metals? What precautions should be taken to reduce this risk? How can dental alloys cause an allergic reaction in patients, dentists, and dental laboratory technicians?

BIOLOGICAL HAZARDS OF BASE METAL ALLOYS

Allergy-inducing substances can be (1) leached from an alloy into the oral environment by dissolution; (2) released to the environment by airborne particulates during grinding and polishing; or (3) propagated by vapor during casting. The amount of vapor released during casting depends on the vapor pressure, the quantity of the cast mass, and the atomic concentration of the element in an alloy. Beryllium has a low-atomic-weight element and high vapor pressure (0.1 Torr at casting temperature). An alloy that contains 80% Ni, 11.4% Cr, 5% Mo, 1.8% Fe, and 1.8% Be on a weight basis contains 73.3% Ni, 11.8% Cr, 2.6% Mo, 1.6% Fe, and 10.7% Be on an atomic basis. Thus, toxicity considerations for beryllium vapor should be based on the atomic concentration (10.7 atomic percent in the alloy) rather than the weight percent (1.8%).

RISKS FOR DENTAL LABORATORY TECHNICIANS

The risk of beryllium vapor exposure is greatest for dental technicians during alloy melting, especially in the absence of an adequate exhaust and filtration system. When an exhaust system is used, the concentration of beryllium in the breathing zone can be reduced to levels considered safe by the Occupational Safety and Health Administration (OSHA) specification. Workers exposed to moderately high concentrations of beryllium dust over a short period of time or prolonged exposure to low concentrations may experience signs and symptoms representing acute disease states. Physiological responses vary from contact dermatitis to severe chemical pneumonitis, which can be fatal. The chronic disease state is characterized by symptoms persisting for more than a year, with the onset of symptoms separated by a period of years from the time of exposure. Symptoms range from coughing, chest pain, and general weakness to pulmonary dysfunction.

Airborne levels of beryllium can be controlled with a local exhaust system. However, one should not assume that activities such as melting and grinding of Ni-Cr alloys without beryllium and grinding of other dental materials pose no major risk to the health of laboratory technicians. Good ventilation and exhaust facilities should be employed whenever any material is ground. The dental profession should investigate methods to minimize such risks.

POTENTIAL PATIENT HAZARDS

Of greater concern to dental patients is the intraoral exposure to nickel, especially for patients with a known allergy to this metal element. Shown in Figure 7-5, *A*, is an example of nickel allergy on the hand of an individual who has had frequent exposure to nickel metal. In 1983, Moffa et al. have reported that for patients between the ages of 24 and 44 who had a nickel alloy fixed prosthesis, 9.7% of the females and 0.8% of the males experienced a positive reaction to 2.5% nickel sulfate. The incidence of nickel hypersensitivity for all age groups was 4.5% for females and 1.5% for males. Of the positive reactions to nickel, female patients with pierced ears accounted for 90% of the total. None of the males with pierced ears exhibited positive reactions. No correlation was found between the incidence of nickel sensitivity and the presence of intraoral nickel-alloy restorations. Vreeburg et al. reported similar observations, in that the oral exposure of nickel and chromium to guinea pigs via a fixed appliance or the dietary intake of these elements as metallic powder or salts did not induce an allergic reaction to these metals.

Nickel is a moderate allergen, as detected by patch testing for contact allergies, and the potential carcinogenic risks of nickel are unlikely to be incurred by dental patients and dentists. Because of a far greater time-weighted exposure to nickel and beryllium dust and vapor, dental technicians should have adequate protection facilities so that such risks are minimized.

To minimize exposure of metallic dust in patients and dentists during metal-grinding operations, a high-speed evacuation system should be employed when such procedures are performed intraorally. Patients should be informed of the potential allergic effects of nickel exposure, and a thorough medical history should be taken to determine if the patient is at risk of exhibiting an allergic reaction to nickel. As a conservative approach, one should adopt the policy that evidence of a previous allergic response to any alloy should be sufficient grounds to reject the use of nickel-based alloys.

To ensure the safety of patients, dentists, dental office staff, and dental technicians, manufacturers and laboratory managers should identify the alloys and alloy components used in the fabrication of prosthetic devices in terms of elements that may affect the health of individuals (e.g., nickel, chromium, cobalt, beryllium, and palladium). Dentists and administrators of dental laboratories should be encouraged to inform employees who work as technicians of the need to avoid inhalation of dusts and vapors from alloys. Practitioners are encouraged to document in patient records the contents, batch number (if available), and specific brand name of alloys used in restorative materials. Health histories should include documentation of patients who are allergic to metals. Patch testing for sensitivity to metals should not be performed by dentists but by professionals trained in the administration and interpretation of these tests. Practitioners and manufacturers are encouraged to report case histories of adverse reactions to metals and other biomaterials to reporting agencies in their countries.

CRITICAL QUESTION

What are the differences between soldering, brazing, and welding?

JOINING OF DENTAL ALLOYS

There are three categories of metal-joining operations: soldering, brazing, and welding. The soldering and brazing process involves the metallic components (also called substrate metals) to be joined, a filler metal (usually called solder), a flux, and a heat source. The primary difference between soldering and brazing is that brazing requires a heating temperature above 450 °C and soldering is conducted below that temperature. Both processes are performed below the solidus temperature of the substrate metal or metals. The word *soldering* is used in this section as a general term to describe both processes. Welding may not require a filler metal since the metal surfaces to be joined will melt and fuse locally. The common characteristic of these operations is the achievement of bonding between the workpieces and/or the filler metals by a controlled heating procedure.

Metal joining processes in dentistry are traditionally dominated by the gold-based alloys. Therefore, soldering (or brazing) using a flame torch is the main operation in metal joining. With the new nongold alloys—such as alloys for orthodontic appliances and palladium-based and base metal alloys for dental castings, the requirements of the metal-joining process differ among metals and appliances made of these metals. For example, titanium alloys oxidize readily at elevated temperatures and all high-temperature heating processes require an oxygen-free environment and a nonoxygen heating source.

Spot welding based on electrical resistance has been used to weld orthodontic appliances. New advances in the technology of heating sources have also been adapted for dental applications. They include the plasma torch, Nd:YAG laser, and tungsten inert gas (TIG) arc. The advantages of these technologies are that the area of heating is small—it can be as little as 0.2 mm with the laser and TIG—and the duration of heating can be controlled. When the area of heating is very small, the thermal conductivity of the alloy can be of concern, since the energy provided must not only melt the substrate metal but also compensate for the loss of energy from thermal conduction of the metal. This mode of heating is advantageous for Co-Cr and titanium alloys, which have lower thermal conductivities than gold-based alloys.

Although the advantages of modern heating sources shift the operation of metal joining in dental laboratories toward welding, gold soldering is a simpler procedure that can be conducted in the dental office. It is the focus of this section.

? CRITICAL QUESTION

What materials and methods can be used to enhance or restrict the flow of solder?

SOLDERING FLUX

A metal surface free of any contaminant, such as oxides, is essential for the molten solder to wet the substrate metals. A flux is used to reduce this oxide, inhibit further oxidation, and facilitate its removal. The composition and cleanliness of the substrate metal and the temperature to which it is heated determine the wettability of the substrate by the molten solder alloy. The solder chosen must wet the metal at as low a contact angle as possible to ensure wetting of the joint area. To prevent flow of molten solder onto adjacent areas, an **antiflux** such as rouge mixed with chloroform or graphite can be painted on these areas before heating substrate metals. There are three types of fluxes according to their primary purpose:

Type I. Surface protection—covers the metal surface and prevents access to oxygen so that no oxides can form.
Type II. Reducing agent—reduces any oxides present and exposes clean metal.
Type III. Solvent—dissolves any oxides present and carries them away.

Fluxes for use with noble metal alloys are generally based on boric acid, boric anhydride, and borax. Chromium oxides that form on base metal alloys are more stable and fluoride-containing fluxes are used as solvents to dissolve chromium, nickel, and cobalt oxides. Fluxes also come in temperature ranges for optimal activity. For example, a flux designed for joining metal-ceramic alloys before firing porcelain, which is known as ***presoldering*** (or prebrazing), will be subjected to a higher soldering temperature than that for joining metal-ceramic after sintering the veneer porcelain, which is known as ***postsoldering*** (or postbrazing).

It is of primary importance to minimize the amount of flux used. Entrapment of flux within the filler metal can cause a weakened joint. Residual flux that is covered with porcelain can cause discoloration and bubbling of the porcelain. Flux combines with metal oxides and forms a glass during the soldering process, and the residue should be removed. Sandblasting the joint immediately after removal from the soldering investment with alumina abrasive particles and boiling in water for about 5 minutes are recommended.

The manufacturer is responsible for providing explicit instructions for eliminating the oxide layer during the joining process. The instructions should also include a recommendation for the appropriate filler metal and flux for each alloy. For metal-ceramic alloys, the recommendation should also identify filler metals to be used before and after firing porcelain.

FILLER METAL FOR SOLDERING (BRAZING)

The filler metal must be compatible with the nonoxidized substrate metal, but it does not necessarily need a similar composition. Compatibility requirements include (1) a sufficiently low flow temperature, (2) the ability to wet the substrate metal, and (3) sufficient fluidity at the flow temperature. Other properties considered important are acceptable color, adequate hardness, strength, and tarnish and corrosion resistance.

Flow Temperature

When the filler metal melts (liquefies), wets, and flows on the substrate metal, it bonds the solder (or brazing alloy) to the

workpiece substrate. The flow temperature of the filler metal is usually higher than its liquidus temperature. The flow temperature of the filler metal should be at least 55.6 °C lower than the solidus temperature of the substrate metals. For a presoldered alloy substrate that will be veneered with porcelain later, the melting-range of the filler metal should be higher than the sintering temperature of the porcelain. This condition avoids remelting the filler metal and prevents sag deformation of bridge frameworks during subsequent porcelain firing.

Temperature and time control the diffusion of atoms across the filler-substrate interface. Even if the flow temperature of the filler metal is not too high, alloying can take place by diffusion if the temperature remains constant for a sufficiently long time. An alloy formed at the interface through diffusion can have properties different from those of the filler metal and the substrate metal. As shown in Figure 16-5 for a nickel-based alloy with a gold filler metal, the resultant diffusion process can form an alloy of gold and nickel that can begin to melt at 950 °C. Such an alloy can then melt during the firing of porcelain and lead to distortion of the prosthesis, as demonstrated for a soldered bar at the top of Figure 16-6. For this reason, gold-based filler metals should not be used as a presolder for base metal alloys.



FIGURE 16-5 Micrograph showing alloying at the interface between a gold-alloy solder metal and a base metal substrate (×100). (Courtesy of C. E. Ingersoll.)

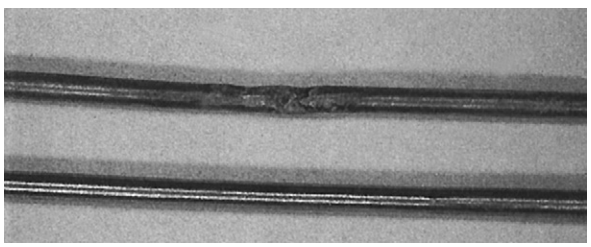


FIGURE 16-6 A sag test in which soldering (brazing) of a nickel-based alloy with a gold-based soldering alloy (*top*) produced a gold-nickel diffusion zone. The soldered rod has sagged as compared with the nonsoldered rod (*bottom*). (Courtesy of C. E. Ingersoll.)

The soldered joint represents a compromise in the structure of the prosthesis. If the flow temperature of the filler metal is close to or above the solidus temperature of either substrate metal, alloying can take place during the soldering process. Figure 16-7 shows such a soldered joint between two different substrate metals. On the left side, the filler-substrate interface is represented by a sharply defined plane. On the right side, the substrate metal appears to have melted and alloyed with solder at the joint surface adjacent to the nodular area (to the right of the solder boundary).

Wetting

Wetting of the substrate metal by the filler metal is essential to produce a bond. Figure 16-8 shows that when pure silver is melted on nickel or nickel-based alloys, it forms a spherical shape (poor wetting), as seen on the right side. In contrast, when pure silver is melted on gold and Pd-Ag alloys, it spreads over the surface (good wetting). Oxides have poor wettability characteristics; therefore, molten metal does not spread on the oxide layer of substrate metals.

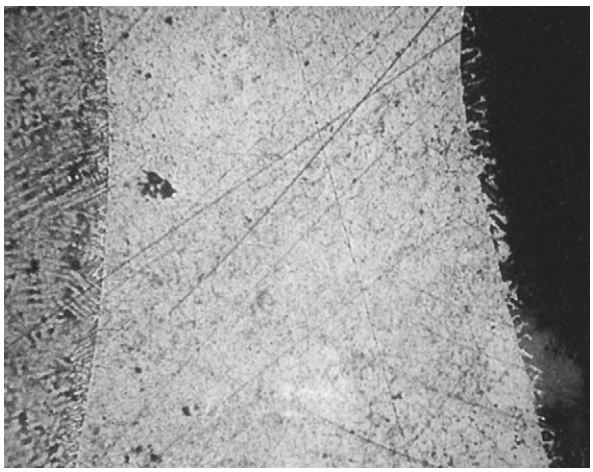


FIGURE 16-7 Joining of two different substrate metals with the filler metal (*in center*). Left: Good bonding with no alloying between the filler metal and substrate metal. Right: A nodular region of alloying that has occurred at the interface between the filler metal and another substrate alloy, which is not distinct in this micrograph. (Courtesy of C. E. Ingersoll.)

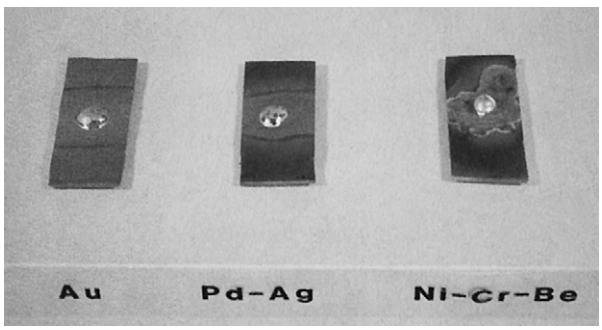


FIGURE 16-8 Pure silver melted on three different alloys. It wets the gold (Au) alloy and palladium-silver (Pd-Ag) alloy but does not flow onto the surface of the base metal (Ni-Cr-Be) alloy. (Courtesy of C. E. Ingersoll.)

Fluidity

Molten filler metals should flow freely into the gap between the two substrate metals. When the surface of a metal prosthesis needs to be extended such as for a deficient interproximal contact area, a filler metal can be used to build up the area. A relatively sluggish fluid filler metal then becomes desirable. This type of filler usually has a wide range of melting temperatures and flow can be controlled to well-defined areas.

? CRITICAL QUESTION

How can one best assess if the quality of a solder joint is acceptable or not?

HEAT SOURCES FOR SOLDERING

The most common instrument for the application of heat is a gas-air or gas-oxygen torch. Another source of heating is a furnace that heats the assembled substrate metals along with flux and solder deposited at the joining site to appropriate temperature for melting and flow of solder.

All gases shown in Table 16-15 have potential flame temperatures high enough to melt any dental casting alloy currently in use. The thermal energy (heat content measured in calories per cubic meter of the fuel) from combustion of the fuel must not only raise the temperature of both the substrate metal and the filler metal to the soldering temperature but also compensate for heat loss to the surroundings. Fuel with a lower heat content requires a longer period of heating at the desired temperature and is associated with increasing danger of oxidation during the soldering process.

Hydrogen

The low heat content of hydrogen indicates that heating is a slow process with hydrogen as a fuel. It may be impossible for a hydrogen flame to heat the joining area of a large bridge to the temperature required for presoldering.

Natural Gas

Usually, natural gas is not uniform in composition and frequently has water vapor in it. The heat content is comparable to that of dry natural gas. Water vapor cools the flame, and this may result in a need for more time to properly melt alloys during the casting process.

TABLE 16-15 Thermal Characteristics of Fuel Gas Combustion

Fuel	Flame Temperature (°C)	Heat Content (kcal/m^3)
Hydrogen	2,660	2,362
Natural gas	2,680	8,898
Propane	2,850	21,221
Acetylene	3,140	12,884

Acetylene

The variation in temperature from one part of an acetylene-oxygen flame to another may be more than 100 °C, which makes the positioning of the torch critical, so that the proper zone of the flame is used. Acetylene is also a chemically unstable gas that readily decomposes to carbon and hydrogen. Carbon can be incorporated into both nickel and palladium solders, resulting in adverse effects on the mechanical properties of the solder joint. Hydrogen can be absorbed by palladium-based alloys, and this can result in increased casting porosity. Only individuals with extensive experience with this gas should consider its use for metal joining procedures.

Propane

Of the fuel gases in Table 16-15, the best choice is propane. Butane, which is more readily available in some parts of the world, has a similar flame temperature and heat content as propane. Both propane and butane have the advantage of being relatively pure compounds; therefore, they are uniform in quality are virtually water-free, and burn cleanly (provided that the torch flame is properly adjusted).

Furnace Soldering

A furnace should be chosen with enough wattage to provide the heat required to raise the temperature of the filler metal to its flow point. The furnace will also provide a high-temperature environment, so less heat is lost to other parts of the appliance or to the ambient atmosphere than with torch soldering. Before the assembled substrate metals are placed into the oven, a uniform coating of a paste flux should be applied to the surface to be soldered. The advantage of furnace soldering is that every component can be heated and cooled uniformly in accordance with a precise schedule that prevents distortion, which might occur under localized heating, such as during soldering of metal-ceramic bridges.

? CRITICAL QUESTION

Which type of torch gas should be used for soldering noble alloys? Why can't all torch gases be used?

TECHNIQUE CONSIDERATIONS FOR SOLDERING

For fixed prostheses, where accurate alignment is needed, the parts to be joined are first indexed and joined by a temporary material like acrylic resin or sticky wax. The indexed assembly is then mounted in a soldering investment, which hardens and holds the parts together during the soldering procedure. This process is called investment soldering. In assembling orthodontic and other appliances, the parts to be joined are manually held in contact during the soldering procedure. As soon as the filler metal has flowed to position, the heating is discontinued and the appliance is cooled. This process is called free-hand soldering.

The investment soldering technique involves several critical steps: (1) cleaning and preparing the surfaces to be joined, (2) assembling the parts to be joined, (3) preparation and

fluxing of the gap surfaces between the parts, (4) maintaining the proper position of the parts during the procedure, (5) control of the proper temperature, and (6) control of the time to ensure adequate flow of solder and complete filling of the solder joint.

Other factors that may influence the result of soldering are described below.

Gap Width

The optimal gap between parts of substrate metal to be joined has never been precisely defined. If the gap is too great, the joint strength will be dictated by the strength of the filler metal. If the gap is too narrow, flux inclusions and porosity caused by incomplete flow of the filler metal may occur and lead to decreased strength. Inclusions or porosity can lead to distortion if any heating, such as porcelain application, takes place after the soldering operation.

The two bars shown in Figure 16-9 are of the same nickel-based alloy. The gap for the upper bar was 1.0 mm, whereas the gap for the lower bar was 0.3 mm. Both bars were soldered with the same filler metal. The upper bar failed in the filler metal. The lower bar failed in the substrate metal even though the tensile strength of the substrate metal was greater than that of the filler metal.

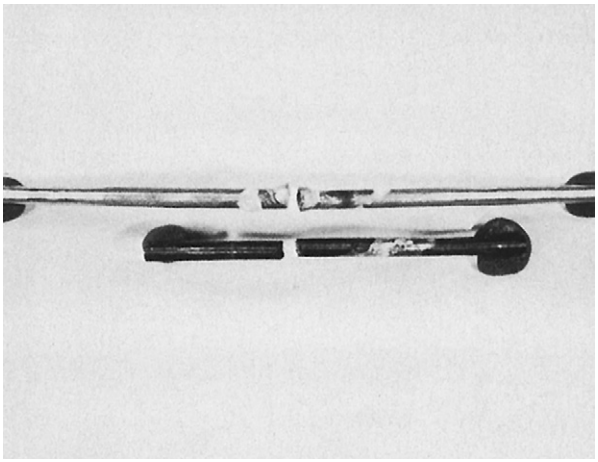


FIGURE 16-9 The two bars are of the same nickel-based alloy that were cut into halves and soldered together at the cut. The gap width was 1.0 mm for the upper bar and 0.3 mm for the lower bar. When it was tested to failure under tension, the upper bar, with a large gap width, failed within the filler metal. The lower bar, with a proper gap, failed in the substrate metal. (Courtesy of C. E. Ingersoll.)

Flame

A torch flame can be divided into four zones, as shown in Figure 16-10. The portion of the flame used to heat the soldering assembly should be the tip of the reducing zone, in which the most efficient burning process occurs and the most heat is generated. An improperly adjusted torch or improperly positioned flame can lead to oxidation of the substrate or filler metal and result in a poor solder joint. It is also possible to introduce carbon into the substrate and filler metal by using the unburned gas portion of the flame. To prevent oxidation, the flame should not be removed once it has been applied to the joint area until the soldering process has been completed. The flame provides protection from oxidation, especially at the soldering temperature.

Temperature and Time

The flame or furnace chamber should provide enough heat to the substrate metal to reach the flow temperature of the filler metal. Thus, the substrate metal will be hot enough to melt the filler metal as soon as the filler metal contacts the area to be joined.

The flame should be maintained in place until the filler metal has flowed completely into the connection and a moment longer to allow the flux or oxide to separate from the fluid filler metal.

? CRITICAL QUESTION

What kind of heating source and surrounding environment are needed for joining titanium components?

LASER WELDING OF COMMERCIALLY PURE TITANIUM

Commercially pure titanium is a highly reactive metal that forms oxides readily in air. At temperatures used for soldering procedures, the thickness of the titanium oxide layer increases and it may spontaneously debond from the parent metal surface at temperatures exceeding 850 °C. Thus the quality of the soldered joint is quite variable if a traditional torch-soldering or oven-soldering procedure is used.

Laser welding in an argon gas atmosphere is a method of choice for joining titanium components of dental prostheses, because the coherent, high-intensity laser pulse of light can be focused in a small region and melt the substrate without extensive microstructural damage to the surrounding areas. An advantage of welding is that the joint will be composed of the same pure titanium as the substrate components, thereby preserving the excellent biocompatibility potential of CP Ti

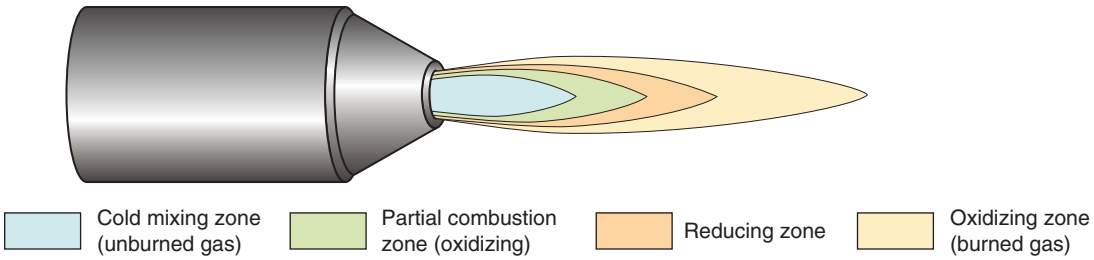


FIGURE 16-10 Flame zones in a propane-oxygen torch flame.

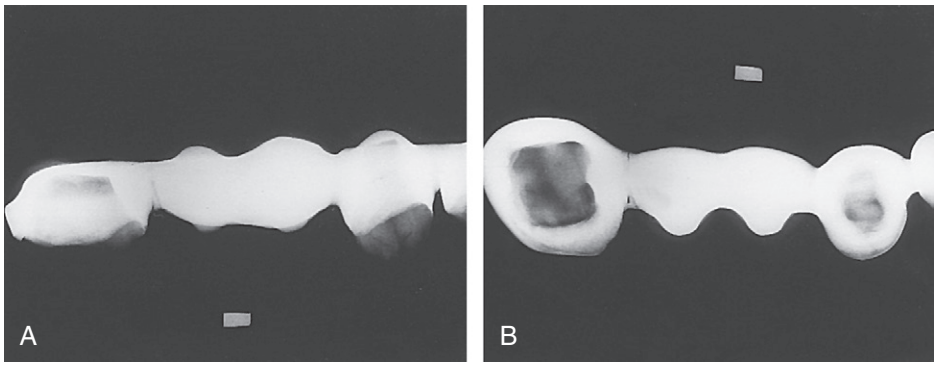


FIGURE 16-11 **A,** Buccolingual radiographic image of metal framework designed for a metal-ceramic fixed partial denture (bridge). **B,** Occlusogingival view. Note the radiolucencies at the buccal and lingual aspects of the posterior soldered connector (**A**).

and avoiding the risk of galvanic corrosion effects within the prosthesis.

Commercial laser welding units consist of a small type of glove box that contains the laser tip, an argon gas source, and a stereomicroscope with lens crosshairs for precise alignment of the laser beam with the CP Ti components. The maximum penetration depth of these laser welding units is 2.5 mm. Since only a small amount of heat is generated, the parts can be handheld during the welding procedure, and welding can be performed close to ceramic or polymeric veneers without causing damage to these materials. This procedure can be used for Co-Cr and Ni-Cr alloys.

RADIOGRAPHIC ANALYSIS OF SOLDER JOINT QUALITY

The presence of solder joint defects, such as porosities and flux inclusions can be identified by a radiographic examination of the joined area. The simplest method is to lay the structure on an unexposed piece of intraoral x-ray film and expose the film with an x-ray beam, using an accelerating voltage of 90 kV and a current of 10 mA for 1 second. Another film should be exposed after rotating the fixed partial denture at a 90° angle to the initial orientation. Shown in Figure 16-11 are radiographic images of a metal-ceramic framework. One can clearly see the radiolucent flaws at the buccal and lingual aspects of the distal (most posterior) presoldered connector, whereas the cast metal in the mesial embrasure area is sound.

ACKNOWLEDGEMENTS

The authors wish to acknowledge Dr. Paul Cascone for his previous contribution to this chapter.

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The study shows posterior three-unit FPDs incorporating milled zirconia frameworks exhibited larger internal gaps than those constructed using conventional metal-ceramic techniques.

CHAPTER
17

Wrought Metals

OUTLINE

Deformation of Metals

Effects of Annealing Wrought Metal

Stainless Steel Alloys

Cobalt-Chromium-Nickel Alloys

Nickel-Titanium Alloys

Beta-Titanium Alloys

Additional Wrought Alloys

Direct Filling Gold

KEY TERMS

Annealing—The process of controlled heating and cooling that is designed to produce desired properties in a metal. Typically, the annealing process is intended to soften metals, to increase their ductility, stabilize shape, and increase machinability (see *stress relief*). In the case of gold foil, the term refers to removal of contaminant from the surface of the foil.

Cold welding—The process of joining metals by metallic bonding. The metal-joining process does not occur by heating or fusion but by pressure applied to the interface between the two parts to be joined; no liquid or molten phase is produced witihn the interface joint.

Cold working—The process of plastically deforming metal at room temperature.

Compaction (condensation)—The process of increasing the density of metal foil, pellets, or powder through compressive pressure.

Degassing—The process of removing gases (or other impurities) from the surface of a solid or liquid, usually by heating.

Desorption—The process of removing molecules that have attached to the surface of a solid by a physical or chemical action; it is a broader term than *degassing*.

Dislocation—An imperfection in the crystalline arrangement of atoms consisting of either an extra partial plane of atoms (edge dislocation), a spiral distortion of normally parallel atom planes (screw dislocation), or a combination of the two types.

Ductility—The ability of a solid to be elongated or thinned plastically without fracturing.

Ductile fracture—The rupture of a solid structure resulting in measurable plastic deformation.

Grain growth—The increase in the mean crystal size of a polycrystalline metal produced by a heat-treatment process.

Grain refinement—The process of reducing the crystal (grain) size in a solid metal through the action of specific alloying elements or compounds.

Interstitial atom—An imperfection in a crystal lattice consisting of an extra atom located between the adjacent atoms in normal lattice sites.

Malleability—The ability (of a metal) to be hammered into thin sheets without fracturing.

Point defect—A lattice imperfection of atomic size in three dimensions, such as a vacancy, divacancy, trivacancy, or interstitial atom.

Precipitation hardening—The process of strengthening and hardening a metal by precipitating a phase or constituent from a saturated solid solution.

Recovery—A stage of heat treatment that results in the partial restoration of properties of a work-hardened metal without a change in the grain structure.

Recrystallization—The process of forming new stress-free crystals in a work-hardened metal through a controlled heat-treatment process.

Springback—The amount of elastic strain that a metal can recover when loaded to and unloaded from its yield strength; an important property of orthodontic wires.

Strain hardening—The increase in strength and hardness and decrease in ductility of a metal that is caused by plastic deformation below its recrystallization temperature; also called work hardening.

Stress relief—The reduction of residual stress by heat treatment.

Superelasticity—The ability of certain nickel-titanium alloys to undergo extensive deformation resulting from a stress-assisted phase transformation, with the reverse transformation occurring on unloading; sometimes called pseudoelasticity.

Vacancy—An imperfection in a crystal lattice consisting of an unoccupied atom site.

Work hardening—See *strain hardening*.

Working range—The maximum amount of elastic strain that an orthodontic wire can sustain before it plastically deforms.

Wrought metal—A metal that has been plastically deformed to alter the shape of the structure and certain mechanical properties, such as strength, hardness, and ductility.

Whenever a cast pure metal or alloy is permanently deformed in any manner it is considered a ***wrought metal***. Because of plastic deformation, the microstructure of an alloy is altered and the alloy exhibits properties that are different from those it had in the as-cast state. The most significant changes are its proportional limit and **ductility**, which will be discussed later. The applications of wrought metals in dentistry include orthodontic wires, clasps for removable partial dentures, direct-filling gold, root canal files and reamers, preformed crowns in pediatric dentistry, and surgical instruments. The primary metals are wrought noble alloys wrought metals are mostly base metal alloys, such as stainless steel, cobalt-chromium-nickel, nickel-titanium, and beta-titanium. Some wrought noble alloys are also available.

Objects of any design, intricate or simple, can be produced by using the lost-wax technique as long as a pattern can be formed in a wax and embedded in an investment material or alternative processing techniques such as CAD/CAM milling and thee-dimensional printing. On the other hand, objects of a simpler configuration, such as round orthodontic wire, can be made easily by drawing a cast alloy through a series of dies, with intermediate heat treatments to eliminate the effects of severe **work hardening** (discussed later) before the next step of drawing.

Many accessory dental materials and instruments are fabricated from cast alloys that have been rolled to form sheets or rods, drawn into wire or tubing, or forged into a finished shape. Forging is the process of plastically deforming heated metals in a die under compressive pressure. If one considers the many metallic articles encountered in everyday life, most are wrought metals and not castings.

Direct filling gold, also called gold foil, is a metallic restorative material that relies on its ductility and **malleability** to adapt to a cavity preparation. The restorative process requires **condensation** that makes the final restoration practically a wrought metal. The goal of this chapter is to become familiar with the process of plastic deformation and its effect on the properties of pure metals and alloys that leads to their specific application in dentistry. Several types of wrought metals used in dentistry are described. In this chapter, the terms *metal* and *alloy* are frequently used interchangeably. In cases where the topic specifically refers to pure metals, this distinction is noted.

CRITICAL QUESTION

Why does the ductility of a pure metal depend on its crystal structure?

DEFORMATION OF METALS

In Chapter 4, the principles of elastic and plastic deformation are described relative to their effect on mechanical properties. For example, when the stress induced by an applied tensile force is below the proportional limit, the separation between metal atoms is increased a very small amount from the equilibrium interatomic spacing in the crystal structure (Chapter 2). Plastic deformation occurs when the applied stress increases above the elastic limit. We often use the proportional limit as the property of interest here, since it can be determined easily from stress-strain plots and its value is slightly lower than its elastic limit (Chapter 4). Yield strength, which is slightly greater than the elastic limit, is used when the proportional limit is not well defined. When this force is reduced, the interatomic separation returns toward its equilibrium value. However, once the proportional limit of a metal is exceeded at a sufficiently high applied force, permanent (plastic) deformation of the metal occurs. Some alloys, such as dental amalgams, will undergo brittle fracture rather than a significant amount of permanent deformation, as noted in Chapters 4 and 15. Only the elastic strain is recovered after loading is released from a metal that has been loaded beyond its proportional limit.

THEORETICAL AND OBSERVED SHEAR STRENGTHS OF METALS

An atomic model illustrating permanent deformation of a metal of perfect crystalline structure subjected to an applied shear stress is illustrated in Figure 17-1. Notice that the deformation or slip process requires the simultaneous displacement of plane A atoms relative to the plane B atoms. If the elastic modulus in shear is known for a given metal, this model can be used to calculate the maximum theoretical shear strength. However, studies have shown that theoretical shear strengths are much higher than those observed from

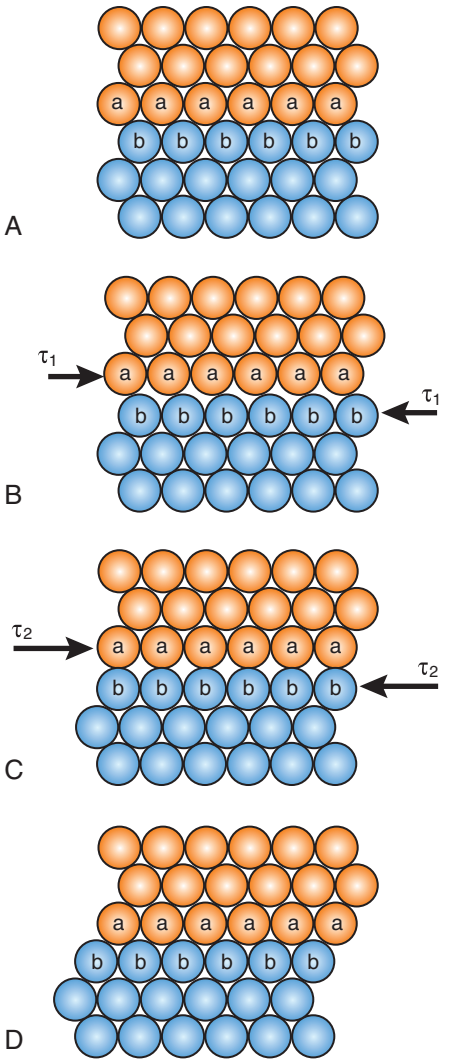


FIGURE 17-1 Slip between adjacent planes of atoms. **A**, A solid subjected to shear stress (τ). Planes A and B are adjacent. **B**, The configuration of planes A and B when the solid is not stressed. χ is the direction of movement. **C**, Application of a shear stress τ_1 causes plane A to move with respect to plane B. **D**, Increasing the shear stress to τ_2 increases the relative lateral displacement of the two planes. This configuration corresponds to the state of maximum stored elastic energy. **E**, The two planes have been displaced by one interatomic distance r_0, shown in **B**, with respect to each other. This configuration will be maintained if the load is removed. If the shear stress (τ_2) remains, the planes will continue to slip past each other.

mechanical testing of polycrystalline metals. For example, the differences for copper and iron are approximately 40 times greater and can be as much as 190 times greater for SiC (Table 17-1). The table also shows that only whisker specimens, which are very thin single crystals of pure materials that have near perfection in their atomic lattice, exhibit shear strengths approaching their theoretical values. The key difference between whiskers and bulk polycrystalline specimens of the same material is the presence of crystal imperfections at the atomic level in the bulk material.

? CRITICAL QUESTION

Why are the observed strengths of metals always lower than the theoretical strengths?

CRYSTAL IMPERFECTIONS

Crystallization (Chapter 5) from starting nuclei during solidification of a metal does not occur in a regular fashion of atomic plane by atomic plane; instead, growth is likely to be random and imperfect. When lattice positions have missing atoms, displaced atoms or extra atoms, they are called **point defects**. The edge of an extra plane of atoms in the crystal is called a line defect. The boundaries between crystals or the external surface of the crystal are also considered imperfections in the crystal.

Point Defects

A **vacancy** or vacant atom site in a crystalline lattice may occur at a single site in the atomic arrangement (Figure 17-2, *A*), and two vacancies may condense as a divacancy (Figure 17-2, *B*); a trivacancy may also exist. An **interstitial atom** is illustrated in Figure 17-2 ,*C*. Vacancies and other point defects are equilibrium defects, and a crystalline material that is in equilibrium will contain a certain number of these defects at a given temperature. The most important point defects are vacancies, which provide the principal mechanism for atomic diffusion in crystalline materials.

Line Defect (Dislocations)

The simplest type of line defect, known as an edge **dislocation**, is illustrated in Figure 17-3, *A*, for a simple cubic structure. It can be noted that the atomic arrangement is regular except for the single vertical plane of atoms that is discontinuous. The edge dislocation (symbolized by ⊥) is located at the edge of the half plane.

If a sufficiently large shear stress is applied across the top and bottom faces of the metal crystal in Figure 17-3, *A*, the bonds in the row of atoms adjacent to the dislocation will be broken and new bonds with the next row will be established, resulting in movement of the dislocation by one interatomic distance, as indicated in Figure 17-3, *B*. Continued application of this shear stress causes similar movements of one interatomic distance until the dislocation reaches the boundary of the crystal. The plane along which an edge dislocation moves is known as a slip plane. It can be seen in Figure 17-3, *C*, that the result of this dislocation movement across the crystal is that the atomic planes on one side of the slip plane have been displaced one interatomic spacing (one unit of slip) with respect to the atomic planes on the other side of the slip plane. The crystallographic direction in which the atomic planes have been displaced is termed the *slip direction*, and the combination of a slip plane and a slip direction is termed a *slip system*.

The inherent ability of a metal to deform plastically is generally dependent on the number of slip systems associated with the crystal structure. For example, the face-centered

TABLE 17-1 Theoretical and Observed Shear Strength

Materials	Shear Modulus (GPa)	Observed Ultimate Shear Strength* (MPa)	Calculated Ultimate Shear Strength (GPa)	Observed Ultimate Shear Strength† (GPa)
Copper	48	220	7.7	2.1
Iron	80	290	12.4	9.5
Nickel	76	480	—	2.7
Al_2O_3	170	—	12.1	14.6
BeO	140	280 (tension)	21.7	9.2
SiC	200	170 (tension)	32.3	14.6

*Polycrystalline.
†Whisker; the shape of the whiskers is not conducive to shear testing.
The tabulated values were calculated from tensile strength data given by Broutman IJ and Krock RH: *Modern Composite Materials,* Reading, MA, Addison-Wesley, 1967. From Eisenstadt M: *Introduction to Mechanical Properties of Materials.* Upper Saddle River, NJ, Prentice-Hall, Inc, 1971.

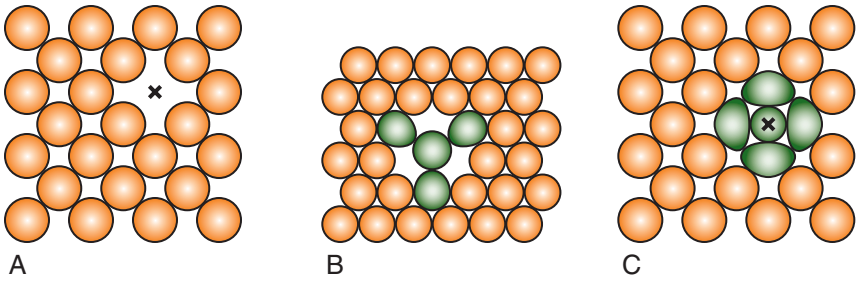


FIGURE 17-2 Point defects. **A**, Vacancy. **B**, Divacancy (two missing atoms). **C**, Interstitial (extra atom). Different colors are used to show that the atoms have been distorted by adapting to the space available. (Adapted from Van Vlack LH: *Elements of Materials Science*, ed 4, Reading, MA, Addison-Wesley, 1980.)

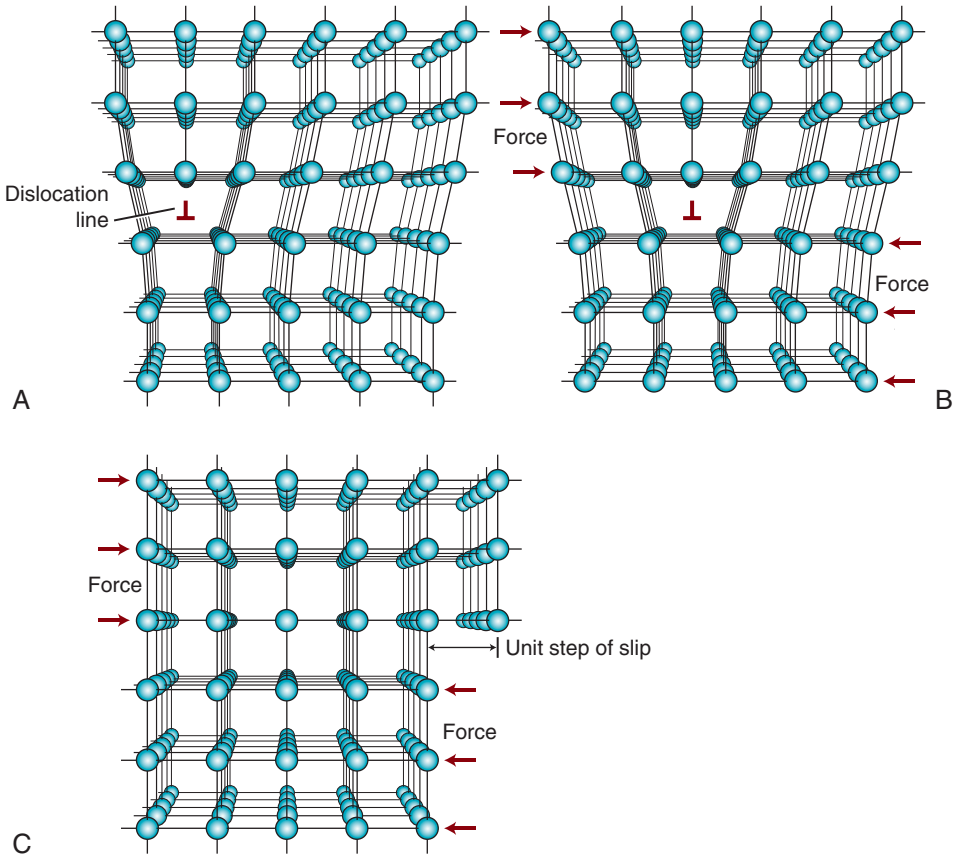


FIGURE 17-3 **A**, An edge dislocation in a schematic cubic crystal structure. **B**, The dislocation has moved one interatomic distance along the slip plane under the action of the shearing force indicated by the arrows. **C**, The dislocation has reached the edge of the crystal, and a unit amount of slip has been produced. (Adapted from Guy AG: *Elements of Physical Metallurgy*, ed 2, Reading, MA, Addison-Wesley, 1959.)

cubic (fcc) structure has the largest number of slip systems, and metals with this crystal structure—such as gold, silver, copper, platinum, palladium, and nickel—are highly ductile. The hexagonal close-packed (hcp) structure of metals, such as zinc, has far fewer slip systems, and these metals have very low ductility. The body-centered cubic (bcc) structure has fewer slip systems than those of the fcc structure but more than hcp; metals with the bcc crystal structure have intermediate levels of ductility.

It is evident that much less shear stress is required to cause permanent deformation of the metal crystals that contain edge dislocations (Figure 17-3), since only one row of atomic bonds is broken at a time, compared with the perfect crystal, where all rows of atomic bonds across the two planes (Figure 17-1) must be simultaneously broken for shear deformation to occur. This accounts for the difference in Table 17-1 between the values of theoretical shear strength for a dislocation-free metal whisker and a polycrystalline metal containing dislocations. The proportional limit for a metal generally corresponds to the onset of significant movement of dislocations. The slip lines in Figure 17-4 correspond to slip planes where large numbers of dislocations exit the metal, causing surface offsets that scatter the light used for observation. Thus, one can conclude that plastic deformation of metal is the result of dislocation movement and slip between atomic planes.

? CRITICAL QUESTION

What fundamental strengthening mechanisms are available for alloys that are not possible for pure metals?

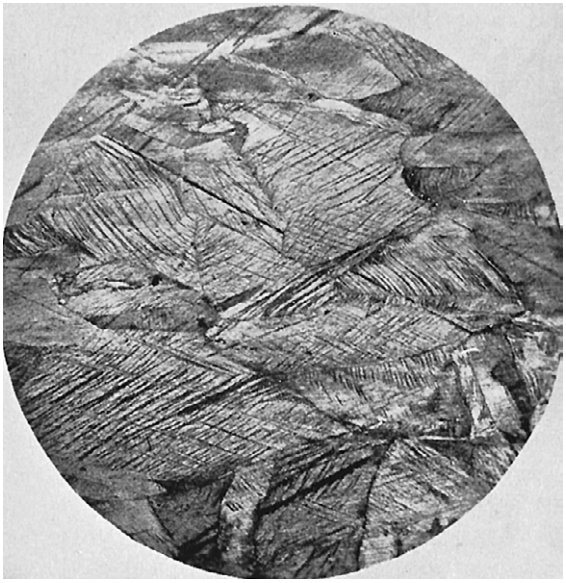


FIGURE 17-4 Photomicrograph of cold-worked gold, showing deformed grains and slip lines (the parallel lines within grains) at surface offsets where dislocations have exited their slip planes (×100). (Courtesy of S. D. Tylman.)

DISLOCATION MOVEMENT IN POLYCRYSTALLINE ALLOYS

Figures 17-3 and 17-5, *A*, illustrate one dislocation moving in a pure metal crystal; it appears that there is little hindrance of a moving dislocation along its slip plane. In reality there are several scenarios in which dislocation movement can be impeded in pure metals and alloys. Alloys contain multiple phases, such as solid solutions and/or precipitates (Chapter 5), in addition to the numerous dislocations and grain boundaries found in pure metals. These crystal structural features represent obstacles that may be overcome by an application of increased stress to promote dislocation movement.

For solid solution alloys, the atomic arrangement near solute atoms is locally distorted. The movement of dislocations along the slip plane will be impeded by the presence of such solute atoms (Figure 17-5, *B*). Precipitates can be coherent, where the atomic bonds are continuous across the interface with the solid solution matrix, or incoherent, where interatomic bonds are not continuous across the interface. Coherent precipitates generate localized distortion in the atomic arrangement and have the same crystal structure as the matrix phase. Dislocations cannot move through incoherent precipitates but instead form loops of increasing size around these particles (Figure 17-5, *C*). Additional stress is needed to move dislocations through distorted regions, including coherent precipitates, or around incoherent precipitates.

Metals with a reasonable amount of ductility can be permanently deformed under mechanical stress at temperatures below their **recrystallization** temperatures, discussed later. This process, also known as **cold working**, can create vast numbers of point defects and dislocations within the metals. These dislocations will interact with each other, mutually impeding their movements. Increased stress is required for further dislocation movement to continue the permanent deformation process.

It is difficult for a dislocation to pass into another grain, especially if the adjacent grain is misaligned (Figure 17-6). Grain boundaries represent the end of slip planes where dislocations cease to move and accumulate. As the grain size decreases, there will be more grain boundary area per unit volume to impede dislocation motion. Grain size can be controlled by rapid cooling or quenching (Chapter 5) or by inclusion of a grain refiner (Chapter 16), such as beryllium in Ni-Cr-Be alloys. Cold working also alters the shapes of grains significantly (i.e., the grains may be severely elongated parallel to the wire axis).

A higher stress, which is reflected in higher values of proportional limit, is needed for dislocations to overcome each impeding mechanism to continue moving along the slip plane. Because of the increase in the proportional limit, these obstacles are also considered a mechanism for strengthening of metal alloys. These mechanisms provide the basis for solid solution strengthening, **precipitation hardening**, strain (or work) hardening, and **grain refinement** strengthening. While the proportional limit and yield strength

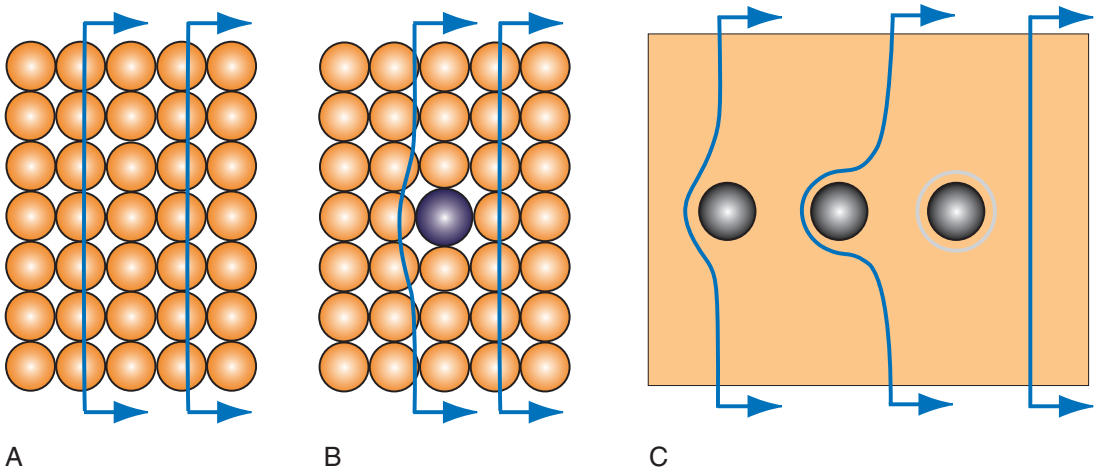


FIGURE 17-5 Movement of a dislocation. The illustrations depict the view taken from the top of the 3-D model shown in Figure 17-3. Each line with right-pointing arrows represents a line defect (dislocation) moving toward the right side of the grain. **A,** A dislocation moves without any impediment within a grain; no extra effort is needed and no strengthening effect occurs. **B,** The darker and slightly larger sphere represents a solute atom or coherent precipitate that presents an obstacle to the movement of the dislocation; bending of the line defect implies that the movement has been impeded and more stress is needed to pass through the obstacle. **C,** The dark spheres represent incoherent precipitates and the background simulates the rest of the grain. The dislocation cannot pass through the incoherent precipitate, since it does not share the same lattice with the hosting grain. The first dislocation (*left*) bends as it moves close to the precipitate. The second dislocation (*middle*) continues to bend around the precipitate while the rest of the dislocation keeps moving toward the right. Finally, the dislocation (*right*) completes its encircling around the precipitate; the rest of the dislocation rejoins and moves on through the nonstrengthened area.

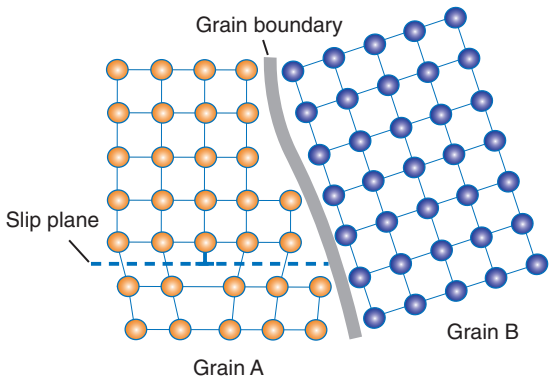


FIGURE 17-6 This illustration shows the spatial lattice of two adjacent grains. Notice that the lattices are not aligned. There is a dislocation moving toward the grain boundary in grain A. Because of misalignment, dislocation in grain A cannot move into grain B but it is trapped at the grain boundary. In essence the grain boundary is an obstacle to dislocation movement. Therefore, the greater the number of grain boundaries the higher is the yield strength of the material.

increase with wrought alloys, the elastic moduli of the for alloys remain the same since there are no changes in the crystalline structure. If phase changes have occurred because of plastic deformation, some changes in the elastic moduli are expected.

? CRITICAL QUESTION

Why does the clasp of a removable partial denture fracture easily after a patient has bent it back and forth repeatedly to relieve discomfort?

EFFECTS OF STRENGTHENING METALS

Based on the principle that impeding the movement of dislocations strengthens cold-worked metals, it follows that the hardness, yield strength, and proportional limit are increased with each of the strengthening mechanisms just described, whereas the ductility is decreased. The corrosion resistance is also decreased for a permanently deformed metal, since the dislocations produce localized regions of strain at the atomic level, which have higher energy than atomic arrangements in the undeformed metal. Corrosion is a process of relieving stored energy (Chapter 3), and it can be minimized by **stress relief** (discussed later).

One can visualize the effects of severe cold working on the grain structure of a copper-zinc alloy (brass). This is shown in the first row of photomicrographs (longitudinal sections) of Figure 17-7, where rolling of the metal took place in the plane perpendicular to the plane of these photomicrographs. One can observe that the thinner the specimen becomes, as designated above each photomicrograph, the flatter or thinner the grain appears to be. Although brass is used in this example, the same effect would occur with wrought dental alloys. For the extreme example of a wire, the grains will be elongated parallel to the wire axis and resemble "strands

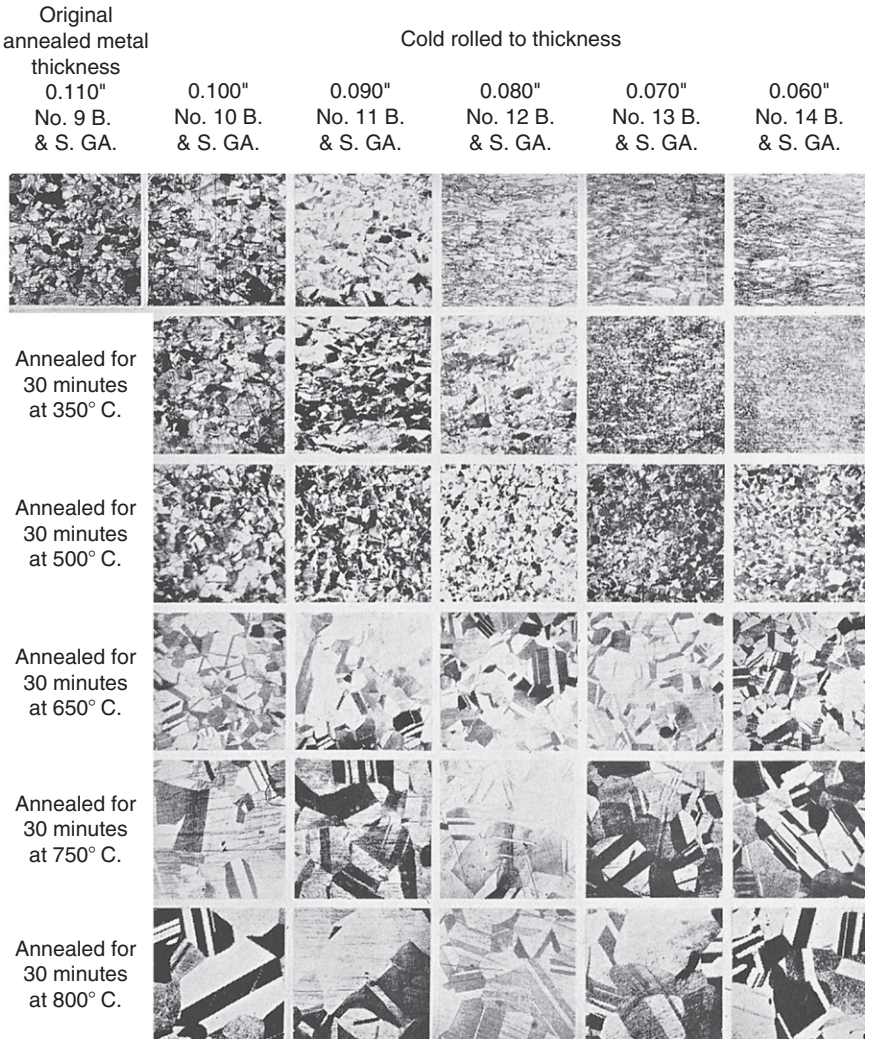


FIGURE 17-7 Grain size and appearance of brass (copper 66%, zinc 34%), after cold working and annealing. Note that as the degree of cold work increases (*to the right of the figure*), the appearance of the grain becomes more distorted. When the recrystallization proceeds, the grain size is inversely proportional to the degree of cold work (×40). (Prepared by L. H. DeWald.)

of spaghetti" in a photomicrograph showing a longitudinal section.

We should be familiar with practical examples of cold work and **strain hardening** at room temperature. For example, a wire can be fractured by bending it back and forth repeatedly. During each bend, the wire is cold worked, which requires greater stress to achieve subsequent bending deformation. However, this results in decreased ductility. Eventually, the wire fractures after extensive permanent deformation as a result of its reduced ductility. The same phenomenon can occur when a patient bends a clasp back and forth several times to relieve discomfort caused by a removable partial denture and this fatigue process leads to fracture of the clasp.

FRACTURE

If the cold-working process is continued, a severely deformed metal eventually fractures. The microcracks that act as sites of fracture initiation can arise from multiple causes, including an accumulation of dislocations or strain boundaries between two different microstructural phases.

Alloys undergo *brittle fracture* or ***ductile fracture***, depending on a variety of factors, such as composition, microstructure, temperature, and strain rate. Figure 17-8 illustrates the appearance of a brittle fracture surface for a carbon steel rotary endodontic instrument subjected to torsional loading. In contrast, Figure 17-9 presents a ductile fracture surface for a gold casting alloy specimen that had been loaded to failure in tension. The ductile fracture surfaces of metals are characterized by a typical rupture morphology, where failure has occurred because of the coalescence of microvoids that typically form at impurity particles during the later stages of permanent deformation. The dimpled rupture pattern reflects a map of the local stress field, which represents a characteristic appearance for bending and torsional fracture surfaces of rotary endodontic instruments that are fabricated from stainless steel.

? CRITICAL QUESTION

What is the difference between twinning and dislocation movement mechanisms of plastic deformation?

PLASTIC DEFORMATION WITHOUT DISLOCATION MOVEMENT

An alternative mode of permanent deformation in metals is twinning. *Twinning* refers to the atomic arrangement within a crystal where a region of the crystal takes on a different

crystallographic axis orientation from the rest of the crystal; the structures on either side of the boundary (between the two different orientations) are crystallographically identical as if they are reflections cross across a mirror plane. The boundary is called a twinning plane (Figure 17-10, *A*). The portion having a lattice orientation that is different from the original orientation is called a twin. Twinning can occur in a metal either during solidification as shown in Figure 17-10, *A*, or as a result of being stressed to a state of plastic deformation (Figure 17-10, *B*).

The stress needed to twin a crystal tends to be higher than that required for slip (see Figure 17-1). Therefore, slip is the normal deformation mechanism. Twinning is the favored mechanism at high strain rates and at low temperatures rather than dislocation movements in metals having relatively few slip systems. One should note that plastic deformation by twinning is merely a reorientation of the lattice, and that although the atoms in the twinned portion have moved, their positions relative to each other remain unchanged. On the other hand, plastic deformation by slip occurs along individual lattice planes for which the position of atoms relative to each other has changed.

Twinning has significance for deformation of α-titanium alloys, which are highly important for some dental implants

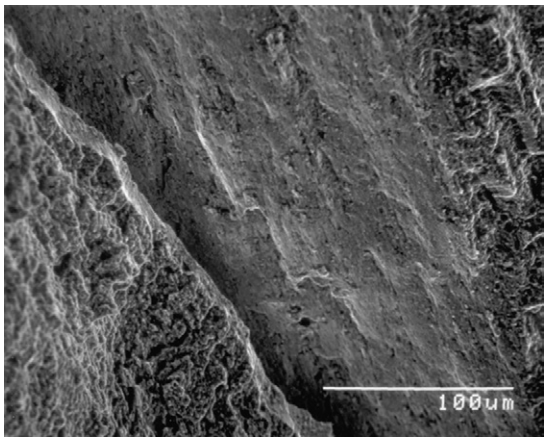


FIGURE 17-8 Brittle fracture surface of a carbon steel rotary endodontic instrument that was subjected to counterclockwise torsional loading (×500). (From Luebke NH, Brantley WA, Sabri ZI, et al: Physical dimensions, torsional performance, and metallurgical properties of rotary endodontic instruments: III. Peeso drills. *J Endodont* 18:13, 1992.)

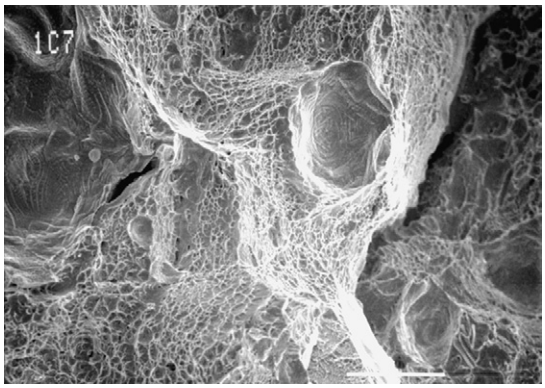


FIGURE 17-9 Ductile fracture surface of a cast gold alloy specimen that was loaded to failure in tension, illustrating the appearance of a dimpled rupture. The overall topography of the fracture surface indicates the grain size of the alloy, and casting porosity can also be seen (×2000, with scale bar length of 10 μm). (From Reisbick MH, Brantley WA: Mechanical property and microstructural variations for recast low-gold alloy. *Int J Prosthodont* 8:346, 1995.)

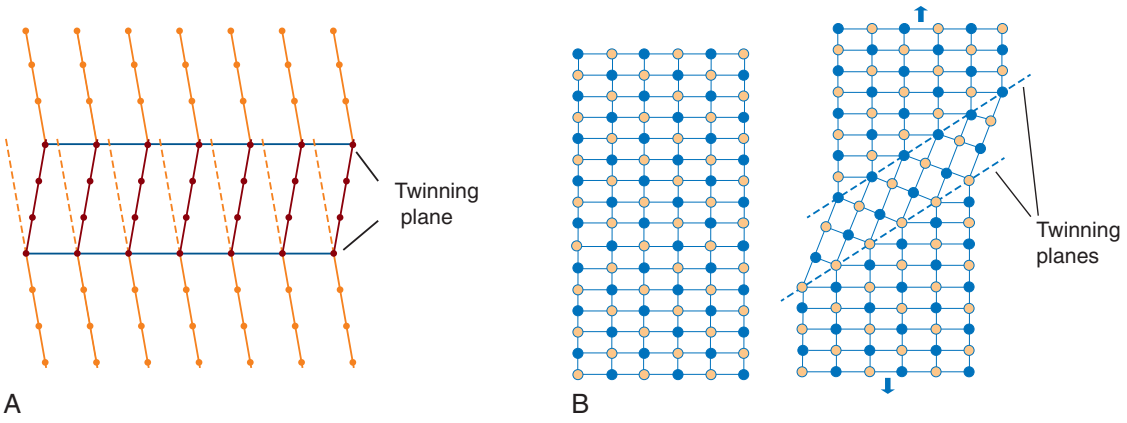


FIGURE 17-10 Schematic illustration of twinning in a metal. **A**, Atomic arrangement at the twinning planes in an fcc metal. The dashed lines show the orientation of the crystal if twinning had not occurred. Note that the atoms on either side of the twinning plane have a mirror relationship. **B**, A lattice structure before and after plastic deformation of a metal by twinning under tension. Note that the shape of the object has changed but the relative position of the atoms remains unchanged. Also note that the atoms on either side of the twinning plane have a mirror relationship. The two colors of spheres provide a contrast of neighboring atoms.

and are gaining interest for cast restorations. In α-titanium the ratio of lattice parameter (*c*) in the perpendicular direction to the basal plane and the lattice parameter (*a*) in the basal plane (see Figure 2-8), which is known as *c*/*a* ratio, is slightly less than the ideal value of 1.633 for the hcp structure, which results in additional slip planes and the tendency to readily undergo twinning. Twinning is also the mechanism for reversible transformation between the austenitic and martensitic structures in nickel-titanium orthodontic wires, which has considerable clinical significance.

APPLICATION OF WROUGHT METAL IN DENTISTRY

Wrought metals are used as wires by orthodontists for correcting displacements of teeth from proper occlusion as well as by prosthodontists and general practitioners as clasps for retention and stabilization of removable partial dentures. Other wrought metals, like files and reamers, are used by endodontists to clean and shape canals or by dentists who use preformed metal crowns for pedodontic patients.

The mechanical properties that enable orthodontic wires to move the teeth to a more desirable alignment are the force the wire delivers and the **working range**. As demonstrated by a cantilever beam (Figure 17-11), for a given design with known elastic modulus (E), the elastic deflection of the beam is proportional to the force applied. The same relationship also shows that for a given elastic deflection, the force needed to maintain that deflection is proportional to the elastic modulus of the material. A properly designed orthodontic appliance applies forces to the teeth. As the teeth move, the deflection of the device decreases. In response to the reduction in elastic deflection of the appliance, the level of force applied to the teeth is gradually reduced below the threshold level. When this happens, the appliance must be reactivated to increase the force level to its original value.

Elastic deflection of a cantilever beam under a load reflects the extent of tooth displacement that the designed appliance can deliver. The maximal amount of force a design can deliver is slightly less than the force needed to cause permanent deformation of the design; therefore, the greater the proportional limit of the wire, the higher the elastic deflection that the wire can deliver. The maximal elastic deflection the wire exhibits is called the *working range*. An obvious benefit of wrought wires is that they have a greater working range than their cast counterparts. Large elastic deflections are clinically desirable for orthodontic wires. The relationship in Figure 17-11 shows that for a given force (P) to be delivered, higher elastic deflection (δ) can be achieved by selecting a wire of lower elastic modulus (E), smaller cross-sectional dimension (*t*, *w*, or *r*), or a greater length (*l*) of the active component of the wire. Thus, it is possible to find the optimal design for an appliance that will deliver the low, constant forces, which are biologically desirable for tooth movement.

From Chapter 4 it follows that the maximal elastic deflection for tensile loading is given by the quotient of the proportional limit and elastic modulus. (Since the bending deformation used by orthodontists involves tensile and compressive strains parallel to the wire axis, these concepts for tensile loading are applicable.) Clinicians usually activate stainless steel wires (and other orthodontic wires including nickel-titanium wires) partially into the permanent deformation range to obtain a suitable configuration for moving the teeth effectively. Consequently, the practical working range is considered to be the elastic strain at the yield strength (YS) of the wire, which is termed ***springback*** that is defined as YS/E. The mechanical principles described here also apply to the design of retentive clasps and root canal files and reamers.

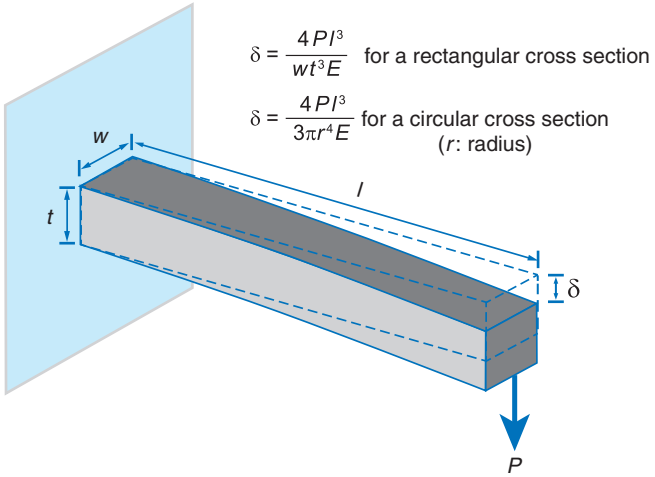


FIGURE 17-11 Bending of a cantilever beam. δ, deflection; *t*, thickness; *w*, width; *l*, length; and *E*, elastic modulus.

? CRITICAL QUESTION

Why must recrystallization of orthodontic wires be avoided when a stress-relief heat treatment is performed after manipulation to minimize fracture during placement?

EFFECTS OF ANNEALING WROUGHT METAL

The effects associated with plastic deformation (e.g., strain hardening, decreased ductility, distorted grains, and increased dislocation density) can be reversed by simply heating the metal to an appropriate elevated temperature without melting it. This process is called **annealing** and it takes place in three successive stages: **recovery**, **recrystallization**, and **grain growth**. The more severe the degree of cold working, the more rapidly the effects can be reversed by annealing. Also the higher the melting point of the metal, the higher the temperature needed for annealing. A rule of thumb is to use a temperature that is approximately half the melting point on the absolute temperature scale.

RECOVERY

Heating increases atom diffusion. At the recovery stage, the results of cold working begin to disappear, but not significantly. As can be seen in Figure 17-12, there is a very slight decrease in tensile strength and no change in ductility during the recovery stage, which reduces the number of dislocations and relieves internal strain energy resulting from cold

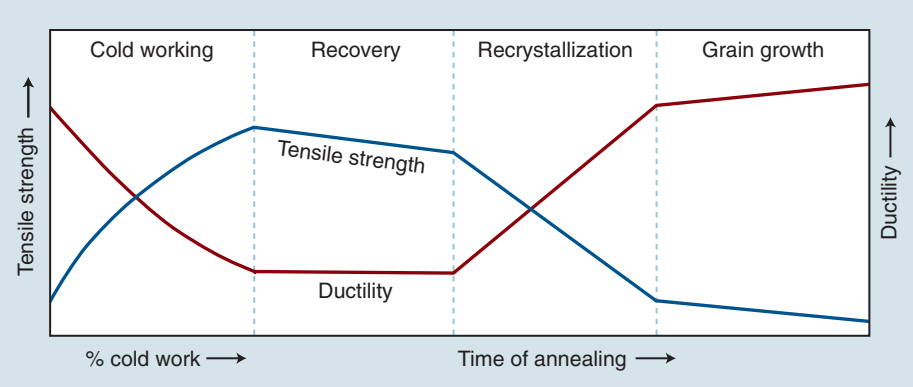


FIGURE 17-12 Tensile strength and ductility of a metal as a function of the percentage of cold work and annealing time. Tensile strength increases and ductility decreases during cold working. These properties change only slightly during recovery. During recrystallization, tensile strength decreases and ductility increases rapidly. Only slight changes occur during grain growth. (Adapted from Richman MH: *Introduction to the Science of Metals*. Waltham, MA, Blaisdell, 1967.)

working. Orthodontic appliances fabricated by bending wires are often subjected to a stress-relief anneal prior to their placement. This heat treatment stabilizes the configuration of the appliance and allows an accurate determination of the force that the appliance can deliver in the mouth. Elimination of residual stresses in the appliance also reduces the likelihood of fracture during clinical adjustments. It is essential that this heat treatment be performed in the recovery temperature range and not at higher temperatures where recrystallization occurs.

CRITICAL QUESTION

Why does the process of recrystallization cause significant reduction in the tensile strength of the alloy?

RECRYSTALLIZATION

When cold-worked metal specimens are annealed, recrystallization occurs after the recovery stage. This process involves a radical change in the microstructure, as seen in second and third row of Figure 17-7. The atoms at this stage are rearranged into a lower energy configuration. The old, deformed grains disappear completely and a new structure of strain-free grains with a lower density of grain boundary per volume emerges. After completion of recrystallization, the metal retains microstructures resembling that before cold-work (upper left of Figure 17-7), and essentially attains its original soft, ductile condition (Figure 17-12). It should now be obvious why recrystallization must be avoided during the stress-relief heat treatment of orthodontic appliances. However, if a metal is not sufficiently cold-worked, recrystallization will not occur during the typical annealing process.

The average grain size of the recrystallized structure depends on the initial number of nuclei. The more severe the degree of cold working, the greater is the number of such nuclei. The grain size for the recrystallized metal can range from rather relatively fine to fairly coarse (second and third row of Figure 17-7).

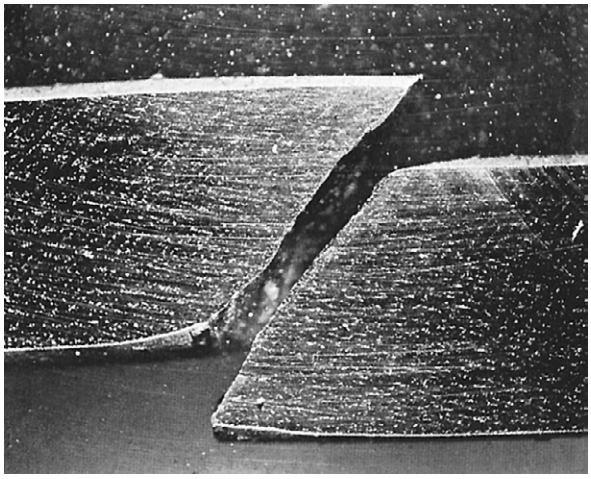


FIGURE 17-13 A cast rod showing a shear fracture through one large grain that occupied the entire cross-sectional area of the rod. Although ductility was high, fracture occurred because of a high stress concentration (×24).

GRAIN GROWTH

When the cold-worked metal is annealed at an elevated temperature, the grain size increases (see Figure 17-7, row 4 to row 6). This increase is called grain growth, which is a process by which the grain boundary area is minimized; large grains grow at the expense of small grains. Grain growth does not proceed indefinitely to yield a single crystal; rather, it ceases after a relatively coarse grain structure has been produced.

A larger grain size is not necessarily beneficial for certain applications. For example, with a sufficiently large grain size in a dental appliance of small cross-sectional thickness, a large grain may have an orientation where the resolved shear stress results in a low proportional limit and a substantial amount of local permanent deformation. Figure 17-13 shows that catastrophic fracture of a cast 9.5-mm-diameter gold alloy rod occurred in one grain that extended across the entire cross section.

CAST STRUCTURE VERSUS WROUGHT STRUCTURE

Metals and alloys are generally produced from castings. Castings can be machined, forged, drawn, extruded, or mechanically worked in some manner to produce the required article or appliance, thereby becoming a wrought metal. Most dental restorations and prostheses are cast and not wrought. However, if the dentist bends a cast removable partial denture clasp or burnishes a cast crown margin during adjustment, that part of the structure may be cold-worked sufficiently to attain the properties of a wrought metal.

When wrought metals are used (e.g., orthodontic bands and wires, appliances in pediatric dentistry, and removable partial denture clasp arms), the strength and fracture resistance of the wrought alloy will be significantly compromised if the metal is exposed to the temperature range at which recrystallization occurs. Such weakening can occur during soldering operations for stainless steel orthodontic appliances because of the reduced corrosion resistance of the affected area.

? CRITICAL QUESTION

What are the differences in the martensitic structures that form in plain carbon steels and austenitic stainless steels?

STAINLESS STEEL ALLOYS

Stainless steels have demonstrated superior performance for curettes and endodontic instruments where carbon steel products are also available. As has been pointed out, stainless steels are the major alloys used in orthodontics, and these alloys have many other applications in dentistry. The metallurgy and terminology of stainless steels are closely related to the binary iron-carbon system, which yields the primary phase of carbon steel. Therefore, a brief outline of the iron-carbon system and carbon steels is presented here.

IRON-CARBON SYSTEM

Carbon steels can be described simply as iron-carbon binary alloys that contain less than 2.1% of carbon by weight. At room temperature, pure iron has a body-centered-cubic (bcc) structure. This phase is stable up to 912 °C, where it transforms to a face-centered-cubic (fcc) structure. The solubility of carbon in bcc is very low and reaches a maximum of 0.02% at 723 °C. This material is known as ferrite. Above 723 °C, a solid solution of carbon in an fcc iron matrix called austenite is formed. The maximal solubility of carbon in fcc matrix is 2.1%.

When a plain carbon steel containing 0.8% carbon is cooled slowly in the austenitic phase to 723 °C, it undergoes a solid-state eutectoid transformation to yield a microstructural constituent called pearlite, which consists of alternating fine-scale lamellae of ferrite and iron carbide (Fe_3C), referred to as cementite, or simply, carbide. The Fe_3C phase is much harder and more rigid than austenite or ferrite. When the carbon content is less than 0.8%, the microstructure consists of ferrite and pearlite, whereas carbon steels containing more than 0.8% carbon will yield much harder alloys with microstructures consisting of carbide and pearlite.

If austenite is cooled very rapidly (quenched), it will undergo spontaneous transformation to a body-centered tetragonal (bct) structure called martensite, which is a very hard, strong, brittle alloy. The high hardness of this structure allows the grinding of a sharp edge, which will be retained in extended use. Martensite is a metastable phase that transforms to ferrite and carbide when it is heated to elevated temperatures. This process is called tempering; it reduces the hardness of the alloy but increases its toughness.

TYPES OF STAINLESS STEELS

When approximately 12% to 30% chromium by weight is added to carbon steel, the alloy is commonly known as *stainless steel*. Chromium forms a very thin, transparent, adherent layer of Cr_2O_3 through a process called passivation, which provides a barrier to diffusion of oxygen and other corrosive species and it prevents further corrosion of the underlying alloy. If the oxide layer is ruptured by mechanical or chemical means, only a temporary loss of protection against corrosion will occur, and the passivating oxide layer eventually forms again in an oxidizing environment such as ambient air.

Based on the previously described crystal structures formed by iron and carbon atoms, there are three major types of stainless steels. This classification, with approximate compositions, is given in Table 17-2.

Ferritic Stainless Steels

These alloys provide good corrosion resistance at a low cost when high strength is not required. They cannot be hardened by heat treatment or readily work-hardened. Consequently they have little application in dentistry.

Martensitic Stainless Steels

These alloys can be heat-treated in the same manner as plain carbon steels, with similar results. Because of their high yield strength and hardness, martensitic stainless steels are used for surgical and cutting instruments. The austenitic stainless steels are the most corrosion-resistant of the three major types and are the stainless steels used for orthodontic wires, endodontic instruments, and crowns in pediatric dentistry.

TABLE17-2 Composition (Percent by Weight) of Three Types of Stainless Steel* by Crystal Structure of Iron

Type of Stainless Steel	Chromium	Nickel	Carbon
Ferritic (bcc)	11.5–27.0	0	0.20 max
Austenitic (fcc)	16.0–26.0	7.0–22.0	0.25 max
Martensitic (bct)	11.5–17.0	0–2.5	0.15–1.20

*Silicon, phosphorus, sulfur, manganese, tantalum, and niobium may also be present in small amounts. The balance is iron.

Austenitic Stainless Steels

The addition of nickel to the iron-chromium-carbon composition stabilizes the austenite phase on cooling. Type 18-8 stainless steel, which contains 18% chromium and 8% nickel by weight, is the most commonly used alloy for orthodontic stainless steel wires and bands.

Austenitic stainless steel is preferable to ferritic stainless steel for dental applications because it has the following properties:

- Greater ductility and ability to undergo more cold work without fracturing
- Substantial strengthening during cold working (some transformation to martensite)
- Greater ease of welding
- Ability to overcome sensitization
- Less critical grain growth
- Comparative ease of forming

? CRITICAL QUESTIONS

How does austenitic stainless steel acquire its corrosion resistance? Can this protection be lost during the fabrication and normal use of a stainless steel appliance?

CORROSION RESISTANCE OF AUSTENITIC STAINLESS STEEL

The surface of stainless steel is highly prone to oxidation, but its passive surface oxide film blocks significant oxygen diffusion to the underlying alloy, thus limiting further oxidation. Nonetheless, stainless steel can corrode under certain conditions. Severe strain hardening produces highly stressed regions that are anodic to less stressed regions in the presence of saliva (Chapter 3). Organic or inorganic deposits and any site of surface roughness on a metal may result in localized concentrations of cell corrosion. Therefore, a stainless steel orthodontic appliance should be polished so that it remains clean and less susceptible to tarnish or corrosion during use. Chlorine-containing cleansers should not be used to clean removable appliances fabricated from stainless steel.

A common cause of stainless steel corrosion is the incorporation of bits of carbon steel or a similar metal in its surface. For example, if a stainless steel wire is manipulated with carbon steel pliers, it is possible for carbon steel debris from the pliers to become embedded in the stainless steel surface. In addition, if the stainless steel appliance is abraded or cut with a carbon steel bur or similar steel tool, some of the carbon steel from the tool may also become embedded in the stainless steel. Such a situation results in an electrochemical cell that may cause considerable corrosion in vivo.

When austenitic stainless steel is heated to between approximately 400 °C and 900 °C, iron-chromium carbides precipitate along the grain boundaries and chromium is depleted near the grain boundaries below concentrations necessary for protection. Thus, the stainless steel becomes susceptible to intergranular corrosion, and partial disintegration of the weakened alloy may result. This phenomenon is called *sensitization*. The temperature range of sensitization is within that used by the orthodontist for soldering and welding. In addition, filler materials that constitute brazed or soldered joints in orthodontic appliances can also form galvanic couples in vivo.

Two methods can be used to minimize sensitization. One is to reduce the carbon content of the steel to such an extent that carbide precipitation cannot occur. If the stainless steel is severely cold-worked and heated within the sensitization temperature range, the iron-chromium carbides precipitate instead at dislocations, which are located on slip planes within the bulk grains. As a result, the carbide formation leads to a uniform distribution throughout the alloy rather than by preferentially depleting chromium near the grain boundary precipitates. The amount of cold work introduced during the manufacturing process for orthodontic stainless steel wires should provide some resistance to intergranular corrosion by this mechanism. Elements such as titanium and tantalum, which preferentially form carbides, can be added to the stainless steel to preserve the level of chromium when the metal is exposed to elevated temperatures. This process is called *stabilization*.

MECHANICAL PROPERTIES OF AUSTENITIC STAINLESS STEEL

Approximate values of the mechanical properties of a stainless steel orthodontic wire are listed in Table 17-3. Strength and hardness may increase with a decrease in cross-sectional dimensions because of the increased cold work that is required for forming smaller wires. (The lack of such changes for certain sizes of the same product is the result of intermediate heat treatments performed during wire drawing.)

X-ray diffraction analyses of as-received 18-8 austenitic stainless steel orthodontic wires have shown that cold working creates a bcc martensitic structure. Because this martensite has a lower elastic modulus than the austenite phase, there is a reduction in the modulus of elasticity of stainless steel orthodontic wires in which the work hardening has not been eliminated by heat treatment. For example, the elastic modulus decreases from approximately 200 GPa for fully annealed austenitic stainless steel to 150 GPa after extensive

TABLE 17-3 Mechanical Properties of Orthodontic Wires

Alloy	Elastic Modulus (GPa)	Yield Strength (GPa)	Ultimate Tensile Strength (GPa)	Number of 90° Cold Bends without Fracture*
Stainless steel	179	1.6	2.1	5
Co-Cr-Ni	184	1.4	1.7	8
Ni-Ti	41	0.43	1.5	2
Beta-Ti	72	0.93	1.3	4

*Formerly required in ANSI/ADA Specification No. 32 for orthodontic wires.

cold working. (This presents no problem clinically, since stainless steel orthodontic wires have a very high elastic modulus relative to the titanium-containing wires, which will be discussed later.) Concomitantly, extensive cold working increases the yield strength to approximately 1100 MPa from a value of 275 MPa for the fully annealed stainless steel.

It is unfortunate that a stainless steel orthodontic wire can become fully annealed (recrystallized) after a few seconds at temperatures from 700 °C to 800 °C, because soldering and welding of the stainless steel are carried out in that temperature range. The yield strength of the wire, and thus, the range of elastic deformation (working range) necessary for a satisfactory orthodontic appliance, are greatly reduced after such annealing, which is a decided disadvantage clinically. However, it can be minimized by using low-fusing solders and minimizing the soldering and welding times. Any softening that occurs under such conditions can be remedied considerably by contouring and polishing of soldered areas.

Recovery Heat Treatment

An increase in the elastic properties of a stainless steel wire can be obtained by heating it to temperatures between 400 °C and 500 °C for 5 to 120 seconds after it has been cold-worked. This *stress-relief heat treatment* promotes the recovery annealing stage, which removes residual stresses introduced during manipulation of the wire. Thus, it stabilizes the shape of the appliance. This is important clinically, since such residual stresses can promote fracture when the appliance is being adjusted by the clinician.

? CRITICAL QUESTION

Which failure processes in soldered and welded joints in stainless steel orthodontic appliances might be observed clinically?

SOLDERING AND WELDING STAINLESS STEEL

Stainless steel components are often joined by silver solders, which are alloys of silver, copper, and zinc to which elements such as tin and indium may be added to lower the fusion temperature. Although such solders corrode in use because they are anodic to stainless steel, this is not objectionable in orthodontic appliances. These appliances are temporary structures, usually not worn in the mouth for more than 6 to 30 months, and frequent inspection by the orthodontist is necessary. In addition to the typical reducing and cleaning agents for soldering described in Chapter 16, a flux used for soldering stainless steel also contains a fluoride to dissolve the passivating surface film formed by chromium. The solder will not wet the metal when such a film is present.

Technical Considerations for Soldering

The freehand soldering of stainless steel is not greatly different from that of gold soldering, described in the previous chapter. A needlelike, nonluminous, gas-air flame may be used to minimize annealing of the metal surrounding the joint. The reducing zone of the flame should be used. The soldering should be observed in a shadow, against a black background, so that the temperature can be judged by the color of the work piece. The color should never exceed a dull red.

Prior to soldering, the parts should be tack-welded for alignment during the soldering procedure. Then flux should be applied, and the heavier-gauge part should be heated first. Flux must cover all of the areas to be soldered before heat is applied. As soon as the flux fuses, the solder alloy should be added and heating continued until the solder flows around and within the joint. After the solder has flowed, the work should be immediately removed from the heat source and quenched in water. From the preceding discussion on the sensitization of austenitic stainless steels, it should be evident that the objective during soldering is to use as little heat for as short a time as possible. Other heating techniques include the use of a hydrogen-oxygen torch, electric resistance heating, and indirect heating using a brass wire intermediary.

A photomicrograph of a cross section within a stainless steel wire-silver solder junction is shown in Figure 17-14. Although intimate contact between the two metals is seen at this moderate magnification, research indicates that no measurable amount of atomic diffusion occurs at the interface and that the bond is strictly mechanical. Interfacial constraint between the thin layer of solder alloy and the stronger wire might account for the higher strength of the solder joint.

? CRITICAL QUESTIONS

Does welding of stainless steel wires subject them to undesired annealing? What can be done to reduce the effect of annealing?

Welding

Flat structures such as bands and brackets are usually joined by spot welding, which produces a large electrical current that is forced by the electrode to flow through a limited area (spot) on the overlapped materials that are to be welded. The interfacial resistance of the materials to the current flow produces intense localized heating and fusion of the overlapped metals.

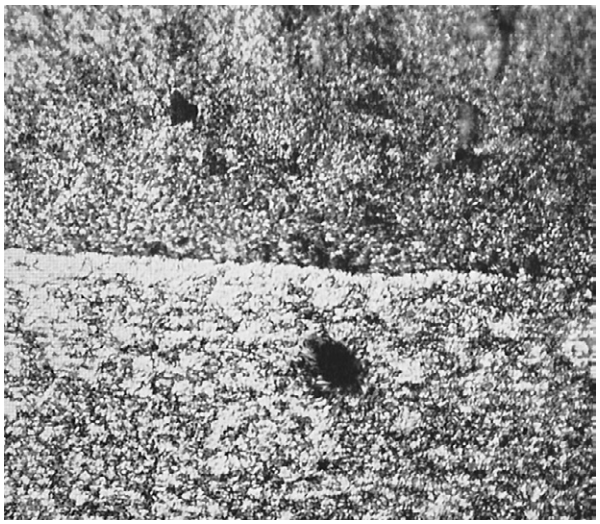


FIGURE 17-14 Photomicrograph of a soldered joint between a stainless steel orthodontic wire and a silver solder (×800).

No solder is employed. Ideally, melting is confined to the junction area, which can be observed metallographically in cross section as a region of resolidified alloy with a distinctive cast microstructure. The grain structure of the surrounding wrought alloy should not be affected, but stress exists at the interface of the cast and wrought structures, which would be the most likely path of joint failure should fracture occur. The strength of the welded joint decreases with an increase in the area of recrystallization of the adjacent wrought structure, and the joint strength increases with the area of the weld. The welded joint is susceptible to corrosion, primarily because of the loss of passivation caused by sensitization and the localized stress at the interface between the weld area and the surrounding wrought structure.

COBALT-CHROMIUM-NICKEL ALLOYS

Cobalt-chromium-nickel alloys were originally developed for use as watch springs (Elgiloy) and first marketed for use in orthodontic appliances during the 1950s. Elgiloy has excellent resistance to tarnish and corrosion in the oral environment and utilizes the same welding and soldering procedures used for stainless steel wires.

One manufacturer offers Elgiloy wires in four different tempers: soft, ductile, semiresilient, and resilient. The most widely used is the soft temper (Elgiloy Blue), which is easily manipulated and then heat treated to achieve increased resilience; other tempers are also responsive to heat treatment. The resulting changes in mechanical properties are associated with precipitation reactions. Clinicians can easily perform heat treatment using an electrical resistance welding apparatus and a special paste provided by the manufacturer to indicate the optimal period of time. Alternatively, furnace heat treatment at approximately 480 °C for 7 to 12 minutes can be employed.

Heat treatment of Elgiloy Blue orthodontic wires with several cross-sectional dimensions increases the elastic modulus in tension from a range of 160 to 190 GPa for as-received wires to a range of 180 to 210 GPa. The springback (YS/E), which varies from 0.0045 to 0.0065 for the as-received wires, increases to a range of 0.0054 to 0.0074 after heat treatment. Because of their nearly identical values of elastic modulus (see Table 17-3), the orthodontic force delivery for Elgiloy Blue and stainless steel orthodontic wires is essentially the same. In the as-received condition, the Elgiloy Blue wires have a "soft feel" compared with the more resilient stainless steel wires because of their much lower yield strength.

NICKEL-TITANIUM ALLOYS

A wrought nickel-titanium orthodontic wire alloy known as Nitinol was introduced commercially during the 1970s. This wire alloy is noted for its much lower elastic modulus and much wider elastic working range than those of stainless steel and Co-Cr-Ni wires (Table 17-3). The alloy name "Nitinol" originally came from the two elements nickel (Ni) and titanium (Ti) and the Naval Ordnance Laboratory (NOL) where these alloys were developed.

The nickel-titanium alloys used in dentistry are based upon the equiatomic intermetallic compound NiTi, which contains 55% nickel and 45% titanium by weight. Orthodontic wire alloys contain small amounts of other elements, such as cobalt, copper, and chromium. The microstructure consists predominantly of NiTi, but small precipitates are also observed. The NiTi intermetallic compound can exist in different crystal structures. The austenitic NiTi phase has a bcc structure, and the martensitic NiTi phase has a distorted monoclinic, triclinic, or hexagonal structure. The names *austenitic* and *martensitic* for these different crystallographic forms of NiTi have been taken from the metallurgical terminology for carbon steel and stainless steel.

MECHANICAL PROPERTIES

Approximate mechanical properties for Nitinol wire are 41 GPa for elastic modulus, 430 MPa for 0.2% offset yield strength, and 1500 MPa for tensile strength (see Table 17-3). Placement of permanent bends by the clinician in Nitinol wires is difficult because of their high resilience. Nitinol has high ductility, and its ability to undergo substantial work hardening is evident from its considerably higher tensile strength compared with its yield strength. The very low elastic modulus of Nitinol results in very low forces delivered by the appliance compared with similarly constructed and activated appliances from the other two alloys, and the springback or elastic range available for tooth movement is much greater for Nitinol.

? CRITICAL QUESTION

What are the clinical advantages of a shape-memory nickel-titanium orthodontic wire compared with a stainless steel orthodontic wire?

SUPERELASTICITY AND SHAPE MEMORY OF NITINOL

Transformation between the austenitic and martensitic forms of NiTi can be induced by both temperature and stress. Austenitic NiTi is the high-temperature, low-stress form, and martensitic NiTi is the low-temperature, high-stress form. Transformation occurs by a twinning process, which is reversible below the elastic limit and also results in changes in volume and electrical resistivity. The detailed NiTi phase relationships can be found in the referenced textbook on orthodontic materials by Brantley (2001) in the Selected Reading section.

Figure 17-15 illustrates the stress-strain behavior for a NiTi wire in bending; the bending moment and the angular deflection are equivalent to the stress-strain relationship tested in tension. Segment *a-b* corresponds to the initial elastic deformation of the wire, followed by segment *b-c*, where the austenitic structure transforms to the martensitic structure. After the transformation is completed at point *c* (typically at approximately 10% strain), further elastic deformation and plastic deformation occur with increasing stress

(bending moment) along segment *c-d*. During unloading, this sequence of events is reversed, with segment *d-e* corresponding to loss of elastic strain (angular deflection) in the martensitic structure, followed by transformation back to the austenitic structure along segment *e-f*, and finally loss of elastic strain in the austenitic structure along segment *f-g* as the bending moment decreases to zero. A small amount of permanent angular deflection remains in the wire because of the permanent deformation induced in segment *c-d*. This phenomenon is called **superelasticity** or pseudoelasticity in engineering materials science. Segment *e-f* delivers a nearly constant force for tooth movement during deactivation (unloading), which does not occur with stainless steel or Co-Cr-Ni wires.

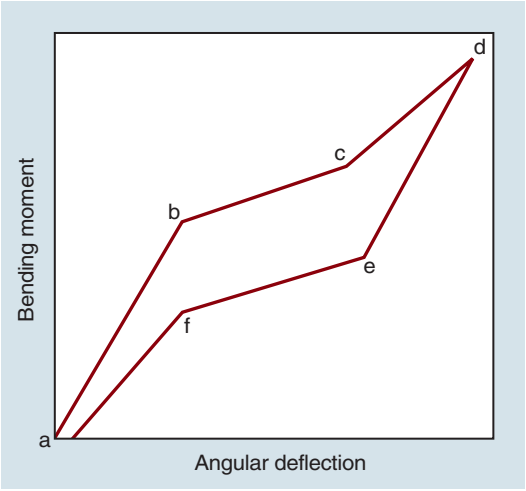


FIGURE 17-15 Schematic bending movement versus angular deflection curve for a nickel-titanium orthodontic wire showing the regions of superelasticity: b–c during loading (activation) and e–f during unloading (deactivation). Such behavior imparts a large working range to the archwire. Region c–d corresponds to permanent deformation during loading, and d–e corresponds to initial unloading of the permanently deformed arch wire. Regions b–c and e–f correspond to the forward and reverse directions, respectively, of the stress-induced transformation between the low-stress austenitic and high-stress martensitic structures.

Tooth movement can be achieved by another property of Nitinol. The shape of the appliance, such as an orthodontic arch wire, is first established when the alloy is heated at a temperature near 480 °C to stabilize austenitic structure (Figure 17-16). When it is cooled to room temperature, it converts to the twinned martensitic phase and retains its shape. The appliance is then reshaped at room temperature by the clinician; the martensitic structure becomes detwinned because of the stress induced by plastic deformation. When it is placed into brackets bonded to malpositioned teeth, exposure of the wire to the body temperature will promote the detwinned (deformed) martensitic structure to revert back to the austenitic structure and it regains its shape established near 480 °C, allows for further tooth movement. This phenomenon is called shape memory and the temperature that induces conversion from the detwinned martensitic to austenitic structure is called the transformation temperature. The transformation temperature can be lowered by elemental additions, such as copper, to ensure that the transformation to an entirely austenitic NiTi structure is completed.

As noted previously, nickel-titanium orthodontic wires are difficult to reconfigure into clinical shapes, and they must be joined by mechanical crimps, since the alloy can be neither soldered nor welded. In addition, nickel-titanium

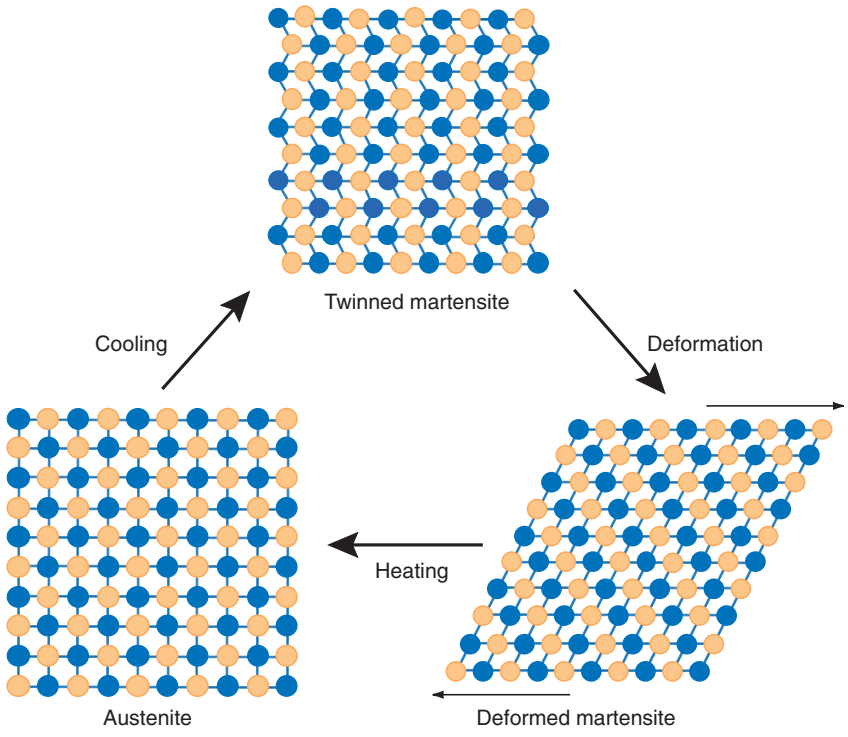


FIGURE 17-16 Shape memory process. The austenite crystal is stable at a higher temperature and can be plastically deformed to some desired shape without altering its crystalline structure. When austenite is cooled to room temperature, it converts to a twinned martensite without undergoing a shape change. When the twinned martensite is deformed plastically under a stress, the structure detwins and takes up a new shape. Note that the overall shape of the object has changed but the relative position between atoms did not change. Upon heating to body temperature (for orthodontic wire), the deformed martensite (detwinned martensite) will revert back to austenite and regain its original shape, since there is no change in the relative position of the atom arrangement. Heating of twinned martensite will also recover the austenite structure.

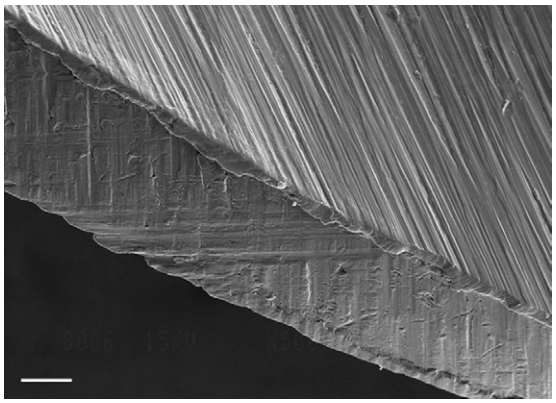


FIGURE 17-17 Photomicrograph of a nickel-titanium rotary endodontic instrument, showing permanent deformation at the edges of the flutes (rollover) and other surface defects that resulted from the machining process used for fabrication. (Courtesy of S. B. Alapati.)

orthodontic wires have relatively rough surfaces, which result in high friction between arch wires and brackets; this can potentially prolong the time needed for clinical treatment.

CRITICAL QUESTION

Why is the superelasticity of NiTi alloy advantageous for endodontic applications?

NICKEL-TITANIUM ENDODONTIC INSTRUMENTS

Within the upper superelastic plateau region shown by the segment *b-c* in Figure 17-15, the markedly increased strain for a small increase in bending moment indicates that the instrument can adapt along a sharply curving root canal with a small increase in the stress applied on the canal wall, thereby minimizing the risk for perforation of the root.

The drawback of this alloy is that nickel-titanium endodontic instruments must be fabricated by machining the starting wire blanks, in contrast to stainless steel endodontic instruments, for which a special apparatus twists the tapered starting wire blank. The manufacturing process results in substantial permanent deformation (Figure 17-17) at the edges of the cutting flutes and surface flaws that lead to premature fracture of the instrument. It is likely that the NiTi alloy is inherently notch-sensitive, because the coexisting austenitic and martensitic NiTi phases have very different crystal structures.

CRITICAL QUESTION

What is a potential clinical disadvantage of an orthodontic wire fabricated from β-titanium?

BETA-TITANIUM ALLOYS

Commercially pure titanium (CP Ti) exists in a stable hcp crystal structure at temperatures below 882 °C and a stable bcc structure above that temperature. These structures are referred to as α-titanium and β-titanium, respectively. Certain elements—such as aluminum, carbon, oxygen, and nitrogen—will stabilize the α-titanium structure; other elements—such as vanadium, molybdenum, and tantalum—will stabilize the β-titanium structure. Depending upon the quantity of stabilizer used, an alloy, such as Ti-6Al-4V, can contain both the α-titanium and β-titanium phases, which can be varied substantially with appropriate heat treatment (Chapter 16).

The first commercial β-titanium wires have had an approximate composition (by weight) of 79% titanium, 11% molybdenum, 6% zirconium, and 4% tin. The addition of molybdenum stabilizes the bcc β-titanium structure at room temperature and yields an alloy of lower elastic modulus and higher ductility than those of α-titanium alloys. This means that β-titanium can easily be drawn into wires for orthodontic applications. One commercial alloy has the trade name of TMA (titanium-molybdenum alloy).

MECHANICAL PROPERTIES OF BETA-TITANIUM WIRES

The elastic modulus of β-titanium wires is intermediate between that for stainless steel and Elgiloy wires and that for Nitinol wires (see Table 17-3). The springback (YS/E) for β-titanium wires is much greater than that for the stainless steel and Elgiloy wires and very similar to that for the Nitinol wires. The β-titanium wires can be highly cold-worked and, because of the bcc structure of the β-phase, the wires have high formability, which is comparable to that of austenitic stainless steel, and can be readily bent into various orthodontic configurations.

Because of the high reactivity of titanium, careful control of the original cast ingot quality, the atmosphere, and other processing parameters during wire drawing are essential. (This is also true for manufacturing of the nickel-titanium orthodontic wires.) Whereas heat treatments can be performed to alter the mechanical properties of β-titanium wires, these wires should not be heat-treated by the clinician.

Welding

Titanium alloys are highly reactive with oxygen at high temperature. Because of their high melting temperatures and this reactivity, soldering of these alloys with torches is not advisable. To prevent the potential reaction of titanium alloys with the oxygen in ambient air during the metal joining process, these procedures are often performed in a vacuum or in an argon environment. The β-titanium wires are the only orthodontic wire alloy type that demonstrates true weldability, and clinically satisfactory joints can be made by electrical resistance welding. Such joints need not be reinforced with solder, which is necessary for welded joints in stainless steel and Elgiloy wires. A weld made with insufficient heat will fail at the interface between the wires, whereas overheating may cause a failure adjacent to the joint. Figure 17-18 is a cross section of a welded β-titanium joint, showing minimum distortion of the original cold-worked structure.

Corrosion Resistance

Because of a passive TiO_2 surface film, which is analogous to the Cr_2O_3 film on stainless steel and Elgiloy, titanium and its

alloys generally have excellent corrosion resistance and environmental stability. There has been some concern about the biocompatibility of orthodontic wires containing nickel, which may cause localized tissue irritation or an allergic reaction in some patients, and it should be noted that β-titanium is the only major orthodontic wire alloy that is nickel-free.

Surface Property

The surface roughness of the TMA wires is much greater than that of the stainless steel and Elgiloy wires. Scanning electron microscopy observations suggest that the surface roughness originates from adherence of the titanium in both wire alloys to the dies or rollers used in the wire manufacturing process. During orthodontic treatment, the rough arch wire surfaces increase sliding friction and localized **cold welding** of the arch wire alloy to the metal bracket has also been hypothesized.

Surface treatment of nickel-titanium and beta-titanium orthodontic wires with nitrogen ion implantation has been performed to decrease adhesion between wires and brackets. One study reported significant differences for in vitro tooth movement with ion-implanted TMA and nickel-titanium wires, compared to their non-ion-implanted counterparts. However, the results of a recent clinical study suggest that there were no significant differences for the rate of space closure when ion-implanted TMA, conventional TMA (not ion-implanted), and stainless steel wires were used.

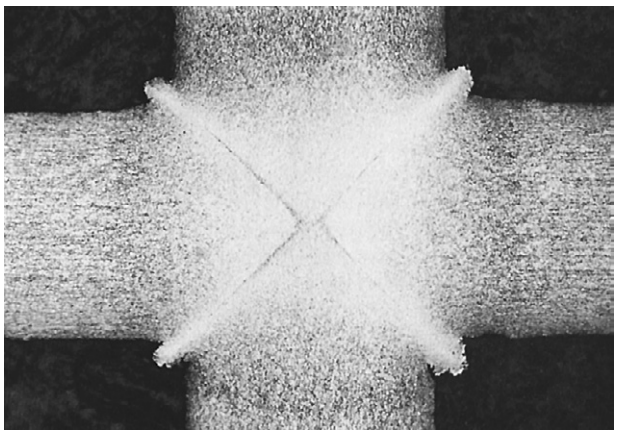


FIGURE 17-18 Photomicrograph of a weld joint between two 0.43- by 0.63-mm beta-titanium orthodontic wires showing minimum distortion of the original cold-worked microstructure. (Courtesy of T. C. Labenski and A. J. Goldberg.)

ADDITIONAL WROUGHT ALLOYS

Noble metal wires are still occasionally employed in the construction of removable partial denture clasps and orthodontic appliances as well as in retention pins for restorations and endodontic posts. The elastic modulus of these gold alloy wires is approximately 100 to 120 GPa, which is higher than that for titanium-based wrought alloys but considerably lower than those of stainless steel and Co-Cr-Ni wrought alloys. Table 17-4 shows specifications of noble metal wrought wire and the properties of two noble alloy wires: platinum-gold-palladium (P-G-P), which contains 40% to 50% platinum, 25% to 30% gold, and 25% to 30% palladium by weight, and palladium-silver-copper (P-S-C) wire, which consists of 42% to 44% palladium, 38% to 41% silver, 16% to 17% copper, and 0% to 1% platinum by weight. The high fusion temperature (hence high recrystallization temperature) of P-G-P wire would be especially useful for casting a removable partial denture framework to this alloy. It is the high fusion temperatures of platinum and palladium that raise the fusion temperature of P-G-P wire. P-S-C wires have also been considered useful for dental applications because their fusion temperatures are higher than those of the gold-based alloy wires.

In addition to the uses of wrought base metal alloys summarized earlier in this chapter, cobalt-chromium alloys for partial denture clasps are available. For example, a cobalt-chromium-tungsten-nickel wire (Ticonium) has a yield strength of approximately 920 MPa, a tensile strength of nearly 1400 MPa, and a percent elongation of 19%. This

TABLE 17-4 Physical Properties of Noble Metal Wires

			ELONGATION (%)		
Wire Type	**Yield Strength Oven-Cooled (MPa)**	**Tensile Strength Oven-Cooled (MPa)**	**Quenched**	**Oven-Cooled**	**Fusion Temperature (°C)**
Formerly ANSI/ADA Type I	860	930	15	4	960
Formerly ANSI/ADA Type II	690	860	15	2	870

			MINIMUM ELONGATION (%)		
Wire Type	**Proportional Limit (MPa)**	**Tensile Strength (MPa)**	**Quenched**	**Oven-Cooled**	**Fusion Temperature (°C)**
Platinum-Gold-Palladium	550–1030*	860–1240*	14–15	—	1500–1530
Palladium-Silver-Copper	690–790†	960–1070†	16–24	8–15	1040–1080

Data from *Dentists Desk Reference: Materials, Instruments and Equipment. Metals and Alloys: Precious Metal Wrought Wire.* Chicago, American Dental Association, 1981; Lyman T: *Metals Handbook*, ed 8, Vol 1. Properties and Selection of Metals. Metals Park, OH, American Society for Metals, 1964.
*Quenched (alloy does not age-harden); †Age-hardened.

wrought alloy is not heat-treatable and is designed for use with the lower-fusing nickel-chromium-beryllium casting alloy from the same manufacturer.

CRITICAL QUESTION

Pure gold can be used as a direct filling restorative material. What are the properties of gold that make this restorative material possible?

DIRECT FILLING GOLD

Pure gold is the noblest of all dental metals, rarely tarnishing or corroding in the oral cavity. It is inactive chemically, and it is not affected by air, heat, moisture, or most solvents. At room temperature, two thin sheets of atomically clean pure gold can be welded under pressure. The procedure is also called cold welding because it is conducted at room temperature. Pure gold is very soft (22 VHN), and the most ductile and malleable metal used in restorative dentistry. As a result, pure gold in the form of foil or powder can be adapted to the walls of a cavity preparation with only a minimal marginal gap. When the gold segments (like increments of amalgam or composite) are compacted with designated instruments to build up the bulk of material, the segments are bonded by metallic bonds (cold welding), and the bulk of material is work-hardened by the pressure. Therefore, the final restoration retains characteristics of a wrought metal. The process of gold compacting is also known as condensation. After work hardening, its hardness (52 to 75 VHN) is equivalent to and may exceed that of type I gold alloy (50 VHN), and approaches that of type II gold alloy (90 VHN). This category of gold is also known as cohesive gold and direct filling gold for restorations.

FORMS OF DIRECT FILLING GOLD

Direct filling gold is supplied in three basic forms: foil (also known as fibrous gold), electrolytic precipitate (also called crystalline gold), and granular gold (also called powdered gold). They can all be cold welded. However, the efficacy of restorations made from these materials is adversely affected by improper handling, contamination, deviations from established cavity design principles, inefficient placement methods, and faulty finishing techniques. With the exception of platinized foil and alloyed electrolytic precipitate, the chemical purity of most types of direct-filling gold is 99.99% or higher.

Gold Foil

Gold foil is provided in sheets, which can also be transformed to other physical form like pellets, cylinders, ropes prepared by the dentist, or partially precondensed laminates of varying thickness produced by the manufacturer. Platinized gold foil is a laminated structure with one sheet of platinum foil between two gold foils. The objective of adding platinum to the gold foil is to increase the hardness and wear resistance of restorations made from this material. Standard No. 4 gold foil is supplied in 100- by 100-mm (4- by 4-inch) sheets that weigh 4 grains (0.259 g) and are about 0.51 μm thick. The numbering system refers to the weight of a standard sheet. The surface of gold foil is shown in the SEM image in Figure 17-19.

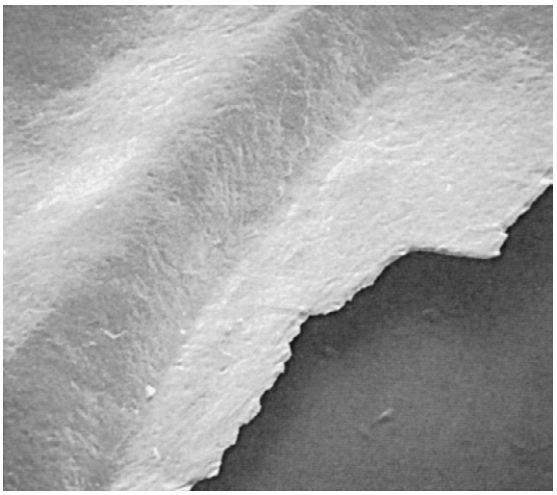


FIGURE 17-19 Scanning electron micrograph of the surface of gold foil (×750). (Courtesy of C. E. Ingersoll.)

During storage, gold foil, like most metals, attracts gases to its surface from the environment, and any adsorbed gas film prevents the intimate atomic contact required for cold welding. To ensure the cleanness of the foil, most gold sheets are provided with an adsorbed protective gas film, such as ammonia. The ammonia-treated foil is called noncohesive foil. The volatile film on the foil is removed by heating immediately before inserting into the cavity preparation.

Electrolytic Precipitate Gold

Another form of direct filling gold is microcrystalline gold powder formed by electrolytic precipitation, which is sandwiched between sheets of gold foil and formed into strips. It is also called mat or sponge gold. The powder consists of dendritic crystals approximately 0.1 mm in length (Figure 17-20).

This form of gold can be cut to a desired size and is often preferred for its ease in building up the internal bulk of the restoration. Mat gold made of electrolytic precipitate from gold, which is alloyed with a trace amount of calcium, can yield a further increase in hardness by dispersion strengthening without affecting the handling properties.

Granular (Powdered) Gold

Gold powders in agglomerated form can also be prepared by chemical precipitation or atomization from molten gold. To prevent agglomerates from disintegrating, the atomized and chemically precipitated powders are first mixed with a soft wax to form pellets. These wax-gold pellets are wrapped with foil. The resulting pellets are cylindrical in shape and are available in several diameters and lengths. Heating to burn away wax is mandatory before insertion into the cavity preparation.

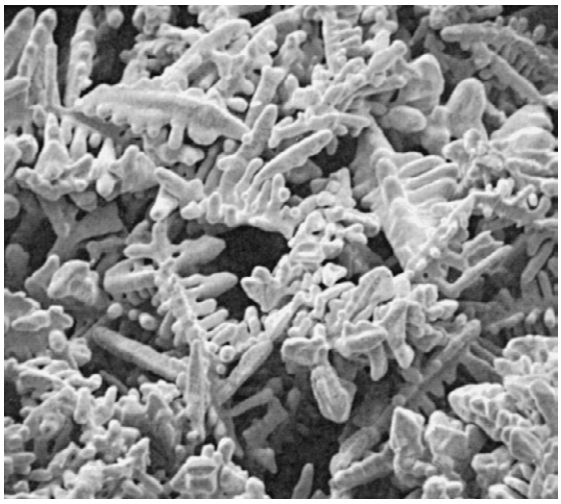


FIGURE 17-20 Scanning electron micrograph of mat gold (×750). (Courtesy of C. E. Ingersoll.)

CRITICAL QUESTION

Why do direct filling golds have to be flamed before insertion in cavity preparation?

PREPARATION OF DIRECT FILLING GOLD FOR RESTORATION

Prior to placing direct filling gold in the cavity preparation, the dentist heats the material to remove the protective coating or wax introduced by the manufacturer, or contaminants on the surface acquired during storage and packaging. Individual pellets can be held over an open flame of pure alcohol, or a group of pellets or other gold forms can be placed on a so-called annealing plate heated by electricity. This step is commonly called annealing, heat treatment, or **degassing**. A more appropriate term would be ***desorption***.

Proper desorption is a matter of heating long enough at a temperature that removes contaminants and, in the case of powdered gold, that burns away the wax. Heating times vary depending on the size and configuration of the gold segment. Powdered gold pellets may take 15 to 20 seconds, whereas gold foil pellets and electrolytic gold pellets may require only 1 or 2 seconds. Underheating can compromise cohesion between segments. Overheating can lead to excessive sintering and possibly contamination by the tray, instruments, or flame. The result may be incomplete cohesion, embrittlement of the portion being heated, and poor compaction characteristics.

Powdered gold must be heated in a flame to ensure the complete elimination of the wax. When heating in bulk on a tray, an excessive amount of gold should be avoided because of the difficulties that prolonged and repeated heating can create. Care should be taken to handle pieces with stainless steel wire points or similar instruments that will not contaminate the gold.

Regardless of the type of direct gold used, flame desorption of surface contaminates will occur when the gold segment has exhibited a dull-red glow. The fuel for the flame may be alcohol or gas, but alcohol is preferred because there is less danger of contamination. The alcohol should be pure methanol or ethanol without colorants or other additives. Advantages of flame desorption include the selection of a piece of appropriate size, desorption of only those pieces used, and reduced exposure to contamination.

COMPACTION OF DIRECT FILLING GOLD

Two of the main processes that control the quality of the final direct gold restoration are cold welding and wedging. *Wedging* refers to the pressurized adaptation of the gold form within the space between tooth structure walls or corners that have been slightly deformed elastically.

A totally dry cavity is mandatory throughout the compaction process to ensure complete cohesion. The increments of gold must be of a proper size for insertion and in the proper "atomically clean" condition for condensing or compacting. The first segment must be sufficiently large that it is secured by compacting it within the prepared cavity. The second and subsequent segments must cold weld to each other, and this will occur only if the surface is free of contaminants and moisture.

Condensers

The condenser can be straight, curved, angled, round, square, or rectangular, and the surface of the tip can be smooth or serrated. The tip can be flat-faced or convex-faced. The condenser tip should also be kept atomically clean.

Size of the Condenser Tip

As in condensation of amalgam, the force distribution to the gold depends on the area of the point working surface of the instrument. It follows that small condenser tips are indicated to achieve the desired compaction at lower forces than those that might damage oral structures. The lower limit of the condenser tip size is based on the tendency of the tip to penetrate an area of the condensed foil.

Compaction Method

The gold segments can be compacted by hand pressure alone, by hand pressure combined with a hand mallet, or by a mechanical device that is activated by a spring, pneumatic pressure, or electronically (using an electromallet). The direction of force application, the amount of applied pressure, and the compaction pattern are critically important factors controlling the quality of the gold restoration.

Condenser penetration should be less than the thickness of each segment that is compacted. The depth of each cold-welded mass is usually between 0.2 and 0.3 mm. The final density is controlled by the direction and the magnitude of the compaction force and by the size and shape of the condenser tip. The condenser tip must be stepped in a controlled overlapping pattern with the condenser tip placed approximately the distance of the tip radius away from the last area to be compacted. Porosity is likely to occur in all direct gold

restorations. Each type of gold requires a slight variation in technique to avoid either closed pores or open pores that intersect the surface.

A small amount of excess material is provided to ensure a proper contour and an adequate surface finish. The excess material is trimmed away with sharp gold knives and files of suitable shapes and sizes, and with abrasive disks, stones, and strips. Whenever the strips are used, cooling water spray must be applied to dissipate heat and reduce trauma to the pulpal tissue.

? CRITICAL QUESTION

Pure gold has a density of 19.3 g/cm^3. Why is the apparent density of the direct filling gold restoration after condensation often less than 16 g/cm^3?

PHYSICAL PROPERTIES OF COMPACTED GOLD

Table 17-5 shows some representative property values of various methods of compacting golds. Transverse (bending) strength reflects three types of stresses: compressive, tensile, and shear (see Chapter 4). In direct filling golds, the failure usually occurs from tensile stress because of incomplete cohesion. Bending strength represents an indirect indicator of cohesive strength. Hardness indicates the overall quality of compacted gold.

The maximal density of gold is 19.3 g/cm^3. The density values shown in Table 17-5 indicate the presence of voids in all direct gold restorations. Apparently, voids are inevitable, but they should be kept to a minimum to achieve the maximal strength attainable.

Hardness may not be a valid measure of the effectiveness of a particular restorative material for its intended purpose of restoring the tooth. It may, however, indicate the overall quality of compacted gold.

There is no evidence that the differences in physical properties among the various forms of gold are clinically significant. The physical properties of the compacted gold (restoration) are probably more greatly influenced by the competence of the dentist in manipulating and placing the gold material.

TABLE 17-5 Representative Physical Properties of Direct-Filling Golds

Materials and Technique	Transverse Strength (MPa)	KHN	Apparent Density (g/cm^3)*
Mat gold			
Hand	161	52	14.3
Mechanical	169	62	14.7
Combined	169	53	14.5
Powdered gold			
Hand	165	55	14.4
Mechanical	155	64	14.5
Combined	190	58	14.9
Gold foil			
Hand	296	69	15.9
Mechanical	265	69	15.8
Combined	273	69	15.8
Mat gold and gold foil			
Hand	196	70	15.0
Mechanical	206	71	15.1
Combined	227	75	15.0

*Density is calculated by dividing the weight of the specimen by its volume.
KHN, Knoop hardness number.
Data from Richter WA, Cantwell KR: A study of cohesive gold. *J Prosthet Dent* 15:722, 1965.

THE DIRECT GOLD RESTORATION

Restorations made with the direct filling golds do not exhibit the high strength and hardness of those made with dental casting alloys, described in Chapter 16. The use of direct filling golds is generally limited to areas where they simply "fill" a space (such as pits and small class I, II, III, V, and VI restorations) and for repairing casting margins. The concerns for possible damaging effects on the pulp have been disputed. Apparently direct gold that is compacted properly into sound tooth structure produces only a minimal pulpal response.

High-quality direct-gold restorations can be ensured only when four principal conditions are satisfied: (1) the appropriate gold form is used for each specific clinical situation, (2) the material is used only where it is indicated, (3) a perfectly dry and clean field is provided, and (4) the material is properly manipulated with the correct instruments. Obviously these conditions can be satisfied only if the clinician has acquired the necessary knowledge, skills, and experience. The cavity preparation is critically important, since it must provide adequate access form, retention, adequate support, well-defined finish lines, and adequate pulp protection. The chief disadvantages of using direct filling gold are its yellow metallic color, high thermal conductivity, and technical difficulties in forming a dense restoration.

The American Academy of Gold Foil Operators posts clinical cases by their members at its website (http://www.aagfo.org/Procedures.html and http://www.goldfoil.org/Procedures.htm). Note that these restorations were placed under rubber dam isolation. The use of a rubber dam is essential to minimize the risk of contamination by saliva, water, and other contaminants during placement. Figure 17-21 is a clinical example of a class II gold foil restoration.

ACKNOWLEDGMENT

The previous contributions of Dr. William A. Brantley to this chapter in the 11th edition of the book are greatly appreciated.



FIGURE 17-21 Clinical example of direct gold foil restoration. **A,** Class II MO preparation filled with cohesive gold foil. **B,** Finished gold foil restoration. (Courtesy of Dr. Richard D. Tucker and Dr. John Sechena.)

SELECTED READINGS

American Academy of Gold Foil Operators: http://www.goldfoil.org/
The website provides links to gold foil study groups and organizations, gold foil procedures, and instructional materials, articles, historical materials, and meeting news.

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CHAPTER
18

Dental Ceramics

OUTLINE

What Are Ceramics?

Applications of Ceramics in Dentistry

History of Dental Ceramics

Classification of Dental Ceramics

Metal-Ceramic Systems: Composition and Properties

Fabrication of Metal-Ceramic Prostheses

Cast Metal for Metal-Ceramic Prostheses

Technical Aspects of Metal-Ceramic Products

Methods for Strengthening Ceramics

All-Ceramic Systems

CAD-CAM Processing of Ceramics

Abrasiveness of Dental Ceramics

Clinical Performance of All-Ceramic Restorations

Chemical Attack of Glass-Phase Ceramics by Acidulated Phosphate Fluoride

Porcelain Denture Teeth

Factors Affecting the Color Appearance of Ceramics

Ceramic Veneers, Inlays, and Onlays

Critical Observation and Analysis of Fractures

Principles Governing the Selection of Dental Ceramics

Ident-Ceram System for Identification of Ceramic Products

KEY TERMS

Alumina core—The substructure or framework of a crown or bridge that is made of Al_2O_3.

CAD-CAM ceramic—A partially or fully sintered ceramic blank that is used to produce a dental core or veneer structure using a computer-aided design (CAD) and computer-aided manufacturing or milling (CAM) process.

Castable ceramic—A glass specially formulated to be cast into a mold and converted by heating to a glass-ceramic as a core coping or framework for a ceramic prosthesis (see Glass-ceramic).

Ceramic frits—Powdered ceramic material fired in a dental lab to produce a dental porcelain veneer layer over a core material (metal or ceramic). Frits may be glass or a mixture of glass and crystalline particles, which commonly contain inorganic pigments.

Ceramic, glaze—Fine glass powder that can be fired on a dental ceramic core or dental porcelain to form a smooth, glassy surface. (See *natural glaze*.)

Ceramic, pressable (hot-pressed ceramic)—Ceramic with a high glass content that can be heated to a temperature and forced to flow under uniaxial pressure to fill a cavity in a refractory mold.

Ceramic, stain—A fine glass powder containing one or more pigments (colored metal oxides) that is applied superficially to a ceramic restoration.

Ceramic—Inorganic, nonmetallic material composed of metallic or semi-metallic oxides, phosphates, sulfates, or other nonorganic compounds. Glass, which is amorphous, is a subset of ceramics.

Copy milling—Process of cutting or grinding a structure using a device that traces the surface of a master pattern, similar to a key-cutting procedure in three dimensions.

Core ceramic—An opaque or semi-translucent dental ceramic having sufficient strength, toughness, and stiffness to withstand masticatory forces. Core materials can be glazed or layered with a veneering ceramic to obtain the desired shade, form and function, and/or esthetics.

Dental ceramic—A specially formulated ceramic material that exhibits adequate strength, durability, and color that is used intraorally to restore anatomic form and function, and/or esthetics. Many formulations are available depending on whether the indication is for a crown, a bridge, an endodontic post or core, an orthodontic bracket, or a veneer. Ceramic products that are used primarily for crowns and bridges include alumina, ceria-stabilized zirconia, glass-infiltrated alumina, glass-infiltrated magnesia-alumina spinel, glass-infiltrated alumina/zirconia, lithium disilicate glass-ceramic, yttria-stabilized zirconia, and various glasses and glazes.

Fixed dental prosthesis (FDP)—An inlay, onlay, veneer, crown, or bridge that is cemented to one or more teeth or dental implant abutments. The term is most often used to describe a bridge prosthesis.

Fixed partial denture (FPD)—A bridge that replaces one or more missing teeth. However, *fixed dental prosthesis* (FDP) is the universally preferred term.

Glass-ceramic—A ceramic that is formed to shape in the glassy state and subsequently heat treated to partially or completely crystallize the object. Glass-ceramic blanks are also available for CAD-CAM processes.

Glass-infiltrated ceramic—A crystalline core (framework) ceramic whose interconnected pore network is infiltrated during heating by the capillary inflow of a low-viscosity highly wetting glass. These infiltrasted core materials are veneered with porcelain. Alumina, magnesia-alumina spinel, or alumina/zirconia core ceramics can be used for this process.

Green state—The semi-hard, prefired condition of a ceramic object. A green ceramic may be wet, as produced by slip-casting, or it may be isostatically pressed to shape prior to firing. Green ceramics are always porous. They are too fragile for use intraorally.

Glaze ceramic—A specially formulated ceramic powder that is mixed with a liquid, applied to a ceramic surface, and heated to an appropriate temperature for a sufficient time to form a smooth glassy layer. (See *natural glaze*.)

Metal-ceramic prosthesis—A partial crown, full crown, or multiple-unit fixed dental prosthesis made from a metal substrate and an adherent oxide to which dental porcelain is bonded for esthetic enhancement and functional anatomy. The terms *porcelain fused to metal* (PFM), *porcelain bonded to metal* (PBM), *porcelain to metal* (PTM), and ceramometal are also used to describe these prostheses, but *metal-ceramic* (MC) is the internationally accepted term. Opaque, body, and incisal porcelains and glaze or stains are used to create the outer layer(s) or veneer.

Natural glaze—A superficial layer on a ceramic-ceramic or metal-ceramic prosthesis formed by heating a dental porcelain to form a smooth glassy layer.

Overglaze—A coating of glass formed by fusing glaze particles on a ceramic surface.

Porcelain, dental—A ceramic produced by sintering a mixture of feldspar, silica, alumina, other metal oxides, pigments, and opacifying agents. Except for porcelain denture teeth, dental porcelain is not made from kaolin.

Porcelain, opaque—A fine dental porcelain, provided either as a paste or powder that is used to mask the color of a metal substructure or ceramic core for fixed prostheses.

Porcelain, aluminous—A dental porcelain whose thermal expansion coefficient is suitable for use as a veneer over an alumina core. This porcelain creates the anatomy of the crown and improves the esthetics of the alumina-based prostheses.

Porcelain, body (also dentin or gingival porcelain)—A dental porcelain used to create the anatomy and shade of a fixed prosthesis.

Porcelain, feldspathic—A specially formulated dental porcelain that contains leucite crystals ($KAlSi_2O_6$) in a glass matrix that is used for veneering the metal framework of metal-ceramic prostheses. Leucite crystals have high thermal expansion, which makes the porcelain thermally compatible with the high-expansion noble and nickel-base alloys used in fixed prosthodontics. The leucite crystals are often formed by heat-treating potassium feldspar.

Porcelain, incisal (also enamel porcelain)—A dental porcelain used to create the anatomy and incisal portion of a fixed prosthesis. These porcelains are generally more translucent than opaque and gingival (body) porcelains.

Porcelain, shoulder—A dental porcelain that is used to build up the cervical area of a metal-ceramic crown to produce an esthetic butt-joint margin. This porcelain is usually more opaque than body or incisal porcelains. This porcelain also has a higher sintering temperature than the adjacent body porcelain so as to retain the sharp edge at the margin during subsequent sintering processes.

Sintering—Process of heating closely packed particles below their melting temperature to promote atomic diffusion across particle boundaries and densification of the mass.

Slip casting—Process of forming ceramic shapes by applying an aqueous slurry of ceramic particles to a porous substrate (such as a die material), and removing the water by capillary action. This densifies the deposited ceramic powder into a "green body," which is subsequently sintered to achieve higher density and strength.

Spinel or spinelle—A porous slip-cast ceramic, $MgAl_2O_4$ ($MgO{\cdot}Al_2O_3$), that is glass-infiltrated to produce a core ceramic.

Thermal compatibility—Ability of veneering ceramics in metal-ceramic or ceramic-ceramic structures to contract in a manner similar to that of the core metal or ceramic structure during cooling from temperatures above Tg such that transient or residual tensile stress in the veneer is minimized and a protective compressive stress is produced.

Zirconia—A partially stabilized zirconium oxide, usually in the tetragonal phase (t-ZrO_2), that is used primarily as a **core** (framework) for dental prostheses. It has also been introduced as a monolithic ceramic to be used without a veneering ceramic.

Zirconia core—A partially stabilized tetragonal zirconia (stabilized either by ceria or yttria) that is used for producing the core veneered framework or substructure for crowns or bridges.

Dentists have searched for the ideal restorative material for more than a century. Although direct restorative materials such as amalgam, composites, and restorative cements have been used with reasonably good success during the past several decades, they are not feasible for multiunit restorations. For some single-unit restorations, esthetic results are critically important. In this regard a restorative material should be biocompatible and durable, and it should maintain its surface quality and esthetic characteristics over an extended period of time, preferably for the lifetime of the patient. **Dental ceramics** are attractive because of their biocompatibility, long-term color stability, chemical durability, wear resistance, and ability to be formed into precise shapes, although in some cases, they require costly processing

equipment and specialized training for lab technicians. This chapter provides an overview of the structure, properties, benefits, and drawbacks of ceramic materials used for crown and bridge prostheses. The field of dental ceramics science has evolved rapidly over the past three decades and further novel developments are anticipated in the future. Thus, it is reasonable to focus on the principles of dental ceramic science and to minimize the emphasis on brand names that are likely to change regularly in the future.

CRITICAL QUESTION

Which property best describes the fracture resistance of dental ceramics?

WHAT ARE CERAMICS?

Dental ceramics consist of silicate glasses, **porcelains**, **glass-ceramics**, or highly crystalline solids. They exhibit chemical, mechanical, physical, and thermal properties that distinguish them from metals, acrylic resins, and resin-based composites. Silicate glasses differ from nonsilicate glasses in that silicon is the central divalent cation that is bound to four relatively large oxygen anions that link in a random order to other tetrahedra to form polymeric-type $(SiO_2)_n$ chains. In silica-based ceramics, each oxygen atom invariably connects two (SiO_4) tetrahedra only at the corners, and no edges and faces of tetrahedra are shared. The properties of ceramics are customized for dental applications by precisely controlling the types and amounts of the components used in their production. Ceramics are more resistant to corrosion than plastics. Ceramics do not react readily with most liquids, gases, alkalis, and weak acids. They also remain stable over long time periods. They exhibit good to excellent strength and fracture toughness. One of the strongest and toughest ceramics, zirconium dioxide, has a flexural strength similar to that of steel, but its fracture toughness is much lower than that of steel. However, metals are tougher than either ceramics or plastics. Although ceramics are strong, temperature-resistant, and resilient, these materials are brittle and may fracture without warning when flexed excessively or when quickly heated and cooled (i.e., under thermal shock conditions). Most dental ceramics are compounds of oxygen with metals or semimetals (metalloids) that have some properties of both metals and nonmetals, but, all ceramic products are nonmetallic in nature.

Most ceramics are characterized by their biocompatibility, esthetic potential, refractory nature, high hardness, low to moderate fracture toughness, excellent wear resistance, susceptibility to tensile fracture, and chemical inertness. For dental applications a ceramic with a hardness less than that of tooth enamel and an easily polishable surface are desirable to minimize the wear damage that can be produced on enamel by the ceramic surface. However, adequate fracture resistance is an important requirement of any dental ceramic. In this regard, the fracture toughness is the most critically important property because it is a measure of the resistance to crack growth under a state of tensile stress.

CRITICAL QUESTION

If tensile strength is not a reliable property of dental ceramics, which property is a better measure of the material's fracture resistance?

The susceptibility to tensile fracture is a drawback, particularly when flaws and tensile stress coexist in the same location within a ceramic prosthesis. However, the tensile strength of ceramics is not a useful parameter to describe their fracture resistance for several reasons. Strength is not an inherent property of ceramics because it varies with specimen size, specimen length, specimen shape, loading rate, surface preparation methods, and the environment. For example, the strength of silica-based ceramics increases with a decrease in specimen thickness, an increase in stressing rate, and a smoother surface. Such variability indicates that strength is not necessarily a bulk property since surface conditions can significantly alter the mean strength as well as the spread of experimental values, as indicated by the Weibull modulus and the coefficient of variation. In comparison, fracture toughness is a true material property that is a measure of the resistance to crack propagation.

It is generally believed that dental ceramics fail primarily because of their brittleness, which is inversely related to its ductility or percent elongation. In general, the major reason for fracture of ceramics is their inability to suppress crack growth by deforming plastically in areas adjacent to crack tips that are subjected to tensile stress. Since there is no other property that directly expresses brittleness, except perhaps for the reciprocal of percent elongation, two fracture mechanics properties may better explain this behavior. Fracture toughness or plane-strain fracture toughness, which is designated as K_{Ic}, describes the critical stress intensity factor based on a mode I (tensile loading perpendicular to the crack plane) crack opening under tensile stress. For dental ceramics, K_{Ic} varies between 0.75 $MPa \cdot m^{1/2}$ for **feldspathic porcelain** to 8 $MPa \cdot m^{1/2}$ or more for yttria-stabilized **zirconia**, or ceria-stabilized alumina-zirconia ceramic. In comparison, the K_{Ic} values for enamel, dentin, and resin composites are 0.7 to 1.3, 3.1, and 0.8 to 2.5 $MPa \cdot m^{1/2}$, respectively.

Another property that is used to describe the brittle fracture resistance of ceramics is the critical strain energy release rate, which is designated as G. The energy release rate failure criterion is that a crack will grow when the energy release rate is greater than or equal to a critical value, Gc, which is referred to as the fracture energy. This property is a measure of the unit strain energy that is released per unit increase in crack area as a ceramic with flaws or cracks is loaded progressively. Comparative values of K_{Ic} $(MPa \cdot m^{1/2})$ and G_c (kJ/m^2) for different types of materials are (1) glass: 0.7 versus 0.007; (2) PMMA: 1.1 versus 0.5; and (3)steel: 150 versus 107, respectively.

Chemical inertness is an important characteristic because it ensures that the chemically stable surface of dental

restorations does not release potentially harmful elements, and it reduces the risk for surface roughening and increased abrasiveness or increased susceptibility to bacterial adhesion over time. Other important attributes of dental ceramics are their potential for matching the appearance of natural teeth, their thermal insulating properties (low thermal conductivity and low thermal diffusivity), and their freedom from galvanic effects (low electrical conductivity). Because the metal atoms transfer their outermost electrons to the nonmetallic atoms and stabilize their highly mobile electrons, ceramics are excellent thermal and electrical insulators.

? CRITICAL QUESTION

What roles do oxygen, potassium, and leucite play in the structure and properties of feldspathic veneering (layering) ceramics?

Dental ceramics are nonmetallic, inorganic structures, primarily containing compounds of oxygen with one or more metallic or semi-metallic elements (aluminum, boron, calcium, cerium, lithium, magnesium, phosphorus, potassium, silicon, sodium, titanium, and zirconium). Many dental ceramics contain a crystal phase and a silicate glass matrix phase. Their structures are characterized by chains of $(SiO_4)^{4-}$ tetrahedra in which Si^{4+} cations are positioned at the center of each tetrahedron with O^- anions at each of the four corners (Figure 18-1). The resulting structure is not close-packed and it exhibits both covalent and ionic bonds. The SiO_4 tetrahedra are linked by sharing their corners. They are arranged as linked chains of tetrahedra, each of which contains two oxygen atoms for every silicon atom. The primary structural unit in all silicate structures is the negatively charged silicon-oxygen tetrahedron $(SiO_4)^{4-}$. It is composed of a central silicon cation (Si^{4+}) bonded covalently to four oxygen anions located at the corners of a regular tetrahedron. For feldspathic veneering porcelains, alkali ions such as sodium or potassium occupy sites that allow them to bond to electrons from unbalanced oxygen ions (see Figure 18-1). Alkali cations such as potassium or sodium tend to disrupt silicate chains and increase the thermal expansion of these glasses. The expansion coefficient (TEC) can be further increased by including crystalline particles such as tetragonal leucite ($K_2O{\bullet}Al_2O_3{\bullet}4SiO_2$ or $KAlSi_2O_6$), whose TEC ranges from 22 to 30×10^{-6}/K. Two of the primary phase fields (potash feldspar and leucite) that are found in commercial feldspathic veneering ceramics are shown in a ternary section of the $K_2O{\bullet}Al_2O_3{\bullet}SiO_2$ phase diagram in Figure 18-2. Sanidine ($KAlSi_3O_8$), a potassium aluminosilicate phase, exists at high temperatures although it may be retained on cooling in the form of monoclinic crystals.

VITABLOCS Mk II is the only known dental ceramic with sanidine as the primary crystal phase. The glass matrix phase in these porcelains is formulated from one or more forms of the mineral feldspar ($KAlSi_3O_8$, $NaAlSi_3O_8$, and $CaAl_2Si_2O_8$). Many of the veneering ceramics (also called porcelains) are derived from potash feldspar ($K_2O{\bullet}Al_2O_3{\bullet}6SiO_2$ or $KAlSi_3O_8$), although some may be based on soda feldspar or a combination of both types. Compositions of some dental ceramics are listed in Table 18-1. In industry, the term *porcelain* is generally associated with ceramics produced with a significant amount of kaolinite [$Al_2Si_2O_5(OH)_4$ or $Al_2O_3{\bullet}2SiO_2{\bullet}2H_2O$]. Kaolinite is a form of kaolin, which is a type of clay. None of the modern low-fusing or ultralow-fusing porcelains contains any clay product such as kaolinite. However, it may be used in the formulations for high-fusing porcelain and ceramic denture teeth (see Figure 18-2). Thus, these ceramics are technically not porcelains and they can be considered a type of glass (e.g., leucite glass, fluorapatite glass, or feldspathic glass). However, until the international community sees the need to change our terminology from *porcelain* to *glass*, we will continue to use the term *porcelain*.

Ceramics are composed of metallic and nonmetallic elements that form crystalline and/or noncrystalline compounds. They may form binary compounds such as **alumina** (Al_2O_3) and zirconia (ZrO_2) by the bonding of metals, which

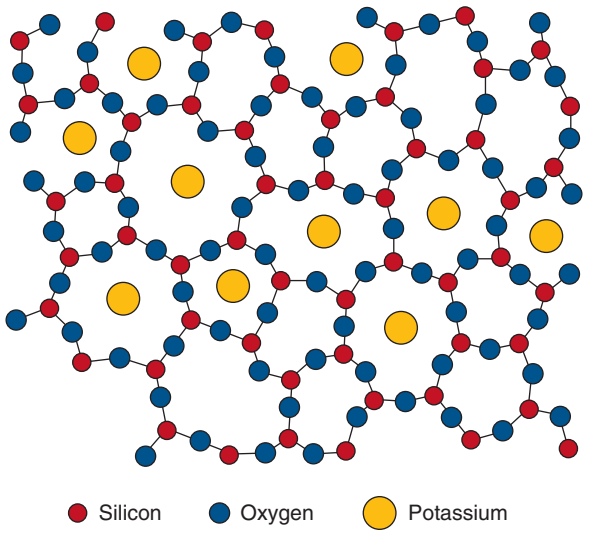


FIGURE 18-1 Two-dimensional amorphous structure of potassium silicate glass.

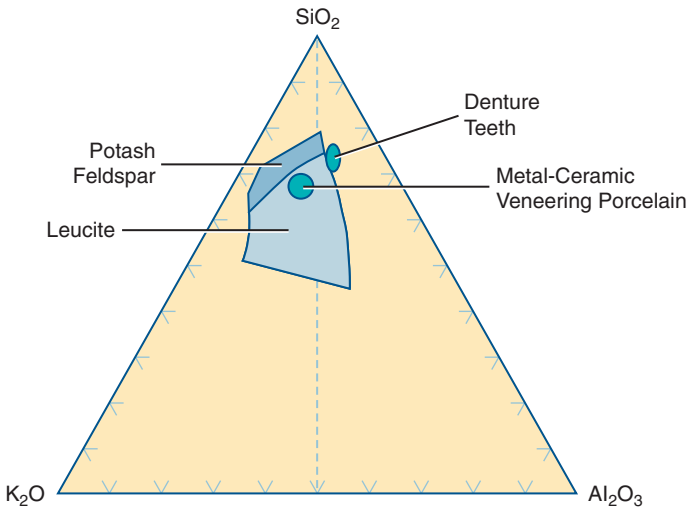


FIGURE 18-2 Principal phase fields of feldspathic ceramics in the ternary K_2O-Al_2O_3-SiO_2 system.

TABLE 18-1 Composition (Percentage by Weight) of Selected Ceramics

	LOW-FUSING VACUUM PORCELAIN			METAL-CERAMIC PORCELAIN			HIP GLASS-CERAMIC	HAP/GLASS
				LOW-FUSING				
Component	Aluminous Porcelain	Dentin	Enamel	Dentin	Enamel	Ultralow-Fusing	IPS e.max Press (Based on $Li_2O•2SiO_2$)	IPS e.max Ceram Veneer Ceramic
SiO_2	35.0	66.5	64.7	59.2	63.5	60–70	57–80	45–70
Al_2O_3	53.7	13.5	13.9	18.5	18.9	5–10	0–5	5–22
CaO	1.1	2.1	1.8	—	—	1–3.0	—	1–11
Na_2O	2.8	4.2	4.8	4.8	5.0	10–15	—	4–13
K_2O	4.2	7.1	7.5	11.8	12.3	10–13	0–13	3–9
B_2O_3	3.2	6.6	7.3	4.6	0.1	0–1.0	—	—
ZnO	—	—	—	0.6	0.1	—	0–8	—
ZrO_2	—	—	—	0.4	0.1	0–1.0	0–8	—
BaO, Y_2O_3	—	—	—	—	—	0–0.2	—	—
SnO_2	—	—	—	—	—	0–0.2	—	—
Li_2O	—	—	—	—	—	0–1.0	11–19	—
F	—	—	—	—	—	0–1.0		0.1–2.5
P_2O_5	—	—	—	—	—	—	0–11	0.5–6.5
Sb_2O_3	—	—	—	—	—	0–1.0	—	—
CeO_2	—	—	—	—	—	0–0.2	—	—
TiO_2	—	—	—	—	—	1–3.0	—	—
Pigments/Other	—	—	—	—	—	—	0–8/0–10	0–3
Sintering/Firing Temperature (°C)	980	980	950	900	900	650–700	945	750

release their positive valence electrons to nonmetals that can accept or share electrons (negative ions). The free energy for bonding of positive metal ions to negative nonmetal ions must be sufficiently low so that the metallic ions preferentially attract nonmetallic ions rather than their own ions or other positive ions. Molecules with one oxygen atom (such as Na_2O, K_2O, or CaO) are useful in dental porcelain as fluxes. They may also act as opacifiers. Molecules that contain three oxygen atoms for every two other atoms (such as Al_2O_3) are used as stabilizers. They are also added as crack blockers or toughening crystals. Silica (SiO_2) is the main glass-forming structure used in all dental veneering ceramics. All silicates of dental interest are derived from silica tetrahedral structures that can be linked as chains, double chains, or three-dimensional distributions of tetrahedra. Fluxing cations such as K^+ or Na^+ neutralize the negative charges of the silicate backbones and disrupt the continuity of silicate networks (see Figure 18-1), leading to lower **sintering** temperatures and increased coefficients of thermal expansion.

Zirconia is of major dental importance because of its high fracture toughness. However, pure ZrO_2 is not useful because cracks occur during sintering as a result of transformation from the tetragonal to the monoclinic phase. This transformation can be fully or partially suppressed by the addition of certain oxides such as MgO, Y_2O_3, CaO, or CeO. Most of the current zirconia ceramic materials for dental prostheses are based on tetragonal zirconia particles (TZP) that are fully stabilized with yttria (Y_2O_3). The addition of yttria to pure zirconia replaces some of the Zr^{4+} ions in the zirconia lattice with Y^{3+} ions. This produces oxygen vacancies, since three O^{2-} ions replace four O^{2-} ions. For several dental zirconia products, approximately 0.25% of Al_2O_3 is added to prevent the leaching of yttria (Y_2O_3).

Multicomponent or mixed oxide structures may also be useful for dental applications. Three examples of this class of ceramics include $MgO•Al_2O_3$ (**spinel**), $3Al_2O_3•2SiO_2$ (mullite, which is located along the right-side border of Figure 18-2), and Al_2TiO_5 or $Al_2O_3•TiO_2$ (aluminum titanate). The spinel structure is used in a **glass-infiltrated ceramic** (In-Ceram Spinell) for applications in which greater translucency is required. Most nonoxide ceramics are not of practical use in dentistry either because of their high processing temperatures, complex processing methods, or their unesthetic color and opacity. Such ceramics include borides (TiB_2, ZrB_2), carbides (B_4C, SiC, TiC, WC), nitrides (AIN, BN, Si_3N_4, TiN), selenide (ZnSe), silicide ($MoSi_2$), sialon (Si_3N_4 with Al_2O_3), and syalon (Si_3N_4 with Al_2O_3 and Y_2O_3).

Glass-ceramics are partially crystallized glasses that are produced by nucleation and growth of crystals in the glass matrix phase. An example of such a product that has been used in dentistry is Dicor glass-ceramic, which was based on the growth of tetrasilicic fluormica crystals in a glass matrix.

This material was originally supplied in a glass ingot form. The glass ingots, which contained a nucleating agent, were melted and cast into a refractory mold and subsequently processed thermally to produce the crystal phase of the glass-ceramic core material. Casting of glass forms is no longer performed for producing dental prostheses. Hot-pressing and CAD-CAM processing are now used to produce glass-ceramic core frameworks for crowns and bridges.

CRITICAL QUESTION

Which property of bilayer ceramics is used as a measure of the **thermal compatibility** of ceramic materials?

Dental ceramics are formed into prosthetic shapes and configurations through a variety of processes including sintering, casting, hot isostatic pressing, **copy milling**, and CAD-CAM machining. The components of the ceramics are based on metal oxides and glasses that are formulated for each particular application. For example, ceramics made as veneering structures on metal frameworks must be capable of bonding to the surface oxide of the metal substructure or to other veneering ceramic layers. The coefficient of thermal expansion (CTE) and coefficient of thermal contraction (CTC) of the ceramic layers must be matched to that of the metal framework in such a way that crack-initiating tensile stresses in the ceramic are avoided or minimized during cooling. The CTEs and CTCs of the veneering ceramics are controlled by varying their composition. In this chapter the calculated TEC differences between two bonded materials are used to describe thermal compatibility between adjacent structural materials. Because of "trapped excess volume" of glass-phase ceramics on cooling after a dilatometry specimen is produced, the subsequent TEC may be significantly lower than the true expansion coefficient because of structural relaxation during the subsequent expansion measurement. This discrepancy can provide misleading information on whether or not a ceramic veneer is thermally matched to its metal or ceramic substructure.

Other component oxides are included to modify the esthetic or appearance characteristics of the final prosthesis, including the hue, value, chroma, opacity, and luminescence. Dental ceramic prostheses may also be used without a metal substructure when ceramic teeth are used in dentures or when all-ceramic crowns and fixed dental prostheses are used to satisfy optimal esthetic or biocompatibility requirements. However, because the brittle glass-phase veneering ceramics are susceptible to crack formation at sites of surface and subsurface flaws in the presence of tensile stresses, these materials must be processed carefully and designed in such a way that the magnitudes of these stresses are minimized.

This chapter describes the composition, microstructure, properties, manipulation procedures, and performance characteristics of ceramic materials used for producing metal-ceramic and all-ceramic prostheses cemented on prepared teeth, on implant abutments, or on other material substrates used in the construction process. Although ceramics made from kaolin, feldspar, and quartz have been used for many centuries, major improvements in dental ceramics have occurred only within the past century. To understand the current state of materials science and technology, dental students, graduate students, and practicing dentists should be familiar with the terminology. The Key Terms section provides the definitions required to facilitate an understanding of ceramic science and technology as they relate to dental prosthetic applications and the clinical performance of metal-ceramic and ceramic-ceramic restorations.

CRITICAL QUESTION

Through what mechanism does transformation toughening increase the fracture resistance of yttria-stabilized zirconia?

APPLICATIONS OF CERAMICS IN DENTISTRY

Dental ceramic science and technology represent the fastest growing areas of dental materials research and development. During the past two decades numerous types of ceramics and processing methods have been introduced. Some of these materials can be formed into inlays, onlays, veneers, crowns, and more complex fixed dental prostheses (FDPs). Several of the core ceramics can be resin-bonded micromechanically to tooth structure. The future of dental ceramics is very promising because the increased demand for tooth-colored restorations will lead to an increased acceptance of ceramic-based and polymer-based restorations and the reduced use of amalgam and cast metals.

This chapter describes the ceramics used for metal-ceramic prostheses and the new generation of ceramic products, such as Cercon, Lava, IPS e.max ZirCAD, In-Ceram Zirconia, Denzir, IPS e.max CAD, Denzir, BruxZir, Procera AllCeram, and Procera Zirconia, which are being used currently for ceramic prostheses in dental practices. Previous glass-ceramics were produced either by crystallization of tetrasilic fluormica or leucite crystals. However, further increases in strength and fracture toughness occurred subsequently with lithium disilicate–based products such as IPS Empress 2 and IPS e.max Press, among others. Introduced later were products such as In-Ceram Alumina, a glass-infiltrated **alumina core** ceramic; In-Ceram Zirconia, a glass-infiltrated zirconia-alumina core ceramic; Lava, a partially sintered or fully sintered zirconia core that is formed by a true CAD-CAM process (by scanning dies without the need for a wax pattern); and Cercon, a partially-sintered zirconia ceramic that is milled to an enlarged size in the **green state** based on scanning of a wax pattern. It is also possible to scan prepared teeth and mill a prosthesis using the Cerec system (Sirona Corp., Germany). The Cerec 1 system was introduced in the mid-1980s and improvements in software and hardware led to the Cerec 2 and Cerec 3 systems for production of ceramic inlays, onlays, and veneers, and the commercial InLab system for large-scale processing of ceramic copings, frameworks, and monolithic ceramic prostheses.

Dental ceramics are used primarily for the production of fixed dental prostheses. Although ceramics such as zirconia

can be used for endodontic posts and implant abutments, their primary applications are for crowns and bridges. Because of its lack of translucency, zirconia is better suited for applications involving posterior teeth or for elderly patients whose teeth have lost much of their original translucency. Each family of dental ceramics has specific indications and contraindications for which it is best suited or not suited. The characteristics and uses of the range of dental ceramics are described in this chapter.

? CRITICAL QUESTION

Which two inventions dramatically increased the success and survival probability of metal-ceramic restorations?

HISTORY OF DENTAL CERAMICS

Ceramic-like tools have been used by humans since the end of the Old Stone Age around 10,000 B.C. to support the lifestyles and needs of fisher-hunter-gatherer civilizations. During the Middle Stone Age (10,000 to 5500 B.C.) ceramics were important materials, and they have retained their importance in human societies ever since. Stone Age craftsmen took rocks and shaped them into tools and artifacts by a process called flaking and flintknapping, whereby stone chips could be fractured away from the surfaces of hard, fine-grained, or amorphous materials including chert, flint, ignimbrite, indurated shale, lava, obsidian, quartz, and silicified limestone. For example, craftsmen of the Paleo-Indian culture, from 10,000 to 6000 B.C., made arrowheads, spear points, and flaking tools from a variety of natural rock materials. Such rocks contained mineral phases such as feldspar, mica, and quartz, which have since been used in dental ceramics.

Because natural minerals are not tooth-colored, subsequent civilizations used a variety of materials to produce simulated teeth. In approximately 700 B.C., the Etruscans made artificial teeth of ivory and bone, human teeth, and animal teeth (possibly oxen) that were held in place by gold wires or flat bands and rivets (Figure 18-3). Animal bone and ivory from hippopotami and elephants were used for many years thereafter.

Human teeth that were sold by the poor and teeth obtained from the dead were also used for centuries thereafter, but dentists generally avoided this option. One of the first sets of dentures made for U.S. President George Washington contained extracted teeth (Figure 18-4, center) but later his dentures were made of hippopotamus ivory (Figure 18-4, left). The ivory tooth forms were supported in the maxillary denture by a gold palatal plate and the dentures were retained by pressure applied by coiled springs attached to the sides of the denture bases. President Washington was inaugurated in 1789 with one remaining tooth. He suffered from poor oral health (although it is reported that he had brushed his teeth regularly with tooth powder). His poor-fitting dentures caused him much discomfort during his presidency (1789–1797) and until his death, in 1799, at the age of 67.



FIGURE 18-3 Copy of Etruscan denture recovered from a tomb in Etruria, Italy, circa 700 B.C. Gold bands of this type held human or animal teeth (possibly oxen) that were fastened by means of gold rivets. (Courtesy of the Science Museum, London.)

None of his dentures were ever made of wood, contrary to erroneous reports circulated since his death.

The first porcelain tooth material was patented in 1789 by de Chemant, a French dentist in collaboration with Duchateau, a French pharmacist. This product, an improved version of the "mineral paste teeth" produced in 1774 by Duchateau, was introduced in England soon thereafter by de Chemant. However, this baked compound was not used to produce individual teeth, since there was no effective way at that time to attach the teeth to a denture base material.

In 1808, Fonzi, an Italian dentist, invented a "terrometallic" porcelain tooth held in place by a platinum pin or frame. Planteau, a French dentist, introduced porcelain teeth to the United States in 1817, and Peale, an artist, developed a baking process in Philadelphia for these teeth in 1822. Commercial production of these teeth by Stockton began in 1825. In England, Ash developed an improved version of the porcelain tooth in 1837. In Germany, Pfaff in 1756 developed a technique to make impressions of the mouth using plaster of Paris, but it was not until 1839 that the invention of vulcanized rubber allowed porcelain denture teeth to be used effectively in a denture base. In 1844, the nephew of Stockton founded the S.S. White Company, which became active in the further refinement of the design and mass production of porcelain denture teeth.

Charles Land introduced one of the first ceramic crowns to dentistry in 1903. Land, the grandfather of aviator Charles Lindbergh, published in the *Independent Practitioner* in 1886 and 1887 a technique for preparing the tooth cavity for an inlay, making a platinum foil matrix, and fabricating a ceramic inlay using high-fusing feldspathic porcelain. The sintering temperature was empirically determined as reported by Gilbert ("Notes on Dental Porcelain," Harvard University Dental School, 1906), who described the temperature required to "set" the inlay as one that was between the melting point of pure gold (1084 °C) and the maximum temperature recommended for the porcelain muffle (1370 °C).



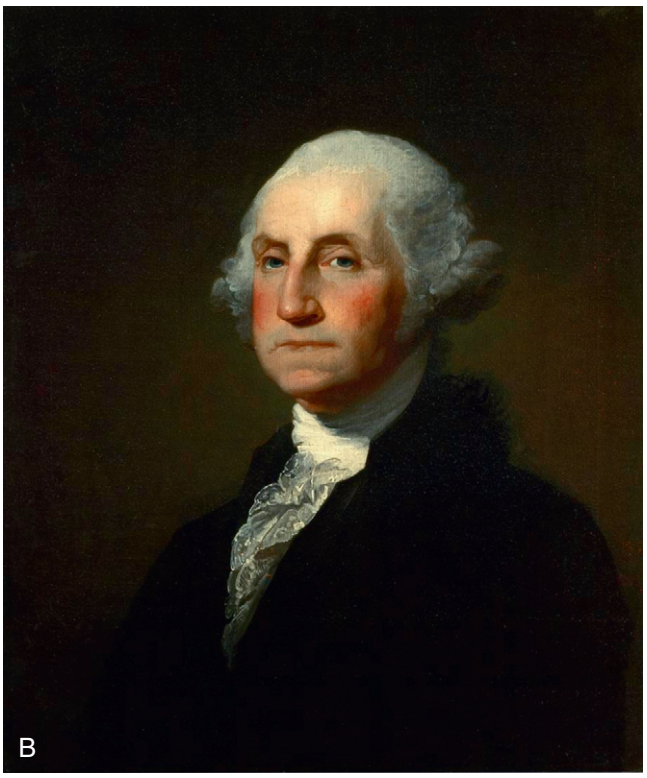


FIGURE 18-4 **A,** (*Far left*) Spring-retained maxillary and mandibular dentures of U.S. President George Washington, made from hippopotamus ivory by dentist John Greenwood. (*Center and Right*) Two of the first dentures made for the president using extracted human teeth. (Courtesy of the New York Academy of Medicine Library.)

B, Portrait of President Washington, who died on December 14, 1799. Technology for producing porcelain denture teeth was not available until 1825, although these prostheses were not refined until vulcanized rubber denture bases were developed in 1839.

These crowns exhibited excellent esthetics, but the low flexural strength of porcelain resulted in a high incidence of fracture. Since the 1960s, feldspathic porcelains with reliable chemical bonding have been used in metal-ceramic prostheses. However, feldspathic porcelains have been considered too weak to be used reliably in the construction of all-ceramic crowns without a tougher ceramic core, a cast-metal core, or metal-foil coping. Furthermore, their firing shrinkage results in significant discrepancies in fit and adaptation of margins unless correction firings are performed.

Two of the most important breakthroughs responsible for the long-standing superb esthetic performance and clinical survival probabilities of metal-ceramic restorations are described in the patents of Weinstein and Weinstein (1962) and Weinstein et al. (1962). One of these patents identified the formulations of feldspathic porcelain that enabled the systematic control of the sintering temperature and coefficient of thermal expansion. The other patent described the components that could be used to produce alloys that bond chemically to and that are thermally compatible with the feldspathic porcelains. The first commercial porcelain was developed by VITA Zahnfabrik in about 1963. Although the first VITA porcelain products were known for their esthetic properties, the subsequent introduction of the more versatile Ceramco porcelain led to thermal expansion behavior that allowed this porcelain to be used safely with a wider variety of alloys.

A significant improvement in the fracture resistance of all-porcelain crowns was reported by McLean and Hughes in 1965, when they introduced a dental **aluminous** core ceramic consisting of a glass matrix containing between 40% and 50% Al_2O_3 by weight. Because of the inadequate translucency (**opaque**, chalky-white appearance) of the aluminous porcelain core materials, a feldspathic porcelain veneer was required to achieve acceptable esthetics. The flexural strength (modulus of rupture) of the core material was approximately 131 MPa. McLean (1979) reported a low 5-year fracture rate of only 2% for anterior crowns but an unacceptably high fracture rate of 15% when aluminous porcelain was used for molar crowns. Another deficiency of the aluminous porcelain crown was the large sintering shrinkage (approximately 15% to 20%) of the core material at its high firing temperature. Because of their relatively high fracture rate in posterior sites, the principal indication for the use of aluminous porcelain crowns was the restoration of maxillary anterior crowns where esthetics was of paramount importance. Since the introduction of aluminous porcelain crowns in the early 1900s and methods to produce durable metal-ceramic crowns in the 1960s, improvements in the composition of ceramics and the method of forming the ceramic core of ceramic crowns have greatly enhanced our ability to produce better-fitting fracture-resistant crowns made entirely of ceramic material.

Significant developments in metal-ceramic properties, design, and performance—such as opalescence, specialized internal staining techniques, greening-resistant porcelains, porcelain-butt-joint margins, and **shoulder porcelains**—have significantly enhanced the overall appearance and "vitality" of metal-ceramic crowns and bridges and the clinical survivability of these restorations. Improvement in all-ceramic systems developed by controlled crystallization of a glass (Dicor) was demonstrated by Adair and Grossman (1984). This glass was melted and cast into a refractory mold

and subsequently crystallized to form the Dicor glass-ceramic containing tetrasilicic fluormica crystals in a glass matrix. A further development was the introduction of a machinable glass-ceramic version (Dicor MGC), which had a tetrasilicic fluormica crystal volume of approximately 70%. In the early 1990s a pressable glass-ceramic (IPS Empress), containing approximately 34% leucite by volume, was introduced. IPS Empress had a strength and marginal adaptation similar to those of Dicor glass-ceramic, but it required no specialized crystallization treatment. Neither of these materials was indicated for producing **fixed dental prostheses.** A more fracture-resistant, pressable glass-ceramic (IPS Empress 2) containing approximately 70% lithia disilicate crystals by volume was introduced in the late 1990s. This core ceramic has been used for three-unit fixed dental prostheses as far posterior as the second premolar. The fracture toughness of IPS Empress 2 glass-ceramic (3.3 MPa•$m^{1/2}$) is more than twice that of its predecessor, IPS Empress glass-ceramic (1.3 MPa•$m^{1/2}$).

These improvements in the composition of ceramics and the method of forming the core of all-ceramic crowns and bridges have greatly enhanced our ability to produce more accurate and fracture-resistant all-ceramic crowns. Significant progress has been made toward the goal of developing less abrasive veneering ceramics. In 1992 Duceram LFC (low-fusing ceramic) was marketed as an ultralow-fusing ceramic with three unique features: (1) it was based on a hydrothermal glass in which water was incorporated into the silicate glass structure to produce nonbridging hydroxyl groups that disrupt the glass network, thereby decreasing the glass transition temperature, viscosity, and firing temperature, and increasing the coefficient of thermal expansion to allow its use as a veneer for certain low-expansion metals; (2) these types of ceramics were also claimed to be "self-healing" through a process of forming a 1-µm-thick hydrothermal layer along the ceramic surface; and (3) the extremely small size of the crystal particles (400 to 500 nm) enhanced the opalescence of the ceramic by reflecting blue light hues from the surface and yellow hues from the interior of the ceramic. Other ultralow-fusing ceramics (sintering temperatures below 850 °C) now commonly referred to as low-fusing ceramics have been introduced with a veneering glass; these materials were claimed to be kinder to opposing tooth enamel either because they were predominantly a glass phase material or because they contained very small crystal particles.

CLASSIFICATION OF DENTAL CERAMICS

In this chapter dental ceramics are divided into two main categories, ceramics used to veneer metal frameworks for metal-ceramic (MC)—that is, porcelain-fused-to-metal prostheses and ceramics used to produce all-ceramic prostheses. Shown in Figure 18-5 is a cross-sectional view of a metal-ceramic crown.

Dental ceramics can be classified according to one or more of the following parameters: (1) uses or indications (anterior and posterior crown, veneer, post and core, **fixed dental prosthesis**, **ceramic stain**, **glaze**); (2) composition; (3) principal crystal phase and/or matrix phase (silica glass, leucite-based feldspathic porcelain, leucite-based glass-ceramic, lithia disilicate–based glass-ceramic, aluminous porcelain, alumina, glass-infused alumina, glass-infused spinel, glass-infused alumina/zirconia, and zirconia; (4) processing method (casting, sintering, partial sintering and glass infiltration, **slip casting** and sintering, hot-isostatic pressing, CAD-CAM milling, and copy-milling); (5) firing temperature (ultralow fusing, low fusing, medium fusing, and high fusing) (Table 18-2); (6) microstructure (amorphous glass, crystalline, crystalline particles in a glass matrix); (7) translucency (opaque, translucent, transparent); (8) fracture resistance (low, medium, high); and (9) abrasiveness (comparison relative to tooth enamel against tooth enamel). To allow a clinician to select the best material for a given clinical situation, the following sections describe the relative characteristics of dental ceramics as a function of one or more of these classifications. Table 18-3 lists the types of dental ceramics by their recommended indications for and contraindications

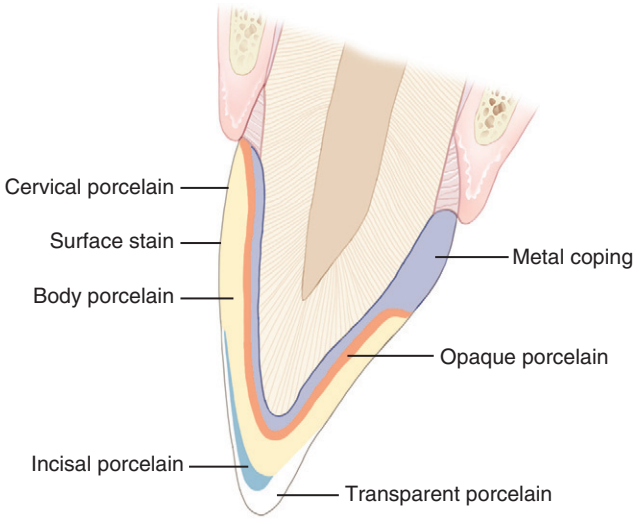


FIGURE 18-5 Schematic illustration of a metal-ceramic (porcelain fused to metal) crown.

TABLE 18-2 Classification of Dental Ceramics by Sintering Temperature

Class	Applications	Sintering Temperature Range
High fusing	Denture teeth, and fully sintered alumina and zirconia core ceramics	>1300 °C (>2372 °F)
Medium fusing	Denture teeth, presintered zirconia	1101 °C–1300 °C (2013 °F–2372 °F)
Low fusing	Crown and bridge veneer ceramic	850 °C–1100 °C (1562 °F–2012 °F)
Ultralow fusing	Crown and bridge veneer ceramic	<850 °C (<1562 °F)

TABLE 18-3 General Indications and Contraindications for Use of Dental Ceramics

Type	Primary Application	Secondary Applications	Contraindications
Feldspathic porcelain	Metal-ceramic veneers Anterior laminate veneers	Single surface inlays/Low stress sites High translucency needed	Inlays, onlays, crowns, and bridges (except as metal-ceramic veneers) Bruxism
Aluminous porcelain	Core ceramic for anterior crowns	Low-stress premolar crowns	Molar crowns Bridges Bruxism
Leucite glass-ceramic	Anterior single-unit crowns Anterior laminate veneers	Low-stress premolar inlays and crowns High translucency needed	High-stress situations Bridges Bruxism
Lithium disilicate glass-ceramic	Anterior and premolar crowns Anterior three-unit bridges Premolar crowns	Anterior laminate veneers Posterior three-unit bridges to second premolar	High-stress posterior situations Bridges involving molar teeth Bruxism
Alumina	Core ceramic for crowns Low-stress anterior bridges	Low-stress posterior bridges	Anterior veneers High-stress posterior bridges Bruxism
Glass-infiltrated spinel	Anterior crowns	High translucency needed	Anterior bridges Posterior crowns and bridges Bruxism
Glass-infiltrated alumina	Anterior and posterior crowns	Anterior bridge substructures up to three units	Anterior veneers Posterior crowns and bridges High translucency needed Bruxism
Glass-infiltrated alumina/zirconia	Posterior crowns Posterior bridge substructures up to three units	Anterior bridge substructures up to three units	Anterior veneers and crowns Where high translucency needed Bruxism
Zirconia (Y-TZP) (with veneering ceramic)	Posterior crowns Posterior bridge substructures up to 5 units		Anterior veneers, crowns, and bridges High translucency is needed Bruxism
Zirconia (Y-TZP) (without veneering ceramic)	Posterior crowns and bridges (limited clinical data available)	Posterior core-ceramic bridges	Anterior veneers, crowns, and bridges High translucency is needed Bruxism
Ce-TZP/Al_2O_3	Posterior crowns and bridge substructures (no clinical data available)	—	Anterior veneers, crowns, and bridges High translucency is needed Bruxism

against their use. Although manufacturers and dental laboratory owners usually list the indications for use of ceramic products, they do not typically state their contraindications. Only after clinical evidence of adverse events occur do the indications change and contraindications become more clearly specified. Table 18-3 reflects a relatively conservative perspective on uses of each type of ceramic based in part on evidence from clinical studies. The information presented does not guarantee success nor is it predictive of failure, because many variables are involved that may shift the balance of risk from low to high. Note that bruxism is a typical contraindication for most ceramics because of the higher risk for fracture as well as the increased risk for wear of opposing tooth enamel surfaces. An example of severe wear of enamel by ceramic is shown in Figure 18-6. Although the extreme abrasion damage shown in this figure may not have occurred primarily because of bruxism, it was related to increased stresses that developed because posterior teeth were not present to distribute the applied mastication forces over posterior teeth as well.

Dental ceramics can be classified by composition. It is not feasible to discuss the compositions of the numerous existing dental products. However, it is useful to be familiar initially with some representative compositions of feldspathic porcelains and an aluminous porcelain. The compositions of typical products are given in Table 18-1. Note that the major component in most of these ceramics is silica, which is the basis of the glass matrix phase of feldspathic porcelains used as a veneering or layering structure of both metal-ceramic and all-ceramic prostheses. These veneering ceramics provide hue, value, chroma, and translucency characteristics to the final restoration. In addition, the fine-grain varieties may cause less wear of opposing enamel or tooth restorations than coarse-grain ceramics.

Classification by processing method is also informative because it is likely that many of the ceramics that fall within

a specific type of processing requirement will behave similarly in a clinical setting, particularly with respect to marginal fit, polishability, failure mechanisms, esthetic potential, wear resistance, abrasiveness, and survivability. A classification of materials by processing method is presented in Table 18-4.



FIGURE 18-6 Excessive wear of mandibular teeth abraded by opposing porcelain surfaces. (Courtesy of Dr. Henry Young.)

To allow a clinician to select the best material for a given clinical situation, the following sections describe the relative characteristics of dental ceramics as a function of one or more of these classifications.

There are four categories of dental ceramics for metal-ceramic systems: (1) manually condensed feldspathic veneering porcelains, (2) hot isostatically pressed (HIP) veneering ceramics, (3) ceramic stains, and (4) glazes. There are six categories of dental ceramics for all-ceramic systems: (1) HIP or CAD-CAM core ceramics, (2) manually condensed veneering ceramics, (3) hot-pressed veneering ceramics, (4) liners, (5) ceramic stains, and (6) ceramic glazes. These material categories are discussed throughout the remainder of this chapter.

The compositions of these ceramics are generally classified by the principal crystal phases controlling their properties. The most common crystal phases are leucite, lithia disilicate, alumina, combinations of alumina and zirconia, zirconia, and apatite. Leucite crystals are included in veneering porcelains for metal-ceramics to opacify and strengthen these glass-matrix materials and to control their thermal expansion and contraction coefficients. Leucite crystals also play similar roles in the formulation of HIP and CAD-CAM core

TABLE 18-4 Methods of Processing the Ceramic Core Component of a Ceramic Prosthesis

Initial Forming Method	Examples	Initial Material Form	Second Processing Step	Subsequent Form	Final Steps
Condensation	Ceramco, VITA VMK, Duceram LFC, IPS d.Sign	Powder and mixing liquid	Sintering of core ceramic	Dense core ceramic with less than 5 vol% porosity	Veneer, glaze
Hot pressing	IPS Empress 2, OPC 3G, Finesse Pressable	High-quality ceramic ingot	Stain only or stain and glaze (inlays), or veneering ceramic	Stained/glazed inlay or veneered core	Stain and/or glaze for crowns and FPDs
Casting	Dicor (obsolete)	Glass core	Crystallization heat treatment (ceramming)	Glass-ceramic core containing a glass phase and tetrasilicic fluormica crystals	Shading porcelain (obsolete)
Slip casting	In-Ceram Alumina In-Ceram Spinell, In-Ceram Zirconia	Powder and mixing liquid	Partial sintering	Partially sintered core	Glass infiltration, trimming of excess glass, veneer, glaze
Computer-aided milling (CAM) of fully sintered form	Cerec VITABLOCS In-Denzir BruxZir	High-quality ceramic ingot	Margin repair (if necessary)	High-quality core possibly with repaired margin	Veneer, glaze (except for BruxZir)
Computer-aided milling (CAM) of partially sintered form	Cercon Lava e.max ZirCAD	Partially sintered ceramic block	Final sintering of machined/ground core and margin repair (if necessary)	Fully sintered core possibly with repaired margin	Veneer, glaze
Copy milling	Variety of ceramic products	High-quality ceramic block	Margin repair (if necessary	High-quality core possibly with repaired margin	Veneer, glaze
Machining, grinding of dry-pressed powder on enlarged die	Procera AllCeram	Dry pressed and machined alumina block	Sintering	High-quality core containing 99.9% alumina	Veneer, glaze

structures of all-ceramic prostheses. Note that although most of the dental literature emphasizes the thermal expansion coefficient (TEC), the thermal contraction coefficient (TCC) is more relevant for analyzing stresses in veneering ceramic that develop during cooling. This difference is most significant for glass-phase ceramics.

Lithia disilicate glass-ceramics, alumina/zirconia, and zirconia are used exclusively for the core structure of the all-ceramic applications. Total core ceramic restorations of posterior crowns and bridges made from either lithia disilicate glass-ceramic or zirconia ceramic have been used to eliminate veneer chipping, gross fracture of veneering (layering) ceramics, and to maximize the size of connectors in fixed dental prostheses (bridges) in order to reduce connector fractures. One of the main concerns on the use of core ceramic prostheses is their potential for increased wear of opposing tooth enamel. Although the surfaces of these prostheses can be glazed to minimize enamel wear, the long-term durability of glaze layers continues to be evaluated.

METAL-CERAMIC SYSTEMS: COMPOSITION AND PROPERTIES

BENEFITS OF METAL-CERAMIC PROSTHESES

Several clinical studies over the past 50 years confirm the high overall survival percentages of metal-ceramic (MC) prostheses. One clinical study revealed that the fracture rate of metal-ceramic crowns as well as bridges made from a high noble alloy was as low as 2.3% over 7.5 years of service. The most outstanding advantage of metal-ceramic restorations is their resistance to fracture. With metal occlusal surfaces, the fracture rate in posterior sites could be reduced further. Another potential advantage of metal-ceramic restorations over total-ceramic restorations is that less tooth structure needs to be removed to provide the proper bulk for the crown, especially if thinner (<0.1 mm) layered noble foil metal is used, where metal alone is used on occlusal surfaces and lingual cusps or porcelain butt-joint margins are used on facial and buccal surfaces. Such designs also cause less wear of antagonist enamel than occurs when enamel is opposed by a ceramic surface.

There are relatively few disadvantages to metal-ceramic restorations compared with all-ceramic choices. One of the most frequently mentioned disadvantages is the potential for metal allergy. However, such allergic reactions are very rare except possibly when nickel-containing alloys are used. Although metal-ceramic restorations have accounted recently for about 60% to 70% of all fixed restorations, a metal-ceramic crown is not the best esthetic choice for restoring a single maxillary anterior tooth. An all-ceramic crown offers a greater potential for success in matching the appearance of the adjacent natural tooth, especially when a relatively high degree of translucency is desired.

A dark line at the facial margin of a metal-ceramic crown associated with a metal collar or metal margin is a significant esthetic concern when gingival recession occurs. This adverse esthetic effect can be minimized by designing the crown with a ceramic margin or by using a very thin knife-edge margin of metal veneered with opaque shoulder porcelain. This ceramic margin should be polished and/or glazed to avoid a rough surface at the margin. The use of metal-ceramic crowns with porcelain shoulder or butt-joint margins or with knife-edge metal margins are successful procedures for improving the esthetics of metal-ceramic prostheses.

CRITICAL QUESTION

Which components of ceramics can cause excessive wear of tooth enamel?

CERAMIC COMPOSITION

Conventional dental porcelain is a vitreous ceramic based on a silica (SiO_2) network and potash feldspar ($K_2O{\bullet}Al_2O_3{\bullet}6SiO_2$), soda feldspar ($Na_2O{\bullet}Al_2O_3{\bullet}6SiO_2$), or both. The ternary diagram in Figure 18-2 for the K_2O-Al_2O_3-SiO_2 system shows the approximate composition ranges of feldspathic porcelain products used for metal-ceramic prostheses and denture teeth. This diagram is based on the use of potash feldspar ($K_2O{\bullet}Al_2O_3{\bullet}6SiO_2$) rather than soda feldspar ($Na_2O{\bullet}Al_2O_3{\bullet}6SiO_2$), which is also used in some products. Pigments, opacifiers, and glasses are added to control the fusion temperature, sintering temperature, coefficient of thermal contraction, and solubility. The feldspars used for dental porcelains are relatively pure and colorless. Thus, pigments must be added to produce the hues of natural teeth or the color appearance of tooth-colored restorative materials that may exist in adjacent teeth.

Feldspathic porcelains contain, by weight, a variety of oxides including a SiO_2 matrix (52% to 65%), Al_2O_3 (11% to 20%), K_2O (10% to 15%), Na_2O (4% to 15%), and certain additives, including B_2O_3, CeO_2, Li_2O, TiO_2, and Y_2O_3. These ceramics are called porcelains because they contain a glass matrix and one or more crystal phases, although the term *porcelain* traditionally refers in industry to products produced from kaolin as a major component. They cannot be classified as glass-ceramics because crystal formation does not occur through controlled nucleation, crystal formation, and growth. There are four types of veneering ceramics. Feldspathic porcelains include (1) ultralow- and low-fusing ceramics (feldspar-based porcelain, nepheline syenite–based porcelain, and apatite-based porcelain); (2) low-fusing specialty ceramics (shoulder porcelains and wash-coat ceramics); (3) ceramic stains; and (4) ceramic glazes (autoglaze and **overglaze**). The compositions of two typical low-fusing veneering porcelains for metal-ceramic prostheses are listed in Table 18-1.

The particle type and crystal particle size may greatly influence the potential abrasiveness of the ceramic prosthesis. The abrasiveness of the finished surface will depend on the thickness of the veneer and the presence or absence of crystalline particles. Excessive wear of enamel may occur by direct two-body contact against core ceramics of all-ceramic restorations or opaque porcelain of metal-ceramic restorations, but core ceramics that are veneered are unlikely to

contact opposing enamel except in situations where inadequate tooth reduction or excessive occlusal reduction has occurred.

CRITICAL QUESTION

How does the leucite content of veneering porcelain for metal-ceramic prostheses control the cracking resistance of the porcelain?

Silicate glass represents the matrix phase of feldspathic porcelains. Silica (SiO_2) can exist in four different forms: crystalline quartz, crystalline cristobalite, crystalline tridymite, and noncrystalline fused silica. Fused silica is a high-melting material whose melting temperature is attributed to the three-dimensional network of covalent bonds between silica tetrahedra, the basic structural units of the glass network. Fluxes (low-fusing glasses) are often included to reduce the temperature required to sinter the porcelain powder particles at sufficiently low temperatures so that the alloy to which it is fired does not melt or sustain sag (flexural creep) deformation.

Potassium and sodium feldspars are naturally occurring minerals composed of potash (K_2O) or soda (Na_2O), alumina (Al_2O_3), and silica (SiO_2). They are used in the preparation of many dental porcelains designed for metal-ceramic crowns and many other dental glasses and ceramics. When potassium feldspar is mixed with various metal oxides and fired to high temperatures, it can form leucite and a glass phase that will soften and flow slightly. The softening of this glass phase during porcelain firing allows the porcelain powder particles to coalesce. For dental porcelains, the process by which the particles coalesce is called liquid-phase sintering, a process controlled by diffusion between particles at a temperature sufficiently high to form a dense solid. The driving force for sintering is the decrease in energy caused by a reduction in surface area.

Another important property of feldspar is its tendency to form crystalline leucite ($K_2O{\bullet}Al_2O_3{\bullet}4SiO_2$) when it is melted. Leucite is a potassium-aluminum-silicate mineral with a high coefficient of thermal expansion (20 to 25 $\times$ 10^{-6}/K) compared with feldspar glasses that have much lower coefficients of thermal expansion (8.6×10^{-6}/K). When feldspar is heated at temperatures between 1150 °C and 1530 °C, it undergoes incongruent melting to form crystals of leucite in a liquid glass. Incongruent melting is the process by which one material melts to form a liquid plus a different crystalline material. This tendency of feldspar to form leucite during incongruent melting controls thermal expansion during the use of porcelains for metal bonding. Some dental glasses do not contain leucite as a raw material. Since feldspar is not essential as a precursor to the formation of leucite, these glasses are modified with additions of leucite to control their coefficients of thermal contraction.

The compositions of the veneering (layering) ceramics used for metal-ceramic restorations (see Table 18-1) generally correspond to those used previously for veneering aluminous porcelain core ceramic except for increased concentrations of K_2O and Na_2O. For metal-ceramic porcelains, specific concentrations of soda, potash, and/or leucite are necessary to reduce the sintering temperature and to increase the thermal expansion to a level compatible with that of the metal coping. The opaque porcelains also contain relatively large amounts of metallic oxide opacifiers to conceal the underlying metal and to minimize the thickness of the opaque porcelain layer.

Veneering ceramics ("porcelains") for metals have higher expansion and contraction coefficients than the ceramics used to veneer alumina or zirconia core ceramics. They should not be subjected to nonessential repeated firings, because this may lead to devitrification and an increased risk of cloudiness within the porcelains as well as potential changes in their coefficient of thermal expansion (α_e) and coefficients of thermal contraction (α_c). It is imperative that a proper matching of these thermal properties of the alloy and porcelain be ensured to reduce the risk for chipping or cracking of the ceramic veneers either during cooling from the sintering or glazing temperatures or at some later time in clinical service.

METAL COMPOSITION

Single-unit crowns and bridges may be made from metal-ceramic systems (combinations of metal substructure and veneering ceramic). In this chapter the term *metal-ceramic* (MC) is used synonymously with *porcelain fused to metal* (PFM), although the former term (MC) is the most internationally accepted descriptor for these types of prosthetic material systems.

Many alloys are available to be veneered with low-fusing and ultralow-fusing porcelains. The compositions of these high noble, noble, predominantly base metal alloys control the castability, bonding ability to porcelain, the esthetics of the metal-ceramic restoration, and the magnitudes of stresses that develop in the porcelains during cooling from the sintering temperature. A typical list of alloy types of one manufacturer is presented in Table 18-5. Some important properties of these alloys are listed. Of particular importance to the section below is the coefficient of thermal expansion (CTE) or contraction, which must match closely to that of the veneering porcelain to be used.

The compositions of the high noble alloys, titanium and titanium alloys, noble alloys, predominantly base metal alloys CPTi, Ti alloys used for metal-ceramic restorations are discussed further in Chapter 16. The reader is referred to this chapter for a description of these systems and of the effects and purposes of the constituent metals.

ULTRALOW-FUSING CERAMICS FOR METAL-CERAMIC PROSTHESES

Most of the ultralow-fusing ceramics (sintering temperatures below 850 °C) have microstructures that exhibit either a well-distributed dispersion of small crystal particles or few or no crystals. Initial results of wear studies are promising in several cases relative to the enamel wear (see Figure 18-6) caused by these ceramics, although not all ultralow-fusing ceramics exhibit this decreased level of abrasiveness. Ultralow-fusing ceramics contain less Al_2O_3 and increased concentrations of CaO, K_2O, Li_2O, and Na_2O.

TABLE 18-5 Composition and Properties of Typical Alloys for Metal-Ceramic Prostheses

	COMPONENTS AND PROPERTIES								
Alloy Product	Principal Elements	Noble Metal (wt%)	ADA Class	2% Proof Stress (MPa)	Elongation (%)	Hardness (VHN)	Elastic Modulus (GPa)	CTE (25 °C –500 °C) 10^{-6}/K	CTE (25 °C –600 °C) 10^{-6}/K
Brite Gold	Au-Pt-In	99.0	HN	230	15.0	100	79	14.8	15.0
Brite GoldXH	Au-Pt	97.9	HN	355–427	11.0	180	107	14.4	14.7
Golden Ceramic	Au-Pt-Pd	97.4	HN	360	12.0	165	64	14.6	14.7
Aquarius Hard	Au-Pt-Pd	97.2	HN	455	12.0	205	88	14.5	14.8
Aquarius	Au-Pt-In	97–98	HN	320	12.0	160	79	14.6	14.8
IPS d.SIGN 98	Au-Pt	98.0	HN	510	8.0	220	80	14.3	14.6
Y	Au-Pt-Pd	96.8	HN	320	12.0	160	81	14.6	14.8
Aquarius XH	Au-Pt-Pd	96.8	HN	510	7.0	220	83	14.1	14.4
Y-2	Au-Pt-Pd	94.6	HN	380	12.0	155	83	15.0	15.1
Y-Lite	Au-Pd-Ag	93.8	HN	500	14.0	225	88	13.9	14.1
Sagittarius	Au-Pd-Pt	95.8	HN	580	10.0	245	94	14.0	14.3
Y-1	Au-Pd-Pt	87.4	HN	340	15.0	185	99	14.8	15.0
IPS d.SIGN 96	Au-Pd-Pt	87.7	HN	405	15.0	214	92	14.3	14.5
IPS d.SIGN 91	Au-Pd-In	90.6	HN	570	31.0	250	136	14.2	14.4
W	Au-Pd-Ag	80.4	HN	455	21.0	220	113	14.2	14.5
W-5	Au-Pd-Ag	78.2	HN	530	20.0	255	118	14.0	14.2
Lodestar	Au-Pd-In	90.0	HN	495	20.0	240	98	14.1	14.3
W-3	Au-Pd-In	88.3	HN	495	17.0	225	128	13.9	14.1
W-2	Au-Pd-Ag	85.3	HN	640	20.0	205	113	14.2	14.6
Evolution Lite	Au-Pd-In-Ag	89.6	HN	375	11.0	280	130	14.2	14.5
Capricorn	Pd-In-Ga-Au	84.1	N	525	21.0	260	101	14.3	14.5
IPS d.SIGN 84	Pd-In-Au-Ag	84.2	N	485	29.0	295	117	13.8	14.0
IPS d.SIGN 67	Pd-Ag-Sn-Au	66.7	N	545	15.0	240	104	13.9	14.2
Spartan Plus	Pd-Cu-Ga-Au	80.8	N	795	20.0	310	97	14.3	14.6
Capricorn 15	Pd-Ag-Au-Pd	66.9	N	490	21.0	255	101	14.3	14.5
Aries	Pd-Ag-Sn	63.7	N	415	46.0	185	98	14.7	14.8
IPS d.SIGN 59	Pd-Ag-Sn	59.2	N	490	14.0	230	139	14.5	14.8
IPS d.SIGN 53	Pd-Ag-Sn-In	53.8	N	545	13.0	250	132	14.8	14.9
W-1	Pd-Ag-Sn	53.3	N	485	11.0	240	114	15.2	15.4
Calisto CP+	Co-Pd-Cr-Mo	25.0	N	640	10.0	365	180	14.4	14.9
Pisces Plus	Ni-Cr-W	0	PB	600	10.0	280	183	14.1	14.4
IPS d.SIGN 15	Ni-Cr-Mo	0	PB	340	13.0	200	200	13.9	14.2
IPS d.SIGN 30	Co-Cr-Mo	0	PB	520	6.0	375	234	14.5	14.7

Ultralow-fusing porcelains generally contain, by weight, 20.1% to 22.6% tetragonal leucite and 0% to 2.6% cubic leucite, although one product contains 11.5% to 11.6% tetragonal leucite and 2.9% to 4.6% cubic leucite. The conventional **frits** have been reported to be admixtures of three kinds of glass frits. One of these ultralow-fusing frits exhibits very small (less than 1 μm) leucite crystals.

Ultralow-fusing dentin and enamel ceramics may be easier to polish and may yield smoother and less abrasive surfaces than conventional low-fusing and medium-fusing porcelains. Because of their lower concentration of leucite crystals compared with conventional porcelains, they have lower expansion and contraction coefficients. Their lower sintering temperatures provide opportunities for use with alloys that have lower fusion temperatures, such as type II and type IV gold alloys, whose compositions have been modified to ensure proper chemical bonding and matched thermal expansion and contraction coefficients.

GLASS MODIFIERS

The sintering temperature of crystalline silica is too high for its use as a veneer on cast dental alloys. At such temperatures the alloys would melt. In addition, the coefficient of thermal contraction of crystalline silica is too low for these alloys. Bonds between the silica tetrahedra can be broken by the addition of alkali metal ions such as sodium, potassium, and calcium. These ions are associated with the oxygen atoms at the corners of the tetrahedra and interruption of oxygen-silicon bonds. As a result, the three-dimensional silica network contains many linear chains of silica tetrahedra that are able to move easily at lower temperatures than the atoms that are locked into the three-dimensional structure of silica tetrahedra. This ease of movement is responsible for the increased fluidity (decreased viscosity), lower softening temperature, and increased thermal expansion conferred by glass modifiers. However, too high a modifier concentration reduces the chemical durability (resistance to attack by water, acids, and alkalis) of the glass. In addition, if too many tetrahedra are disrupted, the glass may crystallize (devitrify) during porcelain firing operations. Hence, a balance between a suitable melting range and good chemical durability must be maintained.

Manufacturers employ glass modifiers to produce dental porcelains with different firing temperatures. Dental porcelains are classified according to their firing temperatures. A typical classification is given in Table 18-2. Other metallic oxides also can be introduced, as indicated in Table 18-1. Boric oxide (B_2O_3) can behave as a glass modifier to decrease viscosity, to lower the softening temperature, and to form its own glass network. Because boric oxide forms a separate lattice interspersed with the silica lattice, it still interrupts the more rigid silica network and lowers the softening point of the glass. The role of alumina (Al_2O_3) in glass formation is complex. Alumina is not a true glass former, but it can take part in the glass network to alter the softening point and viscosity.

Pigmenting oxides are added to obtain the various shades needed to simulate natural teeth. These coloring pigments are produced by fusing metallic oxides with fine glass and feldspar and then regrinding to a powder. These powders are blended with the unpigmented powdered frit to provide the proper hue and chroma. Examples of metallic oxides and their respective color contributions to porcelain include iron or nickel oxide (brown); copper oxide (green); titanium oxide (yellowish brown); manganese oxide (lavender); and cobalt oxide (blue). Opacity may be achieved by the addition of cerium oxide, zirconium oxide, titanium oxide, or tin oxide.

Medium- and high-fusing porcelains are used for the production of denture teeth. The low-fusing and ultralow-fusing types are used as veneering ceramics for crown and bridge construction. Some of the ultralow-fusing porcelains are used for titanium and titanium alloys because of their low-contraction coefficients that closely match those of the metals and because the low firing temperatures reduce the risk for growth of the metal oxide. However, some of these ultralow-fusing porcelains contain enough leucite to raise their coefficients of thermal contraction as high as those of conventional low-fusing porcelains.

To ensure adequate chemical durability, a self-glaze of porcelain is preferred to an add-on glaze. A thin external layer of glassy material is formed during a self-glaze firing procedure at a temperature and time that cause localized softening of the glass phase. The add-on glaze slurry material that is applied to the porcelain surface for an overglaze procedure contains more glass modifiers and thus has a lower firing temperature. However, a higher proportion of glass modifiers tend to reduce the resistance of the applied glazes to leaching by oral fluids.

Another important glass modifier is water, although it is not an intentional addition to dental porcelain. The hydronium ion, H_3O^+, can replace sodium or other metal ions in a ceramic that contains glass modifiers. This fact accounts for the phenomenon of "slow crack growth" of ceramics exposed to tensile stresses and moist environments. It also may account for the occasional long-term failure of porcelain restorations after several years of service.

CERAMIC PROCESSING METHODS

The processing stages of the ceramic core for the production of ceramic prostheses are summarized in Table 18-4. The quality of the final ceramic prosthesis is dependent on each stage of the fabrication process. Machining or grinding of the core structure is of particular importance, since flaws or minute cracks can be introduced that can possibly be propagated to the point of fracture during subsequent intraoral stressing cycles. The use of computer-aided manufacture (CAM) processes is most likely to induce such damage, although ceramics with higher fracture toughness are less likely to sustain such damage. It is possible that subsequent sintering or veneering procedures can reduce the potential for crack propagation of cracks in the prostheses while in service. Although reheating tends to seal surface cracks, it does not necessarily "heal" subsurface cracks.

Feldspathic porcelains that are used to make traditional metal-ceramic restorations, some aluminous porcelains (Vitadur-N, Vitadur Alpha, Hi-Ceram), and pure alumina ceramic (Procera AllCeram) are condensed by vibration and sintered at high temperatures. **Hot-pressed ceramics** (IPS Empress, IPS Empress 2, Finesse All-Ceramic, and OPC-3G) are heated, injected under pressure into a mold, and then veneered. Cast and cerammed crowns, such as Dicor, an obsolete glass-ceramic, were made using the lost-wax technique. The glass was cast into a mold, heat-treated to form a glass-ceramic, and colored with shading porcelain and surface stains.

For slip-cast ceramics (In-Ceram, In-Ceram Spinell, In-Ceram Zirconia), a slurry of liquid and particles of alumina, magnesia-alumina silicate (spinel), or zirconia and alumina are placed on a dry refractory die that draws out the water from the slurry. The slip-cast deposit is sintered on this die and then coated with a slurry of a glass-phase layer. During firing, the glass melts and infiltrates the porous ceramic core. Translucent porcelain veneers are then fired onto the core to provide final contour and color.

For CAD-CAM processes, the ceramic block materials (Dicor MGC, VITA Cerec Mk I, and VITA Cerec Mk II) are shaped into inlays, onlays, or crowns using a CAD/CAM system (Cerec). *CAM* refers to computer-aided machining (or milling). These blocks can also be used in copy-milling devices (Celay) that mill or machine blocks into core shapes in a manner similar to that for cutting a key from a key blank—that is, by tracing over a master die of the shape to be produced out of the ceramic. CAD-CAM processing is described further in the section "All-Ceramic Systems."

? CRITICAL QUESTION

How is the degree of sintering controlled and what parameter defines complete sintering?

FABRICATION OF METAL-CERAMIC PROSTHESES

PORCELAIN CONDENSATION

Porcelain for ceramic and metal-ceramic prostheses as well as for other applications is supplied as a fine powder designed to be mixed with water or another liquid and condensed into the desired form. The powder particles are of a particular size distribution to produce the most densely packed porcelain when they are properly condensed. If the particles are of the same size, the density of packing would not be nearly as high. Proper and thorough condensation is also crucial in obtaining dense packing of the powder particles. This provides two benefits: lower firing shrinkage and less porosity in the fired porcelain. This packing, or condensation, may be achieved by various methods, including the vibration, spatulation, and brush techniques.

The first method uses mild vibration to pack the wet powder densely on the underlying framework. The excess water is blotted away with a clean tissue and condensation occurs toward the blotted area. In the second method, a small spatula is used to apply and smooth the wet porcelain. This smoothing action brings the excess water to the surface, where it is removed. The third method employs the addition of dry porcelain powder to the surface to absorb the water. The dry powder is placed by a brush to the side opposite from an increment of wet porcelain. As the water is drawn toward the dry powder, the wet particles are pulled together. Whichever method is used, it is important to remember that the surface tension of the water is the driving force in condensation and that the porcelain must not be allowed to dry out until condensation is complete.

SINTERING PROCEDURE

The thermochemical reactions between the porcelain powder components are virtually completed during the original manufacturing process. Thus, the purpose of firing is to sinter the particles of powder together properly for a specific time and temperature combination to form the prosthesis. Some chemical reactions occur during prolonged firing times or multiple firings. Of particular importance are the observed changes in the leucite content of the porcelains designed for fabrication of metal-ceramic restorations. As stated earlier, leucite is a high-expansion and high-contraction crystal phase whose volume fraction in the glass matrix can greatly affect the coefficient of thermal contraction of the porcelain. Changes in the leucite content can cause the development of a coefficient of thermal contraction mismatch between the porcelain and the metal and thus can produce stresses during cooling that are sufficient to cause crack formation in the porcelain.

The condensed porcelain mass is placed in front of or below the muffle of a preheated furnace at approximately 650 °C for low-fusing porcelain. This preheating procedure permits the remaining water to evaporate. Placement of the condensed mass directly into even a moderately warm furnace results in a rapid production of steam, thereby introducing voids or fracturing large sections of the veneer. After preheating for approximately 5 minutes, the porcelain is placed into the furnace and the firing cycle is initiated.

The size of the powder particles influences not only the degree of condensation of the porcelain but also the soundness or apparent density of the final product. At the initial firing temperature, the voids are occupied by the atmosphere of the furnace. As sintering of the particles begins, the porcelain particles bond at their points of contact and the structure shrinks and densifies. As the temperature is raised, the sintered glass gradually flows to fill the air spaces. However, air becomes trapped in the form of voids because the fused mass is too viscous to allow all of the air to escape. An aid in the reduction of porosity in dental porcelain is *vacuum firing*. Complete sintering is accomplished when the structure achieves 100% of its theoretical density. However, this is unlikely to occur even in the presence of a vacuum, since it is very unlikely that all porosity will be eliminated under typical dental sintering conditions.

Vacuum firing reduces porosity in the following way. When the porcelain is placed into the furnace, the powder particles are packed together with air channels around them. As the air pressure inside the furnace muffle is reduced to about one tenth of atmospheric pressure by the vacuum pump, the air around the particles is also reduced to this pressure. As the temperature rises, the particles sinter together, and closed pores are formed within the porcelain mass. The air inside these pores is isolated from the furnace atmosphere. At a temperature about 55 °C below the sintering temperature, the vacuum is released and the pressure inside the furnace increases by a factor of 10, from 0.1 to 1 atm. Because the pressure is increased by a factor of 10, the pores are compressed to one tenth of their original size, and the total volume of porosity is accordingly reduced. Not all of the air can be evacuated from the furnace. Therefore, a few bubbles are present, but they are markedly smaller than those obtained with the usual air-firing method. At a condition of 95% to 99% theoretical density, the dental veneering ceramic is claimed to be mature or fully sintered. A list of some veneering ceramics for metal-ceramic prostheses is given in Table 18-6.

TABLE 18-6 Veneering Ceramics for Metal-Ceramic Prostheses

Veneering Ceramic	Compatible Alloys	Manufacturer
Synspar	Most alloys	Jeneric/Pentron
Pencraft Plus	Most alloys	Jeneric/Pentron
Finesse Low Fusing	Most alloys	DENTSPLY Ceramco
Ceramco II	Most alloys	DENTSPLY Ceramco
Ceramco II Silver	Silver-containing alloys	DENTSPLY Ceramco
Ceramco 3	Most alloys	DENTSPLY Ceramco
Duceragold (hydrothermal)	Degunorm Type IV gold alloy for metal-ceramics	Degussa
SymbioCeram (hydrothermal)	Most alloys	Degussa
Duceram Plus	Most alloys	Degussa
Duceram LFC	Most alloys	Degussa
Excelsior	Most alloys	Ney
Porcelfina	Most alloys	Ney
IPS d.SIGN	Most alloys	Ivoclar Vivadent Inc.
IPS Classic V	Most alloys	Ivoclar Vivadent Inc.
VITA Response	Degunorm (Degussa) and Mainbond A (Heraeus), Type IV gold alloys for metal-ceramics	VITA Zahnfabrik
VITA VMK 95	Most alloys	VITA Zahnfabrik
VITA Omega	Most alloys	VITA Zahnfabrik
VITA Omega 900 (Low-fusing)	Most alloys	VITA Zahnfabrik

COOLING

The proper cooling of a porcelain-veneered prosthesis from its firing temperature to room temperature is the subject of considerable importance. The catastrophic fracture of glass that has been subjected to sudden changes in temperature is a sufficiently familiar experience so that most lab technicians are cautious about exposing dental porcelain to extremely rapid cooling (thermal shock) after firing. The cooling of dental porcelain, however, is a complex matter, particularly when the porcelain is bonded to a metallic substrate. Multiple firings of a **metal-ceramic prosthesis** can cause the coefficient of thermal contraction of the leucite-containing porcelain to increase and actually make it more likely to crack or craze because of tensile stress development.

The chief limitation to the use of an all-porcelain crown in fixed prosthodontics is its lack of tensile and shear strength. A method for minimizing this disadvantage is to bond the porcelain directly to a metal coping that fits the prepared tooth. The metal-ceramic restoration shown schematically in Figure 18-5 has a facial metal thickness of 0.3 to 0.5 mm. It is veneered with opaque porcelain approximately 0.3 mm in thickness. The body porcelain is about 1 mm thick.

Since a ductile metal is used as an inner core of a metal-ceramic crown, cracks will not propagate in the metal, but they can progress through the veneering ceramic or within the interfacial region. With proper design and physical properties of the porcelain and metal, the porcelain is protected by a residual compressive stress so that brittle fracture of the veneer can be avoided or at least minimized. Although most metal-ceramic restorations involve cast metal copings, several novel noncast approaches (electrodeposition, milling, swaging, and burnishing) for the fabrication of metal substructures have been developed in recent years. The fracture resistance of metal-ceramic prostheses made from these core metals is less reliable compared with those made from traditional cast metal copings and frameworks.

? CRITICAL QUESTION

What condition is required of cast metals to achieve ionic and/or covalent bonding to veneering porcelain?

CAST METAL FOR METAL-CERAMIC PROSTHESES

The development of the metal-ceramic restoration was the result of advances in the formulation of both alloys and porcelains. To bond to alloys suitable for the copings, porcelains must have a sufficiently low sintering temperature and they also must have CTEs and CTCs that are closely matched to those of the alloys.

A metal oxide is necessary to promote chemical bonding. The gold alloys developed for porcelain bonding have higher melting ranges than typical gold alloys for all-metal prostheses; the higher melting ranges are necessary to prevent sag, creep, or melting of the coping or framework during the sintering and/or glazing of porcelain. These gold alloys contain small amounts (about 1%) of base metals such as iron, indium, and tin, as discussed in Chapter 16. A wide range of high noble and noble alloys is summarized in Table 18-5. The base metals form a surface oxide layer during the oxidation treatment, and this surface oxide is responsible for development of a bond with porcelain. This process is sometimes called degassing, which is a misnomer, because the primary purpose is to produce an adherent metal oxide on the surface to facilitate bonding to porcelain. This porcelain-metal bond is primarily ionic and chemical in nature and is capable of forming even when the metal surface is smooth and little opportunity exists for mechanical interlocking. The chemical bonding may be primarily ionic but is likely to have a covalent component as well.

? CRITICAL QUESTION

Why should a metal coping or framework have a higher expansion coefficient than its veneering porcelain?

The alloys and porcelains used for the construction of such restorations have a number of stringent requirements. For example, the metal framework must not melt during porcelain firing and also must resist high-temperature "sag" deformation. Sag or flexural creep occurs only at high temperatures. It does not occur at oral temperatures. Both the metal and the ceramic must have coefficients of thermal expansion and contraction that are closely matched such that the metal must have a slightly higher value to avoid the development of undesirable residual tensile stresses in the porcelain. If the contraction coefficients are not nearly equal, stresses may occur that weaken both the porcelain and the bond. For example, a difference in the coefficients of thermal contraction of 1.7×10^{-6}/K can produce a shear stress of 280 MPa in porcelain next to the metal-porcelain interface when the porcelain is cooled from 954 °C to room temperature. Because the shear resistance to failure is far less than 280 MPa, these thermal stresses would likely cause spontaneous bond failure or cracking of the veneering ceramic.

High tensile stresses in the veneering ceramic develop from a contraction coefficient mismatch between alloy and porcelain in which the porcelain contracts more than the metal. The tensile stresses induced within the restoration by occlusal forces would be added to the residual thermal tensile stresses. However, for metal-porcelain systems that have an average contraction coefficient difference of 0.5×10^{-6}/K or less (between 600 °C and room temperature), fracture is unlikely to occur except in cases of extreme stress concentration or extremely high intraoral forces. These are known as *thermally compatible systems.* Many restorations made from metal and porcelain combinations having contraction coefficient differences between 0.5 and 1.0×10^{-6}/K are known to survive for many years. These results are explainable by survival probability analyses, which assume that the maximum biting force on anterior crowns rarely exceeds 890 N (200 lb) and the maximum force on posterior crowns rarely exceeds 2224 N (500 lb). However, the *Guinness Book of Records* (1993) cites the maximum clenching force ever recorded for posterior teeth as 4337 N (975 lb) sustained for 2 seconds. The second highest bite force ever recorded was 2447 N (550 lb). Most patients generate typical bite forces of 400 to 800 N (90 to 180 lb) between molar teeth and much lower forces between premolars and between anterior teeth. Thus, a rather small number of patients have bite force capabilities likely to cause fracture of metal-ceramic crowns or bridges even when residual thermal incompatibility stresses are present. As a rule, lower forces are generated by younger children, female patients, a more closed bite, occlusion between natural teeth, a complete denture, and a fixed dental prosthesis. Chipping fractures have been reported at greater frequencies in veneers of zirconia prostheses compared with metal-ceramic prostheses. There are several possible causes, including thermal incompatibility, inadequate substrate design, and contact (Hertzian) stresses.

Another equally important property of metal-ceramic systems is the relatively high proportional limit and high modulus of elasticity of these materials. Alloys with a high modulus of elasticity share a greater proportion of stress than the adjacent porcelain.

TECHNICAL ASPECTS OF METAL-CERAMIC PRODUCTS

CAST METAL COPINGS AND FRAMEWORKS

Copings and frameworks for metal-ceramic prostheses are produced by casting of molten metal, CAD-CAM machining, electrolytic deposition techniques, or swaged metal processes. The most common method is the melting and casting of specialized metals, and this process is highlighted as the principal process in this chapter. For the casting process, the relatively high melting temperatures of most alloys can break down gypsum-bonded investments at the casting temperatures, so the more refractory phosphate-bonded investment must be used.

Each casting should be carefully cleaned to ensure a strong bond to the porcelain. For example, an alloy such as Olympia (Heraeus Kulzer), a gold-palladium, silver-free alloy, is heated in the porcelain furnace to a temperature of 1038 °C to burn off any remaining impurities to form a thin oxide layer. This so-called degassing treatment does not actually degas the interior structure of the alloy. Instead, it produces an oxide layer on the alloy surface that is essential for the formation of the porcelain-metal bond.

The need for a clean metal surface cannot be overemphasized. Metal oxidation is necessary for all gold-porcelain systems. Oil from fingers and other sources such as air lines represents a possible contaminant. The surface may be cleansed adequately by finishing with clean ceramic-bonded stones or sintered diamonds, which are used exclusively for finishing. Final sandblasting with high-purity alumina abrasive before oxidation ensures that the porcelain will be bonded to a clean and mechanically retentive surface.

Frameworks for metal-ceramic bridges must be designed such that the framework will not be deformed at porcelain sintering temperatures, and the connectors must be large enough to resist flexural strains that may cause cracking under intraoral loading.

Opaque porcelain is condensed on the oxidized surface at a thickness of approximately 0.3 mm (see Figure 18-5) and is then fired to its sintering temperature. Translucent porcelain is then applied, and the tooth form is created. Porcelain powder is applied by the condensation methods previously described. The unit is again fired. Several cycles of porcelain application and firing may be necessary to complete the restoration. A final glaze is then produced either by self-glazing (Figure 18-7) or firing an overglaze layer.

? CRITICAL QUESTION

True or false? Creep deformation of a high noble alloy framework for a four-unit bridge occurs at an elevated temperature and continues to increase as the framework cools rapidly to room temperature.

CREEP OR SAG

Creep can be reduced if the metal has the proper composition, so that a dispersion strengthening effect occurs at an elevated temperature. When certain gold alloys are heated to approximately 980 °C, a second phase is precipitated that can harden or strengthen the alloy. Such creep has been reduced in some of the commercial alloys, but it apparently cannot be eliminated. The solidus temperature (the lower end of the melting range) of base metal alloys, such as nickel-chromium, is higher than that of gold alloys; hence, base metal alloys are less susceptible to sag deformation than are gold-based alloys. High-temperature *creep* or *sag* of some high noble and noble alloys occurs when the temperature approaches 980 °C. Once the alloy temperature decreases by 100 °C or more, no further creep deformation occurs. For "high noble" yellow-hued alloys, the spans of fixed partial dentures should not exceed three units, since the mass of the prosthesis may increase the bending stress to the point where permanent deformation occurs at the porcelain sintering temperature.

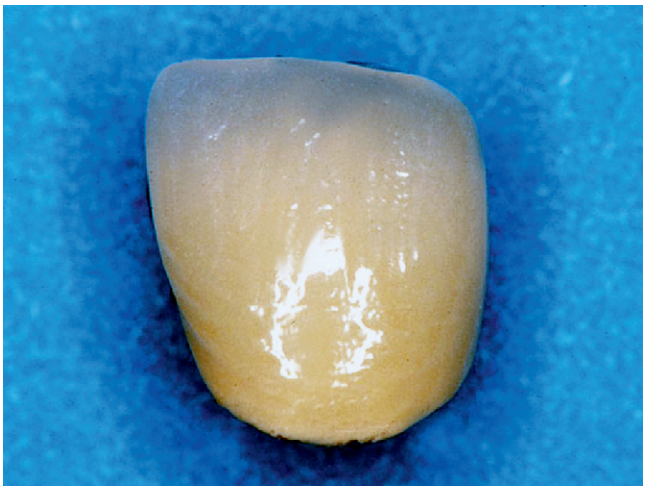


FIGURE 18-7 Autoglazed veneer ceramic.

CRITICAL QUESTION

True or false? The marginal adaptation and fit of a cast crown are equivalent to those of a swaged foil crown.

METAL-CERAMIC CROWNS AND BRIDGES BASED ON SWAGED METAL FOIL LAMINATES

The most widely used product of this type has been Captek (Precious Chemicals Co., Inc., Altamonte Springs, FL), which is an acronym for "capillary assisted technology." The product is designed to fabricate the metal coping of a metal-ceramic crown without the use of a melting and casting process. It is a laminated gold alloy foil sold as a metal strip. Strips of P (Au-Pt-Pd) and G (Au-Ag) metals are applied to a die with a swaging instrument, burnished with a hand instrument or a "P-Press" on the die, and then heated sequentially (P layer followed by the G layer) in a porcelain oven to form a coping with moderate strength. A "bonder" layer is applied and fired, the coping is then veneered with condensed porcelain, and the porcelain is sintered at typical porcelain firing temperatures. Examples of Captek components and a finished bridge are shown in Figure 18-8. For bridges, the pontics are made typically from a palladium-based alloy that is gold-coated. The technology is based on the principle of capillary action to produce a gold-based composite metal. Captek P and G metals



FIGURE 18-8 (*A*) Captek noble metal copings. (*B*) Pontic section attached to two noble metal copings. (*C*) Interior surface of finished Captek crown (left) and finished three-unit FDP (right). Captek three-unit bridge.

can yield thin metal copings for crowns or frameworks for metal-ceramic bridges. The maximal span length recommended for Captek-porcelain bridges is 18 mm, which allows space for up to two pontics. The completed metal coping or framework is a composite metal structure consisting of a gold matrix and small particles of a Pt-Pd-Au alloy with a resulting grain size in the range of 15 to 20 µm. The outer surfaces of the copings contain approximately 97% gold.

The process begins with the preparation of a master refractory die that replicates the prepared tooth. The original gypsum die is sprayed with a surface tension–reducing agent to facilitate flow of the impression material and to reduce bubble formation. Die spacer is applied and undercuts are blocked out. The master die is placed in a duplication flask and silicone impression material is poured into the flask and around the master die. The resulting master impression (mold) is poured with a refractory material (Capvest) to produce a refractory die. The die is heat-treated, and the margins are marked with a red pencil. Captek adhesive is applied to the die to enhance adhesion to the Captek metal and to enhance capillary action.

After heat treatment, Captek P metal, a malleable Au-Pt-Pd alloy, is adapted to the surface. This metal layer provides a three-dimensional capillary network that will subsequently be filled with Captek G metal (97.5% Au, 2.5% Ag by weight) to form an alloy with a high gold content. After this composite material is burnished on the die and the margins are trimmed, it is sintered in a porcelain furnace. The metal copings and Pd-Ag pontics (if needed) are then coated with a slurry of Au, Pt, and Pd powder (Capbond) and liquid, resulting in a thin coating of gold to enhance areas of Captek P that have been ground during adjustment and to provide a gold color similar to that of areas that have not been ground. The completed copings have a thickness of approximately 0.25 mm. Thus, this method provides thinner metal copings than those (0.50 mm) typically produced by the cast-metal process. The metal surfaces are veneered with two thin coats of an opaque porcelain and additional layers of translucent porcelains.

Compared with cast-metal margins formed from the lost-wax process, the accuracy of marginal adaptation for Captek crowns is highly dependent on the skill of the dental technician in trimming the burnished metal copings. In addition, the atomic bonding of veneering ceramics to Captek copings and frameworks is controlled by a special bonder layer, while bonding of ceramics to cast metal is controlled by oxidizable elements within the alloy surface. Another potential concern for the Captek system is the difficulty of bonding the dissimilar metals in the coping and the pontic surfaces. Clinical data for Captek crowns and bridges are very limited. Thus, caution must be exercised in using this system for crowns and bridges in high-stress areas.

? CRITICAL QUESTION

What three conditions control the durability of ceramic bonding to an oxidized metal coping?

BONDING PORCELAIN TO METAL

The primary requirement for the success of a metal-ceramic restoration is the development of a durable bond between the porcelain and the metal oxide. For a metal-ceramic bond to be maintained over time, there should be minimal residual tensile stresses in the porcelain after cooling from the sintering temperature. An unfavorable stress distribution during the cooling process can result in immediate or delayed cracking of the porcelain. Thus, for a successful metal-ceramic restoration to be achieved, both a strong interface bond and thermal compatibility are required. The term *compatibility* has been used in an ISO draft international standard (ISO DIS 9693-1 Dentistry—Compatibility testing—Part 1: Metal-Ceramic Systems) to identify the ability of the composite metal-ceramic system to demonstrate both acceptable adhesion of ceramic to metal oxide and freedom from crack formation associated with tensile stresses attributed to thermal expansion and contraction differences.

Three factors control the durability of metal-ceramic bonding: (1) mechanical interlocking or interatomic bonding at the interface between porcelain and the metal oxide; (2) interatomic bonding across the oxide-porcelain interface; and (3) the type and magnitude of residual stress in the veneering ceramic. Atomic or chemical bonding is primarily responsible for metal-porcelain adherence. However, there is some evidence to support metal-ceramic bonding through a mechanical interlocking mechanism. One Pd-Ag alloy formed an internal oxide but not an external oxide. However, metal nodules were formed on the surface via a creep mechanism. These nodules presumably provided sufficient mechanical retention of porcelain for clinical use, since this alloy has been used for many years without noted problems.

The oxidation behavior of these alloys largely determines their potential for bonding with porcelain. Research into the nature of metal-porcelain adherence has indicated that those alloys that form adherent oxides during the oxidation cycle also form a good bond to porcelain, whereas those alloys with poorly adherent oxides or poor wetting porcelain to the oxide (Figure 18-9) form poor bonds. Although the thickness of the oxide is thought to play a role, there is insufficient evidence to support this theory. Rather, the quality of the oxide and its



FIGURE 18-9 Bond failure of metal-ceramic post and core prosthesis.

adhesion to the metal substrate appear to be the most important factors.

A variety of tests have been advocated for measuring the bond strength. However, because of the inevitable formation of residual tensile and/or compressive stresses during cooling, measurements of bond strength should consider the potential influence of these residual stresses on either increasing or decreasing the "apparent bond strength." If the combination yields residual compressive stress in the porcelain adjacent to the interfacial region, and assuming that a valid test is used to produce interfacial fracture, a higher "apparent bond strength" will result. A fracture that occurs away from the interface does not necessarily prove that the interfacial bond strength is greater than the cohesive strength of either the metal or the ceramic. It may be merely caused by misalignment of loading or such that the maximum tensile or shear stress does not occur within the interfacial region.

GLAZES AND STAIN CERAMICS

? CRITICAL QUESTION

How should the strength of a ceramic three-unit FDP with a polished and glazed porcelain veneer compare with that of an FDP with a highly polished veneer without a glazed surface?

The esthetics of porcelains for metal-ceramic and ceramic prostheses, veneers, and denture teeth may be enhanced through the application of stains and glazes to provide a more lifelike appearance and color match to adjacent teeth or restorations. The fusing temperatures of glazes are reduced by the addition of glass modifiers, typically alkali oxides, which reduce the chemical durability of glazes. Stains are simply tinted glazes that are also exposed to the same chemical durability problems. However, most of the currently available glazes appear to have adequate durability when they are produced in thicknesses of 50 μm or more.

One method for ensuring that the applied characterizing stains will be permanent is to use them internally. Internal staining and characterization can produce a lifelike result, particularly when simulated enamel craze lines and other features are built into the porcelain rather than merely applied on the surface. The disadvantage of internal staining and characterization is that the porcelain must be stripped completely if the color or characterization is unacceptable.

Autoglazed feldspathic porcelain is stronger than unglazed porcelain. The glaze is effective in sealing surface flaws and reducing stress concentrations. Shown in Figure 18-7 is a metal-ceramic crown with a properly fired autoglazed porcelain surface. If the glaze is removed by grinding, the transverse strength may be only half that of the sample with the glaze layer intact. However, some studies indicate that porcelains with highly polished surfaces have strengths comparable to those of specimens that were polished and glazed. This observation is of clinical importance. After the porcelain restoration is cemented in the mouth, it is common practice for the dentist to adjust the occlusion by grinding the surface of the porcelain with a diamond bur. This procedure can weaken the porcelain if the glaze is removed and the surface is left in a rough condition. This can cause increased wear of enamel. For this condition, an acceptable solution is to polish the surface with Sof-Lex (3M, Minneapolis, MN) finishing disks, a Shofu (Shofu, Kyoto, Japan) porcelain laminate polishing kit, or other abrasive system. A smoother surface also reduces the abrasion damage caused to opposing teeth or restorations.

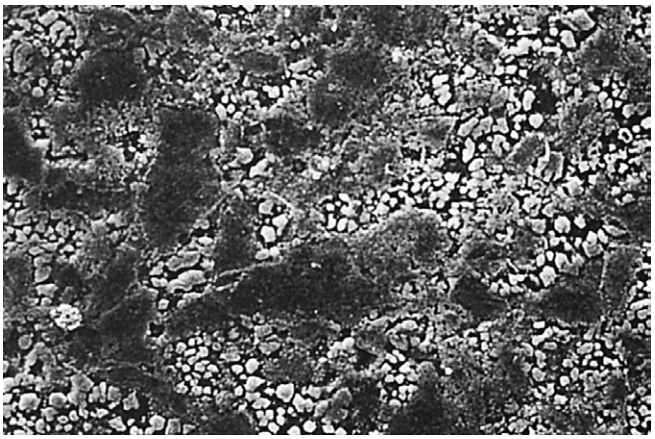


FIGURE 18-10 Surface of feldspathic gingival (body) porcelain after a 30-minute exposure to 1.23% acidulated phosphate fluoride. Most of the degradation has occurred in the glass matrix rather than in the crystal phase.

It is generally believed that glazing of feldspathic porcelain eliminates surface flaws and produces a smoother surface. However, an optimal method of producing the smoothest surface in the shortest time has not been established. It is logical to assume that fine polishing of a roughened surface followed by glazing produces smoother surfaces than polishing alone, sandblasting followed by glazing, or diamond grinding followed by glazing. However, even though one polishes and/or glazes a porcelain veneer surface, the surface will either slowly or markedly break down in the presence of solvents in our everyday diets, which include citric acid, acetic acid and alkalis. Further degradation will occur during exposure of glass-phase ceramics such as porcelain to acidulated phosphate fluoride gel, as shown in Figure 18-10.

BENEFITS AND DRAWBACKS OF METAL-CERAMIC RESTORATIONS COMPARED WITH ALL-CERAMIC RESTORATIONS

A properly made metal-ceramic crown is more fracture-resistant and durable than most all-ceramic crowns and bridges. This technology is well established compared with technologies required of the most recent all-ceramic products. Although the biocompatibility of some metals used for copings and frameworks may be a concern for patients who have known allergies to those metals, these situations are rare. A metal coping or framework provides an advantage compared with zirconia-based ceramic prostheses when endodontic access openings through crowns are required. Temporary repairs for ceramic fractures that extend to the metal framework are possible without the need for intraoral sandblasting treatment by using current resin bonding agents.



FIGURE 18-11 Three-unit all-ceramic posterior bridge.

All-ceramic crowns may be more susceptible to chipping fracture and to bulk fracture in posterior sites. Fractures of ceramic connectors represent another disadvantage of all-ceramic prostheses, especially when the manufacturers' recommendations for connector shape and size cannot be satisfied because of limited space. Overall, the esthetic appearance of an all-ceramic restoration is generally superior to that of a metal-ceramic restoration for anterior as well as posterior situations (Figure 18-11). However, properly designed metal-ceramic crowns are highly esthetic when adequate tooth reduction principles are satisfied. In addition, metal coping designs such as those with thinner facial metal (0.1 to 0.5 mm) and/or knife-edge facial metal margins or collarless metal margins can further enhance the esthetic potential of these anterior crowns.

? CRITICAL QUESTION

What causes stress concentrations? How can they promote fracture of all-ceramic prostheses in the presence of low occlusal forces?

METHODS FOR STRENGTHENING CERAMICS

MINIMIZING THE EFFECT OF STRESS CONCENTRATIONS

Why do dental ceramic prostheses fail to exhibit the strengths that we would expect from the high interatomic bond forces? The answer is that numerous minute scratches and other flaws are present on the surfaces of these materials. These surface flaws behave as sharp slits whose tips may be as narrow as the spacing between several atoms in the material. Under intraoral loading, tensile stresses that develop within the ceramic structure are greatly increased and concentrated at the tips of these flaws. This stress concentration geometry at the tip of each surface flaw can increase the localized stress to extremely high levels even though a relatively low average stress exists throughout the bulk of the structure. When the induced tensile stress exceeds the nominal strength of the material structure, the bonds at the notch tip rupture, forming a crack. This stress concentration phenomenon explains how materials fail at stresses far below their theoretical strength. However, there are other variables that affect the magnitude of these stresses, including prosthesis design, load orientation, loading rate, microstructure, and residual processing stresses. These variables are discussed in other chapters.

Stress raisers are discontinuities in ceramic structures and in other brittle materials that cause a stress concentration in these areas. The design of ceramic dental restorations should be carefully planned with sufficient bulk and a minimum of sharp angular changes to avoid stress raisers in the ceramic. Abrupt changes in shape or thickness in the ceramic contour can act as stress raisers and make the restoration more prone to failure. For example, the **incisal** line angles on an anterior tooth prepared for a ceramic crown should be well rounded and the occlusal reduction for molar teeth should provide sufficient bulk for the ceramic product under consideration.

The brittle fracture behavior of ceramics and their low tensile strengths compared with those predicted from bonds between atoms can be understood by considering stress concentration around surface flaws. Because ceramics, unlike metals, tend to have no mechanism for yielding to stress without fracture, cracks may propagate through a ceramic material at low average stress levels. As a result, ceramics and glasses have tensile strengths that are much lower than their compressive strengths. In the oral environment, tensile stresses are usually created by bending forces, and the maximal tensile stress created by the bending forces occurs within the surface of a restoration or prosthesis. It is for this reason that surface flaws are of particular importance in determining the strength of ceramics.

As the crack propagates through the material, the stress concentration is maintained at the crack tip unless the crack moves completely through the material or until it meets another crack, pore, or crystalline particle, which may reduce the localized stress. The removal of surface flaws or a reduction in their size and number can produce a very large increase in strength. Reducing the depth of surface flaws in the surface of a ceramic is one of the reasons that polishing and glazing of dental porcelain is so important. The fracture resistance of ceramic prostheses can be increased through one or more of the following seven options: (1) select stronger and tougher ceramics; (2) develop residual compressive stresses within the surface of the material by thermal tempering; (3) develop residual compressive stress within interfacial regions of weaker, less tough ceramic layers by properly matching coefficients of thermal expansion and contraction; (4) reduce the tensile stress in the ceramic by appropriate selection of stiffer supporting materials (greater elastic moduli); (5) minimize the number of firing cycles for feldspathic porcelains; (6) design the ceramic prosthesis with greater bulk and broader radii of curvature for connectors in areas of potential tensile stress to minimize stress concentrations and the magnitude of tensile stresses that can develop during function; and (7) adhesively bond the ceramic crowns to the tooth structure.

In all-ceramic crowns, several conditions can produce stress concentrations. For Captek-type crowns, creases or



FIGURE 18-12 Porcelain debonding from a metal pontic substrate of a long-span metal-ceramic bridge.

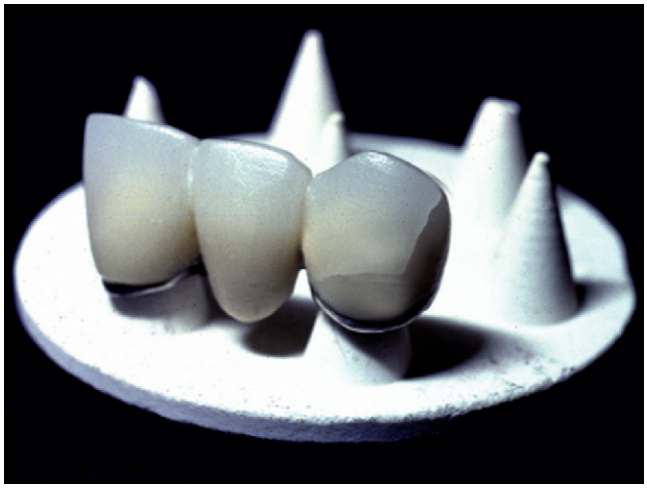


FIGURE 18-13 Crack in metal-ceramic crown after cooling of a three-unit bridge

folds of the platinum or gold foil substrate that become embedded in the porcelain leave notches that act as stress raisers. Sharp line angles in the preparation also create areas of stress concentration in the restoration. Shown in Figure 18-12 is a metal ceramic pontic that has fractured because of a poor framework design. Large changes in porcelain thickness, a factor that is also determined by the tooth preparation, can create areas of stress concentration.

A small particle of porcelain along the internal porcelain margin of a crown also induces locally high tensile stresses. A stray particle that is fused within the inner surface of a shoulder porcelain margin of a metal-ceramic crown can cause localized tensile stress concentrations in porcelain when an occlusal force is applied to the crown.

Even though a metal-ceramic restoration is generally more fracture-resistant than most ceramic crowns of the same size and shape, care must be taken to avoid subjecting the porcelain in a metal-ceramic prosthesis to loading that produces large localized stresses. If the occlusion is not adjusted properly on a porcelain surface, contact points rather than contact areas will greatly increase the localized stresses in the porcelain surface as well as within the internal surface of the crown. These contact stresses can lead to the formation of the so-called Hertzian cone cracks, which may lead to chipping of the occlusal surface.

Fracture mechanics is a science that allows scientists to analyze the influence of flaw/stress interactions on the probability of crack propagation through an elastic, brittle solid. The principles of linear elastic fracture mechanics were developed in the 1950s by Irwin (1957). This pioneering research on fracture phenomena was based on earlier investigations by Griffith (1920) and Orowan (1944, 1949, 1955). Irwin found that when a brittle material was subjected to tensile stresses, specific crack shapes in certain locations were associated with greatly increased stress levels. He also recognized the importance of determining the fracture toughness of these materials as a measure of their ability to resist fracture. The fracture toughness (K_{Ic}) of a material represents the resistance of a material to rapid crack propagation in a stress field. In contrast, the strength of a material depends primarily on the size of the initiating crack that is present. The strength of dental ceramics and other restorative materials is controlled by the size of the cracks or defects that are introduced during processing, production, and handling. In this chapter a description is given of the processing methods used to produce ceramic prostheses and the potential of these methods to introduce flaws or cracks that may limit their clinical survival.

? CRITICAL QUESTION

True or false? Residual compressive stress develops in the veneering ceramic of an all-ceramic crown in the same way as it does in a metal-ceramic crown.

DEVELOPMENT OF RESIDUAL COMPRESSIVE STRESSES

The fabrication of metal-ceramic and all-ceramic prostheses usually involves sintering the ceramic at high temperature or hot-pressing a veneering ceramic onto the metal or core ceramic. The process of cooling to room temperature offers the opportunity to take advantage of mismatches in coefficients of thermal contraction of adjacent materials in the ceramic structure. However, if the porcelain veneer contracts more than the metal coping or framework, axial and hoop tensile stresses develop that can cause cracking of the ceramic (Figure 18-13). Ideally, the ceramic veneer should sustain slight compression in the final restoration. As stated previously, a self-glazed surface layer can also set up compressive stress on cooling. Shown in Figure 18-14 an overglazed glass-ceramic three-unit FDP.

To prevent fracture of a ceramic prosthesis, one must prevent tensile stresses from occurring. Of course this is an unrealistic requirement. Instead, if one could produce a significant amount of compressive stress in the area of the ceramic structure, a greater level of offsetting tensile stress



FIGURE 18-14 Overglazed surface on the veneering ceramic of a three-unit FPD produced with a lithia disilicate–based glass-ceramic framework.

would need to be developed during oral function for the prosthesis to reach the tensile stress needed to cause fracture. One method of introducing residual compressive stresses within the ceramic is to choose veneering ceramics whose thermal expansion or contraction coefficient is slightly less than that of the core ceramic. Consider three layers of porcelain, the outer two of the same composition and coefficient of thermal contraction and the inner layer of a different composition with a higher coefficient of thermal contraction. Suppose that the layers were bonded together and the bonded structure were allowed to cool to room temperature. The inner layer would have a higher coefficient of thermal contraction and tend to contract more as it cooled. Thus, on cooling to room temperature, the inner layer would produce axial and hoop compressive stresses in the adjacent outer layer. In this way the protective compressive stress of the ceramic structure would increase its fracture resistance and survival probability.

Another procedure is to rapidly cool the prosthesis by removing the prosthesis and cooling it on the benchtop rather than slowly cooling the prosthesis in the furnace. This is especially useful for metal-ceramic prostheses, since the thermal conductivity and diffusivity of metal leads to increased compression in the veneer.

We can apply the same principle to a metal-ceramic system as well. The metal and porcelain should be selected with a slight mismatch in their coefficient of thermal contraction (the metal CTC being slightly higher) so that the metal contracts slightly more than the porcelain on cooling from the firing temperature to room temperature. This mismatch leaves the porcelain adjacent to the metal in a state of residual compression, which effectively protects the metal-ceramic restoration against fracture of the veneering ceramic.

MINIMIZING THE NUMBER OF FIRING CYCLES

The purpose of porcelain firing procedures is to densely sinter the particles of powder together and produce a relatively smooth, glassy layer (glaze) on the surface. In some cases a stain layer is applied for shade adjustment or for characterization, such as stain lines or fine cracks. Several chemical reactions occur over time at porcelain firing temperatures; of particular importance are increases in the concentration of crystalline leucite in the porcelains designed for fabrication of metal-ceramic restorations. Leucite, $K_2O{\cdot}Al_2O_3{\cdot}4SiO_2$, a high-expansion crystal phase, can increase the coefficient of thermal contraction of the porcelain. Changes in the leucite content caused by multiple firings can alter the coefficient of thermal contraction of some porcelain products. Some porcelains undergo an increase in leucite crystals after multiple firings, which will increase their coefficient of thermal expansion. If the expansion coefficient increases above that for the metal, the expansion mismatch between the porcelain and the metal can produce stresses during cooling sufficient to cause immediate or delayed crack formation in the porcelain.

ION EXCHANGE

The technique of ion exchange is an effective method of introducing residual compressive stresses into the surface of a ceramic. If a sodium-containing glass article is placed in a bath of molten potassium nitrate, potassium ions in the bath exchange places with some of the sodium ions in the surface of the glass article and remain in place after cooling. Since the potassium ion is about 35% larger than the sodium ion, the diffusion of the potassium ion into the place formerly occupied by the sodium ion creates residual compressive stresses in the surface. Increases of 100% or more in flexural strength of feldspathic porcelains have been achieved with several ion exchange products containing a significant concentration of small sodium ions. However, the depth of the compression zone is less than 100 μm. Therefore, this strengthening effect may be lost if the porcelain or glass-ceramic surface is ground, worn, or eroded by long-term exposure to certain inorganic acids.

THERMAL TEMPERING

Perhaps the most common method for strengthening glasses is by thermal tempering, which creates residual surface compressive stresses by rapidly cooling the surface of the object while it is hot and in the softened (molten) state. This rapid cooling produces a skin of rigid glass surrounding a soft (molten) core. As the molten core solidifies, it tends to shrink, but the outer skin remains rigid. The pull of the solidifying molten core, as it shrinks, creates residual tensile stresses in the core and residual compressive stresses within the outer surface.

Thermal tempering is used to strengthen glass for uses such as automobile windows and windshields, sliding glass doors, and diving masks. Often the rapid cooling of the outer skin is accomplished by jets of air directed at the thermally softened glass surface. If one observes the rear window of an automobile through polarized sunglasses, one can see a regular pattern of spots over the entire window. This pattern of spots corresponds to the arrangement of the air jets employed by the manufacturer in the tempering process. For dental applications, it is more effective to quench hot glass-phase ceramics in silicone oil or other special liquids rather than using air jets that may not uniformly cool the surface. This thermal tempering treatment induces a

protective region of compressive stress within the surface. However, this process is technique-sensitive, since large counterbalancing tensile stresses may develop when excessive cooling rates occur during the tempering process.

CRITICAL QUESTION

What condition is required of cast metals to achieve ionic and/or covalent bonding to veneering porcelain?

ALL-CERAMIC SYSTEMS

Based on a 1994 survey, metal-ceramic crowns and bridges were used for approximately 90% of all fixed restorations. However, recent developments in ceramic products with improved fracture resistance, advanced CAD-CAM technology, and excellent esthetic capability have led to a significant increase in the use of all-ceramic products. Ceramic crowns and bridges have been in widespread use since the beginning of the twentieth century. One of the first hot-isostatically pressed core ceramics was IPS Empress, a leucite-based glass-ceramic. Because of its relatively low flexural strength and fracture toughness, this glass-ceramic was limited to anterior single-unit restorations. Other ceramics that were limited to single-unit restorations were Vitadur N aluminous porcelain, Cerestore magnesia-alumina shrink-free ceramic, and Dicor, a tetrasilicic-fluormica-based glass-ceramic. Although these materials had reasonably good success rates for a few years, their limitations slowly but surely led to the development of stronger and tougher ceramics that allowed for a broader range of uses.

ALUMINOUS PORCELAIN

Until the 1960s, high-fusing feldspathic porcelains had been used to produce all-ceramic crowns. The relatively low strength of this type of porcelain prompted McLean and Hughes (1965) to develop an alumina-reinforced porcelain core material for the fabrication of ceramic crowns. The alumina-reinforced crowns were generally regarded as providing slightly better esthetics for anterior teeth than the metal-ceramic crowns. However, the strength of the core porcelain used for alumina-reinforced crowns was inadequate to warrant its use for posterior teeth.

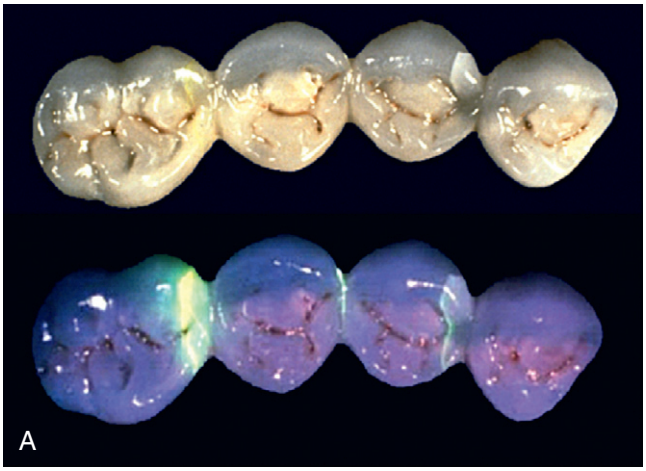
One method of producing aluminous porcelain crowns was to form a tin oxide coating on platinum foil. The objective of this technique was to reduce the weakening effect of surface irregularities on the inner surface of porcelain crowns by bonding a thin platinum foil to the inner surface that would be cemented to the prepared tooth. Atomic bonding of aluminous porcelain was promoted by electroplating the platinum foil with a thin layer of tin and oxidizing it in a furnace to provide a continuous film of tin oxide. The rationale was that the bonded foil served as an inner skin on the fit surface to reduce subsurface porosity and the formation of microcracks in the porcelain, thereby increasing the fracture resistance of the restoration. The clinical performance of these crowns was excellent for anterior teeth, but approximately 15% of molar crowns fractured within 7 years after they were cemented with a glass ionomer cement.

EFFECT OF DESIGN ON FRACTURE SUSCEPTIBILITY OF METAL-CERAMIC AND ALL-CERAMIC RESTORATIONS

There are many examples of atypical designs that lead to ceramic fracture of metal-ceramic prostheses. One of these involves bridges with cast-joined connectors that are used occasionally to avoid soldering bridge framework components that do not fit the prepared teeth. Shown in Figure 18-15A is a four-unit metal-ceramic cast-joined bridge with two connector fractures at the two cast-joined sections in the metal framework. A schematic of a cast-joined connector in the pontic of an FDP is shown in Figure 18-15B. Fluorescent dye illumination allows better visibility of the two areas of ceramic cracking. The results of an in vitro study reveal that design 1 is the most strain-resistant design of the five cross-sectional retention designs shown in Figure 18-15C. Tougher, stronger ceramics can sustain higher tensile stresses before cracks develop in areas of tensile stress. Conventional feldspathic porcelains should not be used as the core of ceramic crowns, especially in posterior areas, because occlusal forces can easily subject them to tensile stresses that exceed the tensile strength of the ceramic. Of major concern are tensile stresses that are concentrated within the inner surface of posterior ceramic crowns (see GLASS-CERAMIC section). Shown in Figures 18-16 and 18-17 are a framework on two galvanometal copings and a fractured three-unit FDP, respectively. The copings were made using the a "galvanometal" process to electrodeposit pure gold onto dies. To minimize the cost of gold used in the process, a base metal pontic was bonded to the copings and it was also coated with a gold layer. As the photos illustrate, cracking of porcelain has occurred at the junctions of the pontic with the crowns and porcelain has also debonded from the gold surface, as is expected, since pure gold cannot form an oxide that is needed for chemical bonding to porcelain.

When fractures occur, a sketch of the observed fracture surface is helpful in determining the cause of fracture. An illustration of the main crack patterns that can develop in a metal-ceramic crown is shown in Figure 18-18. Some cracks travel along the metal-metal oxide interface and others may propagate along the interface between the metal oxide and opaque porcelain. The third type can occur cohesively entirely within porcelain. The first two types are indicative of a material processing error and the third may be indicative of a crown design error, excessive loading, or other uncontrollable factors.

Although ceramic and metal-ceramic prostheses are susceptible to design errors, some variations in design have minimal effects on stress levels generated during loading. For example, the metal-ceramic crown designs shown in Figure 18-19 have quite different metal thicknesses in the facial area, yet finite element analyses reveal no significant differences in the maximum principal tensile stresses that develop under simulated loading.



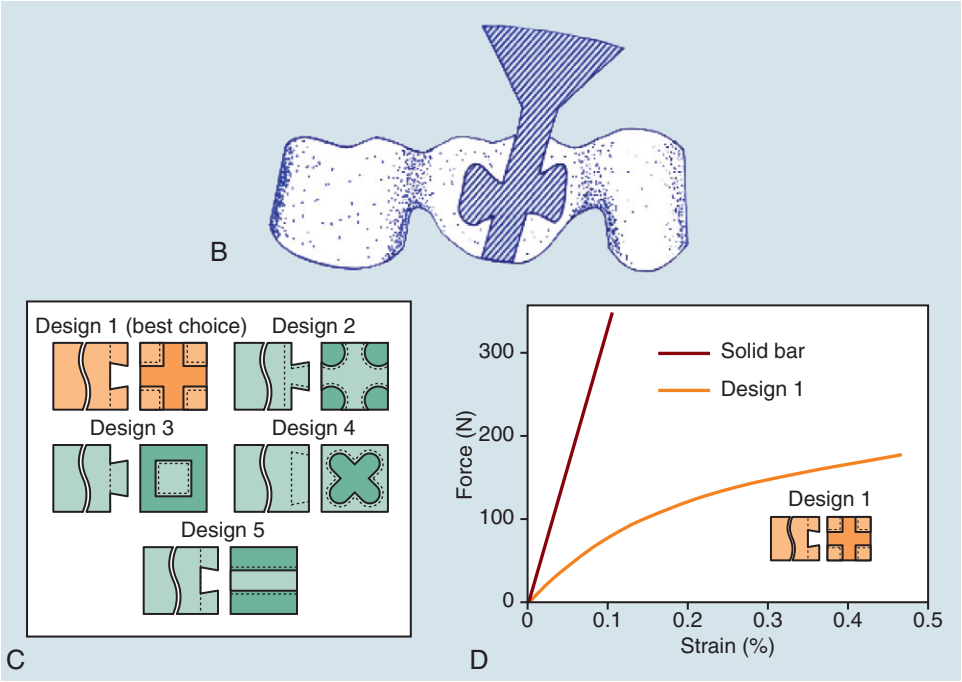


FIGURE 18-15 **A,** Cast-joining fractures in terminal connectors of a four-unit metal-ceramic bridge. Cast-joining designs. The cracks in each of the connectors are highlighted with fluorescent dye in the lower photo. **B,** Schematic of a properly designed cast-joined three-unit bridge framework. **C,** Five possible cross-sectional designs for cast-joining at the pontic. **D,** Plot of force versus strain for a solid bar. Design 1 was the best choice of the five designs on the left. (**C,** and **D,** adapted from DeHoff PH, Anusavice KJ, Evans J, Wilson HR: Effectiveness of cast-joined Ni-Cr-Be structures. *Int J Prosthodont* 3:550–554, 1990.)



FIGURE 18-16 Framework of gold "galvanometal" copings and a base metal pontic. (Courtesy of Dr. Renata Faria.)



FIGURE 18-17 Fractures of metal-ceramic bridge made with gold "galvanometal" copings and a base metal pontic. (Courtesy of Dr. Renata Faria.)

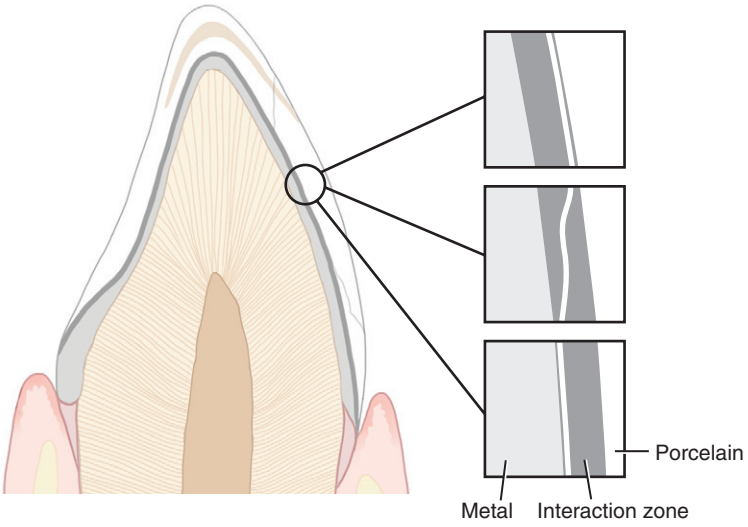


FIGURE 18-18 Cross-sectional illustration of three principal types of interfacial zone fractures.

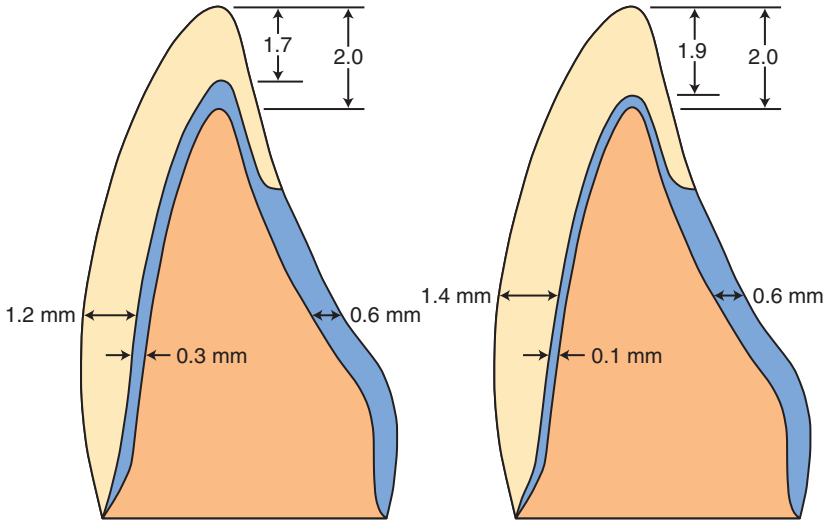


FIGURE 18-19 Cross-sectional illustrations of metal-ceramic crown designs with reduced metal thickness. Metal is represented by a blue color and porcelain by yellow. (*Left*) Facial metal thickness of 0.3 mm. (*Right*) Facial metal thickness of 0.1 mm represents a more esthetic option.

Sharp line angles in the preparation will also create areas of stress concentration in the restoration, primarily where a tensile component of bending stress develops. A small particle of ceramic along the internal porcelain margin of a crown can induce locally high tensile stresses during try-in or final cementation. Furthermore, when grinding of this surface is required for adjustment of fit, one should use the finest grit abrasive that will accomplish the task. This precaution will reduce the probability of forming microcracks and reduce the depth of microfissures produced by the abrasive particles. Grinding flaws in the inner surface of ceramic crowns represents the greatest damage that can be produced in ceramics by processing techniques.

Because the forces on anterior teeth are relatively small, low to moderate tensile stresses can be supported by ceramic crowns more safely. However, if there is a great amount of vertical overlap (overbite) with only a moderate amount of horizontal overlap (overjet), high tensile stresses can be produced.

? CRITICAL QUESTION

Describe four ways in which control of tooth preparations and the design of crowns and bridges can increase the resistance to fracture of all-ceramic crowns.

Most ceramics should be designed in such a way as to overcome their weaknesses—that is, the relatively low fracture toughness and tensile strength of the veneering ceramic and its susceptibility to crack formation in the presence of surface flaws. The design should avoid exposure of the ceramic to high tensile stresses. Knife-edge margins should be avoided because of the risk of cracking or chipping during the try-in phase. The tensile stresses in a ceramic FPD can be reduced by using greater connector heights (Figure 18-20). However, a connector height greater than 4 mm makes the anatomic form in the buccal area of a posterior FPD too bulky and unesthetic (Figure 18-21). Broadening the radius of curvature of the gingival embrasure (Figure 18-22) of the

interproximal connector also can increase the fracture resistance of an FDP. Quinn et al. 2010 studied the effect of connector diameter rather than connector radius of curvature to predict the minimal connector size for a zirconia framework to ensure a 95% survival against fracture over a period of 20 years. The results of this analysis are presented in Figure 18-23.

Fractured connectors are fairly common, especially when the connector size is less than that recommended by the manufacturer. Figure 18-24 illustrates an example of this design deficiency. The distal connector of the three-unit bridge made from a lithia disilicate core ceramic fractured after 1.5 years in service and the mesial connector fractured later. The height of the distal connector was only 3.5 mm, or 0.5 mm less than was recommended.

GLASS-CERAMICS

A glass-ceramic is a material that is formed into the desired shape as a glass and then subjected to a heat treatment to induce partial devitrification—that is, loss of glassy structure by crystallization of the glass. Crystalline particles, needles, or plates formed during this ceramming process interrupted the propagation of cracks in the material when an intraoral force was applied, thereby promoting increased strength and toughness. The use of glass-ceramics in dentistry was first proposed by MacCulloch in 1968. He used a continuous glass-molding process to produce denture teeth. He also suggested that it should be possible to fabricate crowns and inlays by centrifugal casting of molten glass.

The first commercially available castable ceramic material for dental use, Dicor, was developed by Corning Glass Works and marketed by Dentsply International. Dicor was a castable glass formed into an inlay, facial veneer, or full-crown by a lost-wax casting process similar to that employed for metals. After the glass casting core or coping was recovered from the casting investment the glass was sandblasted to remove the residual casting investment and the sprues were cut away. The glass was then covered by a protective "embedment"

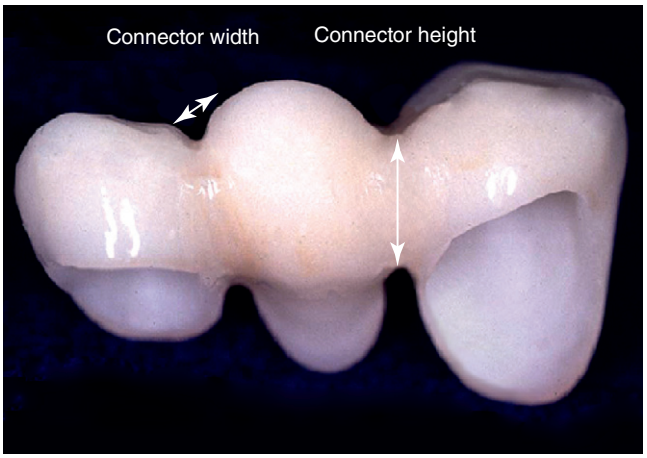


FIGURE 18-20 Connector dimensions for a three-unit ceramic bridge.



FIGURE 18-21 A three-unit ceramic anterior-posterior produced totally with a lithia disilicate-based core ceramic. Note the relatively large connector (4 mm in height) necessary to resist fracture in posterior areas.

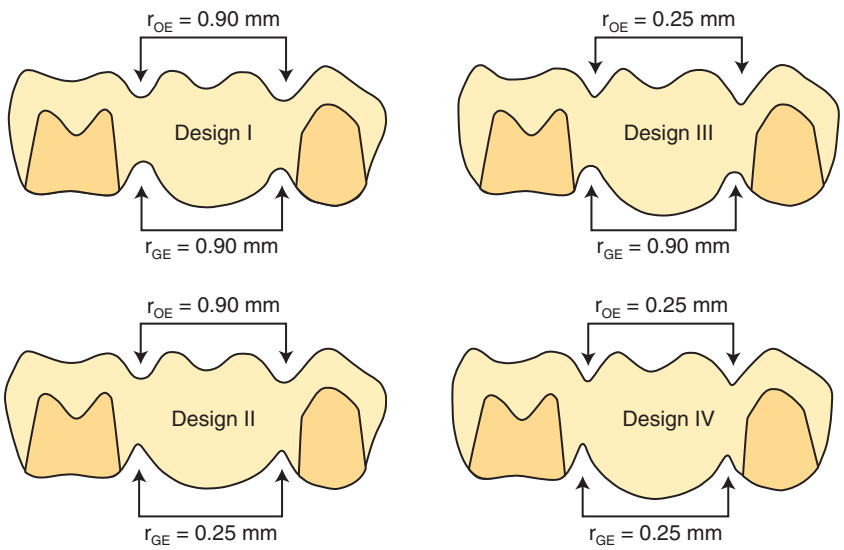


FIGURE 18-22 Ceramic bridges with various radii of curvature in occlusal and gingival embrasures. Designs I and III have the lowest stress concentration factors in the gingival (tensile) embrasure areas, which have the larger radii of curvature.

material and subjected to a heat treatment that caused microscopic platelike crystals of tetrasilicic fluormica to grow within the glass matrix. This crystal nucleation and growth process is called ceramming. Once the glass was crammed, it was fit on the prepared dies, ground as necessary, and coated with veneering porcelain and a stain and glaze layer to match the shape and appearance of adjacent teeth. Dicor glass-ceramic was capable of producing remarkably good esthetics, perhaps because of the "chameleon" effect, in which part of the color of the restoration was picked up from the adjacent teeth as well as from the tinted cements used for luting the restorations.

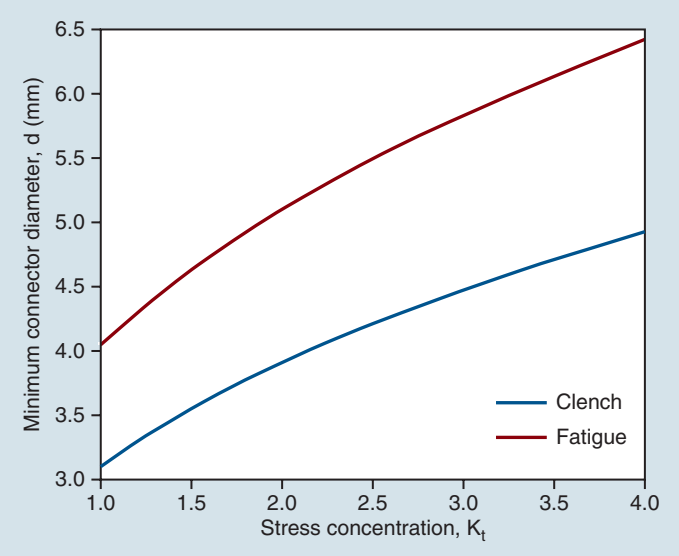


FIGURE 18-23 Predicted minimum connector diameter for four-unit ceramic bridge made from 3Y-TZP to ensure a survival of 95% for at least 20 years. (Adapted from Quinn GD, Studart AR, Hebert C, VerHoef JR, Arola D: Fatigue of zirconia and dental bridge geometry: design implications. *Dent Mater* 26(12):1133–1136, 2010.)

When used for posterior crowns, the Dicor glass-ceramic crowns were more susceptible to fracture than anterior crowns. Shown in Figure 18-25 is the stress pattern (colored areas) computed by finite element analysis in a 0.5-mm-thick molar Dicor crown loaded on the occlusal surface, just within the marginal ridge area. The maximum tensile stress (73 MPa) is shown by the larger red area within the internal surface directly below the point of applied force (above the small white area in the occlusal surface) and just above the 50-µm-thick layer of resin cement (designated by the arrow in Figure 18-25). An SEM image of a fractured clinical crown of Dicor glass-ceramic is shown in Figure 18-26. Note the site of crack initiation indicated by the arrow. This site represents the critical flaw responsible for crack initiation under an applied intraoral force. The location

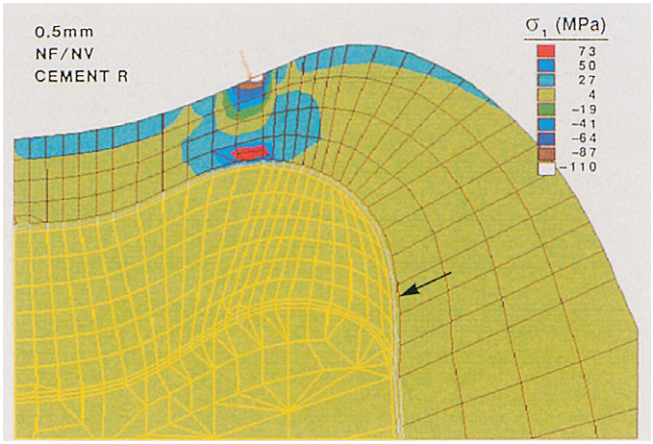


FIGURE 18-25 Stress distribution resulting from loading (close to the marginal ridge area) of the occlusal surface of a finite element model of a ceramic crown with an occlusal thickness of 0.5 mm. The maximal principal tensile stress of 73 MPa is located directly below the point of occlusal loading (red line) within the internal surface of the crown adjacent to the 50-µm-thick layer of resin cement (*arrow*).

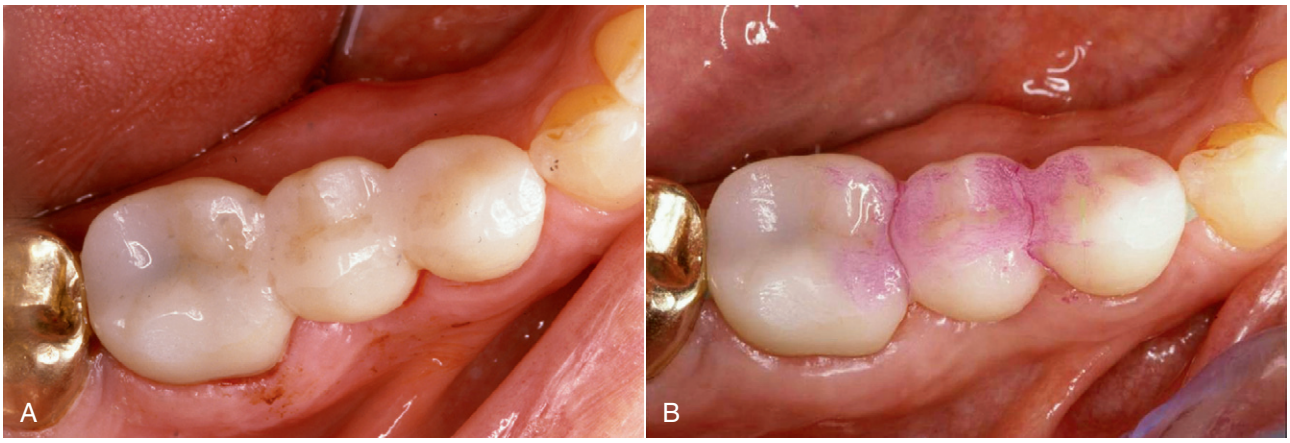


FIGURE 18-24 **A,** Postcementation photo of three-unit ceramic bridge made with a lithia disilicate–based core ceramic. **B,** Fractured connectors of the bridge after approximately 1.5 years. The posterior connector height was found to be 3.5 mm, which was 0.5 mm less than that recommended by the manufacturer.

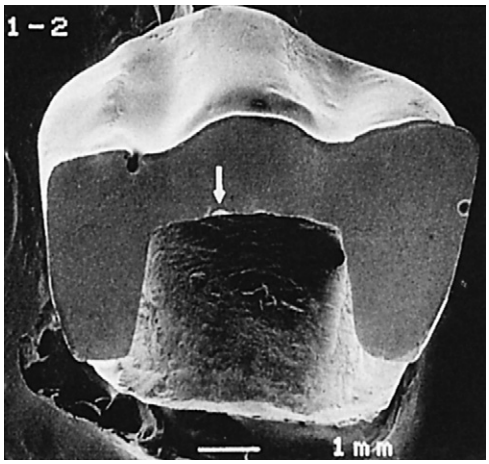


FIGURE 18-26 Scanning electron microscopic image of a fractured Dicor glass-ceramic crown with a tetrasilicic fluormica-based core. The arrow indicates the site of the critical flaw responsible for crack initiation under intraoral loading. (From Thompson JY, Anusavice KJ, Naman A, Morris HF: Fracture surface characterization of clinically failed all-ceramic crowns. *J Dent Res* 73(12):1824–1832, 1994.)

of initial crack formation is consistent with the location of maximal tensile stress predicted by the results of the finite element analysis that are shown in Figure 18-25. Shown in Figure 18-26 is a fractured Dicor glass-ceramic crown. Fractography revealed the crack's origin at the inner glass-ceramic surface, as predicted by the stress patterns (darker gray area within inner surface of crown) shown in Figure 18-25.

More recently, glass-ceramics based on leucite, lithium disilicate, and hydroxyapatite have been used. These ceramics are available as powders or as solid blocks that can be machined through CAD-CAM processes or hot-pressed either as a core ceramic or as a veneering ceramic. The powders are added to a liquid that allows the mixture to be applied as a thick slurry in which the particles are consolidated into a relatively dense mass by a process called condensation. The condensed mass is then sintered at an elevated temperature. These materials are described further in subsequent sections.

CRITICAL QUESTION

Which processing technique is most likely to generate the deepest flaws in a ceramic core framework?

This type of ceramic is characterized by the controlled crystallization (termed *ceramming*) of a glass through the presence of one or more nucleating agents. Dicor, a glass-ceramic that contained 55% by volume of tetrasilicic fluormica ($KMg_{2.5}Si_4O_{10}F_2$), was developed by Corning Glass Works and sold through Dentsply International. This product was derived from the quaternary ceramic system, K_2O-MgF_2-MgO-SiO_2. Dicor was the first castable glass used for dental prosthetic applications. Besides its relatively low flexural strength (110 to 172 MPa) and low fracture toughness (1.6 to 2.1 MPa•$m^{1/2}$), the original cast form was colorless and prostheses had to be colored by the application of a thin layer of shading porcelain. Subsequent products were provided as dark and light shades of machineable glass-ceramic (MGC). The flexure strength of Dicor MGC decreased by up to 88% after the tensile surface was ground. Malament and Socransky (2001) reported the survival of 43% of non-acid-etched and 75% of acid-etched Dicor crowns over a 16-year period. Survival was greater for crowns that were luted with resin cement compared with either glass ionomer or zinc phosphate cement. Dicor and Dicor MGC glass-ceramics are no longer used in dentistry.

We have learned much from the studies of Malament et al. regarding the variables that play a major role in the fracture susceptibility of one type of glass-ceramic. Additional clinical data have been obtained from many other studies of other ceramics as well. At this point in the chapter it may be useful to consider some of the general indications for use of different ceramic products based on existing data. A conservative approach to these recommendations is presented in Tables 18-7 and 18-8. Manufacturers of these products may recommend other applications as possible uses of their ceramics, but the probability of clinical fracture is not provided to give the user an indication of the time-dependent probability of clinical fracture. Thus a conservative approach is recommended until validated clinical evidence supports these applications.

HOT-ISOSTATICALLY PRESSED (HIP) GLASS-CERAMICS

Veneered leucite-based glass-ceramic core restorations are indicated for anterior veneers and crowns and premolar inlays, onlays, and crowns. Hot-pressed leucite-containing glass-ceramics have been used for many years. The technology of hot-pressing leucite-based and lithia disilicate–based glass-ceramics is well established and this technology has recently been applied to the hot-pressing of veneer ceramics on metals and zirconia core ceramics. The most well-known leucite-based products are IPS Empress (Ivoclar Vivadent), Cerpress SL Pressable Ceramic System (Leach and Dillon), and Finesse All-Ceramic System (DENTSPLY Ceramco). These pressed glass-ceramics contain approximately 35% by volume of leucite (K_2O•Al_2O_3•$4SiO_2$) crystals. The glass-matrix layering ceramic for these core materials also contains leucite. These glass-ceramics have relatively low flexural strength (up to 112 MPa) and fracture toughness (0.9 to 1.3 MPa•$m^{1/2}$), so they are not recommended for molar crowns or bridges. A partial listing of HIP core ceramics is given in Table 18-7.

IPS Empress 2 (Ivoclar Vivadent) and Optec OPC 3G (Pentron Laboratory Technologies) contain approximately 65% to 70% by volume of lithia disilicate (Li_2O•$2SiO_2$) as the principal crystal phase. The lithia disilicate materials used as glass-ceramics have a narrow sintering range, which makes processing of ceramic prostheses very technique sensitive. Shown in Figure 18-27 is a schematic cross section of an all-ceramic crown made with a lithium disilicate core ceramic. This glass-ceramic is composed, by volume, of approximately

TABLE 18-7 Pressable Core Ceramics and Associated Veneering Ceramics for All-Ceramic Prostheses

Core Ceramic	Veneering Ceramic	Indications	Manufacturer
Authentic	Authentic	Veneer/Inlay/Onlay/Ant. Crown	Ceramay
Carrara Press Core	Carrara Vincent	Veneer/Inlay/Onlay/Ant. Crown	Elephant
Carrara Press Inlay	Carrara Vincent	Inlay	Elephant
Cergogold	Duceragold	Veneer/Inlay/Onlay/Ant. Crown	Degussa
Cerpress	Sensation SL	Veneer/Inlay/Onlay/Ant. & Post. Crown	Dentagold
Cerapress	Creation LF	Veneer/Inlay/Onlay/Ant. Crown	Girrbach
Empress 2	Eris, e.max Ceram	Veneer/Inlay/Onlay/Ant. & Post. Crown/Ant. FPD	Ivoclar Vivadent
e.max Press	e.max Ceram	Veneer/Inlay/Onlay/Ant. & Post. Crown/Ant. FPD	Ivoclar Vivadent
Evopress	Evolution	Veneer/Inlay/Onlay/Ant. Crown	Wegold
Finesse All Ceramic	Finesse	Veneer/Inlay/Onlay/Ant. Crown	DENTSPLY Ceramco
Fortress Pressable	—	—	Mirage Dental
Magic Coating Caps Schicht-Pressing	Magic Ceram 2	Veneer/Inlay/Onlay/Ant. Crown	D.T.S. Denta TechnoStore
Magic Easy Press Colorier-Pressing	—	Veneer/Inlay/Onlay/Ant. Crown	D.T.S. Denta-TechnoStore
Nuance Presskeramik	Nuance 750	Veneer/Inlay/Onlay/Ant. Crown	Schutz Dental Group
Optec OPC Low Wear	Optec OPC Low Wear	Veneer/Inlay/Onlay/Ant. & Post. Crown	Jeneric Pentron
Optec OPC 3G	Optec OPC 3G Porcelain	Veneer/Inlay/Onlay/Crown/Ant. FPD	Jeneric Pentron
Trendpress	Trendkeramik LFC	Veneer/Inlay/Onlay/Ant. Crown	Binder Dental
PLATINApress	Platina M	Veneer/Inlay/Onlay/Ant. Crown	Heimerle+Meule
Vision Esthetic	Vision Esthetic	Veneer/Inlay/Onlay/Ant. Crown	Wohlwend
VITAPress	VITA Omega 900	Veneer/Inlay/Onlay	Vident

Adapted from Kappert HF, Krah MK: Keramiken—eine Übersicht. *Quintessenz Zahntech* 27(6):668–704, 2001.

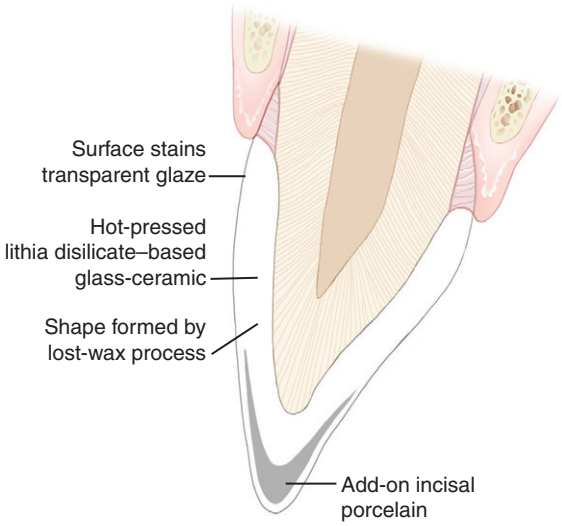


FIGURE 18-27 Cross-sectional illustration of cemented Empress 2 ceramic crown with a lithia disilicate–based ceramic core.



FIGURE 18-28 A three-unit ceramic posterior FPD (tooth numbers 19 to 21; FDI tooth numbers 34 to 36) produced with a lithia disilicate–based core ceramic.

70% lithium disilicate and 30% glass. It is fairly translucent but somewhat more opaque (Figure 18-28) than the leucite-based glass-ceramic (Empress), but it is a stronger core ceramic than leucite-based glass-ceramic. Its mean flexural strength is approximately 350 MPa compared with the 112-MPa strength of leucite-based glass-ceramics. This strength and a fracture toughness of 3.3 $MPa \cdot m^{1/2}$ for lithia disilicate–based glass-ceramics are generally sufficient for most anterior and posterior crowns and for anterior three-unit bridges even though the flexural strength and fracture toughness of their layering ceramics are substantially lower. Although the core ceramic fracture resistance is moderately high, veneered prostheses have been reported to be susceptible to chipping, which may require replacement or

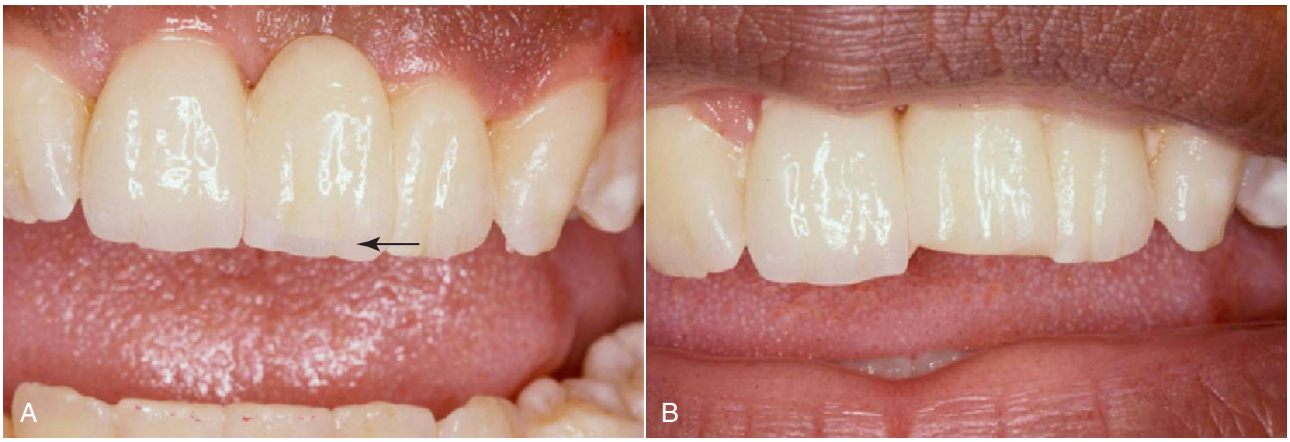


FIGURE 18-29 **A,** Crack (*arrow*) in crown of a three-unit bridge made with a lithia disilicate–based glass-ceramic core. **B,** Fracture of the crown shown on the left.

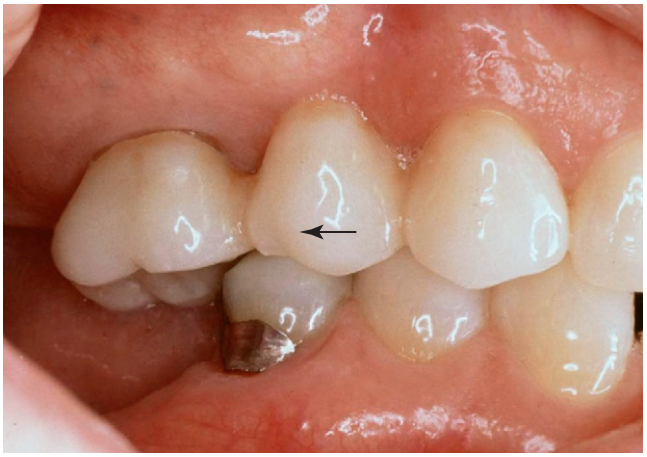


FIGURE 18-30 Chipping of veneer ceramic on the pontic of a three-unit bridge made with a lithia disilicate–based glass-ceramic core.



FIGURE 18-31 Chipped veneer ceramic on a pontic of a bridge made with a lithia disilicate–based core ceramic. Also note the crack in the distal area of the posterior crown.

recontouring of the affected prostheses. Examples of cracking and chipping of these prostheses are shown in Figures 18-29, 18-30, and 18-31.

GLASS-INFILTRATED CORE CERAMICS

To minimize sintering shrinkage and ensure adequate fit of ceramic prostheses, three glass-infiltrated core ceramic systems have been developed, one based on partially sintered alumina, one based on a magnesia-alumina spinel ($MgAl_2O_4$), and one with a zirconia-alumina core. Each of these partially sintered ceramics can be infiltrated with a lanthanum glass without any significant dimensional change.

VITA In-Ceram Alumina contains approximately 85% of alumina by volume. The partially sintered framework is formed by a slip-casting process, which produces dense packing of particles against a porous die. After firing at 1120 °C for 10 hours or more, a partially sintered structure is formed. This porous core ceramic framework is then infused with molten lanthanum glass. A schematic illustration of a cross section of an In-Ceram glass-infiltrated core ceramic crown is shown in Figure 18-32.

The same type of process can also be applied to In-Ceram-Spinell (ICS), which is a magnesia alumina spinel ($MgAl_2O_4$) core ceramic, and In-Ceram Zirconia. After glass infiltration, In-Ceram Spinell ceramic is more translucent than In-Ceram Alumina or In-Ceram Zirconia but its mean strength is significantly lower (approximately 350 MPa versus 600 MPa). The mean flexure strength of In-Ceram Zirconia (about 620 MPa) is only slightly greater than that of In-Ceram Alumina. In-Ceram Zirconia is not made from a pure zirconia core but rather a combination, by weight, of approximately 62% alumina, 20% zirconia, and 18% infiltrated glass. In its glass-infused form it is indicated primarily for crown copings and three-unit anterior and posterior frameworks. Because there is no shrinkage associated with this process, the marginal adaptation is expected to be comparable to that of the hot-pressing method but it is superior to that of the copy-milled technique. A summary of the indications for use of VITA In-Ceram core ceramics, VITABLOCS Mk II

feldspathic ceramic, and VITA VM 9 feldspathic ceramic is presented in Table 18-8. These are the proposed uses that are recommended by the manufacturer. The survivability of ceramic prostheses depends on many factors, some of which are controllable by the dentist and others not. For example, signs of high caries risk, extensive periodontal disease, or severe bruxism are contraindications for all dental ceramic prostheses; under such conditions, Tables 18-3 and 18-8 do not apply.

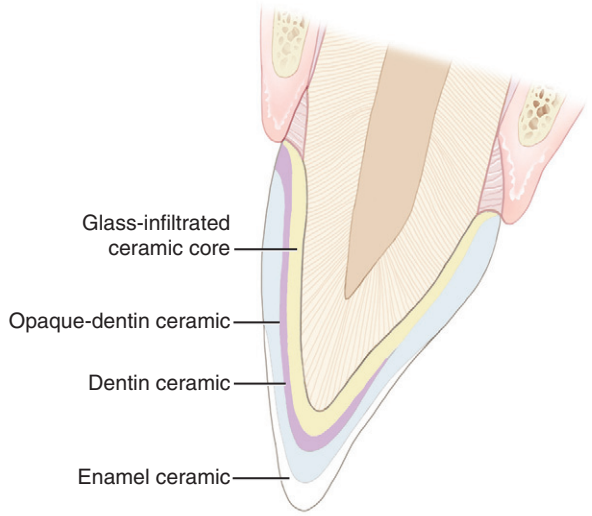


FIGURE 18-32 Cross-sectional illustration of an In-Ceram crown with a glass-infiltrated core ceramic.

ALUMINA CORE CERAMIC

Procera AllCeram (Nobel Biocare) is an alumina core ceramic that is indicated for anterior and posterior crowns. To produce these crowns, a die is first produced from an impression and digitized using a mechanical profiling device and a computer that converts the coordinates of the die surface into a digitized database. An oversized die is then produced onto which pure alumina is dry-pressed. The oversize green alumina body is then sintered and the resulting shrinkage yields the desired size and shape, onto which a feldspathic porcelain veneer is applied and sintered. The Procera AllCeram core is more translucent than In-Ceram Zirconia and it has comparable strength (620 to 700 MPa). Since alumina cannot be acid-etched to produce micromechanical retention, sandblasting the surface with silica-coated alumina particles by a Rocatec system (3M ESPE Minneapolis, MN) is required to ensure sufficient resin bonding. Shown in Figure 18-33, *A,* is a fractured three-unit alumina-based bridge whose retentive flanges were dimpled to promote micromechanical bonding. The fracture surface Figure 18-33, *B,* shows a relatively large void that may have contributed to the fracture.

YTTRIA-STABILIZED ZIRCONIA

Zirconia has been used as a biomaterial since the 1970s. It has been widely used as a hip replacement material and has been used in dentistry for crown and bridge applications since 2004. Zirconium dioxide (ZrO_2), or zirconia, is a white crystalline oxide of zirconium. Dental zirconia should not be confused with cubic zirconia, ZrO_2, which is a cubic crystalline form of zirconia used as a diamond simulant. It should

TABLE 18-8 Indications for Use and Processing of VITA In-Ceram, VITABLOCS, and VM 9 Ceramics

	OXIDE CERAMICS					FELDSPAR-BASED CERAMICS			
	Glass-Infiltrated VITA In-Ceram Core Ceramics (Slip/Grind)			VITA In-Ceram Core Ceramics (Sinter/Grind)		VITABLOCS (Grind)		VITA PM 9 (Press)	
Indications for Use	Spinell	Alumina	Zirconia (Alumina/ Zirconia	AL	YZ	Mk II	Triluxe/Triluxe Forte	Over-Pressing Technique	Substructure-Free Layering Technique*
Anterior Crown	X	X		X	X	X	X	X	X
Anterior 3-unit FDP		X	X	X	X			X	
Anterior 4-unit FDP					X				
Posterior Crown		X	X	X	X	X	X	X	
Posterior 3-unit FDP			X	X	X			X	
Posterior 4-unit FDP					X				
Veneering Ceramic	VITA VM 7	VITA VM 7	VITA VM 7	VITA VM 7	VITA VM 9	VITA VM 9 (individualize only)	VITA VM 9 (Individualize only)	VITA VM 9	VITA VM 9

Adapted from VITA In-Ceram Professionals Web site: http://www.vita-vip.com/index.php?site=VITA_EN_ZT_materials_indicators.

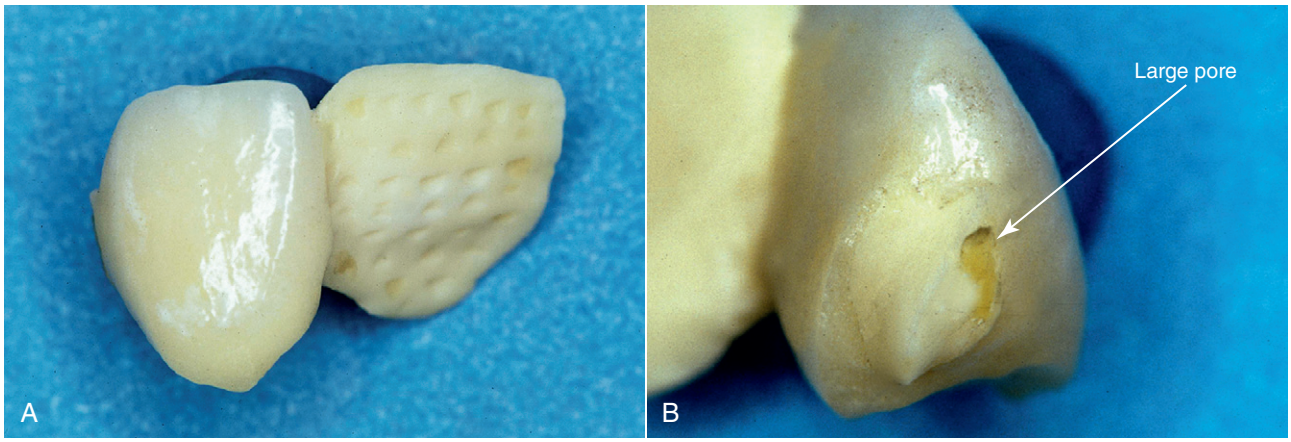


FIGURE 18-33 **A,** Fractured connector of a three-unit resin-bonded bridge made with an alumina core ceramic. **B,** Fracture surface of connector.

also not be confused with zirconium, which is a lustrous, gray-white, strong transition metal, or zircon (also known as zirkon), which is zirconium silicate, $ZrSiO_4$. However, pure zirconium can be obtained from zircon by purification with chlorine.

Zirconia exhibits unique mechanical and electrical properties that make it extremely useful in heat insulators, oxygen sensors, and fuel cells. Under atmospheric pressure, pure zirconia can exhibit three different crystal structures. At temperatures greater than 2367 °C, zirconia has a cubic structure. Between 1167 °C and 2367 °C, zirconia is tetragonal, and below 1167 °C the structure is monoclinic. The tetragonal-to-monoclinic phase transition results in a 3% to 5% volume increase, which produces cracks in bulk zirconia samples and a reduction in strength and toughness. Under this condition pure zirconia would be useless for dental restorative applications. However, if one modifies the composition by doping with Mg, Ca, Sc, Y, or Nd, the high-temperature tetragonal phase can be stabilized at room temperature. In this way, the tetragonal to monoclinic phase transformation stresses are avoided, microcracks are prevented, and the positive mechanical properties of the tetragonal phase are preserved. Another possibility for stabilizing the high-temperature tetragonal phase at room temperature is to reduce the crystal size to less than 10 nm.

Zirconia is a nonmetal with an extremely low thermal conductivity—about 20% as high as that of alumina (Al_2O_3). It is chemically inert and highly corrosion resistant. Pure ZrO_2 has a monoclinic crystal structure at room temperature and transforms to tetragonal and cubic zirconia at elevated temperatures. The large volume expansion that occurs during the transformation of nondoped zirconia from cubic to tetragonal and tetragonal to monoclinic phases leads to structural expansion and high tensile stresses that cause zirconia to crack during cooling from the processing temperatures. To solve this problem, stabilizing oxides such as magnesium oxide (MgO), yttrium oxide (Y_2O_3), calcium oxide (CaO), and cerium oxide (Ce_2O_3) are added to zirconia. The stability of single-phase tetragonal zirconia is enhanced by highly soluble trivalent stabilizers such as yttria, which induce vacancies, or tetravalent stabilizers such as ceria, which are oversized or undersized with respect to zirconium. The most common stabilizer for dental applications is yttria (Y_2O_3). The addition of 3 to 5 mol% of Y_2O_3 results in a stabilized core ceramic referred to as yttria-stabilized zirconia or yttria-stabilized tetragonal zirconia polycrystals (Y-TZP). Magnesia (MgO) has also been used to produce an Mg-PSZ core ceramic (Denzir-M, Dentronic AB, Skellefteå, Sweden). Ceria (Ce_2O_3) is used as a stabilizer in a Ce-TZP/Al_2O_3 core ceramic (NanoZir, Panasonic, Japan).

? CRITICAL QUESTION

Which microstructural changes occur in 3Y-TZP ceramic for transformation toughening to occur at the tip of cracks in the presence of tensile stress?

The structural stabilization of zirconia by yttria results in a significant proportion of metastable tetragonal phase. This metastable tetragonal phase strengthens and toughens the structure by a localized transformation to the monoclinic phase when tensile stresses develop at crack tips. The resulting volume expansion adjacent to the crack tips produces a high local compressive stress around the crack tips, which increases the localized fracture toughness and inhibits the potential for crack propagation. This phenomenon of transformation toughening increases the flexural and tensile fracture resistance of stabilized zirconia prostheses and presumably the survival probabilities of zirconia-based restorations. Although surface grinding may increase surface toughening in principle through the tetragonal to monoclinic phase transformation, excessive grinding by instruments with coarse abrasives or large flutes is not recommended by most zirconia suppliers because deep flaws may offset any advantage presented by localized compressive stresses. The fracture toughness of a 92.2% dense nondoped monoclinic zirconia has been reported to be 2.06 $MPa \cdot m^{1/2}$. An extrapolation to full density yields a value of 2.6 $MPa \cdot m^{1/2}$. In comparison, the fracture toughness of tetragonal 3Y-TZP is approximately 8 to 10.3 $MPa \cdot m^{1/2}$.

When pure ZrO_2 is heated to a temperature between 1470 °C and 2010 °C and cooled, its crystal structure begins to change from a tetragonal to a monoclinic phase at approximately 1150 °C. During cooling to room temperature, a volume increase of several percent occurs when it transforms from the tetragonal to monoclinic crystal structure (Figure 18-34). As stated previously, this polymorphic transformation can be prevented with certain dopant additives such as 3 mol% yttrium oxide (Y_2O_3 or yttria). This ZrO_2 ceramic material is designated as 3Y-TZP (tetragonal zirconia polycrystals). The volume increase in this case is constrained if the zirconia crystals are sufficiently small and the microstructure is strong enough to resist the resulting stresses. This material is extremely strong (flexural strength, ≈900 MPa) and tough (fracture toughness, K_{Ic}, ranges from 8 to 10.3 $MP•m^{1/2}$). Many Y-TZP products are available in dentistry for CAD-CAM processing. These Y-TZP products fall into three groups: (1) products that are milled in the green (compacted) state, (2) products that are milled in a partially sintered state, and (3) products that are milled in the fully sintered state. Product names are given in the CAD/CAM section, below.

The "transformation toughening" mechanism of crack shielding results from the controlled transformation of the metastable tetragonal phase to the stable monoclinic phase. Several types of crack shielding processes are possible including microcracking, ductile zone formation, and transformation zone formation. By controlling the composition, particle size, and the temperature versus time cycle, zirconia can be densified by sintering at a high temperature and the tetragonal structure can be maintained as individual grains or precipitates as it is cooled to room temperature. The tetragonal phase is not stable at room temperature and it can transform to the monoclinic phase and a corresponding volume increase. When sufficient stress develops in the tetragonal structure and a crack in the area begins to propagate, the metastable tetragonal crystals (grains) or precipitates next to the crack tip can transform to the stable monoclinic form. In this process a 3% expansion by volume of the ZrO_2 crystals or precipitates occurs that places the crack under a state of compressive stress (Figure 18-35) and crack progression is arrested. To advance this crack further, additional tensile stress would be required. Because of this strengthening and toughening mechanism, the yttria-stabilized zirconia ceramic is sometimes referred to as "ceramic steel." A cross-sectional view of a Lava crown with a Y-TZP core is shown in Figure 18-36, *A*, and four veneered, Lava zirconia crowns are shown in Figure 18-36, *B*.

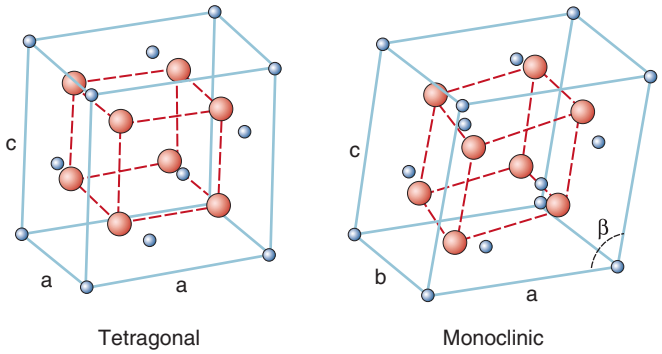


FIGURE 18-34 Tetragonal and monoclinic unit cell structures.

A regeneration heat treatment of machined or superficially ground Y-TZP at 900 °C for 1 h or for less time at 900 °C to 1000 °C converts the monoclinic phase within the surface back to the tetragonal phase. Thus, if veneer firing occurs after a grinding procedure, the thermal treatment can induce the reverse transformation of monoclinic to the tetragonal phase in the ground areas of the zirconia structure.

Another approach for reducing the fracture susceptibility of ceramic restorations is to use only core ceramic and no veneering ceramic. Table 18-9 lists some properties of several core ceramics including a Y-TZP product and its veneering ceramic. Monolithic zirconia may be especially useful in the most posterior areas where high occlusal clenching forces or parafunctional forces are applied. Of course, the most effective way to accomplish this task is to eliminate the veneering ceramic. Several all-zirconia products of this type were marketed in 2010, including Crystal Diamond Zirconia (Crystal,

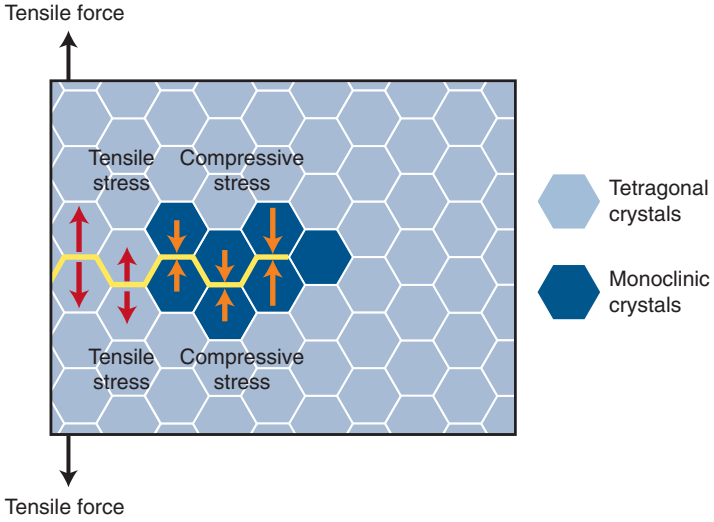


FIGURE 18-35 Schematic illustration of transformation toughening of a Y-TZP ceramic.

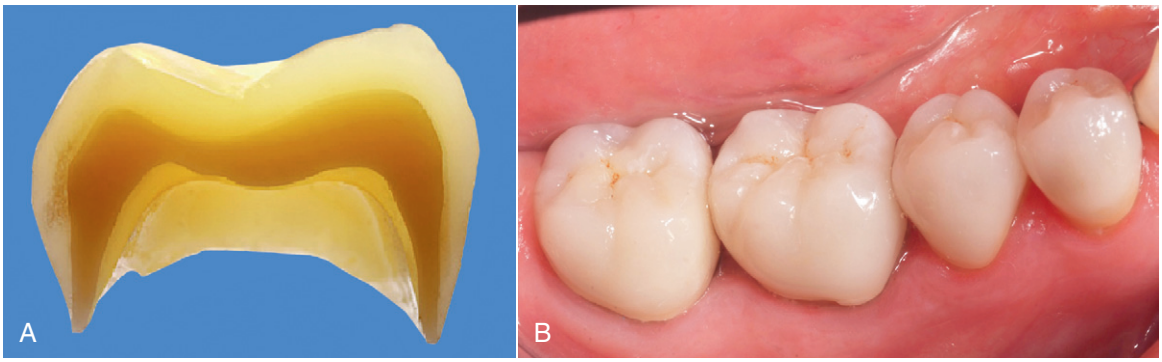


FIGURE 18-36 **A,** Cross section of ceramic crown made with a Lava zirconia-based core. **B,** Four veneered Lava zirconia–based crowns (A, courtesy of 3M ESPE, St. Paul, MN, B, courtesy of Dr. John Sorensen.)

TABLE 18-9 **Properties of Three Types of Core Ceramics and a Veneering Ceramic for All-Ceramic Prostheses**

	PRINCIPAL CRYSTAL FORM			
Property	**Leucite**	**Lithium Disilicate**	**Zirconia (Y-TZP)**	**Ceramic with HAP Nanocrystals for Veneering Y-TZP**
Crystallinity (vol%)	35	70	≥97.5 (may also include crystalline HfO_2, Al_2O_3, Na_2O, SiO_2, and Fe_2O_3, etc.)	N/A
Flexural strength (MPa)	85–112	215–400	900	85–110
Fracture toughness (MPa·$m^{1/2}$)	1.3–1.7	2.2–3.3	8–10.3	0.75–1.0
Vickers hardness (GPa)	5.9	6.3	8.8–11.8	4.8–5.4
Expansion coefficient (10^{-6}/K)	15.0–15.4	9.7–10.6	10.0–11.0	9.8
Elastic modulus (GPa)	65–86	95–103	210	65
Chemical durability* (μg/cm^2)	100–200	30–50	30	10–20

*ISO 6872.

Scottsdale, AZ), BruxZir Solid Zirconia (Glidewell Labs, Newport Beach, CA), Opalite All-Zirconia (The Aurum Group, Calgary, Alberta, Canada), and KZ3 Zirconia (Keller Laboratories, St. Louis, MO). Unfortunately, as of mid-2012 none of these products has been evaluated in a randomized, controlled clinical study or in any controlled clinical study. Although the fracture resistance of all-zirconia crowns is exceptionally high, the risk for catastrophic wear of opposing enamel and dental restorations is one of the major potential challenges to the effective, safe use of solid zirconia prostheses. As of 2012, no validated clinical evidence of the safety and efficacy of these types of crowns and bridges had been reported. Three other disadvantages of an all-zirconia crown are the difficulty in adjusting occlusion when significant premature contacts are present, the cutting difficulty, and the heat generated in removing defective crowns or when making an endodontic access opening with diamond burs.

The apparent fracture strength, σ_f, increases with an increase in fracture toughness K_{Ic} or a decrease in the critical flaw size (c_{crit}), as indicated by the Griffith equation,

$$\sigma_f = \frac{1}{Y}\frac{K_{Ic}}{\sqrt{c_{crit}}} \quad (1)$$

where Y is a geometrical factor.

For zirconia, the fracture toughness tends to increase with increasing grain size. Therefore, the influence of grain size influence on transformation toughening is contrary to the increase in fracture strength for small grain sizes seen in many other materials. One study of the influence of grain size on three-point bending strength and Vickers fracture toughness revealed that the fracture strength increases linearly for 3Y-TZP from 650 MPa for a 0.9-μm grain size up to 1000 MPa for a critical grain size of 1.4 μm, after which it decreases to 750 MPa for a mean grain size of 1.8 μm. However, this relationship probably does not apply to nanocrystalline (grain size below 800-nm) zirconia used in dentistry because the mean grain size is much smaller than the extrinsic defects, such as cracks caused by grinding. Thus, the dependence of fracture strength on grain size should be small for dental CAD-CAM zirconia. The decrease in strength caused by very large grain sizes is likely caused by premature phase transformation, which leads to microcracking. The change in fracture strength is mainly governed by the change in fracture toughness for the grain size between 0.9 and 1.8 μm. Kosmač et al. (2000) reported that grinding reduced the monoclinic content and the flexural strength of fine-grained zirconia but it did not affect the flexural strength of coarse grained zirconia. Curtis et al. (2006) reported that grinding with coarse grit

burs decreased the flexural strength of zirconia but grinding with fine grit burs did not cause a statistically significant change. Other studies listed in the reference section may present conflicting results because of differences in the initial microstructure, composition, particle size distribution, maximum flaw sizes, and flaw size distribution,

The long-term performance of Y-TZP may be compromised by its susceptibility to hydrothermal degradation. Although hydrothermal effects have generally been reported between 200 °C and 400 °C, longer exposure times at oral temperatures may also degrade zirconia, resulting in increased surface roughness, fragmented grains, and microcracks. The degradation process is initiated by a transformation of the surface to the monoclinic phase, which spreads through the surface grains and into adjacent grains by stresses that develop in this process. The controlling mechanism is still unknown although OH^- groups are thought to be responsible for breaking the atomic bonds at the surface, which produces residual stresses and the initial transformation from the tetragonal to monoclinic phase.

ZIRCONIA-TOUGHENED ALUMINA (ZTA)

Zirconia-toughened alumina is composed, by weight, of 70% to 90% alumina and 10% to 20% zirconia. The core of In-Ceram Zirconia before glass infiltration, by weight, is approximately 62% alumina, 20% zirconia, and 18% glass. Thus, it is not strictly a ZTA ceramic. Similar to the toughening of Y-TZP, ZTA is toughened by a stress-induced transformation mechanism. In ZTA microstructures, stress-induced transformation toughening occurs from uniform internal strain that causes the zirconia structure to crack and the zirconia particles to undergo phase transformation. During this process the number of zirconia particles increases and this change induces compressive stress within the alumina structure. The result of this process is that the strength of alumina is doubled and the toughness is increased two to four times. The properties of alumina, ZTA, and Y-TZP are summarized in Table 18-10. The ZTA properties are based on an 85% alumina/15% zirconia product (ZTA-96, Astro Met, Inc. Cincinnati, OH).

DISPERSION STRENGTHENING AND TOUGHENING

Reinforcement of ceramics with a dispersed phase of a different material can prevent or inhibit propagation of cracks. This process is referred to as dispersion strengthening. When small, tough crystals are homogeneously distributed in a glass, the ceramic structure is toughened and strengthened because cracks cannot penetrate the fine particles as easily as it can the glass. This technique was applied many years ago in the development of aluminous porcelains (in which Al_2O_3 particles were dispersed in a glassy porcelain matrix) for all-porcelain crowns. Many current dental veneering ceramics have a glassy matrix that is reinforced by a dispersed crystal phase. Glass matrices in dental ceramics have been strengthened and toughened by a variety of dispersed crystalline phases including leucite, lithia disilicate, alumina, and tetrasilicic fluormica.

TABLE 18-10 Physical Properties of Alumina, Zirconia-Toughened Alumina, and 3Y-TZP

Property	Alumina	Zirconia-Toughened Alumina (ZTA)	Zirconia (Yttria-Stabilized TZP)
Density (g/cm^3)	3.95	4.10	6.07
Vickers hardness (VHN)	1175 11.5 GPa	1750 17.2	1300 12.8
Flexural strength (MPa)	330	760	≥900
Average grain size (μm)	1–5	1.5	≤0.5
Modulus of elasticity (GPa)	300	310	200
Poisson's ratio	0.25	0.26	0.30
Fracture toughness (MPa•m$^{1/2}$)	3.5	5–7	9–13
CTE* (10^{-6} /K)	8.1	8.1	10.3
Thermal conductivity (W/m•°K)	24	21	2.5–2.8

*Coefficient of thermal expansion.

Almost all of the modern higher-strength ceramics derive their improved fracture resistance from the crack-blocking ability of the crystalline particles. Hot-pressed core ceramics and veneering glass-ceramics contain a glass phase strengthened with crystalline particles of leucite ($K_2O•Al_2O_3•4SiO_2$), lithia disilicate ($Li_2O•2SiO_2$), alumina (Al_2O_3), magnesia-alumina spinel ($MgO•Al_2O_3$), and other types of crystals. Some crystal phase additions are not as effective as others in toughening the ceramics. Toughening depends on the crystal type, its size, its volume fraction, the interparticle spacing, and its relative coefficient of thermal expansion relative to the glass matrix. For example, the fracture toughness (K_{Ic}) of soda-lime-silica glass is 0.75 MPa•m$^{1/2}$. If one disperses approximately 34 vol% of leucite crystals in the glass, such as in IPS Empress, K_{Ic} increases only to 1.3 MPa•m$^{1/2}$. However, by dispersing 70% by volume of interlinked lithia disilicate crystals in the glass matrix, as in IPS e.max Press, K_{Ic} increases to 3.3 MPa•m$^{1/2}$.

In contrast to dispersion strengthening, dental ceramics based primarily on zirconia crystals (Cercon, Lava, Denzir, e.max ZirCAD) undergo transformation toughening involving the conversion of ZrO_2 grains from a tetragonal crystal phase to a monoclinic phase at the tips of cracks in regions of tensile stress.

FLUORAPATITE GLASS-CERAMIC

Nano-fluorapatite glass-ceramic veneer, such as e.max Ceram, has a relatively low coefficient of thermal expansion (about 9.5×10^{-6}/K) and is matched to that of lithia disilicate glass-ceramic core material and to some alumina and zirconia

ceramics. Because of the higher expansion coefficients of conventional feldspathic porcelain veneers, these layering ceramics cannot be used on lithium disilicate core frameworks.

CAD-CAM PROCESSING OF CERAMICS

Computer-aided milling of metals, composites, and ceramics is now possible because of advances in imaging devices, software, and CAD-CAM milling systems. **CAD-CAM ceramic** prostheses can be produced either as monolithic lithia disilicate glass-ceramic or zirconia ceramic structures or as bilayer structures made from milled copings and layered manually, by hot pressing, or by fusing a CAM-produced veneer to the framework (CAD-0n method). A ceramic veneer that is pressed on a metal metal is referred to as the POM method. CAD-CAM prostheses can be produced either by industrial milling processes or by chair-side milling units. The industrial CAD-CAM systems are very expensive with typical costs in excess of several hundred thousand USD. However, they are capable of processing multiple jobs with a high level of accuracy and reproducibility. Chairside systems are limited in their processing speed and their ability to process large cases.

Layered zirconia prostheses can be produced from partially sintered ceramics and shaped by carbide burs to enlarged dimensions that compensate for sintering shrinkage. Fully sintered ceramics are shaped by diamond disks and burs to the precise dimensions derived from a scanned image of the prepared teeth. Typically, the external surface must be ground and polished manually, although some CAD-CAM systems are capable of milling the external surface. Shown in Figure 18-37 is a simulated digitized image of a crown to be produced from a ceramic blank and an adjacent image of a partially milled crown. Shown in Figure 18-38 is Cerec ceramic block, a milled inlay form, and the final inlay.

As mentioned previously, zirconia ceramics can be milled in the green state, in the partially sintered state, or in the fully sintered state. A four-unit Cercon core ceramic framework can be milled in the green state (Figure 18-39), after simulated try-in (Figure 18-40), and after sintering, staining, and glazing the veneering ceramic (Figure 18-41). Representative products that fall into each of these categories are as follows:

1. Green-state milling: Cercon (Degudent/DENTSPLY Ceramco), Lava (3M ESPE), ZirkonZahn (USA), Hint-Els Zirkon TPZ-G (DigiDent)
2. Partially sintered-state milling: IPS e.max ZirCAD (Ivoclar Vivadent), VITA In-Ceram YZ Cubes (VITA Zahnfabrik), Everest (Kavo Dental), Hint-Els Zirkon TZP-W (Digident), DC-Shrink (DCS), Precident DCS (DCS)
3. Fully sintered–state milling) Denzir Premium HIP Zirconia (Etkon USA), Zirkon Pro 50 (Cynovad), Kavo Everest ZH Blanks (Kavo Dental)

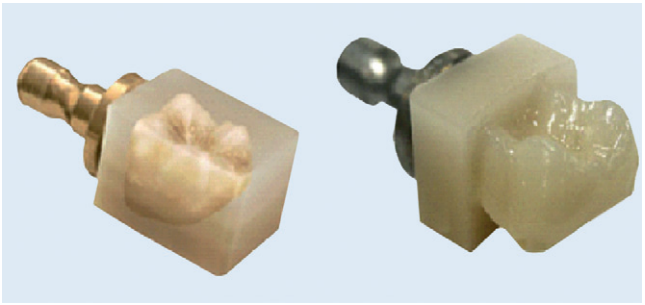


FIGURE 18-37 (*left*) Simulated digitized image, (*right*) partially milled feldspathic ceramic (VITABLOCS Triluxe Forte) processed by the Sirona inLab CAD-CAM system.

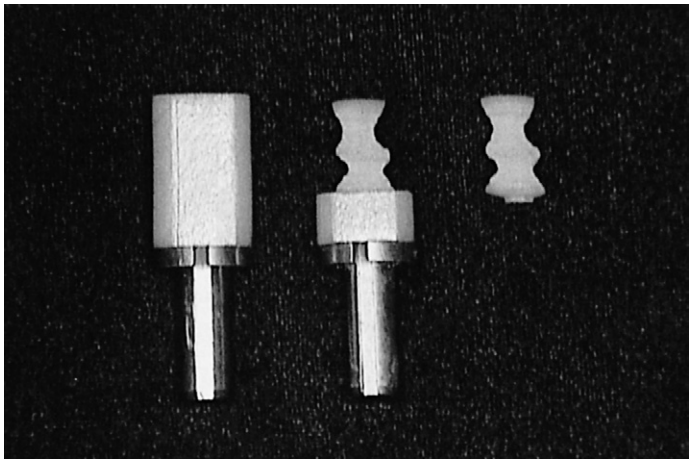


FIGURE 18-38 (*Left*) CAD-CAM ceramic block before milling. (*Center*) An intermediate stage of milling. (*Right*) After removal of the inlay from the mounting stub.

This is by no means a complete list, since new products are introduced each year. For example, the family of ceria-stabilized ceramics has only recently been introduced. Shown in Figure 18-42 is a schematic illustration of the crystalline nanoparticles in a Ce-TZP/Al_2O_3 core ceramic that has a very high fracture toughness and flexure strength. No validated clinical data on this product are yet available. One of the products of this type that has been introduced in Japan is called NanoZir (Panasonic). However, the list is indicative of

the emerging market for dental ceramics and for CAD-CAM systems.

A typical procedural sequence for producing ceramic prostheses by a CAD-CAM system using partially sintered blanks is as follows:

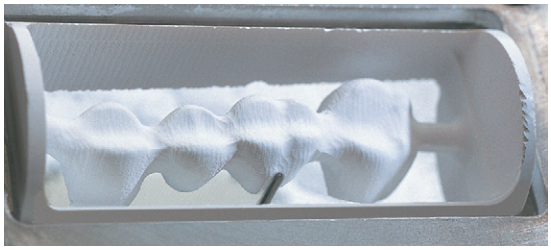


FIGURE 18-39 Cercon zirconia core ceramic after initial milling of the "green state" ceramic. (Courtesy of Dentsply Ceramco, Burlington, NJ.)



FIGURE 18-40 Finished FDP framework made with Cercon core ceramic placed on teeth. (Courtesy of Dentsply Ceramco, Burlington, NJ.)

1. Set the blank in the milling machine holder according to the manufacturer's instructions.
2. Set the enlargement factor to compensate for sintering shrinkage. The factor will vary according to the overall size of the prosthesis.
3. Insert the appropriate machining/milling tool.
4. After machining is completed, remove the framework and residual blank.
5. Cut the framework from the blank using a diamond disc.
6. Clean the partially sintered framework completely.
7. Dry the framework completely.
8. Place the framework in the isothermal hot zone of the sintering furnace.
9. Set the thermal processing conditions according to the sintering instructions for the specific product.
10. Sinter the framework to achieve optimum density.
11. After cooling, remove the sintered framework.
12. Inspect the framework for surface and subsurface flaws using fiberoptic transillumination.



FIGURE 18-41 Final Cercon FDP with veneering ceramic and stain characterization. (Courtesy of Dentsply Ceramco, Burlington, NJ.)

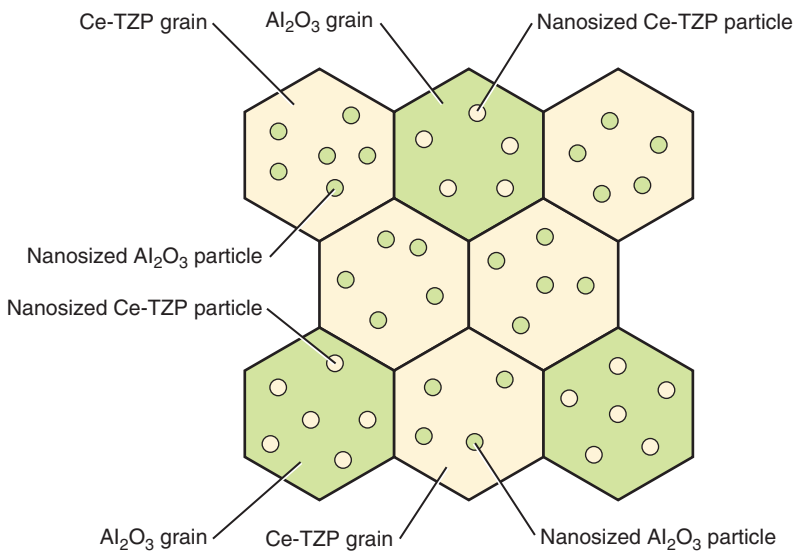


FIGURE 18-42 Schematic illustration of nanostructure crystalline particles in a Ce-TZP/Al_2O_3 core ceramic that has recently been introduced for dental applications.

13. Evaluate the framework for adequacy of wall thickness, ease of seating, and marginal fit.
14. If necessary, use a water-cooled diamond tool to perform minor adjustment corrections.
15. Rinse the framework thoroughly with water and dry it completely.
16. Depending on the zirconia product, the framework may be used with or without a veneering ceramic. If a veneering ceramic is indicated, a transitional liner may be required prior to the application of the veneering (layering) ceramic.

Chair-side milling is the ultimate goal of CAD-CAM processing. Until recently, the ability of a dentist to process his or her own ceramic prostheses was limited by the lack of skills in layering the veneering ceramic on the milled and fully sintered coping or framework. Because of the experience gained over many years with the Cerec system, many dentists are now able to fabricate inlays, onlays, and crowns from leucite-based ceramic blanks (ingots) and lithia-disilicate–based glass-ceramic blanks. Blanks with gradations of translucency and color, such as those developed for the VITABLOCS Triluxe Forte (VITA Zahnfabrik) ceramic line, allow clinicians to produce single-unit finished prostheses without the need for skills in layering of a veneering porcelain. The weak link in all-ceramic prostheses is the relatively low fracture resistance of the veneering ceramics (Table 18-11).

The quality and precision of the more costly commercial imaging, designing, and milling systems has increased markedly since the 1980s because of advances in the software that controls these variables. Thus, it is likely that lab-operated CAD-CAM systems will continue to support crown and bridge needs well into the future.

COPY-MILLING TECHNOLOGY

A copy-milling technique has also been used to machine porcelain. This technology was made possible by means of the Celay system (Mikrona Technologies, Spreitenbach, Switzerland). This system was based on a mechanical device that is used to trace the surface of a prefabricated pattern of the designed restoration made from a blue resin-based composite (Celay-Tech, ESPE, Seefeld-Oberbay, Germany). The resin pattern can be produced directly on prepared teeth or indirectly on dies made from impressions. As the tracing tool passes over the pattern, a milling machine duplicates these movements as it grinds a copy of the pattern from a block of alumina or other ceramic material. Currently, it is possible to machine Celay In-Ceram or In-Ceram Spinell material and then infiltrate the pattern with a sodium-lanthanum glass in a manner similar to that used for conventional In-Ceram crown cores or bridge frameworks. Both types of glass-infiltrated alumina are veneered with Vitadur Alpha porcelain. No long-term clinical data are yet available for Celay-produced restorations. Because the accuracy of the copy-milled crowns is dependent on the care, time, and the profile tracing ability of the technician, the marginal quality of crowns made from the copy-milling technique is likely to be inferior to that of copings made from the hot pressing method. Listed in Table 18-12 are some ceramics that can be processed by copy-milling or by CAD-CAM procedures.

BONDING OF RESIN CERAMIC TO DENTAL CERAMICS

Bonding to resin prosthetic ceramics is important for three reasons: (1) Resin-based composite cements are believed to increase the retention of all-ceramic crowns and bridges. (2) Resin-based composite cements are believed to increase the fracture resistance and survivability of ceramic restorations. (3) The repair of chipped or fractured core or veneer ceramic requires a bonding adhesive to restore the area with composite. However, silane-based bonding adhesives do not bond chemically to all ceramics. For example, as previously shown in Figure 18-33, the framework of the fractured resin-bonded bridge made with an alumina framework could not be etched. The dimpled area on one of the retained flanges of the bridge suggests that macromechanical bonding to the resin cement had been chosen. The clean separation of this framework from the resin-based cement indicates inadequate bonding. Examination of the fractured flange indicates the presence of a large void may have contributed to the fracture of the connector.

It is well known that silane-based resin adhesives can bond to the silica network of silica-based ceramics. In addition, abrasive blasting and acid etching of the glass matrix of these ceramics creates surface irregularities that can further enhance retention of the resin cement. The penetration of the adhesive resin into the macroscopic irregularities combined with chemical bonding may also inhibit water access to the ceramic surface, thereby enhancing durability of bonded ceramic prostheses. Furthermore, acid etching can blunt the tips of microcracks within the ceramic surface. This blunting process reduces the stress concentration at the crack tips. If any voids are trapped within the interface between the crown and cement in the occlusal area, occlusal loads above this site

TABLE 18-11 Properties of Veneering Ceramics for Some Zirconia Core Materials

Veneering Ceramic	Cercon Ceram S	Lava Ceram	Tri-Ceram	VITA VM9	Cerabien CZR
CTE (100 °C–400 °C)	9.6	9.6	8.2	9.1	9.1
Tg (°C)	488	549	561	>590	561
Strength (MPa)	63 ± 8	81 ± 12	81 ± 22	96 ± 8	66 ± 5
Sintering temperature (°C)	830	810	755	910	930

TABLE 18-12 CAD-CAM and Copy-Milled Ceramics Used for All-Ceramic Prostheses

Ceramic Block	Core/Veneer Processing	Ceramic Veneer	Indications	Core/Veneer Supplier
CerAdapt	Highly sintered Al_2O_3	AllCeram	Implant superstructure	Nobel Biocare
Cercon Base	Presintered ZrO_2; postsintered after milling	Cercon Ceram S	Crowns and FPDs	DENTSPLY Ceramco
DC-Kristall	Leucite-based	Triceram	Crowns	DCS Dental AG/ Espident
DC-Zirkon	Presintered ZrO_2; hot isostatic postcompaction	Vitadur D Triceram	Crowns and FPDs	DCS Dental AG/VITA/ Espident
Denzir	Densely sintered; hot isostatic overpressing	Empress2	Crowns and three-unit FPDs	Decim, Ivoclar
IPS ZirCAD	Presintered ZrO_2; hot isostatic postcompaction	IPS ZirPress	Crowns and FPDs	Ivoclar Vivadent
LAVA Frame	ZrO_2; presintered and postsintered	LAVA Ceram	Crowns and FPDs	3M ESPE
ProCad	Leucite-based	Maltechnik	Veneers, inlays, onlays, and crowns	Ivoclar Vivadent
Procera AllCeram	Al_2O_3; presintered and postsintered	AllCeram	Crowns and FPDs	Nobel Biocare
Procera Zirconia	Al_2O_3/ZrO_2; presintered and postsintered	AllCeram	Crowns and FPDs	Nobel Biocare
Synthoceram	Al_2O_3 reinforced; pressed and postsintered	Sintagon	Crowns	Elephant
VITABLOCS Mark II	Feldspathic porcelain block	VITA VM9 (partial veneer only)	Veneers, inlays, onlays, and crowns	VITA Zahnfabrik
VITABLOCS Real Life	Feldspathic porcelain block	VITA VM9 (partial veneer only)	Anterior veneers and crowns	VITA Zahnfabrik
VITABLOCS Alumina	Sintered Al_2O_3: followed by glass infiltration	Vitadur Alpha Vintage AL	Crowns and FPDs	VITA Zahnfabrik Shofu Inc
VITABLOCS Spinell	Sintered MgO-Al_2O_3 spinel followed by glass infiltration	Vitadur Alpha	Crowns	VITA Zahnfabrik
VITABLOCS Zirconia	Sintered Al_2O_3/ZrO_2 followed by glass infiltration	Vitadur Alpha Vintage ZR	Crowns and FPDs	VITA Zahnfabrik Shofu Inc
VITABLOCS Triluxe for Cerec	Feldspathic porcelain block	VITA VM9 (partial veneer only)	Anterior veneers and crowns	VITA Zahnfabrik
Zircagon	ZrO_2; presintered and postsintered	Zircagon	Crowns	Elephant

Modified from Kappert HF, Krah MK, Keramiken—eine Übersicht, *Quintessenz Zahntech* 27(6):668–704, 2001, and from Mantri SS, Bhasin AS. CAD/CAM in dental restorations: An overview. *Ann Esss Dent* II(3):123–128 2010.

can generate tensile stresses in the ceramic that may cause crack formation or fracture.

Silicon dioxide is associated with a large covalent network. The silica molecule is negatively charged. Silicon, an element in group 4A of the periodic chart, has four valence electrons. Silicon bonds covalently with oxygen in SiO_2. Silane primers or coupling agents have dual functionality, including an organic reactive group for bonding to adhesive resins and resin-based composites and methoxy groups ($-OCH_3$) that are hydrolyzed to silanols (Si–OH) for bonding to inorganics such as silica-based ceramics or metal oxide substrates through the formation of siloxane (–Si–O–Si–) bonds. Silane primers provide covalent bonds that promote adhesion at the interface between polymers and hydrolytically stable silica-based substrates, assuming that the substrate is free of contaminants. Shown in Figure 18-43 is a schematic illustration of the bonding stage of silane primer or adhesive to a silica-based ceramic.

Reaction of silanes with silica-based ceramics involves four stages, hydrolysis, condensation, hydrogen bonding, and bond formation. After hydrolysis of the methoxy groups, condensation to oligomers occurs, and the oligomers then hydrogen bond with OH groups of the substrate. Then, during curing, covalent links are formed with the substrate with simultaneous loss of water. These reactions typically occur simultaneously after the initial hydrolysis stage.

Although a monolayer of silane-based primer is preferred, multilayer adsorption generally occurs. Estimated thicknesses from deposition of a 0.25% silane solution onto glass range from three to eight molecular layers. Kitayama et al. (2010) reported that silane-based monomers produced the best bonding to silica-based ceramic and monomers that are

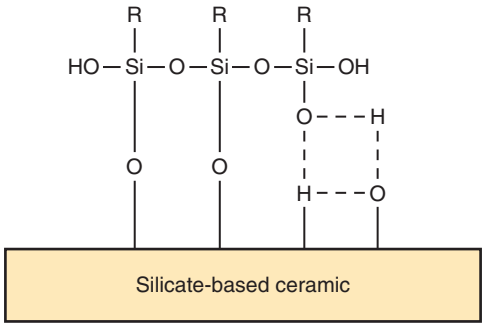


FIGURE 18-43 Schematic illustration of silane bonding to silica-based ceramic.

based on either phosphate ester or phosphonic acid monomers produced better bonding to zirconia. These bonding mechanisms are described further in Chapter 12.

? CRITICAL QUESTION

How can the potential abrasive damage of tooth enamel that opposes ceramic surfaces be minimized? Why is the hardness of a ceramic not a good predictor of wear?

ABRASIVENESS OF DENTAL CERAMICS

Ceramics are generally considered the most biocompatible, durable, and esthetic materials available for rehabilitation of teeth, occlusal function, and facial appearance. Currently available products exhibit variable mechanical properties (hardness, flexure strength, fracture toughness, and elastic modulus), physical properties (index of refraction, color parameters, translucency, chemical durability, and thermal compatibility of core and veneering ceramics), and ability to be bonded to tooth structures and other substrates. In spite of their overall excellence in meeting the ideal requirements of a prosthetic material, dental ceramics have one major drawback: these materials can cause catastrophic wear of opposing tooth structure under certain conditions. The most extreme damage occurs when a roughened surface contacts tooth enamel or dentin under extraordinarily high occlusal forces. This may occur because of bruxing, premature occlusal contacts, and/or inadequate occlusion adjustments. When cuspid-guided disocclusion is ensured, the wear of opposing enamel and dentin will be greatly reduced. The abrasive wear of opposing tooth structure can be reduced further by periodically refinishing the occlusal surface after frequent exposures to carbonated beverages and/or acidulated phosphate fluoride.

Abrasive wear mechanisms for dental restorative materials and tooth enamel include (1) adhesion (metals and composites) in which localized bonding of two surfaces occurs, resulting in pullout, and transfer of matter from one surface to the other, and (2) microfracture (ceramics and enamel), which results from gouging, asperities, impact, and contact stresses that cause cracks or localized fracture. For ceramic and enamel, two-phase brittle structures are involved. The ceramic consists of a glass matrix that contains variable levels and sizes of crystals. Tooth enamel consists of a small volume fraction of organic phase matrix and a high volume fraction of hydroxyapatite crystals. The wear of either material depends on the ease with which cracks can propagate through the structure. If microscopic cracks are forced to pass around the crystal particles rather than through them, the material will usually be more fracture and abrasion resistant. The relative strengthening effect is dependent on several factors including the strength of the glass and crystal phases, the size and spacing of crystalline particles, the interfacial bond strength of the crystal-glass interphase region, and the type and magnitude of residual stresses in the structure. These are factors that are beyond the control of the dentist although the dentist and his/her laboratory technician can select ceramics that are highly fracture resistant.

The microfracture mechanism is the dominant mechanism responsible for surface breakdown of ceramics and the subsequent damage that a roughened ceramic surface can cause to tooth enamel surfaces. Enamel is also susceptible to this kind of microfracture (see Figure 18-6) through four specific mechanisms: (1) asperities extending from the ceramic surface that produce high localized stresses and microfracture; (2) gouging that results from high stresses and large hardness differences between two surfaces or particles extending from these surfaces; (3) impact or erosion that occurs through the action of abrasive particles carried in a flowing liquid such as saliva; and (4) contact stress microfracture that increases localized tensile stress and also enhances the damage caused by asperities, gouging, and impact or erosion. Because of microfracture mechanisms, it may be necessary to polish the ceramic surface periodically to reduce the height of asperities and to minimize enamel wear rates. Of major concern is the potential catastrophic damage that can be incurred by enamel in contact with polycrystalline asperities having high fracture toughness (K_{Ic}) values such as alumina (3.5–4.0 MPa•$m^{1/2}$), magnesium-stabilized zirconia (9–12 MPa•$m^{1/2}$), yttrium-stabilized zirconia (8.0–10.3 MPa•$m^{1/2}$), or cerium-stabilized zirconia (10–16 MPa•$m^{1/2}$). In contrast, glass, which has a fracture toughness of only 0.75 MPa•$m^{1/2}$, should cause less gouging, contact stress, and impact damage to contacting enamel surfaces.

The abrasiveness of ceramics against enamel is affected by numerous factors and properties of the crystal phase particles and the glass matrix (if present). These include hardness, tensile strength, fracture toughness, fatigue resistance, particle-glass bonding, particle-glass interface integrity, chemical durability, exposure frequency to corrosive chemical agents (acidulated phosphate fluoride, carbonated beverages), abrasiveness of foods, residual stress, subsurface quality (voids or other imperfections), magnitude and orientation of applied forces, chewing patterns, bruxing frequency, contact area, lubrication by saliva, and duration of exposure to abrasive particles. As a general rule, the larger the hardness difference between two sliding surfaces, the greater is the degree of wear. However this simple principle does not explain the wide variation in wear rates that are exhibited by different patients under apparently similar conditions. Thus, it is easy to understand why the hardness of the ceramic is not a good predictor of the potential wear of enamel surfaces by a ceramic.

WEAR RATES OF CERAMICS COMPARED WITH OTHER MATERIALS

To minimize enamel abrasion by a contacting ceramic structure, one should use a ceramic that exhibits uniform surface microfracture at the same rate as tooth enamel under the same conditions of loading, antagonist structure, food substance abrasiveness, applied forces, and degree of lubrication. The breakdown of the ceramic surface should be uniform so that asperities such as large crystalline inclusions do not project out of the surface.

These asperities produce high stress concentration areas within the opposing enamel surface that lead to gouging, troughing, and greater localized microfracture of the enamel structure. If such nonuniform surface wear of ceramics occurs during oral function, the only solutions available to reduce enamel wear are to reduce the occlusal load by occlusal adjustment or to polish the ceramic surface periodically to reduce stress concentrations and the height of these asperities. However, polishing of ceramics is a relatively slow process and care must be taken to minimize the generation of heat in the process.

When ultralow-fusing porcelains were initially introduced, the expectation was that because of a smaller particle size, these ceramics would produce less wear of enamel than traditional low-fusing feldspathic porcelains. Duceragold and Duceram LFC (DENTSPLY Ceramco) were introduced between 1991 and 1992. Duceram LFC was classified as a ceramic that was claimed to develop a hydrothermal layer approximately 1 μm thick in vivo and 3 μm thick in vitro. In theory, this property allows a protective layer to seal microscopic surface cracks. Neither Duceram LFC nor Duceragold contains large leucite crystals. The opalescence and fluorescence are greater than those for conventional low-fusing feldspathic porcelains because of their very small crystal particle size (400 to 500 nm). Because of its high expansion coefficient, Duceragold was intended as a veneer for high-expansion alloys such as Degunorm, which exhibits an intense yellow hue and, potentially, exceptional metal-ceramic esthetics.

Duceratin and AllCeram, low-expansion, ultralow-fusing porcelains, were subsequently developed as veneering ceramics for titanium metals and Procera AllCeram (Nobelpharma, Göteborg, Sweden) core ceramics, respectively. TiCeram is another ultralow-fusing ceramic, which has a firing temperature of approximately 740 °C. The initial veneering porcelain for Procera AllCeram was Vitadur N (Vita Zahnfabrik, Bad Säckingen, Germany), a large-particle aluminous porcelain.

WEAR OF ENAMEL BY CERAMIC PRODUCTS AND OTHER RESTORATIVE MATERIALS

Another factor that can increase the wear of enamel by ceramics is the nonuniform clustering of crystals. IPS Empress after hot-pressing at 1180 °C exhibits clusters of relatively large (5- to 10-μm) leucite crystals ($KAlSi_2O_6$) with cracks between the crystal agglomerates. This noninterlocking arrangement of leucite crystals also occurs in the veneering ceramic after it is sintered at 910 °C. In contrast, IPS Empress 2 core ceramic exhibits a uniform dispersion of smaller lithia disilicate ($Li_2Si_2O_5$) crystals after hot pressing at 920 °C and veneering at 800 °C.

One should expect greater wear of enamel by IPS Empress compared with IPS Empress 2. IPS Empress ceramic contains 35 ± 51% by volume of leucite crystals that are formed in a noninterlocking particle cluster pattern (Höland et al., 2000). The core microstructure of IPS Empress 2 is quite different from that of IPS Empress, as evidenced by elongated lithia disilicate crystals 0.5 to 4 μm in length and a smaller concentration of lithium orthophosphate crystals (Li_3PO_4) approximately 0.1 to 0.3 μm in diameter (Höland et al., 2000). An in vitro study involving 50,000 wear cycles in a poppy seed/PMMA-bead slurry revealed significantly greater three-body wear of enamel by IPS Empress veneer ceramic (6.06 mm^2) compared with IPS Empress 2 veneer ceramic (1.82 mm^2). This represents a 238% increase in surface area lost because of ceramic abrasiveness. Enamel wear volume losses caused by other materials were as follows: Vita Omega (4.44 mm^2), Procera AllCeram (4.97 mm^2), Finesse (5.23 mm^2), and Vitadur Alpha (6.61 mm^2), which is an aluminous porcelain.

Studies of ultralow-fusing ceramics have generally revealed significantly lower enamel wear rates than those produced by conventional porcelains. However, the results of one study suggest that one of these ceramics, Duceram LFC, caused significantly more enamel wear (0.197 mm^3) than Creation porcelain (0.135 mm^3) or Vitadur Alpha porcelain (0.153 mm^3), presumably because of the higher void volume within the surface layer of Duceram LFC (Magne et al., 1999). In this study, the combined enamel/ceramic wear rates were significantly greater for Duceram LFC (0.363 mm^3) and Vitadur Alpha (0.333 mm^3) compared with that for Creation porcelain (0.260 mm^3). Veneering ceramics contain either large crystalline filler particles or a glass structure with no crystals or very small crystals such as nanocrystalline fluorapatite.

The results from another study (Al-Hiyasat, 1999) of enamel wear (after 25,000 simulated chewing cycles) by ceramics using a cornmeal slurry (three-body condition) revealed greater relative wear depth in enamel by Duceram LFC (0.74 mm) and Vitadur Alpha (0.80 mm) compared with Vita Cerec Mk II (0.48 mm). The result for Duceram LFC is in contrast with two-body wear data (al-Hiyasat et al., 1998) indicating significantly less enamel wear in distilled water without an abrasive food medium by Duceram LFC (0.54 mm after 25,000 simulated chewing cycles) and Vita Mk II (0.65 mm) and a gold alloy (0.09 mm) compared with Vitadur Alpha porcelain (0.93 mm) and Vita Omega porcelain (0.96 mm). The wear rate of enamel by gold alloy was significantly less than that produced by the four ceramics. The explanation given for the higher wear rate of enamel by Duceram LFC was the presence of porosity within the surface of the ceramic.

One would expect the latter types of ceramics to cause minimal wear of enamel. The results of one study (Metzler et al., 1999) indicate that the relative enamel loss was less for two ultralow-fusing ceramics, Finesse (0.56) and Vita Omega

900 (0.60), compared with Dentsply Ceramco II porcelain (0.85), a large particle leucite-based porcelain.

Krejci and coworkers (1994) reported significantly lower estimated 5-year enamel wear rates for amalgam (50 μm) and a new Cerec CAD-CAM ceramic, Vita Cerec Mk II V7K (95 μm), compared with the original Vita Cerec Mk I ceramic (225 μm). In comparison, the wear of enamel by enamel was 107 μm. Hacker and colleagues (1996) found considerably lower enamel wear rates for a gold-palladium alloy (9 μm) compared with AllCeram veneer ceramic (60 μm) and Dentsply Ceramco porcelain (230 μm).

Jagger et al. (1995) reported the following wear depths of dentin after wear by restorative materials: amalgam (0 μm), microfilled composite (7 μm), gold alloy (16.7 μm), conventional composite (31.7 μm), and Vitadur N aluminous porcelain (100 μm). These results indicate that direct filling materials are less abrasive to dentin than aluminous porcelain. This result is not surprising. What is of importance is the significant potential benefit of amalgam and microfilled composite as the least abrasive restorative materials for situations in which opposing dentin is exposed.

Al-Hiyasat et al. (1998) investigated the effect of a carbonated beverage (Coca-Cola) on the wear of human enamel and three dental ceramics: Vitadur Alpha (feldspathic porcelain), Duceram LFC (ultralow-fusing porcelain), and Vita Mark II, a machinable ceramic. Tooth-ceramic specimens were tested in a wear machine under a load of 40 N, at 80 cycles per minute, for a total of 25,000 cycles. The test was performed in distilled water or with intermittent exposure to a carbonated beverage (Coca-Cola). When tested in water, Vitadur Alpha porcelain caused significantly more enamel wear and also exhibited greater wear than Duceram LFC and Vita Mark II. However, after exposure to the carbonated beverage, the enamel wear produced by Duceram LFC did not differ significantly from that produced by Vitadur Alpha porcelain. Vita Mark II produced the least amount of enamel wear. Exposure to the carbonated beverage significantly increased the enamel wear. The wear of Duceram-LFC and Vita Mark II increased with exposure to the carbonated beverage. It was concluded that exposure to the carbonated beverage accelerated the enamel wear produced by Duceram-LFC and Vita Mark II ceramics. Overall, Vita Mark II was the most resistant to wear and it was also significantly less abrasive than Vitadur Alpha porcelain.

? CRITICAL QUESTION

Why does glazing sometimes not decrease the abrasive potential of ceramic crowns?

REDUCING ABRASIVENESS OF CERAMICS BY POLISHING AND GLAZING

In theory, the smoothest surface should cause the least wear damage to opposing surfaces. Depending on the initial surface roughness of the ceramic surface, glazing the surface may not adequately decrease the surface roughness since the glassy layer may be of insufficient thickness to fill in scratches and grooves within the ground surface. Thus, under certain conditions, polishing or polishing followed by glazing may be required.

Jagger and Harrison (1994) reported that the amount of enamel wear produced by both glazed (28.8 μm) and unglazed Vitadur N aluminous porcelain (29 μm) was similar; however, wear produced by polished porcelain (12 μm) was substantially less. Polished or glazed porcelain caused significantly less wear than unglazed porcelain. Polishing was accomplished with 3M Soflex disks and Shofu rubber points.

After 25,000 cycles of abrasion testing of various porcelain surfaces on human enamel in vitro, Al-Hiyasat et al. (1997) reported no significant difference between the enamel wear of glazed and polished groups, but wear produced by the unglazed groups was significantly higher ($P < 0.05$). Sixty pairs of tooth-porcelain specimens were tested under load in distilled water with and without intermittent exposure to a carbonated beverage. Wear of enamel and Vitadur Alpha porcelain specimens was determined after 5000, 15,000, and 25,000 cycles. Exposure to a carbonated Coca-Cola and Schweppes beverages significantly increased the amount of enamel wear produced by all porcelain surfaces ($P < 0.001$). The finish of the porcelain surface did not influence wear.

GUIDELINES FOR MINIMIZING EXCESSIVE WEAR OF ENAMEL BY DENTAL CERAMICS

To minimize the wear of enamel by dental ceramics, the following steps should be taken: (1) ensure cuspid-guided disocclusion; (2) eliminate occlusal prematurities; (3) use metal in functional bruxing areas; (4) if occlusion is in ceramic, use ultralow-fusing ceramics; (5) polish functional ceramic surfaces; (6) repolish ceramic surfaces periodically; and (7) readjust occlusion periodically if needed.

Ceramic and opposing surfaces should be examined periodically for evidence of excessive wear. Occlusal adjustment and polishing of the ceramic surfaces should be performed to reduce the risk for further surface degradation. Noble metal surfaces are especially indicated for individuals who exhibit evidence of severe bruxing since the wear rates of gold alloys are very low compared with the wear damage caused by either traditional ceramics or recent ultralow-fusing ceramics. A rough ceramic surface that is in hyperocclusion with opposing enamel is very likely to cause great abrasive wear of tooth surfaces. To minimize the risk of such wear damage to tooth enamel or other surfaces, the smoothest possible ceramic surface should be produced. This can be accomplished by (1) polishing only, (2) polishing followed by glazing, or (3) glazing only. The second choice is preferred. Glazing is recommended whenever possible prior to cementation of a prosthesis. If this is not possible, polishing alone is acceptable. Glazing of a very rough ceramic surface may not sufficiently reduce the surface roughness to minimize wear damage. However, it is reasonable to assume that a glazed rough surface is better than a rough, nonglazed surface since the troughs are filled in with glass, which reduces the surface roughness. It is not always possible to polish a ceramic surface

in the clinic. Because of the heat generated during polishing of ceramic-based prostheses, the increased temperature of pulpal tissue may lead to irreversible pulpitis. This is especially true when the tooth has been greatly reduced in size and the pulp chamber is within 0.5 mm of the external surface of the prepared tooth.

There are several clear indications for polishing ceramic surfaces. Polishing of ceramic prostheses should be performed when they cannot be autoglazed. Polishing of ceramic restorations that have functional occlusal pathways or subgingival extensions will ensure optimal smoothness. All CAD-CAM inlays or other ceramic prostheses that will not receive veneering ceramic should also be polished.

Intraoral instrumentation can produce a smoother surface than an autoglazing procedure. Highly polished porcelain may also be naturally glazed or overglazed without significantly increasing the surface roughness. Increased time or cycles of glazing will decrease surface roughness.

Polishing instruments should be selected according to type of ceramic, type of restoration, and level of smoothness desired. If the crown was ground with a 100-µm grit diamond, the first polishing abrasive should be 75 µm or less. If the abrasive is too fine, more time will be needed to polish the surface. Hulterstrom and Bergman (1993) found that two of the best polishing systems were Sof-Lex disks (3M Dental) and Shofu Porcelain Laminate Polishing Kit followed by diamond paste. Polishing is preferred over glazing as a procedure to reduce abrasion damage of enamel. Ceramic surfaces should be refinished periodically after acid exposure, especially acidulated phosphate fluoride. The Shofu porcelain polishing kit followed with diamond paste or SofLex disks (3M) without a diamond paste follow-up are useful as effective finishing products.

For the Sof-Lex disks, one should start with the disk that is the most effective at removing the initial grinding patterns. If the abrasive grit size on the disk is too small, it will take too long to decrease the roughness. If the grit size is too large (e.g., extra-coarse or coarse), the surface will become rougher. Also, if the polishing procedure is performed in the mouth, care should be taken to avoid heat build-up. Sof-Lex disks are made to be used in a wet environment, so water coolant should be used whenever possible.

The Shofu kit contains a series of rubber point abrasives and rubber wheels. The shank of the rubber tips is color coded to distinguish the abrasive grit characteristic. The diamond paste is expressed from a tube or removed from a jar and applied to the ceramic surface using either a Robinson Wheel brush or a felt wheel. This paste is more amenable to use for extraoral polishing of dental ceramics.

CLINICAL PERFORMANCE OF ALL-CERAMIC RESTORATIONS

Malament and Socransky (1999) reported survival probabilities for acid-etched Dicor and nonetched Dicor restorations of 76% and 50%, respectively, after 14 years ($P < 0.001$). Nonetched (nonbonded) Dicor crowns exhibited a 2.2 times greater risk of failure than acid-etched restorations ($P < 0.01$). Ceramic crown survival was greatest for incisor teeth and decreased progressively to a maximum failure level for second molar crowns. All lateral incisor crowns survived during the 14-year study. Survival of acid-etched and resin-bonded Dicor crowns for subjects 33 to 52 years of age was 62% at 14 years compared with 82% for those 52 years of age and older.

Tooth preparation for all-ceramic crowns is virtually the same as that required for metal-ceramic restorations. Occlusal surfaces and incisal edges must be reduced about 1.5 to 2.0 mm. Axial surfaces should be reduced at least 1.0 mm circumferentially, although the guidelines for one all-ceramic product indicate that an axial reduction of 0.8 mm is sufficient. The preparation should be either a shoulder with a rounded gingivoaxial line angle or a 120° chamfer (deep chamfer). Knife-edge margins should never be chosen for any ceramic product.

Clinicians have experienced fractures of crowns during initial seating because of knife-edge margins, overextension of veneering porcelain beyond the support area of the core ceramic (Figure 18-44), undetected or incompletely removed ceramic particles on the internal surface, distortion of impressions or trays, undercut areas on the tooth that were not properly blocked out, and inadequate occlusal or connector thickness under hyperocclusion conditions.

A light seating force combined with internal inspection and correction of these irregularities is indicated as a routine procedure. For cementation, a resin cement is indicated for the weaker products, such as OPC-3G, Finesse All-Ceramic, IPS Empress, IPS Empress 2, and In-Ceram Spinell. Etching of ceramics with a glass matrix creates micromechanical retention areas on the internal surface. A dual-curing or self-curing cement is recommended. A vibratory instrument or a light tapping procedure will ensure complete seating since some of these cements are quite viscous or behave in a thixotropic manner (increased flow under vibratory or light tapping action). The excess cement should be removed completely immediately after seating. After polymerization, residual resin

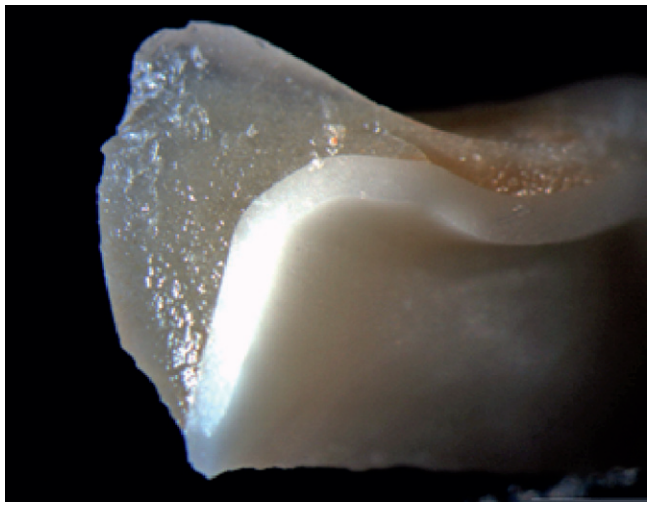


FIGURE 18-44 Fracture of overextended veneering ceramic.

can be removed with abrasive disks, stones, or burs. For any ceramic crown, large voids in the cement must be minimized since the tensile stresses in the unsupported areas of a ceramic crown will be increased under occlusal forces.

CERAMIC VENEERS

The success rate of etched and bonded porcelain veneers has been well established since the concept of acid etching of porcelain was established in 1981. However, limited long-term data are available to compare the longevity of these restorations with the survival times and probabilities for metal-ceramic or ceramic crowns. In general, ceramic veneers are not as esthetically pleasing as full ceramic crowns. Furthermore, crowns that are made from alumina or zirconia core ceramics should not be used for ceramic veneers because of their opacity and their inability to be etched and bonded effectively to tooth enamel.

Ceramic veneers represent a more conservative approach than the use of full crowns. The control of esthetics is technique sensitive since the resin cement, whose color may change over time, plays a key role in the overall appearance. In addition, resin-bonded veneers and crowns that extend into the root area of patients with poor oral hygiene have been associated with leakage and secondary caries caused by improper cementation.

Several products are available for porcelain veneers. Most of these ceramics have relatively high translucency and most are sold with a bonding kit and instructions for etching with hydrofluoric acid (HF) or ammonium bifluoride (NH_4HF_2) gels. Do not etch the ceramic with phosphoric acid from a conditioning kit for composite. Read the instructions carefully. Some ceramics require sandblasting instead of etching when using the bonding kit.

CHEMICAL ATTACK OF GLASS-PHASE CERAMICS BY ACIDULATED PHOSPHATE FLUORIDE

Topical fluorides are routinely used for caries control. The effect of such agents on the surface of ceramic restorations has been studied. Acidulated phosphate fluoride (APF), one of the most commonly used fluoride gels, is known to etch glass by selective leaching of sodium ions, thereby disrupting the silica network. When glazed feldspathic porcelain is exposed to 1.23% APF or by 8% stannous fluoride, a surface roughness is produced within 4 min. As can be seen in Figure 18-10, a 30-min exposure to 1.23% APF gel appears to preferentially attack the glass phase (areas with white precipitate particles) of a gingival (body) porcelain. Obviously this roughness leads to staining, plaque accumulation, and further breakdown of the structure. However, the use of lower concentrations, such as 0.4% stannous fluoride and 2% sodium fluoride, has no significant effect on the ceramic surface. Dentists should be aware of these long-term clinical effects of fluorides on ceramic and composite restorations (because of their glass filler particles) and avoid the use of APF gels when composites and ceramics are present. APF gels should not be used on glazed porcelain surfaces. If such a gel is used, the surface of the restoration should be protected with petroleum jelly, cocoa butter, or wax.

PORCELAIN DENTURE TEETH

The manufacture of denture teeth constitutes virtually the sole current use for high-fusing or medium-fusing dental porcelains. Their composition is slightly higher in the alumina content as shown in Figure 18-2. Denture teeth are made by packing two or more porcelains of differing translucencies for each tooth into metal molds. They are fired on large trays in high-temperature ovens. Porcelain teeth are designed to be retained on the denture base by mechanical interlocking. The anterior teeth are made with projecting metal pins that become surrounded with the denture base resin during processing, whereas the posterior teeth are molded with diatoric spaces into which the denture base resin may flow.

Either porcelain or acrylic resin denture teeth can be employed in the fabrication of complete and partial dentures. Porcelain teeth are generally considered to be more esthetically satisfactory than acrylic teeth. They are also much more resistant to wear, although the development of new polymers has improved the wear resistance of acrylic teeth. Porcelain teeth also have the advantage of being the only type of denture teeth that allow the denture to be rebased (replacement of the entire acrylic denture base).

Compared with acrylic resin teeth, the disadvantages of porcelain teeth are their brittleness, the need for mechanical retention, the extra time required to grind and contour the surfaces, and the clicking sound produced on contact with the opposing teeth. Porcelain teeth also require a greater interridge distance because they cannot be ground as thin in the ridge lap area as acrylic teeth without destroying the diatoric channels that provide their only means of retention to the denture base resin.

FACTORS AFFECTING THE COLOR APPEARANCE OF CERAMICS

In addition to their biocompatibility and chemical inertness, another principal reason for the choice of ceramics as restorative materials is their esthetic qualities in matching the adjacent tooth structure in translucency, color, and chroma. Color phenomena and terminology are discussed in Chapter 3. Perfect color matching is extremely difficult and demands exceptional skill and experience on the parts of the dentist and lab technician. The structure of the tooth influences its color. Dentin is more opaque than enamel and reflects light very well. Enamel represents a predominantly crystalline layer over the dentin and is composed of tiny prisms or rods cemented together by an organic substance. The indices of refraction of the rods and the cementing substance are different. As a result, light rays are dispersed by varying proportions of absorption, transmission, scattering, and reflection to produce a resulting translucent effect and a sensation of depth as the scattered light ray reaches the eye. As the light ray strikes the tooth surface, part of it is reflected, and the

remainder penetrates the enamel and is scattered. Any light reaching the dentin is either absorbed or partially reflected to the eye and partially scattered within the enamel. If dentin is not present, as in the tip of an incisor, some of the light ray may be transmitted into the oral cavity. As a result, this area may appear to be more translucent than that toward the gingival area. Because the law of energy conservation must apply, the following relationship shows the five energy components that are derived from the energy (E) of the incident light:

$$E_{incident} = E_{scattered} + E_{reflected} + E_{absorbed} + E_{transmitted} + E_{fluoresced}$$

Although some of the absorbed light may be converted into heat, some may be transmitted back to the eye as fluorescent energy. Light rays can also be dispersed, giving a color or shade that varies in different teeth. The dispersion can vary with the wavelength of the light. Therefore, the appearance of the teeth may vary according to whether they are viewed in direct sunlight, reflected daylight, tungsten light, or fluorescent light. This phenomenon is called metamerism. The dentist and laboratory technician must reproduce the esthetic characteristics sufficiently such that the appearance of a ceramic prosthesis is discernible only to the trained eye.

Dental porcelains are pigmented by the inclusion of oxides to provide desired shades. Specimens of each shade are distributed in a specific order in shade guides to assist the clinic team in selection of the best match to adjacent natural teeth or other ceramic or resin composite restorations. The colors of dentin (body) porcelain and opaque porcelain vary among manufacturers for a given shade. What are the reasons for this variation? Each manufacturer designs a specific system for developing shades of opaque and dentin porcelains. Ambiguity in the true color of a shade arises from differences among shade guides. Apparently each manufacturer interprets what a given shade should be. Anatomically contoured shade guides are made manually to combine an opaque, dentin, and incisal porcelain on each tab. The porcelains used are uniquely made for shade guides and they are not always produced from dental porcelains. The manual process leads to variations among manufacturers and among shade guides for any shade.

Shade guides are produced by dental ceramic manufacturers to assist dentists and lab technicians in selecting optimum ceramic shades and for communicating the desired prosthesis appearance to each other. Shade guides made of porcelain are used most often by dentists to describe a desired appearance of a natural tooth or ceramic prosthesis. However, there are several deficiencies of shade guides. Shade guide tabs are much thicker than the thickness of ceramic that is used for dental crowns or veneers, and they are more translucent than teeth and ceramic crowns backed by a nontranslucent dentin substructure or veneering ceramics backed by an opaque core ceramic, or a metal framework. Much of the incident light is transmitted through a tab. In contrast, most of the incident light on a crown is reflected except at the incisal edge and at proximal incisal areas. Furthermore, the necks of shade tabs are made from a deeper hue—that is, higher chroma—and this region tends to distract the observer's matching ability in the gingival third of the tab. To avoid this situation, some clinicians grind away the neck area of a set of shade tabs.

The production of color sensation with a pigment is a physically different phenomenon from that obtained by optical reflection, refraction, and dispersion. The color of a pigment is determined by selective absorption and selective reflection. For example, if white light is reflected from a red surface, all the light with a wavelength different from that of red is absorbed and only the red light is reflected. It follows, then, that if a red hue is present in a ceramic crown but the red hue of the same wavelength is not present in the light beam, the tooth will appear as a different shade. If the tooth or restoration surface is rough, most of the light will be scattered and little will penetrate its structure.

CERAMIC VENEERS, INLAYS, AND ONLAYS

The success rate of etched and bonded porcelain veneers has been well established since acid etching of porcelain was established in 1981. Data accumulated for 5 years or more indicate success rates of 95% to 100%. Ceramic veneers represent a more conservative approach than the use of full crowns. The control of esthetics is technique sensitive because the conventional acid-base cements or resin-based luting cements play a key role in the overall appearance.

The discovery that dental porcelains and glass-ceramics can be etched with hydrofluoric acid or other acids to create retentive micromechanical irregularities similar to those in acid-etched enamel has led to the development of resin-bonded, acid-etched ceramic restorations. One must be extremely careful in handling hydrofluoric acid (see Chapter 7) because even short-term contact can cause catastrophic injury to affected tissues. An emergency management plan for laboratories that use hydrofluoric acid should be established.

Ceramic veneers are used primarily for esthetic improvement of stained or hypoplastic anterior teeth. Resin-bonded, acid-etched ceramic inlays and onlays are also used for posterior restorations. A resin cement is used for bonding to the etched metal and enamel. The long-term clinical performance of ceramic veneers and resin-bonded inlays and onlays has been well documented. Their esthetic characteristics are excellent. However, one should be aware of the potential for ceramic veneers to abrade opposing teeth excessively. Thus, the surface of the ceramic restorations should be polished to as smooth a surface finish as possible after they have been adjusted into the desired incisal function prior to cementation.

CRITICAL OBSERVATION AND ANALYSIS OF FRACTURES

Clinical fractures of metal-ceramic restorations, although rare, still occur, especially when a new alloy or veneering porcelain is being used or a new technology (such as POM veneer ceramic for metal frameworks) has been adopted. As is generally true for all dental materials, a learning curve is associated with the initial use of new products. When fractures occur, it is extremely useful to make a vinyl polysiloxane impression of

the fracture site as soon as possible for future fractographic analysis. All information on the crown or bridge should be recorded, including the visual appearance of the fracture site, the location, the approximate size, and occlusion (Anusavice, 2012). A photograph is also very helpful in analyzing the potential cause of fracture. Although there are an infinite number of fracture paths that may occur, three types are of particular importance in diagnosing the cause of fracture. Shown in Figure 18-20 are fracture paths that have occurred primarily at three sites in a metal-ceramic crown: (1) along the interfacial region between opaque porcelain (P) and the bonding zone (I) between porcelain and the metal substrate (top), (2) within the bonding zone (center), and (3) between the metal and the bonding zone (bottom). For conventional metal-ceramic crowns made from cast copings, the bonding zone is synonymous with the metal oxide layer. For copings made using atypical methods such as the technologies associated with the Captek system (Leach and Dillon), and electroforming processes, bonding to porcelain is achieved though the formation of an intermediate layer of material such as the Capbond metal-ceramic "bonder" (bonding agent) for the Captek foil crown system or some other bonding agent.

To characterize the principal site of fracture, a low-magnification examination of the fracture surface may be sufficient in a few cases. However, a magnification of 3 to 100 times is required more often because minute microstructural details such as pores may reveal wake hackle patterns that clearly show the direction of crack propagation in these areas. Fractographers seek important crack features such as hackle, twist hackle, wake hackle, arrest lines, and compression curl to lead them toward the critical flaw or source of crack initiation and the possibility to identifying one or more mechanisms for failure.

Each of the three principal fracture paths in Figure 18-20 is indicative of excessive tensile stress, a material defect, or a processing factor. The location and shape of a fracture surface are major factors used to determine the cause of fracture. For fractures confined to the occlusal surface of posterior crowns, a cone-crack type of fracture (apex of the cone at the fracture surface and the base of the cone extending into the veneer) suggests that localized loading at small contact areas may be the cause. Fractures that occur in the proximal occlusal area of the crowns may be caused by inadequate support of the veneer by the core framework material. Fractures that occur well away from the sites of loading may be caused by thermal incompatibility stresses. The procedures for obtaining evidence from fractured all-ceramic restorations are the same as those used for metal-ceramic restorations. As proposed by Heintze and Rousson (2010), fractures of ceramic-ceramic prostheses can be classified by whether they should be polished (grade 1), repaired (grade 2), or replaced (grade 3).

What is the purpose of the impression? It allows a replica of the fracture surface to be made from an epoxy resin. The replica allows fractographic observations of the fracture surface to be made, and these models can then be examined by a fractography expert under low magnification using optical microscopy and stereoscopic microscopy, followed by scanning electron microscopy. The location of the critical flaw indicates the origin of the fracture. Fracture surface markings observed on the replica assist the expert in determining the origin and to confirm the suspected cause of fracture. Shown in Figure 18-45, *A,* is a residual section of a fractured Procera AllCeram alumina-based crown with a glass-phase veneer that fractured after four years of clinical service. The cause of fracture can be assessed by visual inspection, characterization of principal fracture features, detailed examination of optical microscopy and stereomicroscopy images, and, if necessary, scanning electron microscopy images. These analyses for the fractured crown on the left side of Figure 18-45 revealed fracture paths that are shown by black arrows on Figure 18-45, *B*. These paths suggest that fracture started from an initial crack at the mesial margin (1), propagating 2 mm upward (2), until catastrophic fracture occurred by spreading laterally to areas (4) and area (5), which exhibit an example of compression curl. Area 3 represents another fracture initiation site that is not involved in the bulk fracture process. It

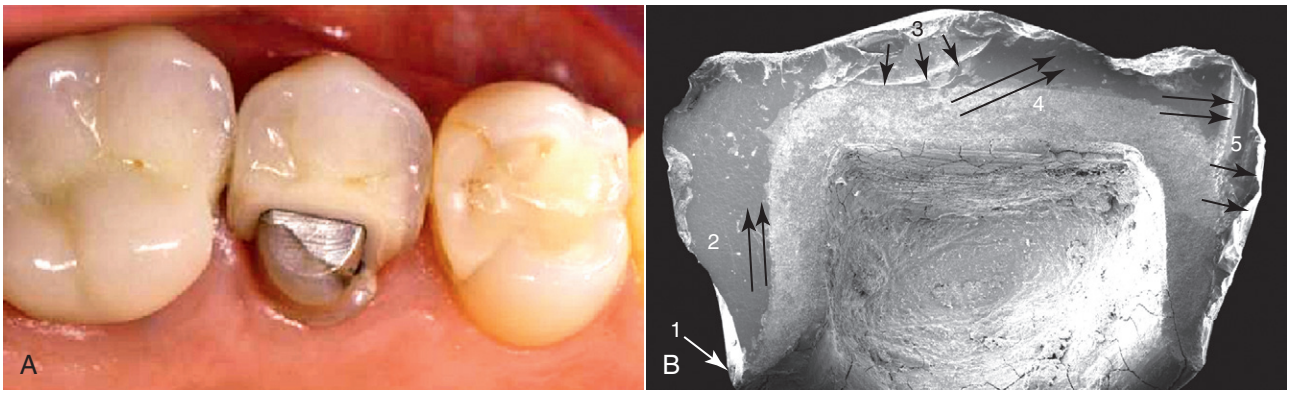


FIGURE 18-45 **A,** Fractured Procera AllCeram premolar crown. **B,** SEM image of the retrieved fractured segment. The initiating crack occurred near the mesial margin (1) and propagated upward approximately 2 mm before crown fracture occurred in areas (2) and (4), terminating in the compression curl area (5). Area (3) represents contact damage within the occlusal veneering ceramic that does not extend into the alumina core ceramic. (From Scherrer SS, Quinn GD, Quinn JB: Fractographic failure analysis of a Procera AllCeram crown. *Dent Mater* 24:1107–1113, 2008.)



FIGURE 18-46 Inspection for cracks using fiberoptic transillumination.

illustrates incidental surface damage in an area where crack propagation was localized only in the veneer ceramic.

The fractographic procedures described above are based on the assumption that the prosthesis was free of cracks during try-in and during cementation. However, dentists are not typically trained to inspect prostheses received from the lab using fiberoptic transillumination. Examination under such lighting can reveal surface and subsurface cracks that may exist in the ceramic and metal-ceramic prostheses either before or after try-in for fit. Shown in Figure 18-46 is a laboratory technician who is using a fiberoptic light source to inspect a ceramic prosthesis for cracks that may be hidden from typical fluorescent or incandescent light sources.

Many factors are associated with the fracture of all-ceramic prostheses. These factors fall into one of eight categories: (1) inherent surface defects, (2) processing defects, (3) loading (bite force and load orientation), (4) design, (5) material properties, (6) residual stress, (7) procedural errors, and (8) diet. Within these categories the following variables may contribute to crack initiation, crack propagation, chipping, and bulk fracture: surface treatment, excessive loading during try-in, bruxing loads, loading location, load distribution, load magnitude, transient cooling stresses, residual cooling stresses, inadequate tooth preparation, improper core framework design, inadequate crown thickness, inadequate core thickness, improper connector size, quality of the cement layer, bond quality of ceramic veneer to core ceramic, voids in the cement layer or at the cement/ceramic interface, and the elastic moduli of component and supporting substrate materials. To reduce the risk for ceramic fracture, sufficient tooth reduction, sufficient thickness of the ceramic, adequate prosthesis design, distributed vertical loading, and meticulous attention to the recommended manufacturers' procedures are required.

? CRITICAL QUESTION

What are the indications and contraindications for the use of all-ceramic crowns?

PRINCIPLES GOVERNING THE SELECTION OF DENTAL CERAMICS

Although an all-ceramic prosthesis usually exhibits superb esthetics, not all such bridges are equally esthetic because the connectors must be sufficiently thick to minimize the risk of fracture and the core ceramic may be excessively opaque. Some ceramic crowns will not be esthetic if the tooth preparations are inadequate, particularly when insufficient tooth structure has been removed. Not all patients will benefit from the placement of all-ceramic crowns or bridges. Some individuals exhibit certain characteristics that would allow only a metal or metal-ceramic bridge to be used. For example, if an individual bruxes frequently and with great force, an all-ceramic bridge would not be likely to survive. A ceramic bridge should not be placed in patients who have a long span across the pontic site, since the higher stresses under function could lead to premature fracture. There are several clear indications and contraindications to be kept in mind when treatment planning involves a crown or bridge made with a ceramic system. Ceramics are preferred over metal-ceramics when esthetics is a prime concern, when metal-ceramic esthetics is unacceptable, or when a history of metal hypersensitivity exists. Contraindications for all-ceramic prostheses include severe bruxism, extensive wear of tooth structure or restorations, excessive bite-force capability, and a previous history of all-ceramic inlay or crown fractures.

The toughest and strongest core ceramics have opaque cores (In-Ceram Alumina, In-Ceram Zirconia, Procera All-Ceram, Cercon, Lava, e.max ZirCAD, Denzir) veneered with layers of translucent ceramic. Other products (e.g., OPC-3G, IPS Empress, IPS Empress 2, and e.max Press) have more translucent cores. However, prediction of the most durable ceramic should be based on the fracture resistance of the entire bilayer or trilayer system, not simply on the core ceramic itself. In the absence of randomized controlled clinical data, in vitro tests of the monolithic ceramic materials and of layered ceramics that simulate the designs used in clinical practice are highly desirable. Shown in Figure 18-47 are the mean fracture loads across three strength ranges for 1.5-mm-thick three-unit bridges made with four ceramic materials. Weibull analyses should be performed on these data to determine the reliability and fracture probabilities over time. More importantly, finite element models can be developed for any prosthesis design that can be applied with dynamic fatigue data for the component ceramic materials using CARES/Life software (NASA) to predict the time-dependent probabilities for fracture.

The success or failure of ceramic restorations can be related to dentist-, lab-, technician-, patient-, and material-related factors. The specific cause of failure often results from failure to follow the manufacturers' guidelines. For example, traditional feldspathic porcelain for metal-ceramic prostheses should not be used as the core ceramic for a ceramic crown because it lacks sufficient fracture toughness for this purpose. The comparative fracture toughness of ceramics are listed in Tables 18-7 and 18-8. Feldspathic porcelain must be

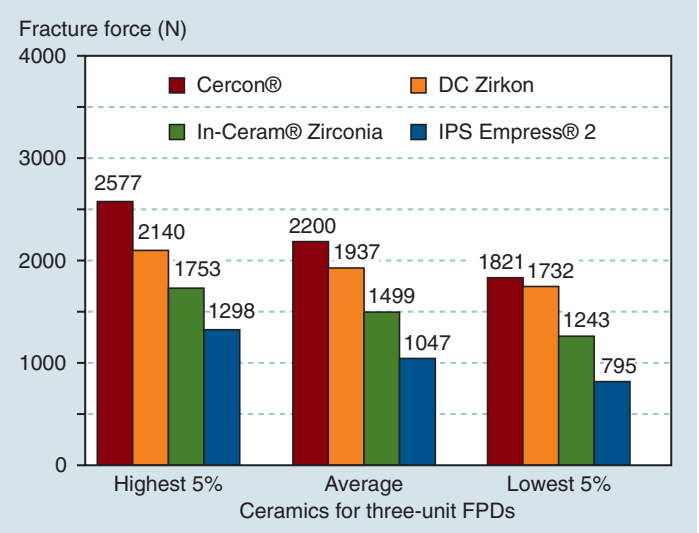


FIGURE 18-47 Distribution of loads (*N*) required to fracture three-unit bridges made from four ceramics in which the core ceramic thickness was 0.8 mm and the veneer thickness was 0.7 mm. Differences between the weakest and strongest ceramic bridges in each grouping were 98.5%, 110%, and 129%, respectively. The core ceramics for the four products are as follows: Cercon and DC Zirkon-Ceram are zirconia-based ceramics, In-Ceram Zirconia is glass-infiltrated zirconia-reinforced alumina ceramic, and Empress 2 is a lithium disilicate–based ceramic. (Adapted from Tinschert J, Natt G, Mautsch W, Augthun M, Spiekermann H: Fracture resistance of lithium disilicate-, alumina-, and zirconia-based three-unit fixed partial dentures: A laboratory study. *Int J Prosthodont* 14:231–238, 2001.)

supported by a metal or high-strength ceramic core to resist occlusal loading and prevent excessive flexural strain. Another cause of fracture is inadequate occlusal reduction on premolar and molar teeth. A minimum of 1.5-mm reduction is recommended for metal-ceramic crowns in molar areas compared with a thickness of 2.0 mm for most ceramic crowns. However, the introduction of all-zirconia crowns made from BruxZir zirconia (Glidewell Labs) and other products mentioned previously suggests that occlusal reductions as low as 0.6 may be adequate in some cases. However, no randomized, controlled, clinical trial reports are available to document the clinical performance of these zirconia products. Clinical data were available at the time of this writing. For any ceramic product, the tooth preparation guidelines recommended by the manufacturer should be followed for the specific ceramic that will be used. These guidelines should be discussed with the lab technician to ensure that standardized procedures are followed.

When a dentist writes a prescription for a metal-ceramic or ceramic prosthesis, specific information is required on the material to be used and the design needed. How should these decisions be made by the clinician? The intraoral conditions and optimal treatment options must first be considered. For missing teeth, restoring the dentition to occlusal function may be accomplished with implants and crowns or fixed dental prostheses. The esthetic needs, expectations, and financial resources of the patient are the next criteria to be considered. The treatment choice is then made on the basis of anticipated success rates, survival times, and minimization of risk factors that are determined from published clinical studies and the previous experience of the clinician, the dental lab technician, and their colleagues. For recent dental school graduates, the previous experience is often based on the materials and techniques learned in dental school. For well-established dentists, experiences in dental practices complement their dental school and advanced education training. Although one may have developed an extensive base of experience, the decision matrix of materials, design options, techniques, experience, patient conditions, and predicted success rates represents an overwhelming combination of variables to factor into optimal treatment decision making.

The dental literature provides convincing evidence that the most durable type of posterior prostheses are those produced from high noble cast alloys, particularly gold-based alloys. However, we have entered into an esthetics-oriented phase of our profession in which decisions tend to favor appearance characteristics of restoration esthetics over long survival times. Thus the selection of dental materials products tends to favor the use of resin-based composites and ceramics for single-unit as well as multiple-unit restorations. In many cases, metal-ceramic material systems are chosen over all-ceramic systems as a compromise between esthetic needs and minimizing the time-dependent probability of failure or maximizing survival.

The dentist and lab technician are faced with a complex challenge of deciding which ceramic should be used for each specific clinical situation. Although some products are recommended for posterior three-unit to five-unit fixed dental prostheses (FDPs), one should first consider the use of all-metal FPDs or metal-ceramic FDPs since these prostheses will have a greater life expectancy. Only when a patient is highly resistant to accepting metallic components during the treatment planning discussions should all-ceramic FDPs be used. Because the fracture resistance of posterior all-ceramic FDPs is based on (1) the strength and fracture toughness of the ceramic components, (2) the connector dimensions (minimum height of 4 mm), (3) connector shape (gingival embrasures must have broad radii of curvature), and (4) the patient's biting force, the selection of a ceramic for these prostheses is a very risky proposition, since optimal conditions for their success are not yet known. For the few clinical studies that have been published, limited data have been reported on connector size and shape and on patients' biting force capabilities.

Before a decision is made to use an all-ceramic crown, six criteria should be considered to minimize the risks of poor esthetics, clinical failures, remakes, and possible disagreements and misunderstandings between dentists, patients, technicians, and manufacturers.

1. The dentist should not consider all-ceramic crowns for patients with evidence of extreme bruxism, clenching, or malocclusion. The use of all-zirconia crowns has been proposed but no randomized, controlled clinical trials of all-ceramic and metal-ceramic restorations have been reported. In this case, metal-ceramic or all-metal prostheses should be used.

2. The experience of the laboratory technician should be extensive to ensure a success rate of at least 98% over a 3-year period. This is the success rate for metal-ceramic crowns and bridges after 7.5 years. Only technicians who demonstrate meticulous attention to detail should be selected. Such technicians are reluctant to accept impressions with unreadable margins.
3. The dentist should judge whether previous esthetic success with metal-ceramic prostheses combined with the esthetic demands of the specific patient would yield more predictable outcomes and longevity than an all-ceramic prosthesis. A metal-ceramic prosthesis made from metal-ceramic systems with which one had previous clinical success is preferred over an all-ceramic prosthesis when the patient has an average or less-than-average appreciation of esthetics.
4. Use all-ceramic crowns when the adjacent teeth exhibit a high degree of translucency. Several relatively translucent core materials are useful for matching adjacent tooth shades for young patients and others who may exhibit a high degree of translucency.
5. Patients must accept the described benefits, risks, and alternatives to the proposed treatment and they must give their consent for the treatment to be performed. This means that informed consent must be obtained from the patient, preferably in writing. As one gains experience and success with these restorations, this precaution will be of secondary importance. Initially, however, the patient should be informed of the higher success rates of metal-ceramic crowns over longer periods of time, especially when used for posterior applications. In addition, the cost differential between the all-ceramic crowns and metal-ceramic crowns should be considered. The initial cost and the expenses associated with remakes for the all-ceramic crowns will be higher than those associated with metal-ceramic crowns. The patient should again be informed of the relative cost of these restorations and their consent should be obtained for the proposed material of choice.
6. The skill of the dentist is of paramount importance in producing perfect impressions derived from smooth preparations free of undercuts with continuous, well-defined margins, and with adequate total tooth reduction. If this performance cannot be consistently maintained without a significant increase in preparation time compared to preparations for metal-ceramic prostheses, the use of the all-ceramic crowns is contraindicated. As stated in criterion 2, a reputable technician should not accept impressions with incomplete or unreadable margins.

IDENT-CERAM SYSTEM FOR IDENTIFICATION OF CERAMIC PRODUCTS

IdentAlloy certificates have been used by dental labs for many years to identify alloys that are used in prosthetic cases sent by the lab to dentists. Because of the strong recent demand for all-ceramic prostheses, IdentCeram certificates were introduced in 2007 to identify the manufacturer/company, brand name, and composition of the materials used for all-ceramic prostheses. Six of the IdentCeram certificates are shown in Figure 18-48. The letter codes are designated as follows: AO (aluminum oxide), YZ (yttrium zirconia), LD (lithium disilicate glass-ceramic), FA (fluorapatite glass-ceramic), FE (fluorapatite glass-ceramic), and LE (leucite glass). The certificates exhibit a recognizable letter code that helps ensure proper insurance coding. These codes correspond to IdentAlloy codes for high noble (HN), noble (N), and predominantly base metal (PB) alloys. By using these widely recognized certificates, labs and dentists gain a proven, practical way to document this information in their patient charts and ensure consistent communication with their dental lab technician.

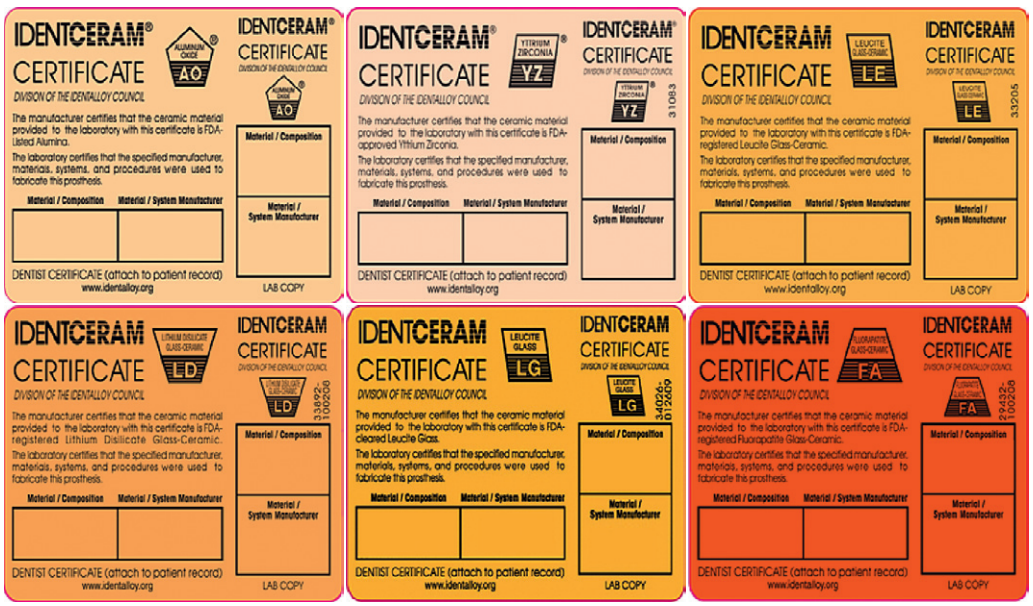


FIGURE 18-48 IdentCeram certificates.

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CHAPTER
19

Prosthetic Polymers and Resins

OUTLINE

Dentures and Denture Base Resins

Fabrication of Dentures

Acrylic Resins

Heat-Activated Denture Base Resins

Compression Molding Technique

Chemically Activated Denture Base Resins

Light-Activated Denture Base Resins

Physical Properties of Denture Base Resins

Miscellaneous Resins and Techniques

Resin Teeth for Prosthetic Applications

Materials for Maxillofacial Prosthetics

KEY TERMS

Inhibitor—A component that prevents or inhibits undesirable polymerization of the monomeric liquid during storage, in order to prolong shelf life. An unintended positive effect of inhibiting or preventing premature polymerization is the increase in working time.

Liner—The polymeric material used to replace the tissue-contacting (intaglio) surface of an existing denture.

Long-term soft liner—A resilient polymeric material that is bonded to the tissue-contacting surface of a denture for cushioning and/or improved retention. Intended for up to a year of service, they are typically heat-processed, and thus, they are more durable than chemically cured, short-term soft liners and tissue conditioners. See also "Denture soft liner."

Rebasing—The process of replacing the entire denture base of an existing complete or partial denture.

Relining—The process of replacing the tissue-contacting surface of an existing denture.

Denture soft liner—A polymeric material that is placed on the tissue-contacting surface of a denture base to absorb some of the mastication impact energy by acting as a type of "shock absorber" between the occlusal surfaces of a denture and the underlying oral tissues. A denture soft liner also may be used to engage natural or prosthetic undercuts so as to provide retention, stability, and support.

Short-term soft liner (tissue conditioner)—A resilient polymeric material that is employed for brief periods (up to 14 days) to absorb masticatory impact and adapt to changing ridge contours (*e.g.*, following the extraction of teeth or surgical alteration of an edentulous or partially edentulous ridge.) Such materials are typically chemically activated polymers that contain plasticizers.

This chapter surveys the materials and techniques used to fabricate prosthetic denture devices and other denture-related materials, as well as prosthetic materials used to replace portions of the facial complex. The emphasis is on the polymeric materials used in denture base resins and denture teeth, plus an overview of the resilient materials used to fabricate maxillofacial prostheses.

DENTURES AND DENTURE BASE RESINS

The Glossary of Prosthodontic Terms (The Academy of Prosthodontics, 2005) defines a complete denture as a removable dental prosthesis that replaces the entire dentition and associated structures of the maxilla or mandible. Such a prosthesis is composed of artificial teeth attached to a denture base. In turn, the denture base derives its support through contact with the oral tissues, teeth, or dental implants.

Although individual denture bases can be formed from metals, the majority of denture bases are fabricated using common polymers. Such polymers are chosen based on availability, dimensional stability, handling characteristics, color, and compatibility with oral tissues.

A description of commonly used denture base polymers is presented in this chapter. Considerable attention is given to individual processing systems and polymerization techniques. In addition, methods for improving the fit and dimensional stability of resin-based prostheses are provided.

FABRICATION OF DENTURES

Several processing techniques are available for the fabrication of denture bases (Figures 19-1 to 19-11). Each technique requires a suitable impression of the associated dental arch followed by fabrication of an accurate gypsum cast. In turn, a resin record base is fabricated on the cast. Wax is added to the record base, and prosthetic teeth are positioned in the wax, related to the opposing dentition, and evaluated in the patient's mouth before proceeding.

In the laboratory, a brass denture flask is chosen, and the completed tooth arrangement is encased in a suitable investing medium. Subsequently, the denture flask is opened and the wax is eliminated. After a thorough cleansing of the mold, a resin denture base material is introduced into the mold cavity and polymerized. Following polymerization, the denture is recovered and prepared for clinical placement.

ACRYLIC RESINS

Since the mid-1940s, the majority of denture bases has been fabricated using polymethyl methacrylate resins. Pure polymethyl methacrylate is a colorless transparent solid. To facilitate its use in dental applications, the polymer can be tinted to provide almost any color, shade, and degree of translucency. Its color, optical characteristics, and dimensional properties remain stable under normal intraoral conditions, and its physical properties have proven to be adequate for dental applications.

One decided advantage of polymethyl methacrylate is the relative ease with which it can be processed. Polymethyl methacrylate denture base material is commonly supplied as a powder-liquid system. The liquid contains mostly nonpolymerized methyl methacrylate and the powder contains predominantly prepolymerized polymethyl methacrylate resin in the form of micro-sized beads (or spheres). When the liquid and powder are mixed in the proper proportions, a workable mass is formed. The material is introduced into a properly formed mold cavity and polymerized. The chemical basis for this reaction is described in Chapter 6.



FIGURE 19-1 A representative heat-activated resin. The majority of heat-activated resins are supplied as powder-liquid systems. (Courtesy of Lang Dental Mfg. Co., Inc. Wheeling, IL)

HEAT-ACTIVATED DENTURE BASE RESINS

Heat-activated materials are used in the fabrication of nearly all denture bases. The thermal energy required for polymerization of such materials can be provided using a water bath or microwave oven. The emphasis in this chapter is on heat-activated systems because of the prevalent use of these resins.

COMPOSITION

As previously noted, most polymethyl methacrylate resin systems include powder and liquid components (Figure 19-1). The powder consists of prepolymerized spheres of polymethyl methacrylate and a small amount of benzoyl peroxide, termed the *initiator,* which is responsible for starting the polymerization process. The liquid is predominantly nonpolymerized methyl methacrylate monomer with small amounts of hydroquinone. Hydroquinone is added as an ***inhibitor***, which prevents undesirable polymerization or "setting" of the liquid during storage. Inhibitors also retard the curing process and thereby increase working time.

A *cross-linking agent* can also be added to the liquid. Glycol dimethacrylate is used commonly as a cross-linking agent in polymethyl methacrylate denture base resins. Glycol dimethacrylate is chemically and structurally similar to methyl methacrylate. Therefore, it can be incorporated into growing polymer chains (Figure 19-2). One should note that methyl methacrylate possesses one carbon-carbon double bond per molecule and glycol dimethacrylate possesses two double bonds per molecule. As a result, an individual molecule of glycol dimethacrylate can participate in the polymerization of two separate polymer chains that unites the two polymer chains. If sufficient glycol dimethacrylate is included in the mixture, several interconnections can be formed and solvent swelling may occur, such as that caused by exposure to ethanol in alcoholic beverages. These interconnections yield a netlike structure that provides increased resistance to deformation. Cross-linking agents are incorporated into the liquid component at a concentration of 1% to 2% by volume.

STORAGE

Manufacturers of heat-activated resin systems generally recommend specific temperature and time limits for the storage of powder and liquid components. Strict observance of such recommendations is essential. If recommendations are not followed, components can undergo changes that may affect working properties of these resins as well as the chemical and physical properties of processed denture bases.

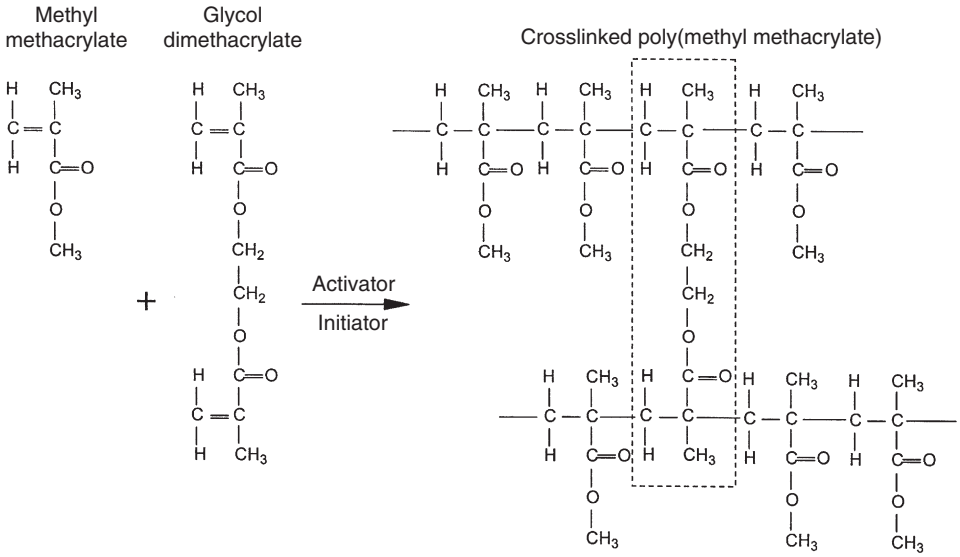


FIGURE 19-2 Chemical basis for the formation of cross-linked polymethyl methacrylate. Glycol dimethacrylate is incorporated into polymethyl methacrylate chains and may "bridge" or "interconnect" such chains.

COMPRESSION MOLDING TECHNIQUE

As a rule, heat-activated denture base resins are shaped via compression molding. Therefore, the compression molding technique is described in detail below.

PREPARATION OF THE MOLD

Before mold preparation, prosthetic teeth must be selected and arranged in a manner that will fulfill both esthetic and functional requirements. In turn, the completed tooth arrangement is sealed to the master cast.

At this stage, the master cast and completed tooth arrangement are removed from the dental articulator (Figure 19-3, *A*). The master cast is coated with a thin layer of separator to prevent adherence of dental stone to the master cast during the flasking process. The lower portion of a denture flask is filled with freshly mixed dental stone, and the master cast is placed into this mixture. The dental stone is contoured to facilitate wax elimination, packing, and deflasking procedures (Figure 19-3, *B*). Upon reaching its initial set, the stone is coated with an appropriate separator.

The upper portion of the selected denture flask is then positioned atop the lower portion of the flask. A surface tension-reducing agent is applied to exposed wax surfaces and a second mix of dental stone is prepared. The dental stone is poured into the denture flask. Care is taken to ensure that the investing stone achieves intimate contact with all external surfaces of the mounted teeth. The investing stone is added until all surfaces of the tooth arrangement and denture base are completely covered. Incisal and occlusal surfaces are minimally exposed to facilitate subsequent deflasking procedures (Figure 19-3, *C*). The stone is permitted to set and is coated with separator.

At this point an additional increment of dental stone is mixed and the remainder of the flask is filled. The lid of the flask is gently seated and the stone is allowed to harden (Figure 19-3, *D*).

After the stone has hardened, the record base and wax must be removed from the mold. To accomplish this task, the denture flask is immersed in boiling water for 4 min. The flask is then removed from the water and the appropriate segments are separated. The record base and softened wax remain in the lower portion of the denture flask while the prosthetic teeth remain firmly embedded in the investing stone of the remaining segment (Figure 19-3, *E*). The record base and softened wax are carefully removed from the surface of the mold. Residual wax is removed from the mold cavity using wax solvent. The mold cavity is subsequently cleaned with a mild detergent solution and rinsed with boiling water.

? CRITICAL QUESTIONS

What is the purpose of a separating medium that is used during denture base fabrication? What is the chemical basis for popular separating media?

SELECTION AND APPLICATION OF A SEPARATING MEDIUM

The next step in denture base fabrication involves the application of an appropriate separating medium onto the surfaces of the mold cavity. This medium must prevent direct contact between the denture base resin and the mold surface. Failure to place an appropriate separating medium can lead to two major difficulties: (1) If water is permitted to diffuse from the mold surface into the denture base resin, it can affect the polymerization rate as well as the optical and physical properties of the resultant denture base. (2) If dissolved polymer or free monomer is permitted to soak into the mold surface, portions of the investing medium can become fused to the denture base. These difficulties often produce compromises in the physical and esthetic properties of processed denture

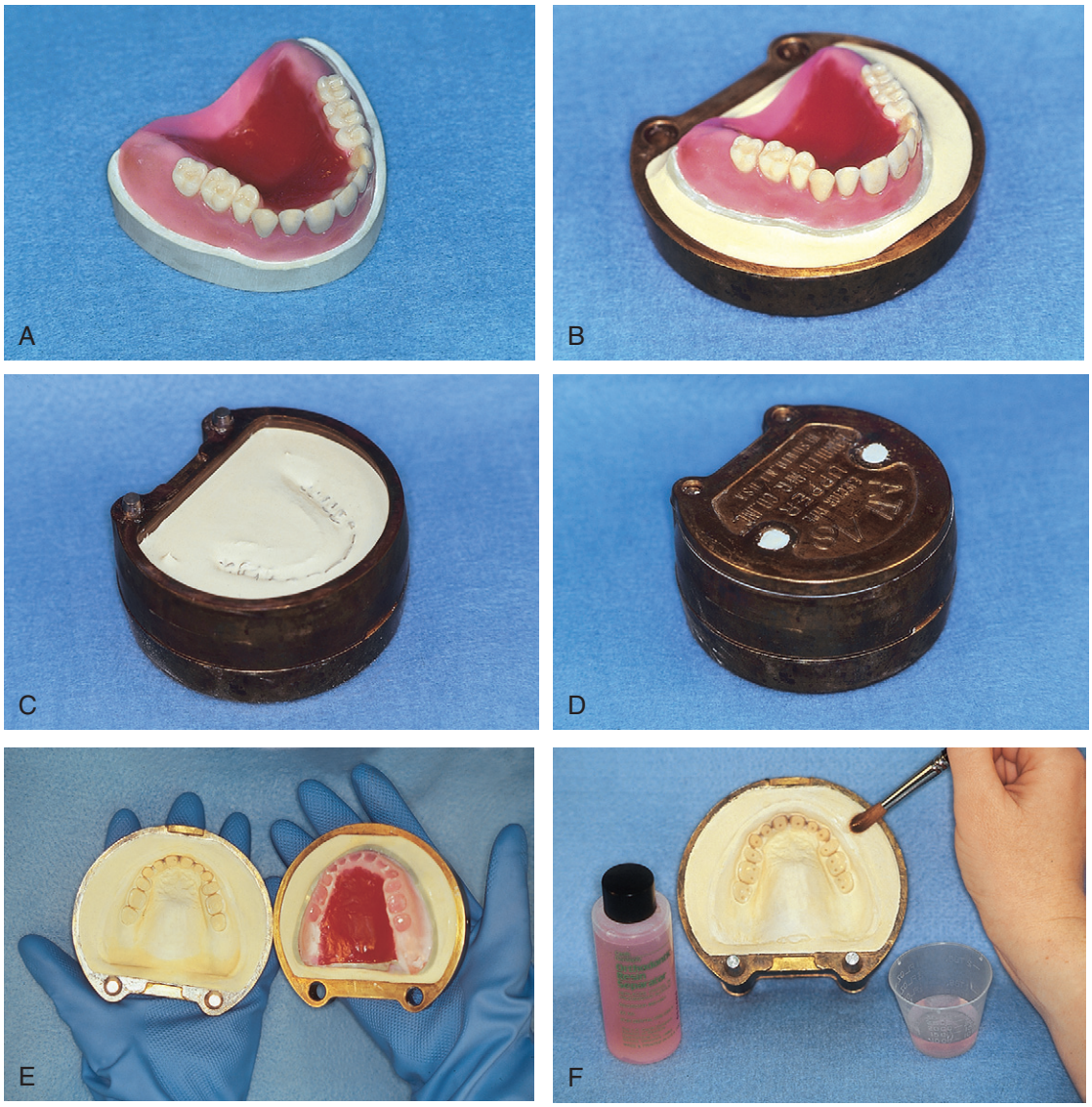


FIGURE 19-3 Steps in mold preparation (compression molding technique). **A,** Completed tooth arrangement prepared for flasking process. **B,** Master cast embedded in properly contoured dental stone. **C,** Occlusal and incisal surfaces of the prosthetic teeth are exposed to facilitate subsequent denture recovery. **D,** Fully flasked complete maxillary denture. **E,** Separation of flask segments during wax elimination process. **F,** Placement of alginate-based separating medium.

bases. Hence the importance of employing an appropriate separating medium should not be overlooked.

Currently, the most popular separating agents are water-soluble alginate solutions. When applied to dental stone surfaces, these solutions produce thin, relatively insoluble calcium alginate films. These films prevent direct contact of denture base resins and the surrounding dental stone, thereby eliminating undesirable interactions.

Placement of an alginate-based separating medium is relatively uncomplicated. A small amount of separator is dispensed into a disposable container. Then a fine brush is used to spread the separating medium onto the exposed surfaces of a warm, clean stone mold (Figure 19-3, *F*). Separator should not be permitted to contact exposed portions of acrylic resin teeth, since its presence interferes with chemical bonding between acrylic resin teeth and denture base resins. Subsequently, the mold sections are oriented to prevent "pooling" of separator, and the solution is permitted to dry.

CRITICAL QUESTIONS

Why do denture base resin systems contain polymer beads? How does the inclusion of polymer beads affect volumetric shrinkage?

POLYMER-TO-MONOMER RATIO

Proper polymer-to-monomer ratio is of considerable importance in the fabrication of well-fitting denture bases with desirable physical properties. Unfortunately, most discussions of polymer-to-monomer ratio provide little practical information for dental personnel. Furthermore, these discussions do not address relationships between molecular events and gross handling characteristics of denture base resins. The

following paragraphs are intended to provide practical, unambiguous information.

The polymerization of denture base resins results in volumetric and linear shrinkage. This is understandable when one considers the molecular events occurring during the polymerization process.

Envision two methyl methacrylate molecules. Each molecule possesses an electrical field that repels nearby molecules. Consequently, the distance between molecules is significantly greater than the length of a representative carbon-to-carbon bond. When the methyl methacrylate molecules are chemically bonded, a new carbon-to-carbon linkage is formed. This produces a net decrease in the space occupied by the components.

Research indicates that the polymerization of methyl methacrylate to form polymethyl methacrylate yields a 21% decrease in the volume of material. As might be expected, a volumetric shrinkage of 21% would create significant difficulties in denture base fabrication. To minimize dimensional changes, resin manufacturers prepolymerize a significant fraction of the denture base material. This can be thought of as "preshrinking" the selected resin fraction.

In practice, the prepolymerized fraction is encountered as a powder, and is commonly referred to as *polymer*. The nonpolymerized fraction is supplied as a liquid, and is termed a *monomer*. When the powder and liquid components are mixed in the proper proportions, a doughlike mass results. Commercial products generally use a polymer-to-monomer ratio of approximately 3:1 by volume. This ratio provides sufficient monomer to thoroughly wet the polymer particles but does not contribute excess monomer that would produce increased polymerization shrinkage. Using a 3:1 ratio, the volumetric shrinkage can be limited to approximately 7%. The initial setting expansion of the gypsum mold and swelling of the polymerized acrylic resin after exposure to water in the denture flask and later, further compensate this shrinkage. The polymerization shrinkage of denture base resin is discussed in depth later in the chapter.

? CRITICAL QUESTIONS

What are the five physical stages through which properly mixed denture base resins pass? During which stage should compression molding be initiated?

POLYMER-MONOMER INTERACTION

When monomer and polymer are mixed in the proper proportions, a workable mass is produced. Upon standing, the resultant mass passes through five distinct stages. These stages can be described as (1) sandy, (2) stringy, (3) doughlike, (4) rubbery or elastic, and (5) stiff.

During the sandy stage, little or no interaction occurs on a molecular level. Polymer beads remain unaltered, and the consistency of the mixture can be described as "coarse" or "grainy." Later, the mixture enters a stringy stage. During this stage, the monomer attacks the surfaces of individual polymer beads and is absorbed into the beads. Some polymer chains are dispersed in the liquid monomer. These polymer chains uncoil, thereby increasing the viscosity of the mix. This stage is characterized by "stringiness" or "stickiness" when the material is touched or drawn apart.

Subsequently, the mass enters a doughlike stage. On a molecular level, an increased number of polymer chains enter the solution. Thus, monomer and dissolved polymer are formed. It is important to note that a large quantity of swollen, but undissolved polymer also remains. Clinically, the mass behaves as a pliable dough. It is no longer tacky and does not adhere to the surfaces of the mixing vessel or spatula. The physical and chemical characteristics exhibited during the later phases of this stage are ideal for compression molding. As a result, the material should be introduced into the mold cavity during the latter phases of the doughlike stage.

Following the doughlike stage, the mixture enters a rubbery or elastic stage. This is because monomer is dissipated by evaporation and by further penetration into remaining polymer beads. The mass rebounds when compressed or stretched. Because the mass no longer flows freely to assume the shape of its container, it cannot be molded by conventional compression techniques.

Upon standing for an extended period, the mixture becomes stiff. This can be attributed to continued evaporation of unreacted monomer. From a clinical standpoint, the mixture appears very dry and is resistant to mechanical deformation.

DOUGH-FORMING TIME

The time required for the resin mixture to reach a doughlike stage is termed *the dough-forming time*. American National Standards Institute/American Dental Association (ANSI/ADA) Specification No. 12 (ISO 20795-1:2008: Dentistry—Base polymers—Part 1: Denture base polymers) for denture base resins requires that this consistency be attained in less than 40 min from the start of the mixing process. In clinical use, the majority of denture base products reach a doughlike consistency in less than 10 min.

WORKING TIME

Working time is defined as the time a denture base material remains in the doughlike stage. This period is critical to the compression molding process. ANSI/ADA Specification No. 12 requires the dough to remain moldable for at least 5 min.

The ambient temperature affects the working time. Hence the working time of a denture resin can be extended via refrigeration. A significant drawback associated with this technique is that moisture may condense on the resin when it is removed from the refrigerator, which may degrade the physical and esthetic properties of a processed resin. Moisture contamination can be avoided by storing the resin in an airtight container. Following removal from the refrigerator, the container should not be opened until it reaches room temperature.

PACKING

The placement and adaptation of denture base resin within the mold cavity are termed *packing*. This process represents one of the most critical steps in denture base fabrication. It is essential that the mold cavity be properly filled at the time of

polymerization. The placement of too much material yields a denture base that exhibits excessive thickness and resultant malpositioning of prosthetic teeth. Conversely, the use of too little material leads to noticeable denture base voids or porosity. To minimize these difficulties, the mold cavity is packed in a well-defined sequence.

While in a doughlike state, the resin is removed from its mixing container and rolled into a ropelike form. Monomer is painted over the necks of the denture teeth to promote bonding to the denture base. Subsequently, the resin form is bent into a horseshoe shape and placed into the portion of the flask that houses the prosthetic teeth (Figure 19-4, *A*). A thin polyethylene separator sheet is placed over the master cast, and the flask is reassembled.

The flask assembly is placed into a specially designed press and pressure is applied incrementally (Figure 19-4, *B*). Slow application of pressure permits the resin dough to flow uniformly throughout the mold space. Excess material is displaced eccentrically. The application of pressure is continued until the denture flask is fully closed. Next the flask is opened and the polyethylene packing sheet is removed from the surface of the resin with a rapid, continuous tug.

Excess resin will be found on the relatively flat areas surrounding the mold cavity. This excess resin is called *flash*. Using a gently rounded instrument, the flash is carefully teased away from the body of resin that occupies the mold cavity (Figure 19-4, *C*). Care is taken not to chip the gypsum surfaces of the mold. Pieces of gypsum that have become dislodged must be removed so that they are not incorporated into the processed denture base.

A fresh polyethylene sheet is placed between the major portions of the flask, and the flask assembly is once again placed in the press. Trial closures are repeated until no flash is observed.

When flash is no longer apparent, the mold is closed for the last time with no polyethylene sheet interposed. The mold sections are properly aligned and placed in the flask press. Again, pressure is incrementally applied. Following definitive closure, the flask is transferred to a flask carrier (Figure 19-4, *D*). The flask carrier maintains pressure on the flask assembly during denture base processing. A cross-sectional representation of the denture flask assembly is presented in Figure 19-5.

INJECTION MOLDING TECHNIQUE

In addition to compression molding techniques, denture bases can be fabricated via injection molding using specially designed flasks. One half of the flask is filled with freshly mixed dental stone, and the master cast is settled into this mixture. The dental stone is appropriately contoured and permitted to set. Subsequently, sprues or ingates are attached to

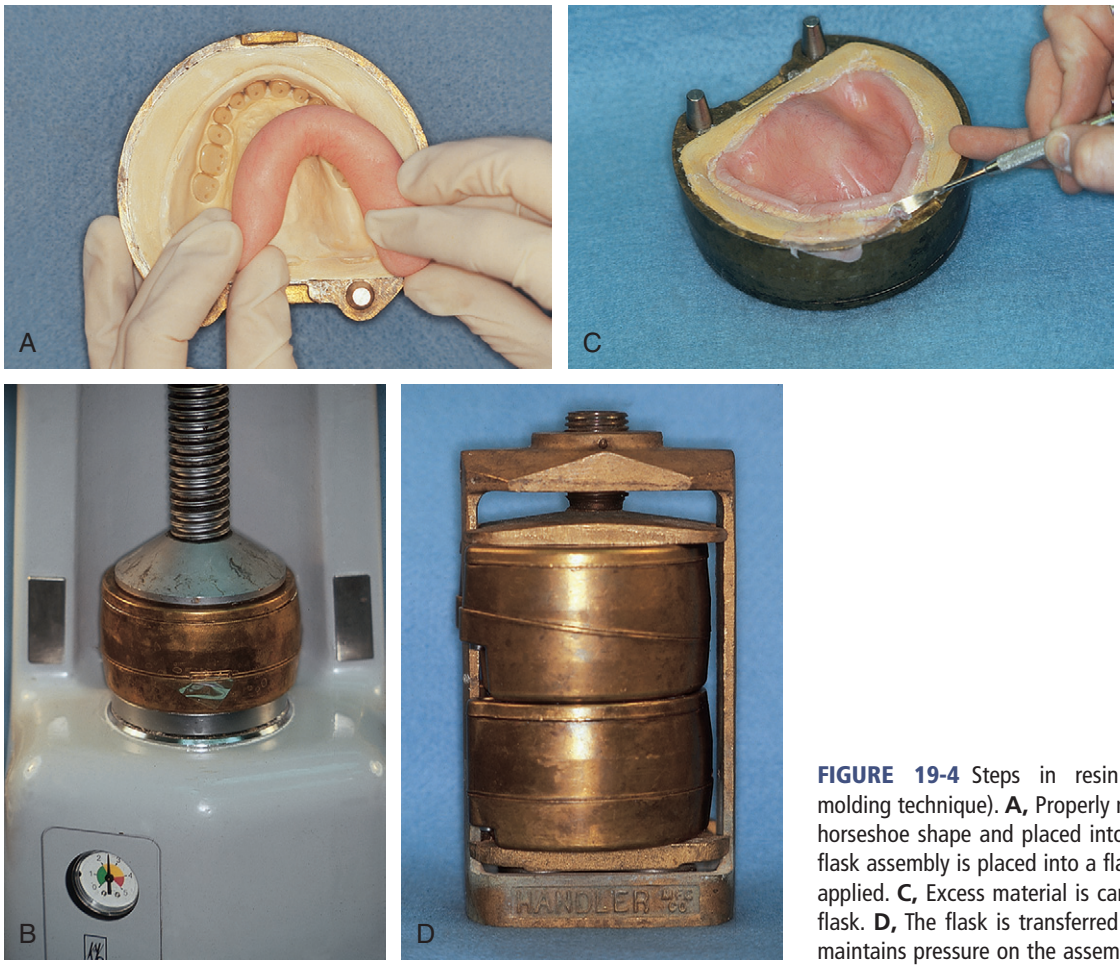


FIGURE 19-4 Steps in resin packing (compression molding technique). **A,** Properly mixed resin is bent into a horseshoe shape and placed into the mold cavity. **B,** The flask assembly is placed into a flask press, and pressure is applied. **C,** Excess material is carefully removed from the flask. **D,** The flask is transferred to a flask carrier, which maintains pressure on the assembly during processing.

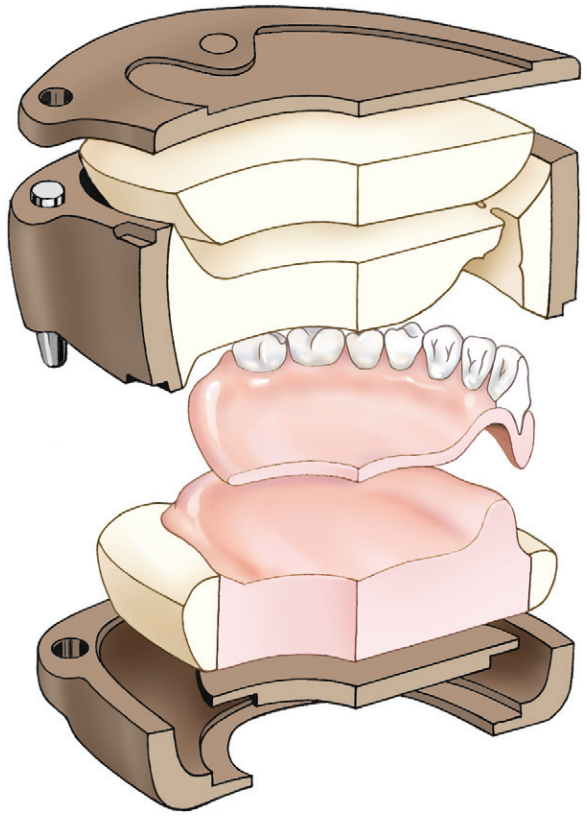


FIGURE 19-5 A cross-sectional representation of the denture flask and its contents.

the wax denture base, which lead to an inlet or pressure port (Figure 19-6, *A*). The remaining half of the flask is positioned, and the investment process is completed (Figure 19-6, *B*). Wax elimination is performed as previously described (Figure 19-6, *C*), and the flask is reassembled. Subsequently, the flask is placed into a carrier that maintains pressure on the assembly during resin introduction and processing.

Upon completion of the foregoing steps, resin is mixed and injected into the mold cavity (Figure 19-6, *D*). The flask is then placed into a water bath for polymerization of the denture base resin if a heat-curing resin is used. Upon completion, the denture is recovered, adjusted, finished, and polished.

Currently there is some debate regarding the comparative accuracy of denture bases fabricated by compression molding and those fabricated by injection molding. Available data and clinical information indicate denture bases fabricated by injection molding can provide slightly improved clinical accuracy.

However, the advantages of injection molding are not straightforward. For example, although tooth movement is minimized, resin viscosity must be considerably lower than that used in compression molding in order to facilitate injection.

This requires a substantially smaller polymer-to-monomer ratio, and consequently results in increased curing shrinkage. Hence, the palatal fit is compromised. This is illustrated in Figure 19-12D, below, in which a greater opening at the posterior palatal seal area is shown for injection molding than for any of the other molding processes.

From a clinical perspective, this requires greater (i.e., deeper) preparation of the post-palatal seal area (on the dental cast) to ensure contact of the polymerized denture base with the patient's palatal tissues.

POLYMERIZATION PROCEDURE

As previously noted, denture base resins generally contain benzoyl peroxide. When heated above 60 °C, molecules of benzoyl peroxide decompose to yield electrically neutral species containing unpaired electrons. These species are termed *free radicals*. Each free radical rapidly reacts with an available monomer molecule to initiate chain-growth polymerization. Since the reaction product also possesses an unpaired electron, it remains chemically active. Consequently additional monomer molecules become attached to individual polymer chains. This process occurs very rapidly and terminates by either (1) the direct connection of two growing chains (i.e., combination) or (2) the transfer of a single hydrogen ion from one chain to another. (See also Figures 6-7, 6-8 and 6-9 in Chapter 6).

In the system under discussion, heat is required to cause decomposition of benzoyl peroxide molecules. Therefore, heat is termed the *activator*. Decomposition of a benzoyl peroxide molecule yields two free radicals that are responsible for the initiation of chain growth. Hence, benzoyl peroxide is termed the *initiator*.

During denture base fabrication, heat is applied to the resin by immersing a denture flask and flask carrier in a water bath. The water is heated to a prescribed temperature and maintained at that temperature for a period suggested by the manufacturer.

TEMPERATURE RISE

The polymerization of denture base resins is exothermic, and the amount of heat evolved can affect the properties of the processed denture bases. Representative temperature changes occurring in water, investing stone, and resin are presented in Figure 19-7. The temperature profile of the investing stone (identified as "plaster") closely parallels the heating curve for the water. The temperature of the denture base resin lags somewhat during the initial stages of the heating process. This can be attributed to the fact that the resin occupies a position in the center of the mold and therefore heat penetration takes a longer time.

As the denture base resin attains a temperature slightly above 70 °C, the temperature of the resin begins to increase rapidly. In turn, the decomposition rate of benzoyl peroxide is significantly increased. This sequence of events leads to an increased rate of polymerization and an accompanying increase in the exothermic heat of reaction. Because resin and dental stone are relatively poor thermal conductors, the heat of reaction cannot be dissipated. Consequently, the temperature of the resin rises well above the temperatures of the investing stone and surrounding water. This can cause the monomer to boil and produce porosity within the processed resin.



FIGURE 19-6 Steps in mold preparation (injection molding technique). **A,** Placement of sprues for introduction of resin. **B,** Occlusal and incisal surfaces of the prosthetic teeth are exposed to facilitate denture recovery. **C,** Separation of flask segments during wax elimination process. **D,** Injection of resin and placement of assembly into water bath.

INTERNAL POROSITY

As indicated earlier, the polymerization process is exothermic. Because resin is an extremely poor thermal conductor, the heat generated in a thick segment of resin cannot be dissipated. When heating is poorly controlled, the peak temperature of this resin can rise well above the boiling point of monomer (100.8 °C). This causes boiling of unreacted monomer and produces porosity within the processed denture base.

CRITICAL QUESTIONS

What causes porosity in denture bases? How can these defects be minimized?

POLYMERIZATION CYCLE

The heating process used to control polymerization is termed the *polymerization cycle* or *curing cycle*. This process should be carefully regulated to avoid the effects of uncontrolled temperature rise.

The curing cycle presented in Figure 19-7 is unsatisfactory because of the marked temperature increase during the early stages of polymerization. Rapid heating of the resin mass may cause the monomer to boil, producing porosity within the polymerized denture base. Fortunately this process can be controlled by heating the resin more slowly during the polymerization cycle.

The relationship between the rate of heating and temperature rise within the denture base resin is illustrated in Figure 19-8. The polymerization cycle represented by curve C probably would yield porosity in thick portions of the denture, since the temperature of the resin exceeds the boiling point of the monomer (100.8 °C). On the other hand, the polymerization cycle represented by curve A probably would result in the presence of unreacted monomer, since the resin temperature fails to reach the boiling temperature of the monomer (100.8 °C). Thus, it is logical to assume that an optimum polymerization cycle lies somewhere between curves A and C.

Research has led to the development of guidelines for polymerization of denture base resins. The resultant polymerization cycles have been quite successful for denture bases of various sizes, shapes, and thicknesses.

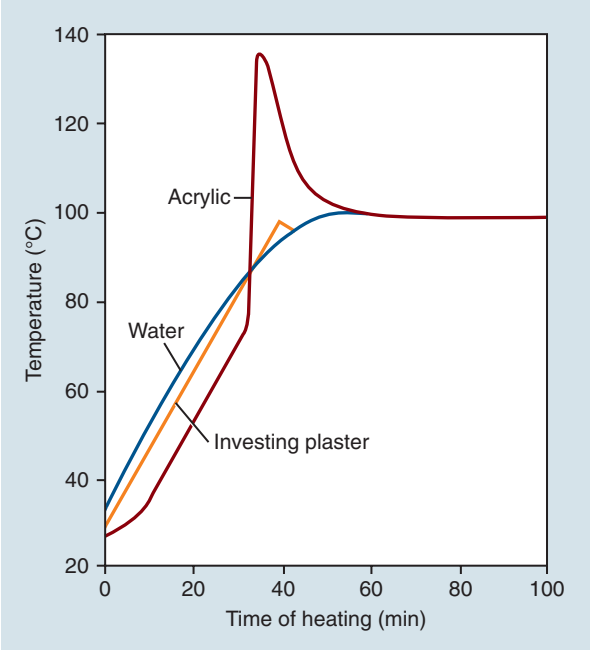


FIGURE 19-7 Temperature-time heating curves for the water bath, investing plaster, and acrylic resin during the polymerization of a 25.4-mm cube of denture resin. (Modified from Tuckfield WJ, Worner HK, Guerin BD: Acrylic resins in dentistry. *Aust Dent J* 47:119–121, 1943. Reproduced with permission from the *Australian Dental Journal*.)

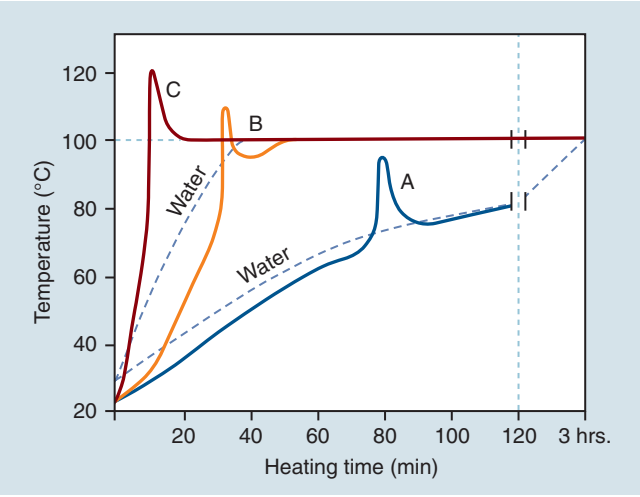


FIGURE 19-8 Temperature changes in acrylic resin when subjected to various curing schedules. (Modified from Tuckfield WJ, Worner HK, Guerin BD: Acrylic resins in dentistry. *Aust Dent J* 47:119–121, 1943. Reproduced with permission from the Australian Dental Journal.)

One technique involves processing the denture base resin in a constant-temperature water bath at 74 °C (165 °F) for 8 h or longer, with no terminal boiling treatment. A second technique consists of processing in a 74 °C water bath for 8 h and then increasing the temperature to 100 °C for 1 h. A third technique involves processing the resin at 74 °C for approximately 2 h and increasing the temperature of the water bath to 100 °C and processing for 1 h.

Following completion of the chosen polymerization cycle, the denture flask should be cooled slowly to room temperature. Rapid cooling can result in distortion of the denture base because of differences in thermal contraction of resin and investing stone. To minimize potential difficulties, the flask should be removed from the water and bench cooled for 30 min. Subsequently, the flask should be immersed in cool tap water for 15 min. The denture base can then be deflasked and prepared for delivery. To decrease the probability of unfavorable dimensional changes, the denture should be stored in water until it is placed in the oral cavity.



FIGURE 19-9 A representative nonmetallic microwave flask (**A**) and microwave resin (**B**). (Courtesy of GC America, Inc. Alsip, IL.)

POLYMERIZATION VIA MICROWAVE ENERGY

Polymethyl methacrylate resin can be polymerized using microwave energy because the methyl methacrylate molecule is asymmetric. This technique employs a specially formulated resin and a nonmetallic flask (Figure 19-9). A conventional microwave oven is used to supply the thermal energy required for polymerization.

The major advantage of this technique is the speed with which polymerization can be accomplished, but overheating can occur in thick sections, causing the monomer to boil and produce porosity. Available information indicates the physical properties of microwave resins are comparable to those of conventional resins. Furthermore, the fit of denture bases polymerized using microwave energy is comparable to those processed via conventional compression molding techniques.

CRITICAL QUESTION

What are the main benefits and drawbacks of denture base resins cured by a chemical-activation process compared with those that are heat-activated?

CHEMICALLY ACTIVATED DENTURE BASE RESINS

As already noted, heat and microwave energy can be used to induce denture base polymerization. The application of thermal energy leads to decomposition of benzoyl peroxide and the production of free radicals. The free radicals formed as a result of this process initiate polymerization.

Chemical activators can also be used to induce denture base polymerization. Chemical activation does not require the application of thermal energy. Therefore, it can be completed at room temperature. As a result, chemically activated resins often are referred to as *cold-curing, self-curing,* or *autopolymerizing* resins.

As discussed in Chapter 7, in most instances, chemical activation is accomplished through the addition of a tertiary amine, such as dimethyl-para-toluidine, to the denture base liquid (i.e., monomer). Upon mixing of the powder and liquid components, the tertiary amine causes decomposition of benzoyl peroxide. As a result, free radicals are produced and polymerization is initiated. Polymerization progresses in a manner similar to that described for heat-activated systems.

It should be noted that the fundamental difference between heat-activated resins and chemically activated resins is the method by which benzoyl peroxide is divided to yield free radicals. All other factors in this process (e.g., initiator and reactants) remain the same.

As might be expected, denture bases fabricated using chemically activated resins and heat-activated resins are quite similar. Nonetheless, chemically activated resins exhibit certain advantages and disadvantages that are worthy of discussion.

As a general rule, the degree of polymerization achieved using chemically activated resins is not as complete as that achieved using heat-activated systems. This indicates there is a greater amount of unreacted monomer in denture bases fabricated via chemical activation. This unreacted monomer creates two major difficulties. First, it acts as a plasticizer, resulting in decreased transverse strength of the denture resin. Second, the residual monomer serves as a potential tissue irritant, thereby compromising the biocompatibility of the denture base.

From a physical standpoint, chemically activated resins display slightly less shrinkage than their heat-activated counterparts. This imparts greater dimensional accuracy to chemically activated resins.

The color stability of chemically activated resins generally is inferior to the color stability of heat-activated resins. This property is related to the presence of tertiary amines within the chemically activated resins. Such amines are susceptible to oxidation and accompanying color changes that affect the appearance of the resin. Discoloration of these resins can be minimized via the addition of stabilizing agents that prevent such oxidation.

TECHNICAL CONSIDERATIONS

Chemically activated denture base resins are most often molded using compression techniques. Therefore, mold preparation and resin packing are essentially the same as those described for heat-activated denture resins.

Polymer and monomer are supplied in the form of a powder and a liquid, respectively. These components are mixed according to the manufacturer's directions and permitted to attain a doughlike consistency. The working time for chemically activated resins is shorter than for heat-activated materials. Therefore, special attention must be paid to the consistency of the material and rate of polymerization.

A lengthy initiation period is desirable since this provides adequate time for trial closures. One method for prolonging the initiation period is to decrease the temperature of the resin mass. This can be accomplished by refrigerating the liquid component and/or mixing vessel before the mixing process. When the powder and liquid are mixed, the polymerization process slows down. As a result, the resin mass remains in a doughy stage for an extended period and the working time is prolonged.

Mold preparation and resin packing are accomplished in the same manner described for heat-activated resins. In cases of chemically activated resins with minimal working times, it is doubtful that more than two trial closures can be made. Therefore, extreme care must be taken to ensure that a proper amount of resin is employed and a minimal number of trial closures are needed.

PROCESSING CONSIDERATIONS

Following definitive closure of the denture flask, pressure must be maintained throughout the polymerization process. The time required for polymerization will vary with the material chosen.

Initial hardening of the resin generally will occur within 30 min but polymerization continues for an extended period. To ensure sufficient polymerization, the flask should be held under pressure for a minimum of 3 hours.

The polymerization of chemically activated resins is never as complete as the polymerization of heat-activated materials. Resins polymerized via chemical activation generally display 3% to 5% free monomer, whereas heat-activated resins exhibit 0.2% to 0.5% free monomer. Therefore, it is important that the polymerization of chemically activated resins be as complete as possible. Failure to achieve a high degree of polymerization will predispose the denture base to dimensional instability and can lead to tissue irritation.

FLUID RESIN TECHNIQUE

The fluid resin technique employs a pourable, chemically activated resin for the fabrication of denture bases. The material is supplied in the form of powder and liquid components. When mixed in the proper proportions, these components yield a low-viscosity resin. This resin is poured into a mold cavity, subjected to increased atmospheric pressure, and allowed to polymerize at ambient temperature. Laboratory aspects of the fluid resin technique are described in the following paragraphs.

Tooth arrangement is accomplished using accepted prosthodontic principles. The completed tooth arrangement is then sealed to the underlying cast and placed in a specially designed flask (Figure 19-10, *A*). The flask is filled with a reversible hydrocolloid investment medium, and the assembly is cooled. (See the section on Agar [Reversible Hydrocolloid] in Chapter 8) Following gelation of the hydrocolloid, the cast with the attached tooth arrangement is removed from the flask (Figure 19-10, *B*). At this stage, sprues and vents are cut from the external surface of the flask to the mold cavity (Figure 19-10, *C*).

Wax is eliminated from the cast with hot water. The prosthetic teeth are retrieved and carefully seated in their respective positions within the hydrocolloid investing medium. Subsequently, the cast is returned to its position within the mold (Figure 19-10, *D*).

The resin is mixed according to the manufacturer's directions and poured into the mold via the sprue channels (Figure 19-10, *E*). The flask is then placed in a pressurized chamber (i.e., a pressure pot) at room temperature and the resin is



FIGURE 19-10 Steps in mold preparation (fluid resin technique). **A,** Completed tooth arrangement positioned in a fluid resin flask. **B,** Removal of tooth arrangement from reversible hydrocolloid investment. **C,** Preparation of sprues and vents for the introduction of resin. **D,** Repositioning of the prosthetic teeth and master cast. **E,** Introduction of pour-type resin. **F,** Recovery of the completed prosthesis.

permitted to polymerize. According to available information, only 30 to 45 minutes are required for polymerization. Nevertheless, a longer period is suggested.

Following completion of the polymerization process, the denture is retrieved from the flask (Figure 19-10, *F*) and the sprues are removed. The denture/cast assembly is returned to the articulator for correction of processing changes. Subsequently, the denture base is finished and polished. After finishing and polishing, the denture should be stored in water to prevent dehydration and distortion.

Advantages claimed for the fluid resin technique include (1) improved adaptation to underlying soft tissues, (2) decreased probability of damage to prosthetic teeth and denture bases during deflasking, (3) reduced material costs, (4) and simplification of the flasking, deflasking, and finishing procedures.

Potential disadvantages of the fluid resin technique include (1) noticeable shifting of prosthetic teeth during processing, (2) air entrapment within the denture base material, (3) poor bonding between the denture base material and acrylic resin teeth, and (4) technique sensitivity.

In general, denture bases fabricated in this manner exhibit physical properties that are somewhat inferior to those of conventional heat-processed resins. Nonetheless, clinically acceptable dentures can be obtained using fluid resins.

LIGHT-ACTIVATED DENTURE BASE RESINS

Visible light-activated denture base resins have been available to the dental community for several years. These materials have been described as resin-based composites having matrices of urethane dimethacrylate (Chapter 6, Figure 6-18), microfine silica, and high-molecular-weight acrylic resin monomers. Acrylic resin beads are included as organic fillers. Visible light is the activator, while a photosensitizing agent such as camphorquinone serves as the initiator for polymerization. Single-component denture base resins are supplied in sheet and rope forms and are packed in lightproof pouches to prevent inadvertent polymerization (Figure 19-11, *A*).

As might be expected, denture base fabrication using a light-activated resin is significantly different from denture base fabrication using a heat-activated or chemically activated resin. A light-activated resin cannot be flasked in a conventional manner since the opaque investing media prevent the penetration of light. Instead, the denture base is molded on an accurate cast and subsequently the teeth are positioned (Figure 19-11, *B*). In turn, the denture base is exposed to a high-intensity visible light source for an appropriate period (Figure 19-11, *C*). Following polymerization, the denture is removed from the cast, finished, and polished in a conventional manner.

The most recent generation of light-activated denture base resins consists of three resins. These include (1) a base-forming resin, (2) a tooth-setting resin, and (3) a contouring resin. The base-forming resin is adapted to the dental cast. The cast and denture base are placed into a high-intensity light chamber to induce polymerization. Subsequently, the tooth-setting resin is used to attach the prosthetic teeth to the polymerized base. A high-intensity light source is used to polymerize the tooth-setting resin, thereby maintaining prosthetic teeth in the desired positions. Next, a contouring resin is used to generate the desired final surface form. The resultant prosthesis is placed into the light chamber to complete the denture base fabrication process. The denture is then removed from the cast, finished, and polished in a conventional manner.

PHYSICAL PROPERTIES OF DENTURE BASE RESINS

The physical properties of denture base resins are critical to the fit and function of removable dental prostheses. Characteristics of interest include polymerization shrinkage, porosity, water absorption, solubility, processing stresses, and crazing. These characteristics are addressed in the following sections.

POLYMERIZATION SHRINKAGE

When methyl methacrylate monomer is polymerized to form polymethyl methacrylate, the density of the mass changes from 0.94 to 1.19 g/cm^3. This change in density results in a volumetric shrinkage of 21%. When a conventional heat-activated resin is mixed at the suggested powder-to-liquid ratio, about one third of the mass is liquid monomer. The remainder of the mass is prepolymerized polymethyl methacrylate. Consequently, the volumetric shrinkage exhibited by the polymerized mass should be approximately 7%. This figure is in agreement with values observed in laboratory and clinical investigations.

There are several possible reasons why materials exhibiting such high volumetric shrinkages can be used to produce clinically satisfactory denture bases. It appears the shrinkage exhibited by these materials is distributed uniformly to all surfaces. Hence the adaptation of denture bases to underlying soft tissues is not significantly affected, provided the materials are manipulated properly.

In addition to volumetric shrinkage, one also must consider the effects of linear shrinkage. Linear shrinkage exerts significant effects upon denture base adaptation and cuspal interdigitation.

By convention, the magnitude of linear shrinkage is determined by measuring the distance between two predetermined reference points in the second molar regions of a completed tooth arrangement. Following polymerization of the denture base resin and removal of the prosthesis from the master cast, the distance between these reference points is measured once again. The difference between pre- and postpolymerization measurements is recorded as linear shrinkage. The greater the linear shrinkage, the greater is the discrepancy observed in the initial fit of a denture.

? CRITICAL QUESTION

Why is the relatively high volumetric shrinkage of a denture base resin not usually considered as a significant clinical problem?



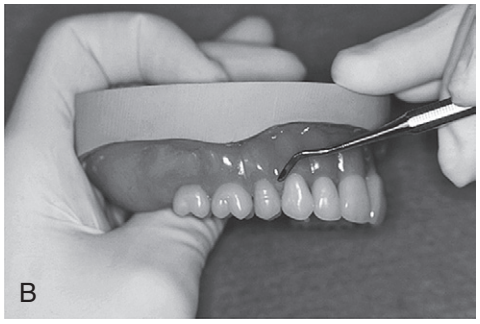




FIGURE 19-11 Steps in denture fabrication (light-activated denture base resins). **A,** Representative light-activated denture base resin. Sheet and rope forms are supplied in light-proof pouches to prevent inadvertent polymerization. **B,** Teeth are arranged and the denture base sculpted using light-activated resin. **C,** The denture base is placed into a light chamber and polymerized according to the manufacturer's recommendations. (Parts **A** and **C** courtesy of Densply International, York, PA.)

TABLE 19-1 Polymerization Shrinkage of Maxillary Denture Bases

Material	Linear Shrinkage (%)
High-impact acrylic resin	0.12
Vinyl acrylic resin	0.33
Conventional acrylic resin	0.43
Pour-type acrylic resin	0.48
Rapid heat-cured acrylic resin	0.97

Data from Stafford GD, Bates JF, Huggett R, Handley RW: A review of the properties of some denture base polymers. *J Dent* 8:292, 1960.

Based on a projected volumetric shrinkage of 7%, an acrylic resin denture base should exhibit a linear shrinkage of approximately 2%. In reality, linear shrinkage rarely exceeds 1% (Table 19-1).

Examination of the polymerization process indicates thermal shrinkage of resin is primarily responsible for the linear changes observed in heat-activated systems. During the initial stages of the cooling process, the resin remains relatively soft. Consequently, the resin mass contracts at about the same rate as the surrounding dental stone.

As cooling proceeds, the soft resin approaches its glass transition temperature, T_g (see Chapter 6, Dental Polymers). The glass transition temperature is a thermal range in which the polymerized resin passes from a soft, rubbery state to a rigid, glassy state. Cooling the denture base resin beyond the glass transition temperature yields a rigid mass. As might be expected, this rigid mass contracts at a rate different from that of surrounding dental stone. The shrinkage occurring below the glass transition temperature is thermal in nature and varies according to the composition of the resin.

To illustrate the effect of thermal shrinkage, consider the following example. The glass transition temperature for polymethyl methacrylate is approximately 105 °C. Room temperature is 20 °C. The generally accepted value for linear coefficient of thermal expansion, α, for polymethyl methacrylate is 81 ppm/°C. Therefore, as the denture base resin cools from the glass transition temperature to room temperature, it undergoes a linear shrinkage, which can be expressed as:

$$\text{Linear shrinkage} = \alpha\Delta T = (81\ \text{ppm/°C})(105\ \text{°C} - 20\ \text{°C})(100\%) = 0.69\% \quad (1)$$

This value is in agreement with linear shrinkages of 0.12% to 0.97% reported for various commercial denture resins (see Table 19-1).

Complete dentures constructed using chemically activated resins generally display better adaptation than those constructed using heat-activated resins. This phenomenon can be attributed to the negligible thermal shrinkage displayed by chemically activated resins. Processing shrinkage has been measured as 0.26% for a representative chemically activated resin, compared with 0.53% for a representative heat-activated resin.

Given the preceding information regarding polymerization shrinkage and denture base adaptation, chemically activated resins appear to provide significant advantages over heat-activated resins. However, there are several other factors that affect the overall dimensional characteristics of processed denture bases including the type of investing medium, method of resin introduction, and temperature used to activate the polymerization process.

On completion of the polymerization process, individual denture bases and master casts are retrieved and returned to their respective dental articulator(s). Dimensional changes are assessed with respect to the proposed vertical dimension of occlusion.

Fluid resin techniques used in conjunction with hydrocolloid investing media generally yield decreases in vertical dimension. Conversely, dentures processed using heat-activated or chemically activated resins in conjunction with compression molding techniques usually display increases in overall vertical dimension. Minimal increases in vertical dimension are considered desirable since they permit a return to the proposed occlusal vertical dimension via occlusal grinding procedures. Dimensional changes occurring in denture bases fabricated from various resins are illustrated in Figure 19-12. Additional dimensional factors include setting expansion of the gypsum product used to make the master cast and investing component and expansion from water sorption of the cured acrylic resin after polymerization is complete.

CRITICAL QUESTIONS

What are the causes of porosity when fluid resin denture fabrication techniques are used? How can these difficulties be minimized?

POROSITY

The presence of surface and subsurface voids can compromise the physical, esthetic, and hygienic properties of a processed denture base. It has been noted that porosity is likely to develop in thicker portions of a denture base. Such porosity results from the vaporization of unreacted monomer and low-molecular-weight polymers when the temperature of a resin reaches or surpasses the boiling points of these species. Nonetheless, this type of porosity may not occur equally throughout the affected resin segments.

To facilitate our understanding of these effects, consider the specimens in Figure 19-13, *A*, no porosity, and 19-13, *B*, localized subsurface porosity. Specimens B and C were flasked in such a manner that the section displaying porosity was nearer the center of the investment mass, whereas the nonporous section was nearer the surface of the metal flask. As might be expected, the metal of the flask conducts heat away from the periphery with sufficient rapidity to prevent a substantial temperature rise. As a result, the low-molecular-weight species does not boil and porosity does not develop. In contrast, resin specimens occupying central positions in the mold are surrounded by larger amounts of gypsum. Because gypsum is a poor thermal conductor, heat was not

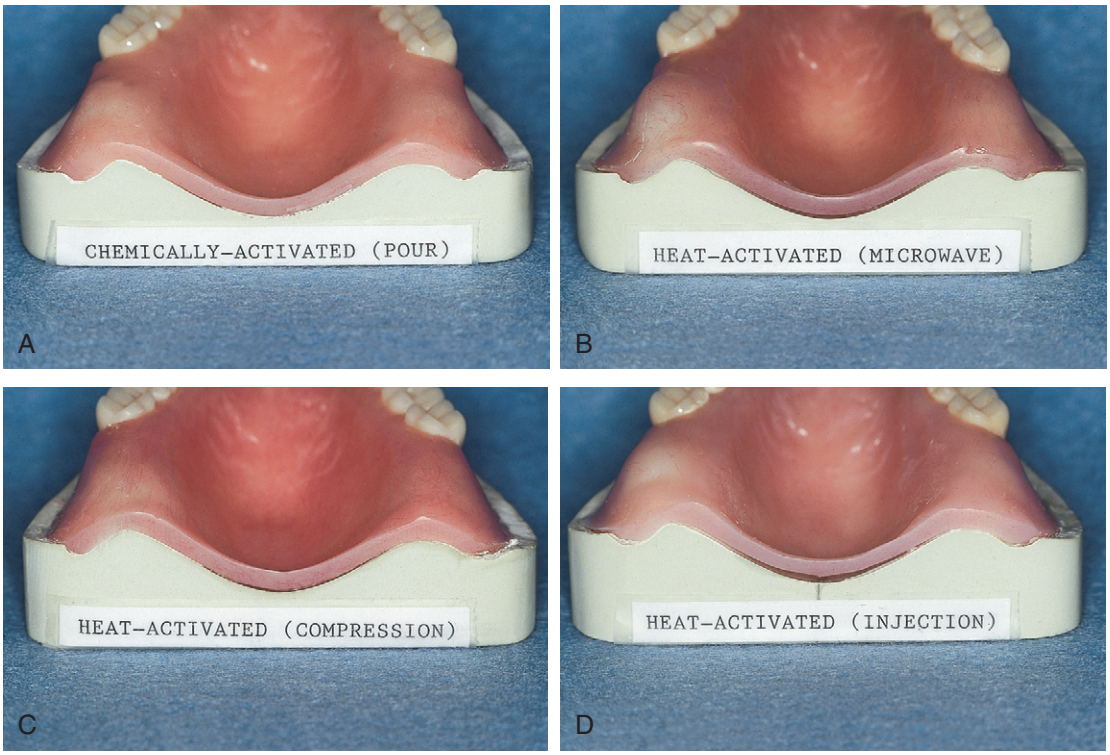


FIGURE 19-12 Dimensional changes resulting from polymerization. **A,** Chemically activated resin, pour technique. **B,** Microwave resin, compression molding. **C,** Conventional heat-activated resin, compression molding. **D,** Heat-activated resin, injection molding. (Demonstration and photographs courtesy of Dr. Rodney Phoenix).

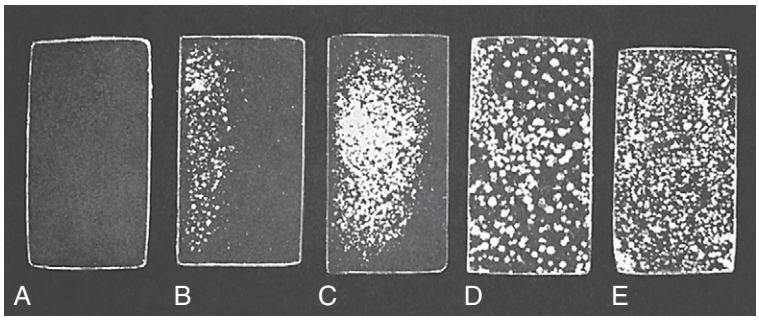


FIGURE 19-13 Heat-activated denture base resin exhibiting different types and degrees of porosity. **A,** Properly polymerized; no porosity. **B** and **C,** Rapid heating, relatively small subsurface voids. **D,** Insufficient mixing of monomer and polymer; large voids resulting from localized polymerization shrinkage. **E,** Insufficient pressure during polymerization; relatively large, irregular voids. (From Tuckfield WJ, Worner HK, Guerin BD: Acrylic resins in dentistry. *Aust Dent J* March 1943.)

readily dissipated. Consequently low-molecular-weight species are vaporized and noticeable porosity is produced.

Porosity can also result from inadequate mixing of powder and liquid components. If this occurs, some regions of the resin mass will contain more monomer than others. During polymerization, these regions shrink more than adjacent regions, and the localized shrinkage tends to produce voids (Figure 19-13, *D*).

The occurrence of such porosity can be minimized by ensuring the greatest possible homogeneity of the resin. Proper polymer-to-monomer ratios and well-controlled mixing procedures are essential. Because the material is more homogeneous in the doughlike stage, it is wise to delay packing until this consistency has been reached. A third type of porosity can be caused by inadequate pressure or insufficient material in the mold during polymerization (Figure 19-13, *E*). Voids resulting from these inadequacies are not spherical; they assume irregular shapes. These voids may be so abundant that the resultant resin appears significantly lighter and more opaque than its intended color.

A final type of porosity is most often associated with fluid resins. Such porosity results from air entrapment during mixing and pouring procedures. If air inclusions are not removed, sizable voids may be produced in the resultant denture bases. Therefore careful mixing, spruing, and venting are essential.

WATER ABSORPTION

Polymethyl methacrylate absorbs small amounts of water when placed in an aqueous environment. This water exerts significant effects on the mechanical and dimensional properties of the processed polymer.

Although absorption is facilitated by the polarity of polymethyl methacrylate molecules, a diffusion mechanism is primarily responsible for the ingress of water. As water molecules penetrate the polymethyl methacrylate mass, they occupy positions between polymer chains. Consequently, the affected polymer chains are forced apart. The introduction of water molecules produces two important effects. First, it causes a slight expansion of the polymerized mass. Second, water molecules interfere with the entanglement of polymer chains and thereby act as plasticizers (see the section, *Solvation and Dissolution Properties* in Chapter 6, Dental Polymers).

Polymethyl methacrylate exhibits a water sorption value of 0.69 mg/cm^2. Although this amount of water may seem inconsequential, it produces significant effects in polymerized resins. It has been estimated that for each 1% increase in weight produced by water absorption, acrylic resin exhibits a linear expansion of 0.23%. Laboratory trials indicate the linear expansion caused by water absorption is approximately equal to the thermal shrinkage encountered as a result of the polymerization process. Hence, these processes very nearly offset one another.

As previously noted, water molecules can also interfere with entanglement of polymer chains and thereby change the physical characteristics of the resultant polymer. When this occurs, polymer chains generally become more mobile. This permits the relaxation of stresses incurred during polymerization. As stresses are relieved, polymerized resins may undergo changes in shape. Fortunately, these changes are relatively minor and do not exert significant effects on the fit or function of the processed bases.

Because the presence of water adversely affects the physical and dimensional properties of denture base resins, diffusion coefficients also warrant consideration. The diffusion coefficient (D) of water in representative heat-activated denture acrylic resin is 0.011×10^{-6} cm^2/s at 37 °C. For a representative chemically activated resin, the diffusion coefficient is 0.023×10^{-6} cm^2/s. Since the diffusion coefficients of water in representative denture resins are relatively low, the time required for a denture base to reach saturation can be considerable. This is dependent upon the thickness of the resin as well as the storage conditions. A typical denture base may require a period of 17 days to become fully saturated with water.

Results of laboratory investigations indicate there are very slight differences in the dimensions of heat-activated and chemically activated denture bases following prolonged storage in water. Compression-molded heat-activated denture bases are slightly undersized when measured from second molar to second molar. Conversely, compression-molded chemically activated denture bases are slightly oversized when measured in the same regions. The clinical significance of this difference is negligible.

ANSI/ADA Specification No. 12 identifies guidelines regarding the testing and acceptance of denture base resins. To test water absorption, a disk of material with specified dimensions is prepared and dried to a constant weight. This weight is recorded as a baseline value. The disk is then soaked in distilled water for 7 days. Again, the disk is weighed, and this value is compared with the baseline value. According to the specification, weight gain following immersion must not be greater than 0.8 mg/cm^2. Additional information regarding ANSI/ADA Specification No. 12 is presented in subsequent sections.

SOLUBILITY

Although denture base resins are soluble in a variety of liquids, they are virtually insoluble in the fluids commonly encountered in the oral cavity. ANSI/ADA Specification No. 12 prescribes a testing regimen for the measurement of resin solubility. This procedure is a continuation of the water sorption test described in the preceding section. Following the required water immersion, the test disk is permitted to dry and is reweighed. This value is compared with the baseline value to determine weight loss. According to the specification, weight loss must not be greater than 0.04 mg/cm^2. Such a loss is negligible from a clinical perspective. Non-cross-linked polymethyl methacrylate dentures made in the 1940s swelled and warped when exposed to ethanol in the diet. Addition of cross-linking agents (see Figure 6-2, Chapter 6, Dental Polymers) to the resin composition has solved this problem.

CRITICAL QUESTIONS

What are the causes of processing stresses? What are the clinical implications of these stresses if any?

PROCESSING STRESSES

Whenever a natural dimensional change is inhibited, the affected material sustains internal stresses. If stresses are relaxed, distortion of the material can occur. This principle has important ramifications in the fabrication of denture bases, since stresses are always induced during processing.

For purposes of this discussion, consider the events that occur during denture base polymerization. As previously noted, a moderate amount of shrinkage occurs as individual monomers are linked to form polymer chains. During this process, it is possible that friction between the mold walls and soft resin may inhibit normal shrinkage of these chains. As a result, the polymer chains are stretched and tensile stresses exist within the material.

Stresses also are produced as the result of thermal shrinkage. As a polymerized resin is cooled below its glass transition temperature, the resin becomes relatively rigid. Further cooling results in thermal shrinkage. The clinician must remember that a denture base resin generally is encased in a rigid investing medium, such as dental gypsum, during this process. Since denture base resins and dental stone contract at markedly different rates, a contraction differential is established. This disparity in contraction rates also yields stresses within the resin. Additional factors that may contribute to processing stresses include improper mixing and handling of

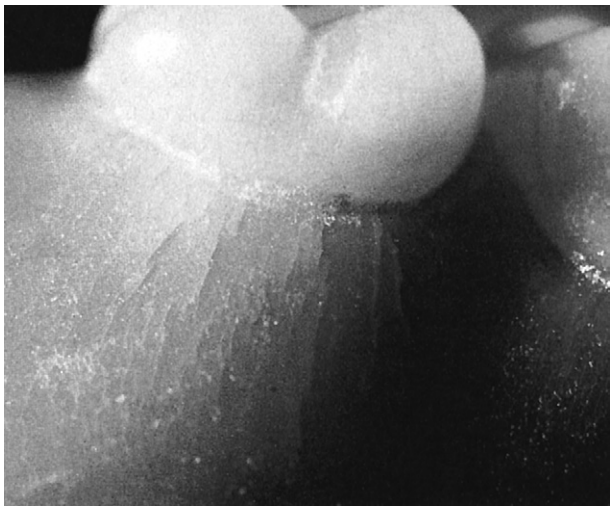


FIGURE 19-14 Crazing around porcelain teeth.

the resin and poorly controlled heating and cooling of the flask assembly.

CRAZING

Although dimensional changes can occur during relaxation of processing stresses, these changes generally do not cause clinical difficulties. In contrast, stress relaxation can produce small surface flaws that may adversely affect the esthetic and physical properties of a denture. The production of such flaws, or microcracks, is termed *crazing*.

In a clinical setting, crazing is evidenced by small linear cracks that appear to originate at a denture's surface. Crazing in a transparent resin imparts a "hazy" or "foggy" appearance. In a tinted resin, crazing imparts a whitish appearance. In addition to esthetic effects, these surface cracks predispose a denture resin to fracture.

From a physical perspective, crazing may result from stress application or from partial dissolution by a solvent. Tensile stresses are most often responsible for crazing in denture base applications. It is believed that crazing is produced by mechanical separation of individual polymer chains that occurs upon application of tensile stresses.

Crazing generally begins at the surface of a resin and is oriented at right angles to tensile forces. Microcracks formed in this manner subsequently progress internally. An example of crazing is presented in Figure 19-14.

As noted, crazing can also be produced as a result of solvent action. Microcracks produced in this manner are oriented more randomly than those depicted in Figure 19-14. Solvent-induced crazing generally results from prolonged contact with liquids such as ethyl alcohol. The development of improved acrylic resin teeth and cross-linked denture base resins has resulted in a decreased incidence of denture base crazing.

CRITICAL QUESTIONS

What variables reduce the strength of acrylic resin denture bases? What processing method is most likely to produce denture bases with decreased fracture resistance?

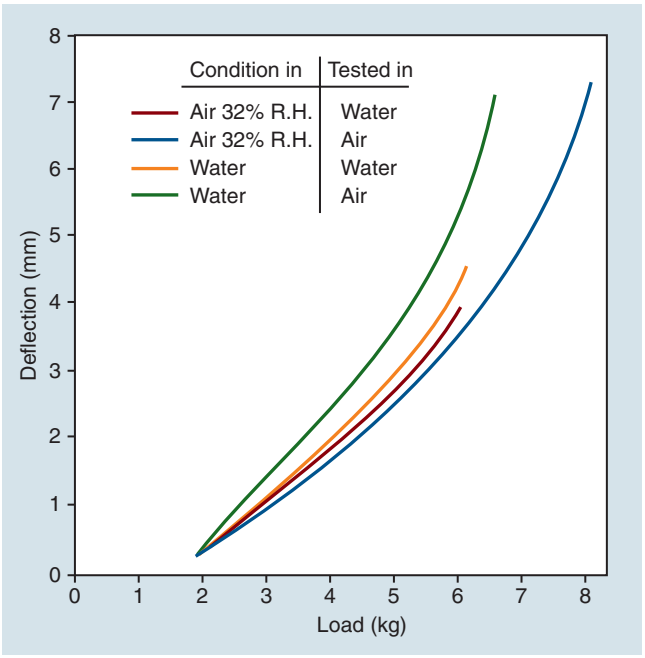


FIGURE 19-15 Transverse deflection-load curve for a typical denture base resin, showing the influences of different conditioning procedures and testing environments. All specimens were conditioned for 3 days as indicated before testing. (Data from Swaney AC, Paffenbarger GC, Caul HJ, Sweeney WT: American Dental Association Specification No. 12 for denture base resin, ed. 2, *J Am Dent Assoc* 46(1):54–66, 1953. Reprinted by permission of ADA Publishing, a Division of ADA Business Enterprises, Inc.) (R.H. = relative humidity.)

STRENGTH

The strength of an individual denture base resin is dependent on many factors. These factors include composition of the resin, processing technique, and conditions presented by the oral environment.

To provide acceptable physical properties, denture base resins must meet or exceed the standards presented in ANSI/ADA Specification No. 12. A transverse test is used to evaluate the relationship between the applied load and resultant deflection in a resin specimen of prescribed dimensions. Typical deflection-load results are presented in Figure 19-15.

Inspection of Figure 19-15 reveals a curvature to each component of the deflection load plot. Since no straight-line portion is evident, one may assume that plastic deformation (i.e., irreversible deformation) occurs during the loading process. Some elastic deformation (i.e., recoverable deformation) also occurs. From a clinical standpoint, this means that load application produces stresses within a resin and a change in the overall shape of the denture base. When the load is released, stresses within the resin are relaxed and the denture base begins to return to its original shape. Nevertheless, plastic deformation prevents complete recovery and some permanent deformation will remain.

Perhaps the most important determinant of resin strength is the degree of polymerization exhibited by the material. As the degree of polymerization increases, the strength of the resin also increases. In this regard, the polymerization cycle

employed with a heat-activated resin is extremely important. Figure 19-16 reveals the effects that processing cycles exert upon deflection-load properties. Note that increased duration of the polymerization cycle appears to yield improved physical properties.

In comparison with heat-activated resins, the chemically activated resins generally display lower degrees of polymerization. As a result, chemically-activated resins exhibit increased levels of residual monomer as well as decreased strength and decreased stiffness. Despite these characteristics, heat- and chemically activated resins display similar elastic moduli.

CREEP

Denture resins display viscoelastic behavior. In other words, these materials act as rubbery solids. When a denture base resin is subjected to a sustained load, the material may exhibit deformation with both elastic (recoverable) and plastic (irrecoverable) components. If this load is not removed, additional plastic deformation can occur over time. This additional deformation is termed *creep*.

The rate at which this progressive deformation occurs is termed the *creep rate*. This rate can be elevated by increases in temperature, applied load, residual monomer, and the presence of plasticizers. Although creep rates for heat-activated and chemically activated resins are very similar at low stresses, creep rates for chemically activated resins increase more rapidly as stresses are raised.

MISCELLANEOUS PROPERTIES

The Charpy impact strength for a heat-activated denture resin can range from 0.98 to 1.27 J, whereas that for a chemically activated resin is somewhat lower (0.78 J). The impact strength of high-impact resins such as Lucitone 199 can be twice as high as the values reported for conventional polymethyl methacrylate resins. Increased impact strength of these products is associated with the addition of a rubbery, branched comonomer such as butyl acrylate. Clinicians should recognize that these figures are useful only for comparison of products, since the energy absorbed by an individual specimen is dependent on specimen size and geometry, distance between specimen supports, and the presence or absence of notching.

The Knoop hardness for heat-activated resins may be as high as 20, whereas chemically activated resins generally display a Knoop hardness between 16 and 18.

? CRITICAL QUESTION

What is the optimal technique for repairing a fractured acrylic denture base?

MISCELLANEOUS RESINS AND TECHNIQUES

REPAIR RESINS

Despite the favorable physical characteristics of denture base resins, denture bases sometimes fracture. In most instances, these fractures can be repaired using compatible resins. Repair resins may be light-, heat-, or chemically activated.

To accurately accomplish repair of a fractured prosthesis, the clinician must realign and lute components together using an adherent wax or modeling plastic. When this has been accomplished, a repair cast is generated using dental gypsum. The denture is then removed from the cast and the

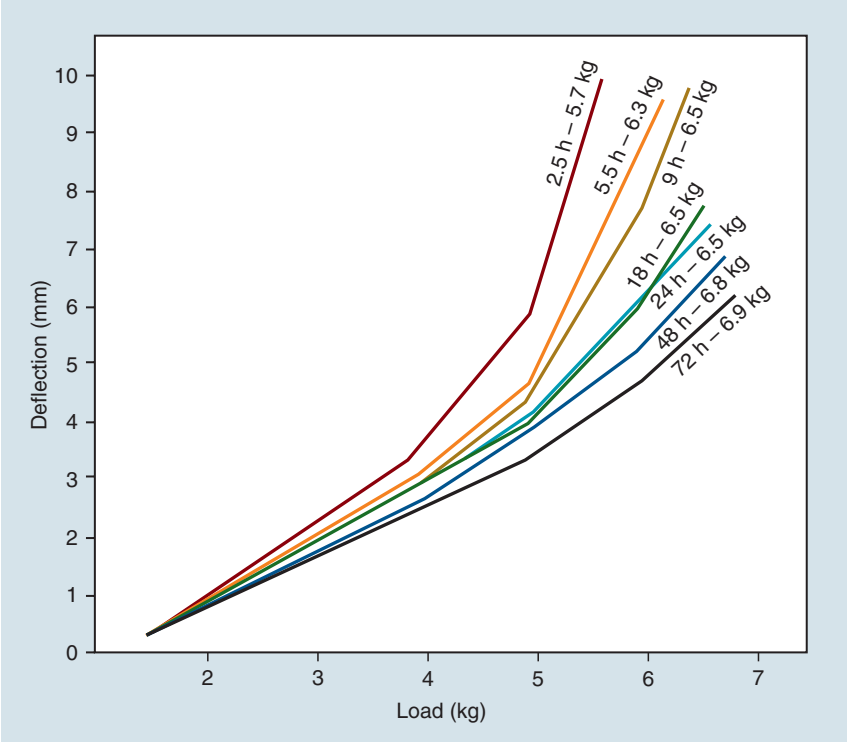


FIGURE 19-16 Deflection-load curves for samples of polymethyl methacrylate polymerized for different periods at 71 °C (160 °F). Processing times and fracture loads are noted on individual curves. (Data from Harman IM: Effects of time and temperature on polymerization of a methacrylate resin denture base. *J Am Dent Assoc* 38(2):188–203, 1949. Reprinted by permission of ADA Publishing, a Division of ADA Business Enterprises, Inc.)

luting medium is eliminated.Then, the fracture surfaces are trimmed to provide sufficient room for repair material. The gypsum cast is coated with separating medium to prevent adherence of repair resin, and the denture base sections are repositioned and affixed to the cast.

At this point a repair material is chosen. Chemically activated resins are generally preferred over heat- and light-activated resins despite the fact that chemically activated resins display lower transverse strengths. The principal advantage of chemically activated resins is that they can be polymerized at room temperature. Heat- and light-activated repair materials must be placed in water baths and light chambers, respectively. Heat generated by water baths and light chambers often causes stress release and distortion of previously polymerized denture base segments.

The following sequence is employed to accomplish denture base repair using a chemically activated resin. A small amount of monomer is painted onto prepared surfaces of the denture base to soften and swell the old resin and thereby facilitate bonding of the repair material. Increments of monomer and polymer are added to the repair area using a small sable-hair brush or suitable substitute. A slight excess of material is placed at the repair site to account for polymerization shrinkage. The assembly is placed in a pressure chamber and allowed to polymerize. The repair site is then shaped, finished, and polished using conventional techniques.

The minimum requirements for chemically activated resins used in repair applications are identified in ANSI/ADA Specification No. 13.

? CRITICAL QUESTION

Why are denture reliner materials considered temporary-use products?

RELINING RESIN DENTURE BASES

Because ridge contours change during denture service, it is sometimes necessary to alter tissue surfaces of prostheses to ensure proper fit. In some instances, this can be achieved by selective grinding procedures. In other instances, tissue surfaces must be replaced by **relining** or **rebasing** existing dentures.

Relining involves replacement of the tissue surface of an existing denture, whereas rebasing involves replacement of the entire denture base except for the denture teeth. In both instances an impression of the soft tissues is made using the existing denture as an impression tray. A gypsum cast is generated in the impression, and the resultant assembly is invested in a brass denture flask. Subsequently, the flask is opened and prepared for the introduction of resin.

If the denture is to be relined, the impression material is removed from the denture. The tissue surface is cleaned to enhance bonding between the existing denture base and the reline material. Next, an appropriate resin is introduced and shaped using a compression molding technique.

For relining, a low polymerization temperature is desirable to minimize distortion of the remaining denture base. Hence, a chemically activated resin is usually chosen. The selected material is mixed according to the manufacturer's recommendations, placed into the mold, compressed, and permitted to polymerize. Finally, the denture is recovered, finished, and polished.

If a chemically activated resin is selected for relining the existing denture, a specialized mounting assembly may be used in lieu of flasking. This assembly maintains the correct vertical and horizontal relationships between the cast and the denture while eliminating the need to encase the remaining denture base in dental gypsum. This facilitates recovery of the denture at the end of the relining process.

Several manufacturers offer chemically activated resins for relining dentures intraorally. Unfortunately many of these materials generate enough heat to injure oral tissues. To receive ADA approval, materials must comply with ANSI/ADA Specification No. 17, which places limits on the rate of temperature rise and maximum acceptable temperature.

Relining can also be accomplished using resins that are activated by heat, light, or microwave energy. In all of these instances, significant heat can be generated and distortion of the existing denture base will be more likely.

Some materials are manufactured for repair as well as relining purposes. Practitioners should be extremely cautious in using such products. Some of these materials comply with ANSI/ADA Specification No. 13 for repairs but fail to meet temperature requirements set forth in ANSI/ADA Specification No. 17. Other materials comply with Specification No. 17 but fail to meet the requirements of Specification No. 13. Such materials often discolor, harbor microorganisms, and separate from underlying denture bases.

Similar materials are marketed for home use. Unfortunately, the majority of patients do not possess adequate knowledge to manipulate these materials correctly; therefore the use of such products can result in damage to the oral tissues. Thus, the purchase and use of such products should be discouraged.

REBASING RESIN DENTURES

The steps required in denture rebasing are similar to those described for relining. An accurate impression of the soft tissues is made using the existing denture as a custom tray. Subsequently, a gypsum cast is fabricated in the impression. The cast and denture are mounted in a device designed to maintain the correct vertical and horizontal relationships between the stone cast and surfaces of the prosthetic teeth. The resultant assembly provides indices for the occlusal surfaces of the prosthetic teeth. After these indices have been established, the denture is removed and the teeth are separated from the existing denture base. The teeth are repositioned in their respective indices and held in their original relationships to the cast while they are waxed to a new baseplate.

At this point, the denture base is waxed to the desired form. The completed tooth arrangement is sealed to the cast, and the assembly is invested as previously described. Following elimination of the wax and removal of the baseplate, resin

is introduced into the mold cavity. The material subsequently is processed. After processing, the denture is recovered, finished, and polished. The completed prosthesis consists of a new denture base in conjunction with teeth from the patient's previous denture.

CRITICAL QUESTION

Under what conditions might soft denture **liners** be used rather than rebasing an acrylic denture base?

SHORT- AND LONG-TERM SOFT DENTURE LINERS

The purpose of a soft denture liner is to absorb some of the energy produced by masticatory impact. Hence a soft liner serves as a "shock absorber" between the occlusal surfaces of a denture and the underlying oral tissues. The most commonly used liners are plasticized acrylic resins. These resins can be heat-activated or chemically activated and are based on addition polymerization chemistry that are described previously and in Chapter 6.

Chemically activated soft liners generally employ polymethyl methacrylate or polyethyl methacrylate as principal structural components. These polymers are supplied in powder form and subsequently are mixed with liquids containing 60% to 80% of a plasticizer. The plasticizer commonly is a large molecular species such as dibutyl phthalate or an alcohol for **short-term tissue conditioners**. The distribution of large plasticizer molecules reduces entanglement of polymer chains, thereby permitting individual chains to "slip" past one another. This slipping motion permits changes in the shape of the soft liner and provides a cushioning effect for the underlying tissues. It is important to note that the liquids used in such applications do not contain acrylic monomers. Consequently the resultant liners are considered short-term soft liners or tissue conditioners.

Unlike chemically activated soft liners, heat-activated materials generally are more durable and can be considered **long-term soft liners**. Nonetheless, these materials degrade over time and should not be considered permanent.

A number of heat-activated soft liners are supplied as powder-liquid systems. The powders are composed of acrylic resin polymers and copolymers, whereas the liquids consist of appropriate acrylic monomers and plasticizers. When mixed, these materials form pliable resins exhibiting glass transition temperatures (T_g) below mouth temperature.

Although plasticizers impart flexibility, they also present certain difficulties. Plasticizers are not bound within the resin mass. Therefore they may be "leached out" of soft liners. As this occurs, soft liners become progressively more rigid. Consequently, it is advantageous to use liners that are less prone to leaching phenomena.

In recent years the phthalate esters plasticizer have raised concerns, as they mimic estrogenic hormones in the body after they are released from the liner. Alternatives are now in use, including trimellitates, aliphatic dibasic esters, phosphates, benzoates, citrate esters, polymeric plasticizers, sulfonic acid, chloroparaffins, and sorbitol.

As polymethyl methacrylate is replaced by higher methacrylates (e.g., ethyl, n-propyl, and n-butyl), the T_g becomes progressively lower. As a result, less plasticizer is required and the effects of leaching can be minimized.

Vinyl resins have also been used in soft liner applications. Unfortunately plasticized polyvinyl chloride and polyvinyl acetate are subject to leaching and will harden during sustained use.

Perhaps the most successful materials for soft liner applications have been the silicone rubbers. These materials are not dependent upon leachable plasticizers; therefore, they retain their elastic properties for prolonged periods. Unfortunately, silicone rubbers may lose adhesion to underlying denture bases.

Silicone rubbers may be chemically activated or heat-activated. Chemically activated silicones are supplied as two-component systems that polymerize via condensation reactions.

Placement of chemically activated soft liners is not complicated. The denture base is relined to permit an acceptable thickness of the chosen material. A special adhesive is then applied to the surface of the denture base to facilitate bonding. The resilient material is mixed, applied to the denture base via compression molding, and permitted to polymerize. Then, the denture is recovered, finished, and polished.

Heat-activated silicones are one-component systems supplied as pastes or gels. These materials are applied and contoured using compression molding techniques. Heat-activated silicones can be applied to polymerized resin bases, or they can be polymerized in conjunction with freshly mixed resins.

To promote adhesion between silicone soft liners and rigid denture base materials, rubber-polymethyl methacrylate cements often are used. These cements serve as adhesive intermediates that bond to both soft liners and denture resins.

At least one silicone liner does not require an adhesive when it is cured together with an acrylic denture base material. This material is actually a silicone copolymer that contains components capable of bonding with acrylic resins.

Laboratory procedures for heat-activated silicones are similar to those described for other chemically activated materials. Bases are invested and mold spaces prepared as required. Relief is provided to permit an acceptable thickness of the chosen material(s). Packing, compression molding, and processing are performed in accordance with manufacturer's recommendations. The denture is then recovered, finished, and polished.

All of the described liners display certain shortcomings. For instance, silicone liners adhere poorly to denture base resins. Silicone liners are also porous, which allows water uptake and harbors fungal growth. Many soft liners bond well to denture bases but become progressively more rigid as plasticizers leach from the liner materials. Hardening rates for these liners are associated with the initial plasticizer content. As the plasticizer content is increased, the probability for plasticizer loss also is increased. Hence materials exhibiting high initial plasticizer content tend to harden rather rapidly.

Soft liners also exert significant effects on associated denture bases. As the thickness of a soft liner is increased, the thickness of the accompanying denture base must be decreased, and this results in decreased denture base strength. Furthermore, materials used in conjunction with soft liners (e.g., adhesives and monomers) may cause partial dissolution of denture bases. This can result in fracture during clinical service.

Perhaps the greatest difficulty associated with long- and short-term silicone soft liners is that these materials cannot be cleaned effectively. As a result patients often report disagreeable tastes and odors related to these materials. Research indicates that the liners themselves do not support mycotic growth, but such growth is supported by debris accumulating in the pores of these materials. The most common fungal growth that develops on soft liners is *Candida albicans*.

Several cleaning regimens have been used in conjunction with soft liners; however, these regimens have met with limited success. Both oxygenating and hypochlorite-type denture cleansers have been employed. Unfortunately, these agents can cause color change and significant damage to soft liners, especially the silicone materials.

Mechanical cleaning of soft liners may lead to damage, but such debridement is often necessary. If mechanical cleaning is undertaken, a soft brush should be used in conjunction with a mild detergent solution or nonabrasive dentifrice.

In attempts to address potential problems, antimycotic agents have been incorporated into soft liners. Although this approach is promising, the limited duration of antimycotic activity is far from ideal. Therefore additional research is warranted.

Based on the preceding information, none of the soft liner materials discussed above are completely satisfactory for other than short-term applications. However, a material suitable as a permanent soft liner was introduced in 1989 (Gettleman et al., 1989; Gettleman, 2004) following extensive NIH-supported research and clinical trials. This soft liner material uses a polyphosphazene fluoroelastomer (PNF, a polymer with –[–P=N–]– as the main chain, and fluorocarbon side groups). PNF forms an interpenetrating network with di- and trifunctional cross-linking acrylics, formulated with barium sulfate filler for radiopacity. The liner material is compression molded in the laboratory, polymerized in hot water, and bonded to new or existing acrylic denture bases. It has no plasticizers that can leach out of the liner surface. Therefore, the liner stays soft permanently, provides comfort by absorbing chewing forces due to its high-energy damping, is nonporous to resist fungus growth, and is easily adjusted to customize fit. (Novus™ Resilient Liner, Lang Dental Manufacturing Co, Wheeling, IL)

RESIN IMPRESSION TRAYS AND TRAY MATERIALS

Resin trays are often used in dental impression procedures. Unlike stock trays, resin impression trays are fabricated to fit the arches of individual patients. Therefore, resin impression trays are commonly called custom trays.

The overwhelming majority of custom trays are fabricated using light-activated and chemically activated resin systems. Each system has advantages and disadvantages. Light-activated materials eliminate methyl methacrylate exposure, but are more expensive and require high-intensity light units for polymerization. Chemically activated resins are less expensive but have been associated with contact dermatitis, particularly in laboratory personnel. Because each material exhibits advantages and disadvantages, the choice of custom tray material is commonly based upon individual preference.

The steps in custom tray fabrication are described as follows: A preliminary impression is made using a stock tray and an appropriate impression material. In turn, a gypsum cast is generated. A suitable spacer is placed on the stone cast to provide the desired relief. Subsequently a separating medium is applied to the surface of the cast. At this stage, fabrication techniques for light-activated materials and chemically activated materials become divergent.

Light-activated resins are supplied in sheet and gel forms. Sheet forms are preferred for custom tray fabrication because of their favorable handling characteristics. Individual sheets are pliable and can be adapted to the associated casts and spacers with relative ease. A handle is added to facilitate removal of the tray from the mouth and the entire assembly is placed in a light chamber and the resin is polymerized.

Chemically activated resins typically are polymethyl methacrylates and are supplied as powder-liquid systems. The components are mixed to form a dough-like mass. The dough is then rolled into a sheet approximately 2 mm thick, adapted to the diagnostic cast with a handle as above, and allowed to polymerize.

Upon completion of the fabrication process, both light-activated and chemically activated custom trays are removed from the associated casts and mechanically trimmed. The peripheries are rounded to make sure that patients will not be harmed by sharp or irregular edges. At this point, trays can be evaluated intraorally and refined as necessary.

DENTURE CLEANSERS

Patients use a wide variety of agents for cleaning artificial dentures. These include dentifrices, proprietary denture cleansers, mild detergents, household cleansers, bleaches, and vinegar.

The most common commercial products are based upon immersion techniques. These cleansers are marketed in powder and tablet forms containing alkaline compounds, detergents, sodium perborate, and flavoring agents. Dissolved in water, sodium perborate decomposes to form an alkaline peroxide solution. This solution subsequently releases oxygen, which loosens debris via mechanical means.

Household bleaches (hypochlorites) also are used in denture cleaning applications. Dilute bleach solutions can be used to remove certain types of stains. Unfortunately, prolonged use of bleach-containing solutions can remove color from denture base and relining materials.

Bleaches and bleach solutions should not be used for cleaning metal prostheses such as removable partial denture frameworks. These solutions produce significant darkening of base metals and can damage the serviceability of affected prostheses irreparably.

The use of brushes and abrasive cleansers can produce a range of effects on resin surfaces. Toothbrushes alone produce minimal wear of resin surfaces. Toothbrushes in conjunction with most commercial dentifrices, mild detergents, and soaps also appear to be relatively nondestructive. Conversely, household cleansers, such as kitchen and bathroom abrasives, are definitely contraindicated. Prolonged use of such cleansers may cause noticeable wear of resin surfaces and adversely affect the function and esthetics of these prostheses. Therefore, patients should be educated regarding the care and cleaning of resin prostheses.

INFECTION-CONTROL PROCEDURES

Care should be taken to prevent microbial and viral cross-contamination between patients and dental personnel, including personnel in the dental laboratory. New appliances should be disinfected before leaving the dental laboratory. Existing prostheses should be disinfected before entering the laboratory and after completion of laboratory procedures. All materials used for finishing and polishing should be handled according to established infection-control guidelines. Items such as rag wheels should be autoclaved, and materials such as pumice should be used according to unit-dose recommendations.

? CRITICAL QUESTION

Which components of denture resins are most likely to cause an allergic reaction?

ALLERGIC REACTIONS

Possible toxic or allergic reactions to polymethyl methacrylate have long been postulated. Reactions can occur following contact with the polymers, residual monomers, benzoyl peroxide, hydroquinone inhibitor, pigments, or a reaction product between some component of the denture base and its environment.

Clinical experience indicates that true allergic reactions to acrylic resins seldom occur in the oral cavity. Irritation is slightly more common and is related to residual monomer. Irritation reactions are relatively rare, since the residual monomer content of a properly processed denture is less than 1%. Furthermore, surface monomer is completely eliminated following storage in water for 17 hours.

Reactions to residual monomer should occur shortly after prosthesis delivery. However, the majority of patients reporting sore mouth due to denture wear have worn the offending prostheses for months or even years. Clinical evaluation of these cases indicates that tissue irritation is commonly related to 24-h denture wearing and fungus overgrowth under the denture, other unhygienic conditions, or trauma caused by poorly fitting denture bases.

Repeated or prolonged contact with monomer can also result in contact dermatitis. This condition is most commonly experienced by personnel involved in the manipulation of denture resins. Hence dental personnel should refrain from handling such materials with bare hands. The high concentration of monomer in freshly mixed resins may produce local irritation and serious sensitization of the fingers.

Finally, it should be noted that inhalation of monomer vapor may be detrimental. Therefore, the use of monomer should be restricted to well-ventilated areas.

TOXICOLOGY

There is no evidence that commonly used dental resins produce systemic toxic effects in humans. As previously noted, the amount of residual monomer in processed polymethyl methacrylate is extremely low. To enter the circulatory system, residual monomer must pass through the oral mucosa and underlying tissues. These structures function as barriers that significantly diminish the volume of monomer reaching the bloodstream.

Residual monomer that does reach the bloodstream is rapidly hydrolyzed to methacrylic acid and excreted. It is estimated that the half-life of methyl methacrylate in circulating blood is 20 to 40 minutes.

Metal oxide (cadmium/selenium) red pigments were used for many years to color denture base resins. Although toxic in all concentrations, the pigments are locked within the denture base polymer network and used in very small concentrations. Nevertheless, most manufacturers have switched to organic pigment systems, i.e., cromophtal red BRN, to avoid such effects.

? CRITICAL QUESTIONS

What precautions should be taken in using porcelain teeth in a denture? What are the clinically relevant differences between porcelain teeth and acrylic resin teeth?

RESIN TEETH FOR PROSTHETIC APPLICATIONS

The majority of preformed artificial teeth sold in the United States is made of acrylic or vinyl-acrylic resins. As might be expected, the majority of resin teeth are based on polymethyl methacrylate compositions.

Polymethyl methacrylate resins used in the fabrication of prosthetic teeth are very similar to those used in denture base construction. The degree of cross-linking at the occlusal and incisal surfaces of prosthetic teeth is much greater that that exhibited by polymerized denture base materials. The increased cross-linking of prosthetic teeth in conjunction with the addition of inorganic filler yields enhanced stability, increased wear resistance, and improved clinical properties.

Cervical portions of prosthetic teeth often exhibit reduced cross-linking. This facilitates chemical bonding with denture base resins. Additional retention may be achieved by removing the glossy "ridge-lap" surfaces of resin teeth preparing mechanical undercuts.

Chemical bonding between resin teeth and heat-activated denture base materials has proven extremely effective.

Nevertheless, bond failures can occur if ridge-lap surfaces are contaminated by residual wax or misplaced separating media. To optimize bonding, gypsum molds must be flushed with hot water and the exposed cervical portions of prosthetic teeth must be thoroughly cleaned with mild detergent solutions. Separating media must be applied to gypsum mold surfaces but should not extend onto the exposed surfaces of resin teeth. As a final measure, ridge-lap surfaces should be wet with monomer immediately before resin introduction.

More recently, manufacturers have introduced "hybrid" teeth to enhance the wear resistance of prosthetic dentitions. These teeth include composite resin-based and polymethyl methacrylate components. Composite resins are found primarily on occlusal and incisal surfaces of the prosthetic teeth, and are intended to provide improved wear resistance. Unfortunately, chemical bonding between composites and heat-activated denture base materials is inferior to that which occurs between resin teeth and such denture base materials. To address this shortcoming, manufacturers have incorporated polymethyl methacrylate at the ridge-lap and lingual surfaces of hybrid teeth. The presence of polymethyl methacrylate on these surfaces facilitates predictable bonding with heat-activated polymethyl methacrylate denture base resins. Nevertheless, operators must be certain not to eliminate the polymethyl methacrylate surfaces while setting the prosthetic teeth.

As might be expected, the laboratory steps prescribed for hybrid teeth in conjunction with heat-activated resins are identical to those prescribed for resin teeth used in combination with heat-activated resins. Proposed bonding surfaces such as ridge-lap areas must be free from residual wax, separating media, and other contaminants. To facilitate chemical bonding, these surfaces should be wet with monomer immediately before denture base resin is introduced in place.

Despite shared chemistries, chemically activated polymethyl methacrylate denture base resins and their heat-activated counterparts display distinct differences. Notably, mechanical retention is the primary method for securing resin teeth to chemically activated denture base materials. While chemical bonding also may be used, it requires a distinct modification of the fabrication process. To achieve predictable chemical bonding, a mixture of equal volumes of methylene chloride and chemically activated methyl methacrylate monomer is applied to the necks of resin teeth for approximately 5 minutes. Excess solution is then removed. This treatment softens and swells the resin and facilitates development of an interpenetrating network between the denture teeth polymers and those of the denture base during polymerization. The resultant bond strengths are similar to those obtained between resin teeth and heat-activated denture base resins.

Despite the current emphasis on resin teeth, prosthetic teeth also can be fabricated using dental vacuum- or pressure-fired porcelains. Hence a comparison of resin and porcelain teeth is provided in the following photographs.

Resin teeth display greater impact resistance and ductility than porcelain teeth. As a result, resin teeth are less likely to chip or fracture on impact, as when a denture is dropped. Furthermore, resin teeth are easier to adjust and display greater resistance to thermal shock. In comparison, porcelain teeth display better dimensional stability and increased wear resistance. Unfortunately, porcelain teeth often cause significant wear of opposing enamel, metal, and resin tooth surfaces, especially when contacting surfaces have been roughened. Therefore, porcelain teeth should not oppose such surfaces, and if they are used, they should be polished periodically to reduce abrasive damage.

As a final note, resin teeth are capable of chemical bonding with commonly used denture base resins. Porcelain teeth, however, do not form chemical bonds with denture resins and must be retained by bonded pins, mechanical undercuts, and/or silanization. Leakage at the tooth-denture base junction can be seen as a dark line when food and microbes penetrate the interface.

CRITICAL QUESTION

What are the benefits and drawbacks of materials used in the construction of maxillofacial prostheses?

MATERIALS FOR MAXILLOFACIAL PROSTHETICS

For centuries, prostheses have been used to mask maxillofacial defects. The ancient Egyptians and Chinese used waxes and resins to reconstruct missing portions of the craniofacial complex. In the sixteenth century, the French surgeon Ambroise Paré described a variety of simple prostheses used for the cosmetic and functional replacement of maxillofacial structures. During subsequent years, restorative techniques and materials were improved and refined. Casualties in World Wars I and II established an increased need for maxillofacial prosthetics, and the dental profession assumed a major role in maxillofacial reconstruction and rehabilitation processes.

Despite improvements in surgical and restorative techniques, the materials used in maxillofacial prosthetics are far from ideal. An ideal material should be inexpensive, biocompatible, strong, and stable. In addition, the material should be skinlike in color and texture. Maxillofacial materials must exhibit resistance to tearing, and should be able to withstand moderate thermal and chemical challenges. Currently, no material fulfills all of these requirements. A brief summary of maxillofacial materials is included in the following paragraphs.

LATEXES

Latexes are soft, inexpensive materials that can be used to create lifelike prostheses. Unfortunately, these materials are weak, degenerate rapidly, and exhibit color instability. Therefore, latexes are rarely used in the fabrication of long-term maxillofacial prostheses.

One synthetic latex is a terpolymer of butyl acrylate, methyl methacrylate, and methyl methacrylamide. Superior

to natural latex, this material is nearly transparent. Colorants are sprayed onto the reverse or tissue side of the prosthesis, thereby providing enhanced translucency and improved blending. Despite these advantages, the associated technical processes are lengthy and the resultant prostheses last only a few months. Therefore, synthetic latexes have limited applications.

VINYL PLASTISOLS

Plasticized vinyl resins sometimes are used in maxillofacial applications. Plastisols are thick liquids composed of small vinyl particles dispersed in a plasticizer. Colorants are added to these materials to match individual skin tones. Subsequently, vinyl plastisols are heated to impart desired physical characteristics. Unfortunately, vinyl plastisols harden with age as a result of plasticizer migration. Ultraviolet light also has an adverse effect on these materials. For these reasons, the usefulness of vinyl plastisols is limited.

SILICONE RUBBERS

Silicones were introduced in the mid-1940s and have been used in maxillofacial applications since the 1950s. Both heat-curing and room-temperature–curing silicones are in use today, and both exhibit advantages and disadvantages.

Room-temperature–curing silicones are supplied as single-component materials that cure by evaporation of acetic acid. They are "characterized" by a natural flesh-like appearance by using dyed rayon fibers, dry earth pigments, and/or oil paints. Prostheses are polymerized by bulk packing in two- or three-part gypsum molds made from the sculpting of the facial part, but more durable molds have been made from epoxy resins or metals.

Heat-curing silicones are supplied as semisolid or putty-like materials that require milling, packing in two- or three-part molds under pressure, and a 30-minute heat application cycle at 180 °C. Pigments are milled into these materials. Thus intrinsic color can be achieved. Heat-curing silicones display better strength and color stability than room-temperature–curing silicones. All of the silicones are susceptible to fungus growth and fraying at the featheredge margins, so a process of bonding to a sheet of polyurethane on the tissue surface has been developed. However, the urethane may discolor over time.

The major disadvantage of heat-curing silicones is the requirement for a milling machine and a press. Furthermore, a metal mold normally is used, and fabrication of the mold is a lengthy procedure. A stone mold may be housed within a brass denture flask, but this increases the risk of damage to the silicone material during deflasking.

POLYURETHANE POLYMERS

Polyurethane also can be used in maxillofacial prosthetics. Fabrication of a polyurethane prosthesis requires accurate proportioning of three components. The material is placed in a stone or metal mold and allowed to polymerize at room temperature. Although a polyurethane prosthesis has a natural feel and appearance, it is susceptible to rapid deterioration and fungus growth.

CHLORINATED POLYETHYLENE

In an effort to overcome the deficiencies of the latex, vinyl plastisol, silicone, and polyurethanes as maxillofacial materials, a thermoplastic elastomer based on chlorinated polyethylene (CPE) was investigated in the 1970s and 1980s. With further development, CPE was shown to provide higher edge strength, permanent elasticity, and minimal fungus growth (Gettleman, 1992). In a recent randomized, controlled clinical trial, it was found that the material was equally preferred by patients who had never worn facial prostheses before, but patients who had worn silicone rubber prostheses in the past favored that material in the trial. Methods of layering the prosthetic material in the molds to develop color at depth were also reported, which may be useful when future maxillofacial prosthetic materials are introduced (Kiat-amnuay et al., 2010).

Additional information may be found in a review by Lemon et al. (2005), which presents current concepts regarding facial prosthetic rehabilitation of patients with head and neck cancer and facial prosthetic biomaterials.

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CHAPTER 20

Dental Implants

OUTLINE

History of Dental Implants

Classification of Implants

Implant Components

Evaluation of Clinical Success

Implant Biomaterials

Selecting an Implant Biomaterial

Biocompatibility of Implants

Biomechanics

KEY TERMS

Alloplastic—Related to implantation of an inert foreign body.

Ankylosis—A condition of joint or tooth immobility resulting from oral pathology, surgery, or direct contact with bone.

Anodization—An oxidation process in which a film is produced on the surface of a metal by electrolytic treatment at the anode.

Bioacceptance—The ability to be tolerated in a biological environment in spite of adverse effects.

Bioactive—Capable of promoting the formation of hydroxyapatite and bonding to bone.

Biocompatibility—The ability of a material to elicit an appropriate biological response in a given application in the body.

Biointegration—The process by which bone or other living tissue becomes integrated with an implanted material with no intervening space.

Endosteal implant—A device placed into the alveolar and/or basal bone of the mandible or maxilla that transects only one cortical plate.

Epithelial implant—A device placed within the oral mucosa.

Implantation—The process of grafting or inserting a material such as an inert foreign body (alloplast) or tissue within the body.

Ion implantation—The process of altering the surface of a metal with desirable ionic species.

Osseointegration—The process by which living bony tissue forms to within 100 Å of the implant surface without any intervening fibrous connective tissue.

Osteoinductive—Ability to promote bone formation through a mechanism that induces the differentiation of osteoblasts.

Passivation—The process of transforming a chemically active surface of a metal to a less active surface.

Replantation—Reinsertion of a tooth back into its jaw socket soon after intentional extraction or accidental removal.

Subperiosteal implant—A dental device that is placed beneath the periosteum and overlies cortical bone.

Texturing—The process of increasing roughness of the implant surface area to which bone can bond.

Toxicity—The ability of a material to cause cell or tissue death.

Transosteal implant—A device that penetrates both cortical plates and the thickness of the alveolar bone.

HISTORY OF DENTAL IMPLANTS

The restoration and replacement of missing teeth are important aspects of modern dentistry. As teeth are lost to decay, disease, and trauma, there is a demand for improvement of esthetics and restoration of function.

Conventional methods of restoration include a removable complete denture, a removable partial denture, a fixed prosthesis, or combinations of these approaches.

There are different indications for each method, with associated advantages and disadvantages. Removable dentures have long been considered problematic because of their varying mobility/stability over time and the inconvenience of removing them each day. Also, many removable dentures were bulky, others complicated chewing, and some were not adequately esthetic. Fixed prostheses were considered more esthetic and comfortable for the patient, but they involved the preparation of adjacent teeth and they were associated with problems such as secondary decay or irreversible pulpitis. If the adjacent teeth did not have restorations, the decision to prepare them for a fixed prosthesis was difficult because two or more natural teeth would have to be surgically altered to provide retention for one or more artificial teeth (a bridge).

For centuries people have attempted to replace missing teeth by implanting synthetic and natural substances. ***Implantation*** has been defined as the insertion of any object or material, such as an **alloplastic** substance or other tissue, either partially or completely, into the body for therapeutic, diagnostic, prosthetic, or experimental purposes. Implantation is usually differentiated from other, similar procedures such as **replantation** and transplantation. *Replantation* refers to the reinsertion of a tooth back into its jaw socket after its accidental or intentional removal, whereas transplantation is the transfer of a body part (homogeneous or heterogeneous) from one host to another.

? CRITICAL QUESTION

How did the concept of implantation evolve into a widely used restorative technique in dentistry?

Dental implants began as far back as the early Greek, Etruscan, and Egyptian civilizations, employing different designs and materials ranging from jade and other stones and metals to bone and ivory. Some of the design concepts used then have evolved into the implants of today.

Sea shells were used in place of teeth in 600 A.D., evidence of which was found in Honduras, and tooth restorations made of jade and turquoise, were found in Mayan skulls. Albucasis de Condue (936–1013) of France used ox bone to replace missing teeth; this was one of the early documented placements of implants. Through the centuries various tooth transplants made of either human or animal teeth were tested. These transplants became status symbols and they quickly replaced other artificial alternatives for restoring missing teeth. Toward the eighteenth century, Pierre Fauchard and John Hunter further documented tooth transplantation and specified conditions for the success of this procedure. They claimed that success was greater with anterior teeth, premolar teeth, and transplants placed in young people with healthy tooth sockets. Failure was believed to be the result of the incompatibility of the type of tooth used or the lack of conformity of the tooth to the socket.

The recognition of failure rates of transplants increased interest in the implantation of artificial tooth roots. In 1809 Maggiolo fabricated gold roots that were fixed to teeth by means of a spring. These gold implants were placed into fresh extraction sites, although they were not truly submerged into bone. The crowns were placed after healing had occurred around the implant. Many attempts followed. Harris (1887) proposed the use of a platinum post coated with lead. The post was shaped like a tooth root, and the lead was roughened for retention in the socket. Bonwell (1895) implanted gold or iridium tubes to restore a single tooth or support complete dentures. Payne (1898) implanted a silver capsule as a foundation for a porcelain crown that was cemented after weeks. Scholl (1905) demonstrated a porcelain corrugated root-shaped implant that lasted for two years and was anchored to adjacent teeth by pins. Greenfield (1913) introduced and patented a hollow "basket" implant made of a meshwork of 24-gauge iridium-platinum wires soldered with 24-karat gold. This device was used to support single implants as well as fixed dental prostheses comprising as many as eight implants.

Consistent problems with these artificial implant designs and materials supported the need for a scientific approach to implant selection and placement. Some have proposed that the "modern era" started in 1925. In 1937 Venable et al. analyzed the interactions of cobalt alloy and other available metals and alloys with bone. They concluded that certain metals produced a galvanic reaction, which led to corrosion when these metals contacted tissue fluids. They proposed the use of Vitallium, a cast alloy, which was composed of cobalt, chromium, and molybdenum. This alloy was considered to be relatively inert, compatible with living tissue, and resistant to the adverse reactions with body fluids. Vitallium has also been used in different forms of surgical devices, such as dental **subperiosteal implant** and orthopedic plates, screws, nails, and joints. Early evaluations documented Vitallium implants with survival times of 10 or more years.

The background of research, development, and applications of biomaterials for dental implants began with the application of available substances, often of metallic origin. Some separate the period before 1950 as an era of applications driven by need and availability. Examples include the early use of wires, pins, and rods fabricated from gold and other noble metals and alloys. In the 1950s, the cobalt-based alloys were cast and finished for subperiosteal and some root-form designs. The austenitic iron-based stainless steels constituted from iron-chromium and nickel (sometimes with molybdenum as well) were also utilized in wrought and machined conditions. Within a decade, titanium and other reactive-group metals—plus carbons, ceramics, and eventually polymers—were considered.

The more "modern" era of biomaterials arose by the 1970s, when materials known and tested in many disciplines were constituted, fabricated, and finished as biomaterials. Consensus standards rapidly evolved for these biomaterials, which resulted in more consistent control of their properties. A very important aspect of this evolution—which included biomaterials, designs, and clinical application—was the clinical research led by P. I. Brånemark in Sweden. His studies utilized unalloyed titanium, a root-form design and very controlled conditions for surgery, restoration, and maintenance. Data

presented in literature reviews and consensus conferences over the period 1972–2002 have demonstrated significant improvements in dental implant survival statistics. When outcomes were evaluated by objective criteria, the average survival at 5 years was about 50% in the 1970s. In the 2000s, average survival at 10 years was above 90%.

CLASSIFICATION OF IMPLANTS

Implants can be classified according to anatomic location, device design, implant properties, or implant attachment mechanism. In a broad context, there are four implant design types that can be classified by anatomic location and they have evolved over centuries of development.

IMPLANT DESIGN

The first and most commonly used type of design is the endosteal (called endosseous) implant, a device placed into an alveolar and/or basal bone of the mandible or maxilla that usually transected only one cortical plate. These implants were formed in many different shapes, such as root-form cylindrical cones or screws or thin plates called plate or blade forms, and they were used in all areas of the mouth. One example of an **endosteal implant** was called the blade implant (Figure 20-1), which was developed independently in 1967 by two groups led initially by Roberts (1970) and Linkow (1968). Endosteal blade implants consisted of thin plates placed into bone; they were most commonly used for narrow anatomic structures such as posterior edentulous areas after significant resorption of bone. Because of various issues with blade implants, their application in more recent implantology has decreased. Another example of an endosteal implant was the ramus frame implant, a horseshoe-shaped stainless steel device inserted into the ascending rami (bilateral) and the anterior symphysis area of the mandible. As with the blade implants, the number of applications have been limited. The most popular endosteal implant has been the root-form (Figure 20-2), which was designed initially to mimic the shape of tooth roots for directional load distribution as well as for positioning in bone. In longitudinal studies, the root-form implant has the most documentation of the endosteal implants, although several surgical stages may be needed for completion.

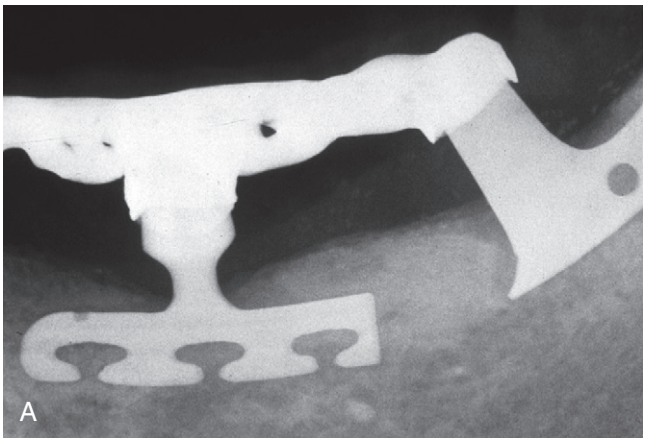




FIGURE 20-1 **A,** Blade implants embedded in bone, with some bone loss. **B,** Failed blade implant prosthesis that was also attached to natural teeth. (Courtesy of Dr. Mickey Calverley.)

The second implant design was the subperiosteal implant (Figure 20-3), which employed an implant substructure and superstructure. The custom-cast frame was placed directly beneath the periosteum overlying and fitting along the bony cortex. This implant was first developed by Dahl (1943) and refined by Berman (1950), who used a direct bone impression technique. These devices were used to restore partially dentate or completely edentulous jaws when there was inadequate bone for endosseous implants. Use of the subperiosteal implant has been limited because of numerous considerations, including the difficulty of retrieval.

The third design was the **transosteal implant** (Figure 20-4), which combined subperiosteal and endosteal components. This type of implant penetrated both cortical plates and passes through the full thickness of the alveolar bone. Use of the transosteal implant has been restricted to the anterior area of the mandible and provides support for tissue-borne overdentures. The concept of transosseous implants was first conceived in Germany in the early 1930s; early examples were made of a cobalt alloy. Small (1968) developed the mandibular staple implant made of a titanium alloy, which was modified by Bosker (1983), who produced the transmandibular implant (TMI) made of a gold alloy. Other names for transosteal implants have included *staple bone implant, mandibular staple implant,* and *transmandibular implant.*

The fourth implant design was the **epithelial implant**, which was inserted into the oral mucosa. This type was associated with a simple surgical technique where the mucosa was used as an attachment site for metal inserts placed into an acrylic denture. Several disadvantages were associated with the epithelial implant, most notably a painful healing process and a requirement for continuous wear. The current use of "mucosal inserts" or epithelial implants is very limited.

Some oral implantologists also include the endodontic stabilizer as an anatomy-specific application system. These smooth or threaded pins (or screws) were placed through endodontically treated teeth with the implant extending into the bone. They were constructed from alloys or ceramics made of alumina or zirconia. Reported difficulties included sealing the transition zone from tooth to bone and the limited strength of small-diameter pins or screws.

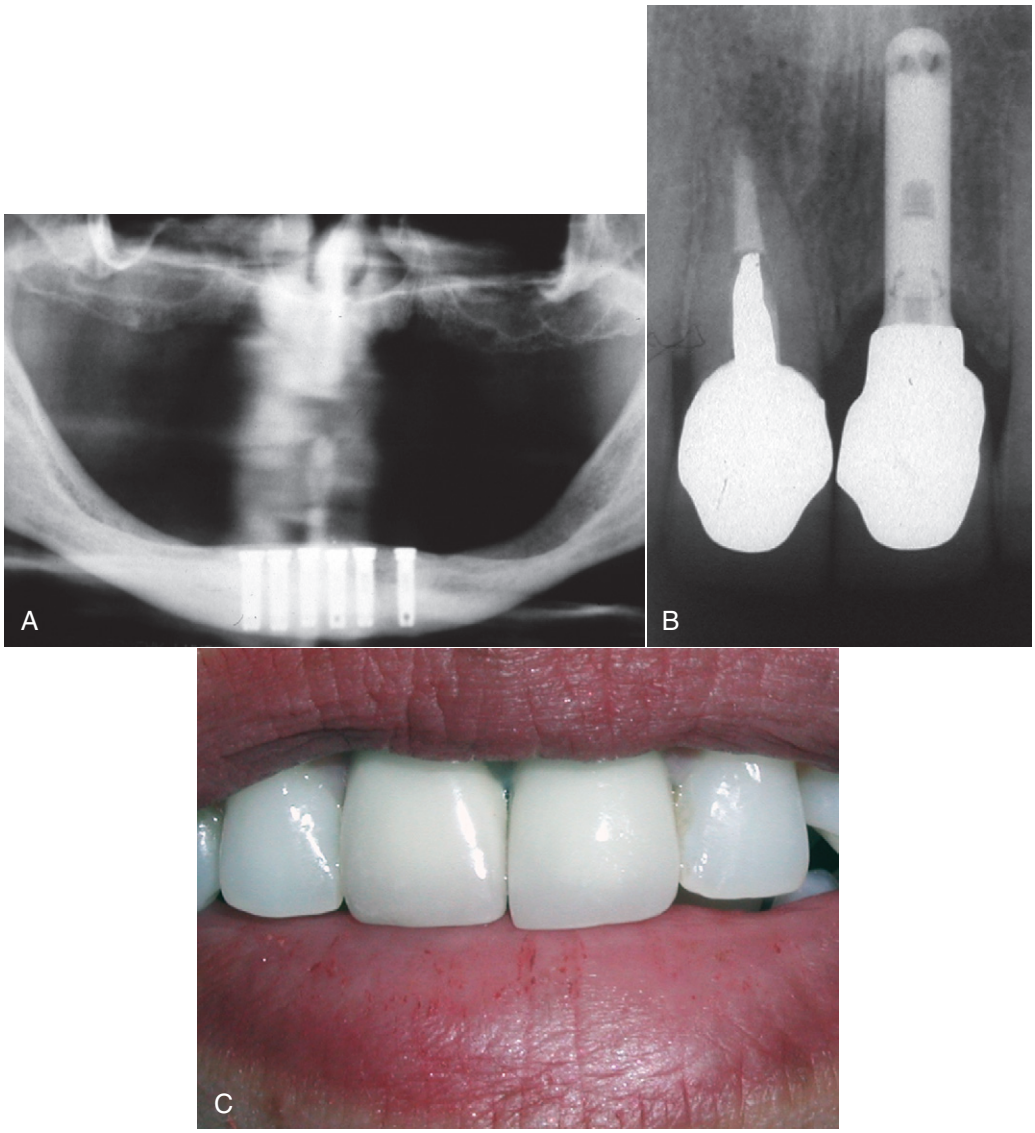


FIGURE 20-2 **A,** Endosteal implants are placed directly into bone; they mimic root forms for proper placement and location in bone. **B** and **C,** Restored anterior implant blending well with adjacent teeth.

From a historical and applications perspective, these systems were reviewed in the early 1970s by Natiella et al. (1972) and subsequently in each decade by researchers who participated in professional society–based consensus conferences. To summarize the various biomaterials and designs tested for dental implants, examples of devices received for examination prior to 1990 are shown in Figures 20-5 through 20-7.

IMPLANT PROPERTIES

Implant biomaterials can also be classified according to their composition and their physical, mechanical, chemical, electrical, and biological properties. These classifications often include ranked comparisons of properties such as elastic moduli, tensile strength, and ductility to determine optimal clinical applications (Table 20-1). These properties are used to aid in the design and fabrication of the prosthesis. For example, the elastic modulus of the implant is inversely related to the strain transferred across the implant-tissue interface during loading of the implant; that is, the greater the elastic modulus of an implant, the greater is the stress in the implant and the lower is the stress transferred to bone.

An implant with a elastic modulus comparable to that of bone should be selected to produce a more uniform stress distribution across the interface. Metals possess high strength and ductility, whereas the ceramics and carbons are brittle materials. Ductility is also important because it relates to the potential for permanent deformation of abutments or fixtures in areas of high tensile stress.

CRITICAL QUESTIONS

What is the preferred implant-to-tissue interaction? How has this influenced the popularity of implant applications?

TISSUE INTEGRATION

Another way of classifying implants is through interactions at the implant-to-tissue interface. Periodontal structures,

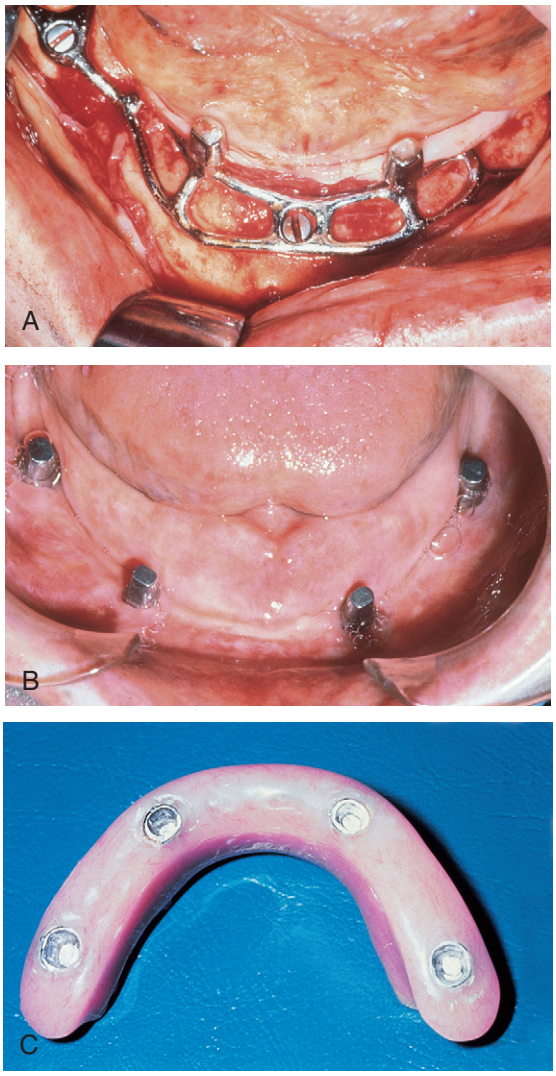


FIGURE 20-3 **A,** Subperiosteal implant positioned beneath the periosteum. Impression making often requires a difficult surgical technique. **B,** Superstructure for subperiosteal implant allowing for attachment of prosthesis. **C,** Denture prosthesis for subperiosteal implant. (Courtesy of Dr. Joseph Cain and Dr. Richard Seals.)

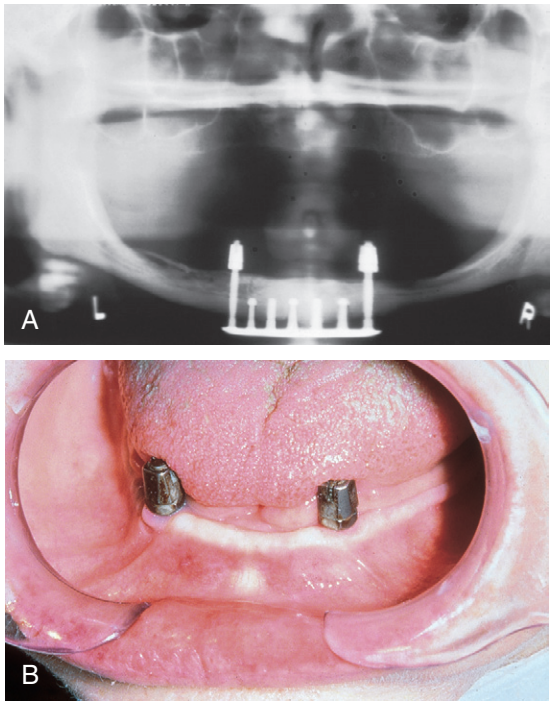


FIGURE 20-4 **A,** Panoramic radiograph of a transosteal implant showing perforation of both cortical plates, hence the name *staple implant*. **B,** Transmucosal abutment for transosteal implant allowing for placement of denture restoration. (Courtesy of Dr. Joseph Cain and Dr. Richard Seals.)

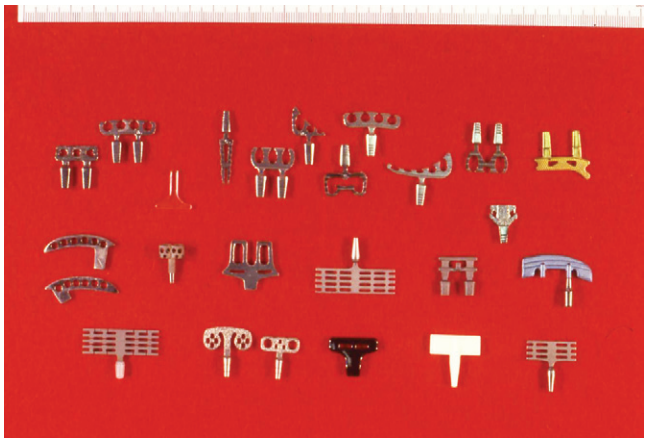


FIGURE 20-5 Collection of endosteal blade implant designs for restoring single or adjacent teeth.

which attach teeth to bone, consist of highly differentiated fibrous tissue. These fibers are replete with numerous cells and nerve endings that allow for functional force transfer, sensory function, bone formation, and tooth movements. Although this is the ideal form of integration, there are no known implant biomaterials or designs at present that can stimulate the growth of these fibers and fully mimic the function of the periodontal ligament and a natural tooth.

Historically, implant interactions occurred through fibrous connective tissue, and this was accepted as a measure of successful implant function (the pseudoligament concept). This type of interaction was reported to be very susceptible to acute or chronic inflammatory responses, which were accompanied by pain and eventual loss of the implant. Such an implant has also been called a pseudoperiodontium. Despite numerous reports of implant success, clinical studies indicate that this type of interaction is susceptible to a greater amount of progressive loosening and infection, with subsequent loss of the implant construct.

The implant-to-bone interaction (called **osseointegration**) is characterized by direct contact between bone and the surface of a functional implant after one year. This central theme of the Brånemark group was called "direct anchorage to bone" and has become a major attribute of dental implants. This mode is described as the direct adaptation of bone to implants without any other intermediate nonbony tissue and has been described by some as similar to tooth **ankylosis**, where no periodontal ligament or fibrous tissue exists. The



FIGURE 20-6 Collection of endosteal implants for partial arch restorations.

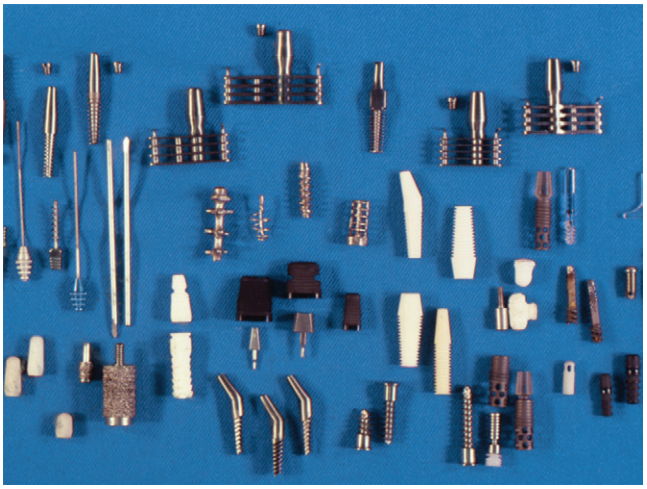


FIGURE 20-7 Collection of different designs and materials used for endosseous implants.

strength of this contact has been shown to be stable, which is advantageous compared with the soft tissue interface described previously.

This type of osseous interface has been described extensively and includes a process wherein bone-producing cells migrate along the implant surface through the connective tissue scaffolding that forms adjacent to the implant surface. Integration at the implant interface is highly dependent on the implant surface's chemistry and design. Bone apposition has been reported at higher rates when microscopic surface ridges are present. Osseous integration has also been achieved through the use of **bioactive** materials that stimulate the formation of bone along the surface of the implant. Another way of achieving osseous integration involves de novo bone formation, wherein a mineralized interfacial matrix and/or active growth factors are deposited along the implant's surface. Once again, the implant's surface topography influences the strength of its attachment to bone.

? CRITICAL QUESTION

What is the implication of having direct bone contact and the absence of a periodontal ligament on the prosthetic superstructure?

Implant-supported restorations differ from tooth-supported restorations in that the former lack a periodontal ligament, which reduces shear stress and strain, provides shock absorption, and reduces the development of dangerously high occlusal forces. These benefits of the periodontal ligament reduce the potential for inadvertent damage to the tooth or restoration. With the increased popularity of all-ceramic restorations, the effect of no periodontal ligament attachment in implant-supported restorations must be

TABLE 20-1 Mechanical Properties and Density of Metallic and Ceramic Implant Materials

Material	Grade or Condition	Yield Strength (MPa)	Elongation (%)	Modulus of Elasticity (GPa)	Tensile Strength (MPa)	Density (g/cm^3)
CP titanium	1	170	24	102	240	4.5
	2	275	20	102	345	4.5
	3	380	18	102	450	4.5
	4	483	15	104	550	4.5
Ti-6Al-4 V		860	10	113	930	4.4
Ti-6Al-4 V ELI		795	10	113	860	4.4
Co-Cr-Mo	Cast	450	8	240	700	8.0
Stainless steel	Annealed	190	40	200	490	8.0
	Cold-worked	690	12	200	860	8.0
Aluminum oxide	Polycrystalline	400* (500/flexure)	0.1	380	220	3.96
Zirconium oxide	Y_2O_3 (stabilized)	1200 (flexure)	0.1	200	350	6.0
Cortical bone		N/A	1	18	140	0.7
Dentin		N/A	0	18.3	52	2.2
Enamel		N/A	0	84	10	3.0

*ASTM standard: minimum values.

established. Ceramic materials are brittle by nature and because of inherent processing flaws, they cannot withstand any stress above their yield point, which is equivalent to their tensile strength. These stresses can be generated during occlusal loading. Implants, on the other hand, are directly anchored to the bone and cannot readily flex laterally under extremely high occlusal loads to relieve some of the excessive loading. Based on an in vitro study, Vult von Steyern et al. (2005) analyzed the fracture strength of all-ceramic prostheses on abutment teeth and implants. They concluded that implant-supported ceramic prostheses fractured at higher loads than those supported by natural teeth because of the lack of a periodontal ligament. To date, there are no clinical studies comparing the performance of ceramic FDPs supported by implants and natural teeth.

Conversely, studies have analyzed whether the type of prosthetic material can affect the longevity of an implant. Brånemark and Skalak advocated the use of acrylic for the prosthetic superstructure to act as a shock absorber and essentially dissipate the load on the implants and the bone surrounding them. To date, acrylic, gold, and ceramic are being used in implant superstructures. In the absence of a periodontal ligament, minimizing the load along the bone-implant interface is logical. However, there is no evidence to associate the use of any prosthetic material with the longevity and survival of the implants.

? CRITICAL QUESTION

What is the purpose of pretreating implant surfaces?

IMPLANT COMPONENTS

To understand the material characteristics and function of an implant, one must first be knowledgeable about its numerous component parts. Although each implant system varies, the parts are basically consistent. The body of the implant (called a fixture for the Brånemark system) (Figure 20-8, *A*) is the implant component that engages with bone. Depending on the implant system, the body section can have different surfaces—threading, grooved, perforated, plasma-sprayed, or coated. These characteristics are often classified as subtraction (acid etch) or addition (coating) types. Each surface type is meant to serve a particular purpose—for example, increased surface area enhances bone integration, and better cortex engagement plays an important role in immediate and long-term bone anchorage. The coated or plasma-sprayed biomaterials, discussed later in this chapter, are used to enhance attachment to bone. The second component (Figure 20-8, *B*) is the transmucosal abutment, which provides the connection between the implant body and the intraoral prosthesis to be fabricated (Figure 20-8, *C*), which will provide intraoral function. The abutment is usually connected to the implant body by means of a screw; however, it can also be cemented or connected by a Morse taper-type design. Abutments can become engaged to the implant body either by an internal or external geometry (initially a hexagon) within the implant body, which also serves as an antirotation device and is particularly important for single-unit restorations. The last part of an implant is the prosthesis. This can be attached to the abutments through the use of screws, cement, precision attachments, magnets, or other designs, such as those used for removable implant overdentures.

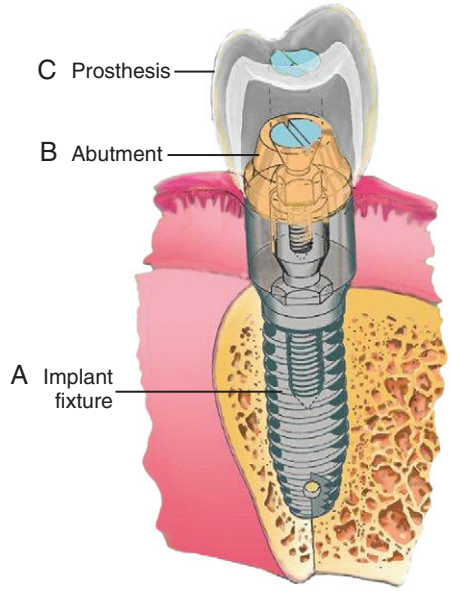


FIGURE 20-8 Diagram of implant components. **A,** The implant fixture (endosteal root form). **B,** Transmucosal abutment serving as the attachment between fixture and the actual prosthesis. **C,** The actual prosthesis, which can either be cemented, screwed, or swaged.

Placement and restoration of implants intended to integrate with bone are usually performed in stages. The first stage involves the surgical part, where the implant is placed into the bone. The implant is left within the bone (passive) for a period of months, depending on the bone quality, and allowed to heal and become integrated. A secondary surgery is sometimes required whereby the implant is uncovered and exposed through the oral environment using a healing cap, which is placed to ensure proper healing of soft tissue around the site of the future abutment. The restorative phase then follows the placement of abutments and a crown, a partial denture, or a removable denture, with or without a bar construct. Some implant systems utilize only one surgical intervention, where the implant is immediately placed in contact with the oral environment and is sometimes able to function in a limited way within days. Some of these systems have even been advocated for immediate functional loading, with reports of relative success.

? CRITICAL QUESTIONS

When can an implant restoration be considered successful? What criteria are used to determine this success? What clinical situations can affect the success rate of dental implants?

EVALUATION OF CLINICAL SUCCESS

There have been several long-standing debates about what is considered successful in implant dentistry. Some consider

that the encapsulation of an implant with a pseudoperiodontium is a successful implant condition. The most frequently cited success criteria from the 1970s are those in the publication edited by Schnitman and Schulman (1979). More recently, summaries from Cochran and Fritz (1996) and Albrektsson et al. (1986 and 1991) are often cited. Proposed early requirements included (1) implant mobility less than 1 mm when tested clinically; (2) no evidence of x-ray radiolucency; (3) bone loss less than one third the height of the implants; (4) absence of infection, damage to structures, and violation of body cavities—inflammation, if present, must be amenable to treatment; and (5) a success rate of 75% or more after 5 years of functional service using objective criteria for evaluation. As an example, these conditions were somewhat different from the criteria of Albrektsson et al. (1986), which included the following: (1) the implant must be immobile when tested clinically; (2) there must be no evidence of periapical x-ray radiolucency; (3) vertical bone loss should be less than 0.2 mm annually following the implant's first year; (4) absence of signs and symptoms such as pain, infections, neuropathies, paresthesias, or violation of the mandibular canal; and (5) a success rate of 85% or more at the end of a 5-year observation period and 80% at the end of a 10-year period when evaluated by objective criteria for success.

Smith and Zarb (1989) recommended an addition to Albrektsson's criteria by stating that the patient's and dentist's satisfaction should be the primary consideration and that esthetic conditions should be met. Patient satisfaction and patient attitude toward the prosthesis have been included in some subsequent lists of criteria for success. Although these criteria have become more stringent in recent years, success in implant dentistry is still difficult to quantify.

In 2008, the International Congress of Oral Implantologists arrived at a consensus for rating implant success, survival, and failure. The scale ranges from 1 to 4, with 1 being deemed successful and optimal health and 4 as clinical failure. The consenus evaluates the presence of pain or tenderness, mobility, bone loss, and exudate history (Table 20-2).

Standardized criteria for success should continue to evolve to enable proper evaluation of implant dentistry as the systems and treatments change over time.

TABLE 20-2 International Congress of Oral Implantologists Health Scale for Rating the Success or Failure of Dental Implants

Quality Scale	Clinical Condition
I. Success	a) No pain or tenderness at function
	b) 0 mobility
	c) <2-mm bone loss
	d) No exudate history
II. Satisfactory	a) No pain or tenderness at function
	b) 0 mobility
	c) 2–4-mm bone loss
	d) No exudate history
III. Compromised	a) May have pain or tenderness at function
	b) 0 mobility
	c) >4-mm bone loss and < ½ implant length
	d) No exudate history
IV. Failure	a) Pain or tenderness at function
	b) Mobility
	c) Bone loss > ½ implant length
	d) Uncontrolled exudates
	e) No longer in the mouth

From Misch CE et al: Implant success survival and Failure: International Congress of oral Implantologists, Pisa, Italy, Consensus Conference, Implant Dentistry 17(1):5–15, 2008.

? CRITICAL QUESTION

What is the primary mechanism of failure involved with dental implants?

LONGEVITY OF DENTAL IMPLANTS

The popularity of dental implants to restore full or partial edentulism has been the result of predictable outcomes with high success rates. Success rates of 96% to 98% are reported for mandibular implants and 94% to 96% for maxillary implants, depending on the quality of bone, surgical technique, and primary implant stability. Implant failure can occur at an early stage or a late stage. Early-stage failures occur prior to loading or placement of the prosthesis and are most commonly associated with poor surgical techniques or inability to achieve primary stability.

Brånemark and Albrektsson reported strict protocols required to achieve proper osseointegration. These include following proper aseptic techniques and allowing the bone to heal around the implant for a period of 4 to 6 months. The healing process allows the bone to be generated around the implant free from bacteria and micromovements, which can disrupt bone deposition around the implant. Micromovements above 150 µm have been shown to encourage soft tissue deposition and eventual encapsulation of the implant body with fibrous tissue. This occurrence is classified as a failure of osseointegration. Allowing the bone surrounding the implant to heal necessitates a two-step surgical technique in implant placement. Stage 1 occurs when the implant is surgically placed into the bone. A flap is reflected and the implant is screwed into the bone (Figure 20-9). The soft tissue is placed over the implant body to allow healing of the bone to occur. Stage 2 or the uncovering stage occurs when the soft tissue is removed to expose the implant to the oral cavity (Figure 20-10). This exposure is performed 4 to 6 months after implant placement and after proper bone healing has occurred.

In 1990 Schnitman et al. reported on the success of immediate loading of dental implants. This technique eliminates the need for a second surgery and allows the implant to be used immediately to support a temporary or permanent prosthesis (Figure 20-11). There are mixed results regarding the success rates between immediately loaded and conventionally loaded implants. While the success rates vary, there

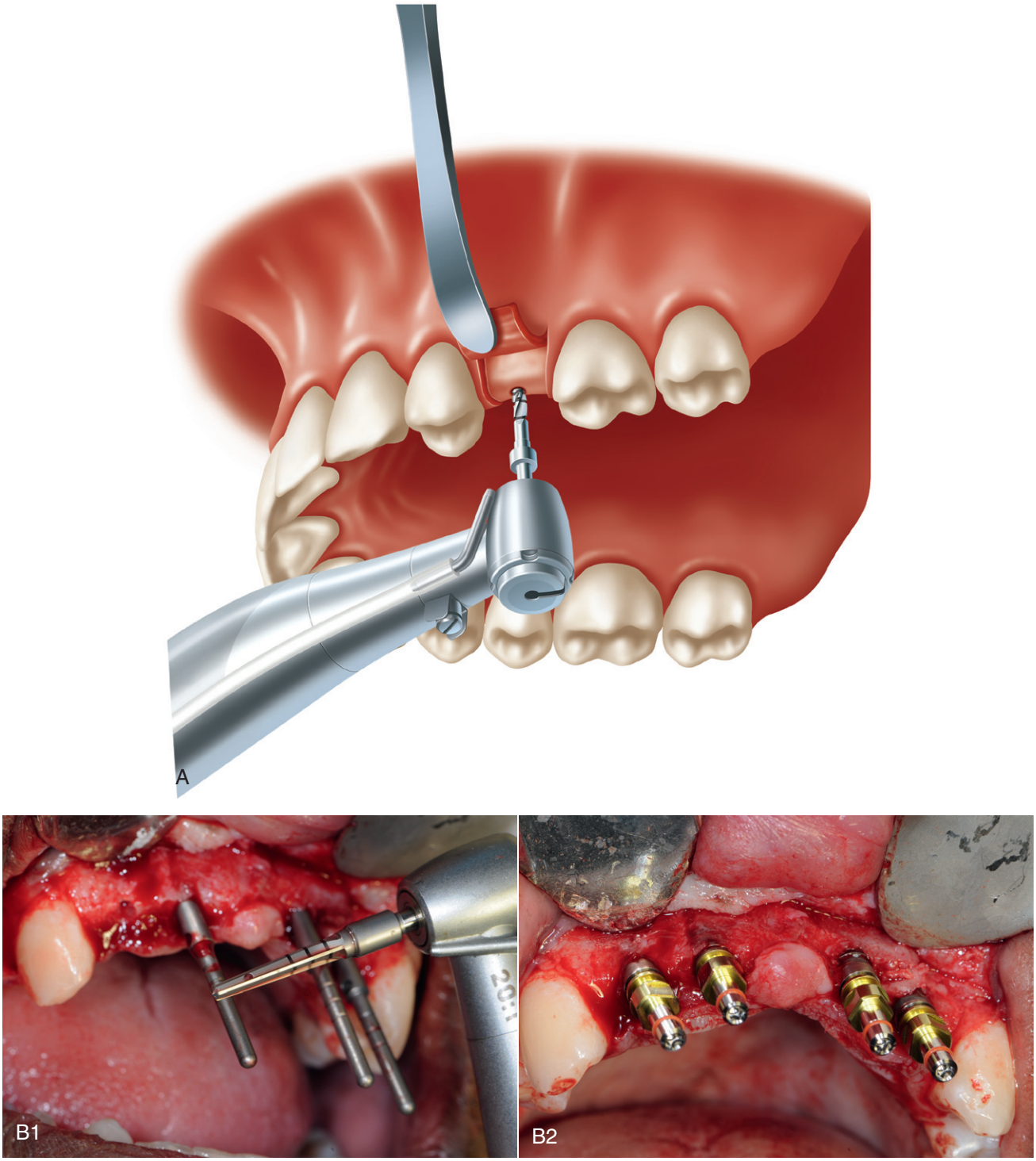


FIGURE 20-9 Stage 1 surgery for implant dentistry involves placing the implant in bone. **A,** Several drills are needed to accommodate the size of the implant in bone. **B,** Osteotomies must be double checked for parallelism and proper positioning. Multiple implants being placed must be verified with placement pins. (Part A ©2012 Zimmer Dental Inc., all rights reserved. Part B From Garg AK: *Implant Dentistry*, ed 2, St. Louis, Mosby, 2010.)

is consensus that immediate loading constitutes a more technique-sensitive process and patient-selective endeavor. Researchers conclude that if these guidelines are followed, the success rates for immediately loaded implants are more favorable. As with conventional implants, primary stability is important in achieving proper osseointegration. The problem with immediately loading implants is that micromovement can occur and jeopardize the bone formation around the implant body. However, research has shown that there is a range of allowable micromovement from 30 to 150 μm, where

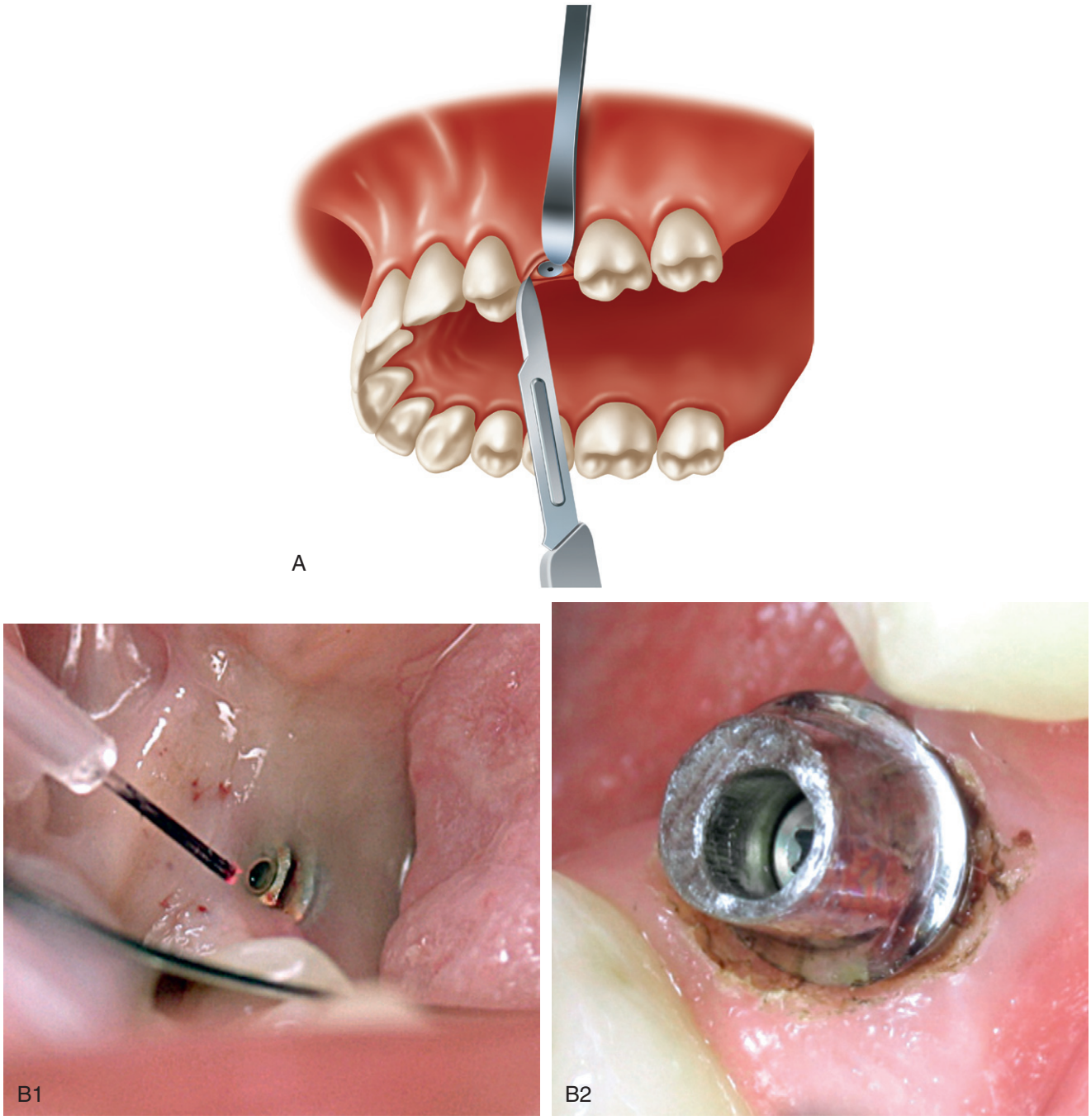


FIGURE 20-10 Stage 2 surgical technique where implants are exposed to the oral cavity after proper bone healing has occurred. Uncovering can be done by several methods. **A,** Technique using standard incision. **B,** Stage 2 technique utilizing laser surgery. (Part A ©2012 Zimmer Dental Inc., all rights reserved. Part B From Garg AK: *Implant Dentistry*, ed 2, St. Louis, Mosby, 2010.)

bone deposition is not hindered. The advantages of immediate loading are shorter treatment times, which lead to greater patient convenience and comfort by reducing the number of surgeries and allowing the immediate placement of a prosthesis.

Late-stage failures occur after loading or placement of a prosthesis and can be the result of complications stemming from uncontrolled periodontal disease or overloading of the implant. Overloading can be due to lateral or oblique forces exerted on the prosthesis from improper occlusal loading or parafunctional habits. Bone is susceptible to microfractures or fatigue fractures, depending on the type and amount of occlusal load being exerted. Once the bone reaches the tolerance limit for the occlusal loads, these fractures can occur and can lead to implant failure. Excessive bone deformation has been shown to occur between 2000 and 3000 microstrain

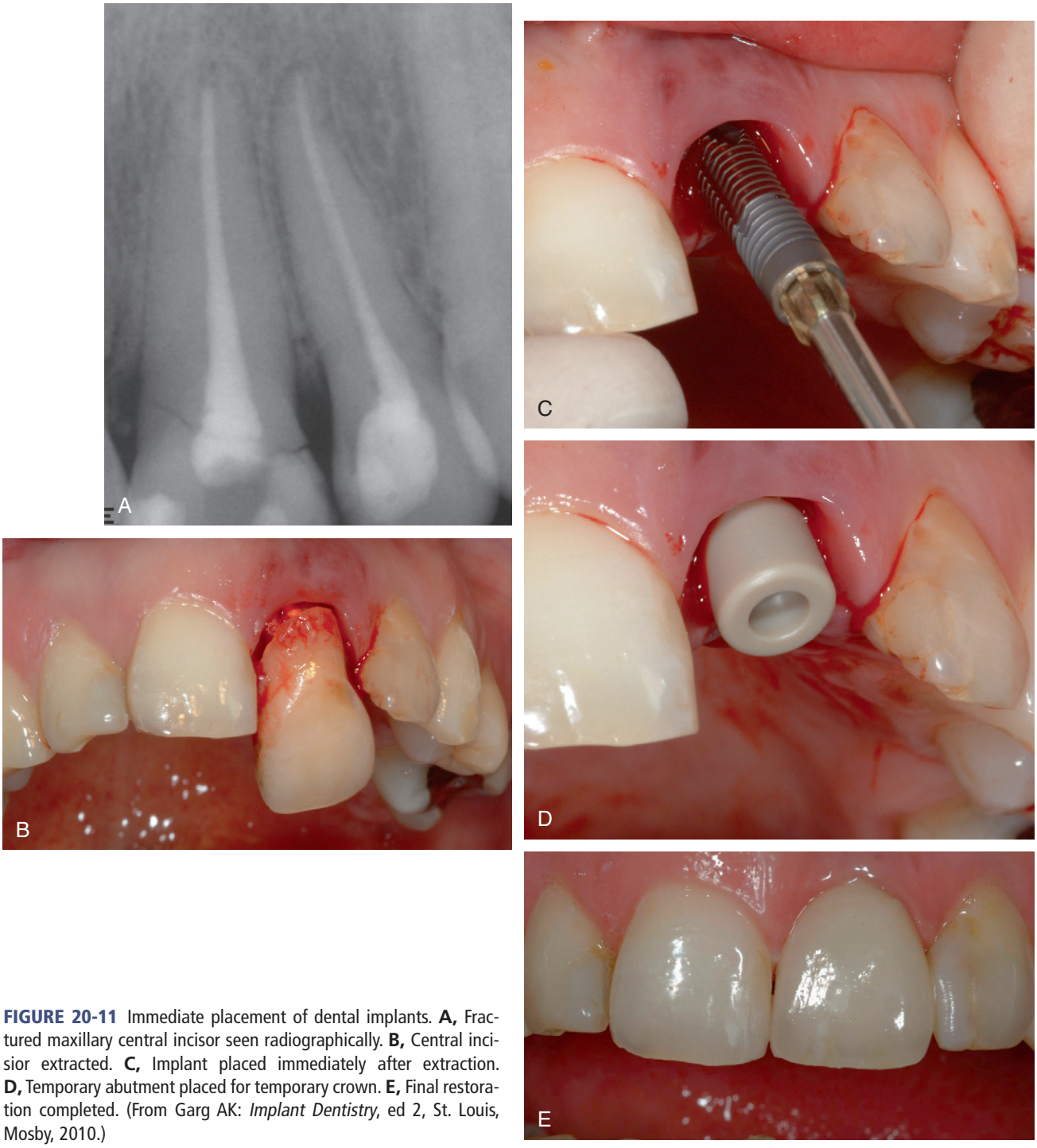


FIGURE 20-11 Immediate placement of dental implants. **A,** Fractured maxillary central incisor seen radiographically. **B,** Central incisor extracted. **C,** Implant placed immediately after extraction. **D,** Temporary abutment placed for temporary crown. **E,** Final restoration completed. (From Garg AK: *Implant Dentistry*, ed 2, St. Louis, Mosby, 2010.)

units, and pathological overloading can be seen at over 4000 microstrain units (a microstrain unit equals the strain that produces a deformation of one part per million).

? CRITICAL QUESTION

Which factors in the implant and prosthesis design affect the load transfer to bone?

A delicate balance must be achieved in load transfer from implant to bone to maintain proper bone health. Excessive occlusal forces lead to overloading of the bone surrounding the implant, which can, in turn, lead to bone resorption and microfracture. Conversely, minimal load transfer to bone can lead to bone atrophy from disuse. Rough surfaces along the implant are typically conducive to transferring more load to the bone due to the increased surface area contact. This reduction in localized stress decreases the strain around the

implants. On the other hand, smooth-surfaced implants have the opposite effect, as evidenced by resorption along the marginal areas, where there is a smooth transition from the implant to bone.

The type of prosthesis used can also have an effect on how the forces are transferred along the implants. Prosthesis design should minimize long cantilever arms so as to avoid offset loads or high bending moments on the implants. Lateral forces are not tolerated as well as direct axial loading. Cement-retained prostheses have been found to be more favorable in maintaining proper axial loading as opposed to screw-retained restorations. The absence of a screw hole allows proper occlusal design for the prosthesis to adequately direct loading to the implant. Conversely, the presence of a screw hole will redirect occlusal forces and introduce bending moments to the implant.

? CRITICAL QUESTION

Which biomaterial is best for certain types of implants?

IMPLANT BIOMATERIALS

Today, implant materials are subjected to significant scientific scrutiny, which includes regulatory approval of implant devices used in vivo. The most commonly used implant materials are made from metallic biomaterials. Implants also differ in the nature of their surface condition. Some implants are machined and finished; others are coated with different types of biomaterials. Of the four types of implants, endosteal implants are the most commonly used for dental applications. Thus, the nature of the biomaterials used for these devices is a central focus of the following discussion.

METALLIC IMPLANTS

Metallic implants undergo one or more of several surface treatments prior to final packaging for implantation. Some of these modifications include **passivation**, **anodization**, **ion implantation**, and **texturing** by several different methods. *Passivation* refers to the enhancement of the oxide layer to minimize the release of metallic ions as a result of surface transfers. The minimization of ion release contributes to the **biocompatibility** of these materials. Passivation treatments can be performed through immersion in 40% nitric acid or anodization, a process by which an electrical current is passed through the implant when it is placed in a specialized solution. The former method of treatment minimally increases the thickness of the oxide layer, whereas the latter treatment can result in a thicker oxide layer, which has been shown to be beneficial in enhancing corrosion resistance. Surface texturing increases the surface area of the implant and enhances tissue interactions by increasing the area through which stresses are transferred to bone. This is accomplished by several methods, including plasma spraying with titanium, acid etching, and blasting with aluminum oxide or another ceramic or ceramic-like material. It is important that the increased implant surface area remain passive, because a greater surface area influences the overall release of metallic ions. Another surface modification for the implant is ion implantation, which consists of bombarding the surface of the implant with high-energy ions up to a surface depth of a few micrometers. This procedure has been claimed to increase the corrosion resistance of the metal through the formation of a titanium nitride TiN surface layer if the ion is nitrogen.

The most popular implant biomaterials in use today are titanium, titanium alloy, and calcium-phosphate–coated materials. One result of the current extensive research focus is that titanium has become one of the most popular implant biomaterials. Titanium exists in nature as a pure element with an atomic number of 22. With an atomic weight of 47.9, titanium makes up about 0.6% of the earth's crust and is a million times more abundant than gold. This metal exists as rutile (TiO_2) or ilmenite ($FeTiO_3$) compounds and requires specific extraction methods to be recovered in its elemental state. The Kroll process involves reduction of $TiCl_4$ by magnesium, whereas the iodide process involves formation of titanium iodide through the reaction of titanium with iodine. The titanium iodide is later decomposed on a heated titanium wire. Titanium has several favorable physical properties, which include low density of 4.5 g/cm^3 and a relatively high flexure strength comparable to that of cast forms of cobalt and stainless steel alloys. Titanium is also very resistant to corrosion; as a result of this property, it can be passivated by a thin layer of titanium oxide, which is formed instantly on its surface. This metal has the ability to form an oxide layer of nanometer thickness within a millisecond, and this oxide reforms if lost because of mechanical removal. If left unchecked, this oxide layer can become thicker over time. Pure titanium has the ability to form several oxides, including TiO, TiO_2, and Ti_2O_3. Of these, TiO_2 is considered the most stable and is found after exposure to physiological conditions.

The most commonly used titanium products are grades 1 to 4 of unalloyed Ti. Titanium alloys, namely, Ti-6Al-4 V and Ti-6Al-7Nb, are used in extralow interstitial (ELI) grades. The ELI contains low levels of oxygen dissolved in interstitial sites in the metal. Lower amounts of oxygen and iron improve the ductility of the ELI titanium alloy, which can be alloyed with different elements to modify its properties. For example, titanium undergoes a transformation from a hexagonal-close-packed alpha phase to a body-centered-cubic beta phase at 883 °C. Alloying elements can be added to stabilize either phase. Ti-6Al-4 V is one of the titanium alloys more commonly used in the United States. Aluminum acts as an alpha stabilizer for the purpose of increasing strength and decreasing density. Vanadium is a beta-phase stabilizer, which is used to minimize the formation of $TiAl_3$ to approximately 6% or less and to decrease the alloy's susceptibility to corrosion. With the exception of pure titanium, the modulus of elasticity of Ti-6Al-4 V is closer to that of bone than that of any other widely used metallic implant biomaterial. Newer titanium alloys have been developed, including Ti-13Nb-13Zr and Ti-15Mo-2.8Nb. These alloys utilize other phase stabilizers instead of aluminum and vanadium, and they may exhibit greater strength and corrosion resistance.

TABLE 20-3 Composition of CP Titanium and Alloys (Percent by Weight)*

Titanium	N	C	H	Fe	O	Al	V	Ti
CP grade I	0.03	0.08	0.015	0.20	0.18	—	—	Balance
CP grade II	0.03	0.08	0.015	0.30	0.25	—	—	Balance
CP grade III	0.05	0.08	0.015	0.30	0.35	—	—	Balance
CP grade IV	0.05	0.08	0.015	0.5	0.4	—	—	Balance
Ti-6Al-4 V alloy	0.05	0.08	0.015	0.3	0.2	5.50–6.75	3.50–4.50	Balance
Ti-6Al-4 V (ELI alloy)	0.05	0.08	0.012	0.25	0.13	5.50–6.50	3.50–4.50	Balance

*ASTM Standard: minimum values.

As listed above, commercially pure (CP) Ti comes in different grades, from CP grades I to IV. The compositions of these metals in weight percentage are given in Table 20-3. The strength of CPTi is less than that of Ti-6Al-4V alloy, although the modulus of elasticity values are comparable. The elastic modulus of a typical Ti alloy (113 GPa) (see Table 20-1) is only slightly higher than that for the CP grade IV Ti (102 GPa). The yield strength of Ti-6Al-4V ELI and Ti-6Al-4V alloys (795 MPa and 860 MPa, respectively) is 65% to 78% greater than that for CPTi. Ti alloys are able to maintain the fine balance between sufficient strength to resist fracture under occlusal forces and to retain a lower modulus of elasticity for more uniform stress distributions across the bone-implant interface.

Another alloy used for surgical implants is stainless steel. Used in the form of surgical austenitic steel, these metals have 18% chromium for corrosion resistance and 8% nickel to stabilize the austenitic structure. Stainless steel is most often used in the wrought and heat-treated state and possesses high strength and ductility. Despite its low cost and ease of fabrication, this alloy is not widely used in implant dentistry because of a potential allergic response to nickel as well as a susceptibility to crevice and pitting corrosion. The corrosion products for stainless steel contain iron, chromium, nickel, and molybdenum. These elements or their ions can accumulate in the tissues surrounding the implant and subsequently be transported to different parts of the body to produce a potentially unfavorable response. Surface treatments such as surface passivation and ion implantation are used to improve the corrosion resistance, although austenitic stainless steels are still prone to localized attack in long-term applications.

Cobalt-chromium-molybdenum cast alloys generally consist of 63% cobalt, 30% chromium, and 5% molybdenum with small amounts of carbon, manganese, and nickel. Molybdenum is a stabilizer; chromium provides the passivating effect to ensure corrosion resistance; and carbon serves as a hardener. Vitallium was introduced by Venable in the late 1930s and is part of the Co-Cr-Mo alloy family. This metal was initially shown to lack electrochemical activity and any tissue reaction. Ticonium, a Ni-Cr-Mo-Be alloy, was also used as a dental implant material, although this alloy revealed some adverse issues related to corrosion and biocompatibility. In later studies, Vitallium was associated with chronic inflammation and no osseous integration for several endosteal and subperiosteal designs. In an attempt to improve implant performance, inert biomaterials in the form of aluminum oxide and other ceramics were deposited on alloy surfaces. Aluminum oxide and zirconium oxide coated on cobalt alloys were found to have no effect on improving biological acceptability of the implants evaluated. Co-Cr-Mo alloys have a high elastic modulus and resistance to corrosion. The additions of ceramic coatings such as calcium phosphate did not significantly alter the bulk portions of the alloy. Studies of cobalt alloys have shown that their lower ductility is a result of the agglomeration of compounds rich in carbon, chromium, and molybdenum. Also, studies have shown that ductility is improved by reducing the carbon content and controlling the processing of the alloy. Co-Cr-Mo and stainless steel alloy continue to be used for some implants, such as subperiosteal and transosteal implants and ramus frames, because of their castability, mechanical properties, and lower cost.

CERAMIC AND CERAMIC-LIKE COATED IMPLANT SYSTEMS

Several synthetic and biological materials have been used specifically for the treatment of bone defects, ridge augmentation, and osteoporotic lesions. These biomaterials are also used to coat metallic implants to produce ceramic-like surfaces, which can be more thermodynamically stable, hydrophilic, and nonconductive of heat and electricity, thereby producing a high-strength integration with bone and the surrounding tissues. These ceramics can either be plasma-sprayed or coated onto the metallic implant to produce a bioactive surface. The term *bioactive* refers to a variety of inorganic biomaterials that can enhance integration with bone. These are generally brittle and may have high elastic moduli and low tensile strengths.

Ceramic implants can withstand only relatively low tensile or shear stresses induced by occlusal loads, but they can tolerate quite high levels of compressive stress. Aluminum oxide (Al_2O_3) is used as a standard biomaterial for ceramic implants because of its inertness (biostability), with no evidence of adverse in vivo reactions. Zirconia (ZrO_2) has also demonstrated a high degree of inertness, although alumina (Al_2O_3) has shown a higher surface wettability compared with other surfaces, such as those of metallic implants. These types of ceramic implants are not bioactive in that they do not promote the formation of bone. They have high strength, stiffness, and

hardness and function very well for some designs of dental implants. Table 20-1 lists the mechanical properties of different metallic biomaterials, including ceramic implant biomaterials.

Of the synthetic types of materials, calcium phosphates are the most successful for grafting and bone augmentation. This performance is probably associated with the fact that bone is composed of 60% to 70% calcium phosphate. These materials are nonimmunogenic and are biocompatible with host tissues. The two most commonly used calcium phosphates are hydroxyapatite (HA), or $Ca_{10}(PO_4)_6(OH)_2$, and tricalcium phosphate (TCP), $Ca_3(PO_4)_2$. Hydroxyapatite and tricalcium phosphate are used as bone graft materials in granular or block form to serve as a template for the formation of new bone. Because these materials are known to promote and achieve a direct bond of the implant to hard tissues, they are classified as bioactive. Both also promote vertically directed bone growth as well as a relatively strong bond to bone.

Biointegration is defined in the seventh edition of the *Glossary of Prosthodontic Terms* as "the benign acceptance of a foreign object by living tissue." More specifically, the biointegration of bone with an implanted material indicates the bond of bone to hydroxyapatite. HA, TCP, and other calcium phosphates are bioactive in part as a result of the release of calcium and phosphate ions within the surrounding tissue. Studies have revealed several differences in the tissue response to these materials following implantation. The beta form of TCP is resorbed more rapidly than HA and results in a breakdown of TCP. Some have reported a replacement of mesenchymal cells with features resembling osteoprogenitor cells. Studies have also shown that after 4 weeks of implantation, osteocytes accumulate adjacent to HA granules, indicating the possibility of osteogenesis with these implants. This is one of the justifications for using calcium phosphate compounds for coatings on implants placed into bone.

Use of these calcium phosphates as coating biomaterials for metallic implants is directly related to their physical and chemical properties. The more crystalline the HA coatings, the more resistant they are to clinical dissolution. A minimum of 50% crystalline HA is considered a preferable concentration for coatings. Implants coated with HA have shown a wide range of properties, from 85% crystalline HA and 15% TCP to 97% crystalline HA. Dissolution of the coating occurs at a higher rate with the more amorphous structural conditions. Heat treatment after the deposition process improves the crystallinity of HA. The major advantage of these ceramic-like coatings is that they can stimulate the adaptation of bone and very often exhibit a more intimate bone-to-implant contact compared with a metallic surface. The amount of bone integration has been compared between metallic implants and ceramic-coated implants in numerous studies, which suggest that there is a greater bone-to-implant integration with the HA-coated implants. However, other studies indicate that there is no significant difference between the HA-coated and the uncoated implants after months of integration, which implies that early integration may be quite different.

The bioglasses (SiO_2-CaO-Na_2O-P_2O_5-MgO) are another form of bioactive ceramic biomaterials. These materials are known to form a carbonated hydroxyapatite layer in vivo as a result of their calcium and phosphorus content. The formation of this layer is initiated by the migration of calcium, phosphate, silica, and sodium ions into tissue as a result of external pH changes. A silica-rich gel layer forms on the surface as elements are released. The silicon depletion initiates a migration of calcium and phosphate ions to the silica gel layer from both the bioglass surface and tissue fluids. This results in the formation of a calcium-phosphorus layer that stimulates osteoblasts to proliferate. These osteoblasts produce collagen fibrils that become incorporated into the calcium-phosphorus layer and are later anchored by the calcium-phosphorus crystals. This layer is 100 to 200 µm thick and has been shown to form a strong bone-bioglass interface. Bioglasses are classified as bioactive materials because they stimulate the formation of bone. They are more often used as grafting materials for ridge augmentation or bony defects than as coating materials for metallic implants because the interfacial bond strength of bioglasses with the metallic substitute and other ceramic substrates is weak and is subject to dissolution in vivo. Despite their favorable **osteoinductive** ability, bioglasses are also very brittle, which makes them unsuitable for use for some stress-bearing implant applications.

OTHER IMPLANT MATERIALS

Carbon and a carbon compound (C and SiC) were introduced in the 1960s for use in dental implantology. Vitreous carbon, which elicits a very minimal response from host tissues, is one of the most biocompatible materials. Studies have confirmed that the morphology of the bone-implant interface is similar to that associated with an HA implant. Compared with the metallic implants, carbon is more inert under physiological conditions and has a modulus of elasticity similar to that of dentin and bone. Thus, carbon deforms at a rate similar to those tissues, enhancing the transmission of biomechanical forces. However, carbon is susceptible to fracture under tensile and stress conditions because of its brittleness and its susceptibility to fracture under tensile stress in the presence of surface flaws, which is usually generated as a component of flexural loading. Carbon-based biomaterials have also been used for ceramic-like coatings on metallic implants.

? CRITICAL QUESTION

What are the indications for the use of mini-implants in dental practice?

Mini-implants have been gaining wide popularity in recent years. More notably, their use in orthodontics for appliance anchorage has increased. Other uses include overdenture retention in areas where there is minimal bone available or in areas that are narrow. They can also be used to anchor temporary prostheses in the case of overdentures on an arch

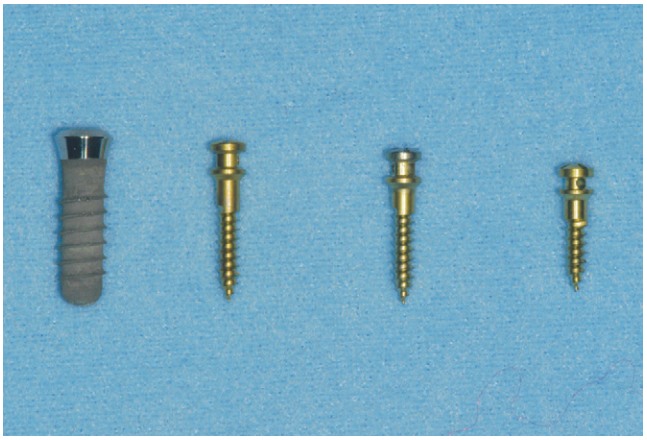


FIGURE 20-12 Mini-implants used for orthodontic anchorage, showing 2-mm diameter of the mini-implants as compared with the 4-mm diameter of standard implants.



FIGURE 20-13 Four qualities of bone.

with newly extracted teeth. These implants were initially used as temporary implants, which helped anchor the prosthesis while the larger-diameter implants were left alone to osseointegrate. They could then be removed once the final prosthesis was fabricated. Over time, the success of these mini-implants has led to their evolution as final restorations for compromised cases. The diameter of mini-implants ranges from 1.8 to 2.9 mm (Figure 20-12). Most mini-implants can be placed without having to reflect a flap in the gingival tissue because of their small diameter. Mini-implants are also designed for immediate loading, offering the convenience of few visits and allowing the patients to have teeth right away. Although these implants are essentially made from the same material as the larger standard implants and are constructed as root-form implants, the main difference lies in their smaller diameter. This smaller size allows placement of these implants in areas where standard implants would normally require a bone grafting procedure, which results in additional trauma and expense to patients. As the applications of mini-implants continue to grow, they are slowly being incorporated for use with fixed dental prostheses, adding additional support along the pontic areas.

? CRITICAL QUESTION

With the abundance of implant materials to choose from, how does a clinician know which biomaterial is best for a particular implant application?

SELECTING AN IMPLANT BIOMATERIAL

Because of the abundance of different implant biomaterials and implant systems, it is important to know the indications for their use. Perhaps the most important consideration is the strength of the implant biomaterial and the type of bone in which the implant will be placed. The other factors to consider are the implant design, abutment choices, abutment availability, surface finish, and biomechanical considerations of restorative treatments.

The strength of an implant is often a consideration, depending on its area of placement. If the implant is located in a zone of higher force transfer (e.g., in the posterior area of the arch), the clinician might consider using a higher-strength material such as grade IV CP titanium or one of the titanium alloys. Some controversy exists as to which titanium metal or alloy to use, because some researchers believe that aluminum and vanadium can be **toxic** if released in sufficient quantities. Other considerations for selection include a history of implant fracture in the placement area of interest, the use of narrower implants, and a history of occlusal or parafunctional habits. Anterior implants, which are designated for use in narrow spaces, have smaller diameters, in the range of 3.25 mm or less. Conversely, single implants placed in posterior areas have larger diameters, up to 7 or 8 mm. Selection of the implant biomaterial must also be evaluated in terms of the abutment and intraoral biomaterials and dental materials. Electrochemical studies of the corrosion of metallics now provide lists of acceptable and unacceptable combinations under conditions where parts touch one another and galvanic corrosion might exist. In general, the titanium and cobalt alloys are relatively stable and both have been combined electrochemically with the high noble dental alloys. Base metal and amalgam combinations are a concern.

? CRITICAL QUESTION

How do implant characteristics and the quality and quantity of bone affect the survival time of implants?

As previously stated, the type of bone in which the implant will be placed is of critical importance. Bone for implantation has been classified into four types: type I consists of mostly homogeneous compact bone; type II consists of a thick layer of compact bone surrounding a core of dense trabecular bone; type III is a thin layer of cortical bone surrounding a core of dense trabecular bone; and type IV is composed of a thin layer of cortical bone with a core of low-density trabecular bone (Figure 20-13). Type IV bone is by far the most compromised bone environment for implant stability because of its inadequate quality and quantity.

There has been much debate about when to use metallic or HA-coated implants. As mentioned earlier, HA-coated implants stimulate bone growth and have been shown to have a greater percentage of bone-to-implant integration. However, there are also some studies showing that HA is a very unstable implant material under some conditions (inflammation, infections, micromotion) and can prove detrimental to bone and tissues in the long term. As one example, Gottlander and Albrektsson (1991) examined the bone-to-implant contact area both at 6 weeks and 12 months for HA-coated and CPTi implants. They concluded that the bone-to-implant contact area at 6 weeks was 65% for HA and 59% for Ti. However, at 12 months, Ti exhibited a 75% contact area versus 53% for HA. Some contend that the interactions of HA with bone are biologically unstable because of this interface exchange. As mentioned earlier, HA can also be subjected to dissolution, and higher crystallinity must be maintained to minimize this occurrence. Unfortunately some amount of amorphous biomaterial is often present during plasma spray processing of the coating, and this substance is susceptible to dissolution. The long-term stability of HA-coated implants is still very controversial. Although the bond between HA and bone is considered to be strong, the mechanical stability of the interface between the coating and the metallic substrate may be unstable under some conditions.

Some studies have shown that the survival rate of HA-coated implants is initially higher than that for titanium plasma-sprayed implants, but in one study, the survival rate significantly decreased after 4 years. Failures were associated with inflammation of the surrounding tissues, with delamination and exfoliation of the implant. Some implants were retrieved before failure; these revealed partial loss of the HA coating, with flattening and thinning in some areas as well as an increase in local Cl and Mg ions. The implications of these factors relative to clinical implant failure remain unknown. Another concern is the adherence of microorganisms to the HA surface. A study of failed titanium and HA-coated implants revealed a colonization of coccoid and rod-shaped bacteria on HA implants, possibly as a result of the bioreactivity of HA. The roughened surface of the HA implants can also contribute to plaque growth, peri-implantitis, and dissolution once the coating is exposed. This can decrease the chance of long-term survival.

In spite of all its possible disadvantages, hydroxyapatite has multiple indications for implant applications. Studies reporting on the biological response to both the coated and uncoated implants suggest that HA-coated implants were interfaced intimately with bone and that the mineralized matrix extended into the microporosity of the HA coating. Numerous osteocytes were found along the periphery of HA-coated implants, which indicates that these implants are a better option for areas of poor bone quality such as the maxilla. In one study, Brånemark-type titanium implants were evaluated in type IV bone and a survival rate of 63% was found for mandibular implants and 56% for maxillary implants. These values are lower than the survival rates of 90% or more when these implants were placed in type I and II bone.

Another study compared the survival rates of titanium screw-type implants and HA-coated cylinders in type IV bone. At 36 months, Ti implants had a survival rate of 78% compared with 98% for HA implants. At 48 months, this survival rate fell to 75% for the metal implants. In a follow-up study, titanium screws exhibited a 91% 3-year survival rate and 89% for a 7-year period in type IV maxillary bone. These rates can be compared with a survival level of 95% for HA implants during a 7-year period. All of these studies indicate that HA-coated implants have a greater survival rate in type IV bone. Therefore, many recommend the use of HA-coated implants in areas of poor or less than ideal bone as sites for implant placement. The bone height available for implant placement is also a factor in considering which type of implant to use. A 5-year study revealed a 70% failure rate in bone for titanium screws with an implant length of 8 mm. HA-coated screws of the same length had only a 4% failure rate over this period. There was no significant difference in the failure rates between the two types of implants when the length of the screws was increased to 12 mm.

Another indication for HA-coated implants was their use in fresh extraction sites, owing to the initial stability afforded by these types of implants. Implant placement can sometimes be performed immediately after an extraction. Initial stability has been reported to be difficult to obtain in some of these cases, and this could lead to implant loss. A comparison of the survival rate of HA-coated implants, metallic implants, and hollow basket implants was made after 7 years of immediate implant placement. Survival rates of 95%, 90%, and 82% were found, respectively. The implant-bone interface contact area was also shown to be 62% for HA-coated implants and 29% for metallic implants after 28 days of placement.

Further advances in the field of dental surgery have allowed placement of implants in areas where bone was not normally present or had been lost. Maxillary and nasal sinus lifts are commonplace in partially dentate individuals who need an implant-based reconstruction. Bone grafts have enabled placement of a sinus lift in posterior areas where bone is deficient. Unfortunately, the quality of bone produced from these bone grafts is of lower quality, and an implant needs a substantial implant-bone contact area for function. Most of these implant sites oppose fully dentate arches, which normally exert a higher amount of masticatory force. Thus, initial stability, enhanced bone integration, and higher strength are important implant properties for these locations. Studies have revealed that HA-coated implants exhibited a push shear bond strength of 7 MPa versus 10 MPa for titanium metallic implants after a period of 10 weeks. After 32 weeks, HA-coated implants continued to have shear strengths five times greater than those of metallic surface implants.

Another study compared the torsional strength of commercially pure titanium, Ti-6Al-4V, and HA-coated implants. Tensile strength for a period of up to 4 months ranged from 74 Ncm for the uncoated implants to 186 Ncm (HA-coated implants). These torsion-resistance values reflect the rotational shear resistance of the implant. Thus, HA-coated implant surfaces in this circumstance provided greater

implant-bone interface area, higher shear tolerance, and higher torsional strengths in areas where a sinus lift procedure had been conducted.

A meta-analytic review was reported on the overall performance of coated and uncoated implants. It suggests that the survival rates are similar for both and that the HA coating did not compromise the long-term survival of these implants. Indications from reviews supporting the selection of HA-coated implants over titanium- or metal-surfaced implants include (1) the need for greater bone-implant interface contact area, (2) the ability to place the implant in type IV bone, (3) fresh extraction sites, and (4) newly grafted sites. It has also been shown that the advantages of HA-coated implants are mainly short term in nature and are related to the initial stability of the implant, which most often determines its prerestorative success or failure.

? CRITICAL QUESTION

Several types of biocompatibility test data may be useful in selecting an appropriate implant. What is the principal factor on the basis of which an implant material should be selected as suitable or unsuitable for osseointegration?

BIOCOMPATIBILITY OF IMPLANTS

The concept of biomaterial biocompatibility does not refer to total inertness but rather to the ability of a material to perform with an appropriate response in a specific application. Biocompatibility is affected by the intrinsic nature of the material as well as its design and construction. Therefore the state of biocompatibility may be specific to a particular situation or function. The American Dental Association outlines some acceptance guidelines for dental implants, including the following: (1) evaluation of physical properties that ensure sufficient strength; (2) demonstration of ease of fabrication and sterilization potential without material degradation; (3) safety and biocompatibility evaluation, including cytotoxicity testing, and tissue interface characteristics; (4) freedom from defects; and (5) at least two independent longitudinal prospective clinical studies demonstrating efficacy.

The primary surface interactions between an implant material and its host take place at the surface of the implant within a region of approximately the size of one water molecule (about 0.1 to 1.0 mm). However, this does not mean that the implant-tissue interactions are isolated to this interface. Some studies have reported high titanium levels in both the spleen and lungs of rabbits immediately following surgery, but these concentrations were well within normal limits. In humans, Ti levels have been reported at 50 ppm, but they can reach levels of up to 200 ppm in tissues surrounding some titanium implants. At this level tissue discoloration may be visible, but it is still well tolerated by the body. Kasemo and Lausmaa (1991) demonstrated the dissolution of corrosion products into the bioliquid and adjacent tissues. Thus the outermost atomic layers of an implant are critical regions associated with biochemical interactions of the implant-tissue interface. These reports emphasize the importance of process controls and a high degree of standardization and surface cleanliness in the production of implants.

? CRITICAL QUESTION

What are the important considerations for intraoral prosthesis design and material?

BIOMECHANICS

The integration of bone with implants serves as the basis for the biomechanical analyses performed for dental implants. Close approximation of bone-integrated conditions with the surface of an implant permits the transfer of forces and site-specific stresses with elastic displacement of the bone and implant. The stresses that are generated are highly affected by four main considerations: (1) masticatory factors (frequency, bite force, and mandibular movements); (2) support for the prosthesis (implant-supported, implant-tissue-supported, implant-tooth-supported; (3) the mechanical properties of the materials involved in the implant restoration (elastic modulus, ductility, fracture strength, etc.); and (4) the design of the implant body and the associated intraoral prostheses. One of the most important variables affecting the close apposition of bone to the implant surface is the relative movement, or micromotion. It has long been documented that movement shortly after implantation prevents the formation of bone and encourages the formation of fibrous connective tissue around the implant surface. This collagen-rich connective tissue is known to be of lower modulus and strength and function is likely to change over time. This is the reason that a delay of months for intraoral restoration has been recommended before loading after surgery. As mentioned previously, success has been reported with immediate loading of implants depending on bone quality, patient selection, and short-term controls of intraoral function. The key issue is control of implant-to-tissue micromotion during the initial healing of bone.

Numerous studies have defined the relationships for the response of bone to the types of biomechanical stresses and strains and their magnitudes. The results have been summarized as the "frost paradigm," where microstrain magnitudes are correlated with bone conditions of disuse atrophy (less than 500 με), normal function (500 to 1500 με), and microtrauma (more than 500 με). This concept is depicted schematically in Figure 20-14. This paradigm affords opportunities to evaluate implant and construct designs on a relative basis using finite element models and analyses (FEM/FEA). Once again, this literature is well developed.

Two main types of loading conditions can occur at an implant site. These are represented by axial forces and bending moments caused by noncentric loading conditions. A bending moment can best be demonstrated by visualizing a cantilever beam design in which the maximum bending moment is located at the fixed base of support and is calculated as force (perpendicular to the beam) times the length of the lever arm.

These bending moments become highly significant depending on the type and design of implant restoration planned.

Rangert (1989), Skalak (1983), and Brunski (1988) analyzed the theoretical effects of cantilever length, number of implants, arrangement of implants, and prosthesis design. Their models were based on the initial Brånemark hybrid prosthesis for the atrophic mandible (Figure 20-15). This type of restoration usually involves four to six implants confined to the area between the mental foramen of the mandible, with cantilevers extending from the most distal implant. These were restored with acrylic resin and denture teeth, which were attached to a metallic superstructure by the use of several types of attachment methods. The most significant aspect of these studies is the optimal ratio of the cantilever length to the interfixture distance.

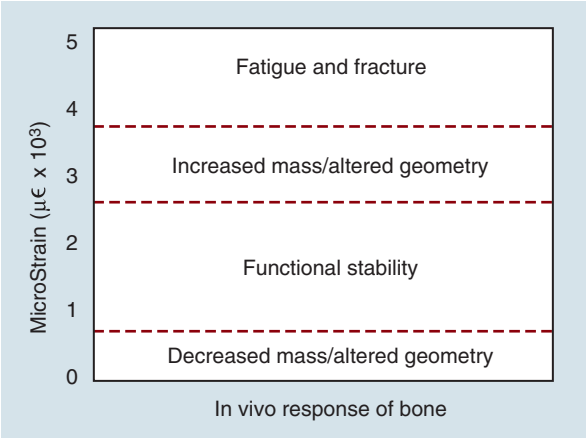


FIGURE 20-14 Schematic diagram of Frost paradigm.

When two or more implants are placed in a straight line, the bending moment will be distributed proportionately to the implants provided that the intraoral prosthesis is designed to be sufficiently rigid. Placement of the implants in an offset manner has been suggested for more favorable positioning because it redistributes the implant loading. However, some recent studies have shown that tripodization of implants does not necessarily minimize stresses as much as the use of wider-diameter implants placed in a straight line. An increase in the anteroposterior placement of implants is also recommended to minimize the off-axis loading of the implant components. The load is greatest at the most distal implant when an anteriorly positioned cantilever prosthesis exists. Thus, the distance between the most terminal abutment and the one adjacent to it should be increased to reduce the stress and stain induced within the most distal abutment.

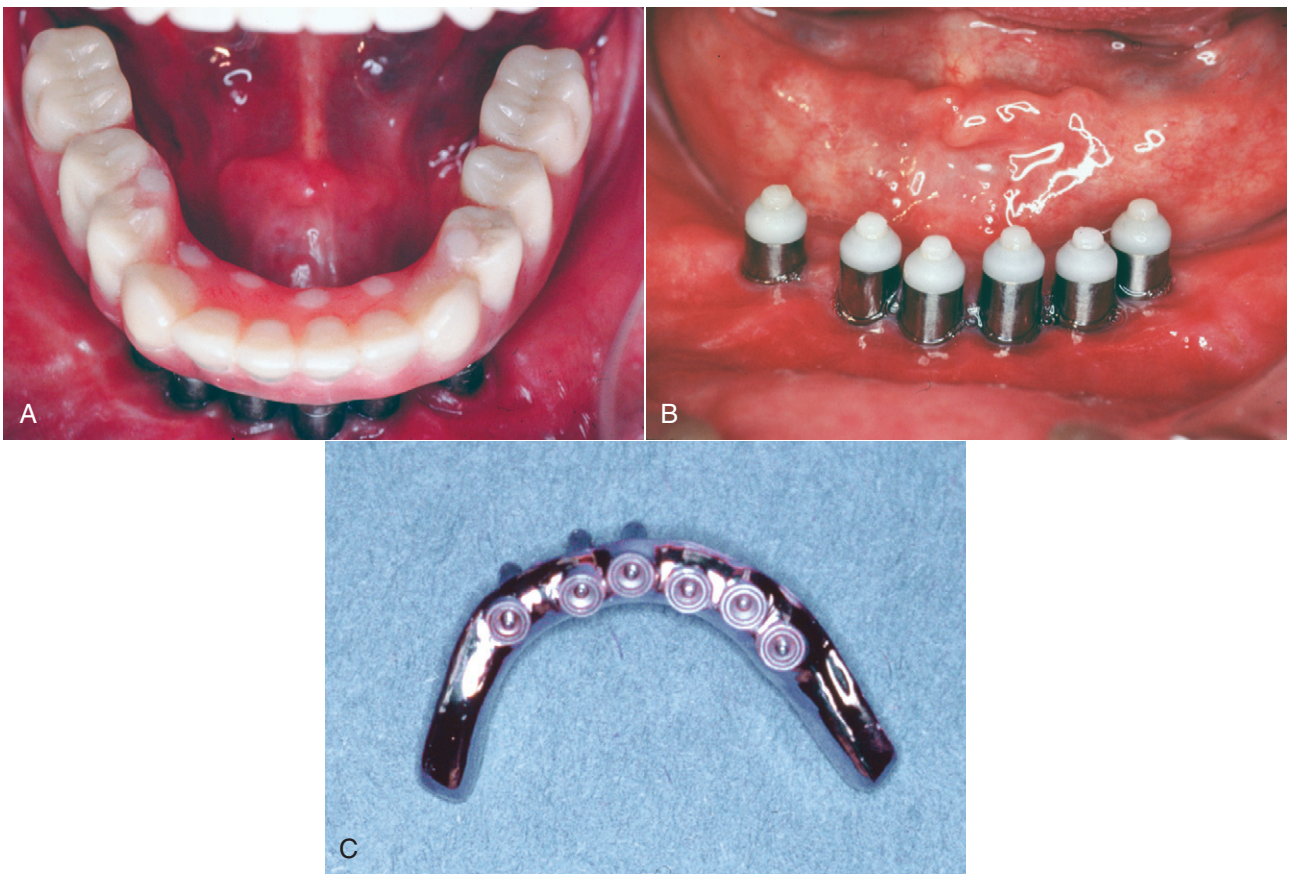


FIGURE 20-15 **A,** The original Brånemark hybrid prosthesis designed to accommodate severely atrophic mandibles. **B,** The hybrid prosthesis usually utilizes four to six implants. **C,** Corresponding superstructure that is screwed onto the implants.

Another important factor to consider is the fit of the prosthesis on the implant. An inaccurate fit will lead to a nonuniform distribution of load, with the unit closest to the load bearing most of the forces. For well-integrated implants, the weakest link in the early systems of Brånemark was the gold or abutment screw, which is regarded as the safety feature for these restorations. The external loads were transferred through the gold screw if an inaccurate fit or overload existed, and the screw would deform and fracture. These screws were fairly retrievable and were easy to replace. The ultimate tensile strength of the gold screw was designed to function within the normal ranges of occlusal force in the molar region.

Some guidelines include computing the anteroposterior span of all the implants and allowing a distance of 1.5 times any cantilever distance while limiting the maxilla to a maximal cantilever of 8 mm because of the limitations of bone quality. Any cantilever length over 7 mm causes a significant increase in microstrain within both the framework and bone. Therefore, for any length over 7 mm, ideal functional conditions should be considered, or the decision to proceed under less ideal conditions should be approached with extreme caution.

Another area of debate is the attachment of implants to natural teeth. The consensus seems to be that attaching implant intraoral prostheses to natural teeth should be limited and that having lone implants is a better restorative option. However, in cases utilizing natural teeth in the restoration (e.g., when a low maxillary sinus position is present), there is disagreement as to whether or not this decreases the survival probability of the entire restoration. This issue stems from the different nature of attachments to bone between the implant and the tooth. The implant is integrated with bone (rigid), meaning that it has a direct connection with bone. On the other hand, a tooth is attached to bone through the periodontal ligament, which provides sensory functions to the tooth and also deforms in response to masticatory loads. Numerous reports have focused on these types of reconstructions; however, they should be approached with caution. Bone formation or resorption is determined by the tension or compression within the periodontal ligament. A concern associated with attachment of an implant to a natural tooth is that the mobility of the tooth might minimize its load-sharing ability and overload the implant, understimulate the tooth, or cause a breakdown of the intraoral prosthesis. Several devices, such as the IMZ intramobile element, have been developed to allow the implant to accommodate the movement of the periodontal ligament. In any event, studies will continue to elucidate the effects of implant and natural tooth attachment on the probability of success. The results from most of the previous studies suggest that the attachment of natural teeth to implants does not compromise the prognosis of the prosthesis. Because these studies also confirm the overall excellent success rates of implant-supported prostheses, it is still recommended that this be the first approach for treatment.

SUMMARY

The implant systems currently available are diverse. In 2011 there were hundreds of companies manufacturing many different systems. The implant biomaterials for the most part range from commercially pure titanium and titanium alloys to HA-coated devices. Manufacturers have developed individualized designs for their implants, which are now mostly root forms, and they are continually altering marketing strategies to highlight the features of each. Although most of the implant materials described in this chapter are believed to be biocompatible, the precise bone-bonding mechanisms are not fully characterized on a molecular level. When the mechanisms that ensure implant **bioacceptance** and structural stabilization are more fully understood, implant failures will become even rarer provided that they are used properly and placed in sites for which they are indicated.

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CHAPTER 21

Emerging Technologies

OUTLINE

Biomaterials

Biological Materials

Instruments and Processes

Environmental Considerations

KEY TERMS

Bioactive—Having an effect on or eliciting a response from living tissue, organism, or cell, such as inducing the formation of hydroxyapatite.

Bioinductive—Capable of inducing a response in a biological system.

Biomaterial—Any matter, surface, or construct that interacts with biological systems.

Biomimetics—Study of the formation, structure, or function of biologically produced substances and materials (such as silk or conch shells) and biological mechanisms and processes (such as protein synthesis or mineralization) for the purpose of synthesizing similar products by artificial mechanisms that mimic natural structures.

CAD-CAM—The term *CAD* refers to computer-aided design technology, which is based on the use of computer software and systems to assist in the creation, modification, analysis, and optimization of two-dimensional or three-dimensional models of objects. Any computer program that embodies computer graphics and an application program that facilitates engineering functions in the design process can be classified as CAD software. The term *CAM* refers to computer-aided manufacturing of a restorative device using the CAD input file. CAM may be additive (buildup) or subtractive (machining of a device from a larger starting piece of material).

Chondrogenesis—The development of cartilage.

Cytology—The harvesting of disaggregated cells and related microscopic material for analysis of disease.

Haptics—Technology that is based on the sense of touch to facilitate computer interactions and control of virtual objects such as the remote control of devices.

Matrix metalloproteinase (MMP)—Any member of a family of at least 19 structurally related zinc-dependent neutral endopeptidases collectively capable of degrading essentially all components of the extracellular matrix.

Nano—The prefix *nano* refers to one billionth or 10^{-9} of a specific unit. A nanometer (nm) is one billionth of a meter (10^{-9} meter) or one thousandth of a micron (10^{-3} μm).

Nanotechnology—The branch of technology that focuses on the atomic and molecular scale (1 to 100 nm) of matter, including materials, devices, and other structures. On this scale, in which at least one dimension must be below 100 nm, quantum mechanics (quantum theory) controls material properties or behavior (Seeman, 2004).

Osteoconductivity—Property of a material that describes its ability to act as a matrix or scaffold and facilitate new bone growth on its surface.

Osteoinductive—The ability of a material to form new bone.

Peri-implantitis—An inflammation that develops in and around the area surrounding a dental implant.

Self-assembling materials—Material systems that automatically transform into prespecified assemblies.

Stem cells—Biological cells in multicellular organisms that can divide by mitosis and differentiate into any one of the 200 or more possible cell types in humans and continuously divide to yield more stem cells of the same type.

Smart materials—Synthetic materials that interact with external stimuli such as light, temperature, stress, moisture, pH, and electric/magnetic fields in such a way as to alter specific properties in a controlled fashion. A key feature of smart behavior is the ability of a material to return to its original state after the stimulus has been removed.

Temporomandibular joint (TMJ)—The junction between the head of the mandible and the temporal bone of the skull.

Voxel—Volumetric picture element that represents a single sample, or data point on a regularly spaced three-dimensional grid.

Emerging applications of dental **biomaterials** are primarily focused on the prevention and treatment of caries, periodontal disease, and oral cancer. The materials being used currently are useful for treating and detecting such diseases, but they need further improvement. Caries prevention treatments have reduced the need for initial restorations, replacement restorations, and removable dentures. Minimally invasive dentistry concepts have led to sealing defective or leaking margins of restorations with sealing resins rather than performing restoration replacement procedures that can destroy healthy adjacent tissue (Mertz-Fairhurst et al., 1998).

The implementation of a cure for caries is likely to take at least 20 more years; therefore, most of the restorative materials in use today will likely remain in use for a decade or more. A cure for dental caries will have a dramatic impact on the use of restorative materials to repair form and function of teeth with cavitated lesions. In the interim, the use of dental amalgam will continue to decline, despite the durability of amalgam restorations, until it is eliminated because of environmental restrictions on mercury release. Improved resin restorative materials will continue to supplant amalgam's use. Before caries can be considered truly "curable," demand will remain high for remineralizing agents, **smart materials**, and durable repair and replacement materials that avoid the need to repeatedly restore a tooth. The need for both repair and replacement will continue because of the time-dependent failure or degradation of the present materials. The developed world has led the way in promoting the use of higher-cost esthetic restorations, sometimes at the expense of durability. Many restorations are being placed for esthetic reasons and not for caries management, a trend that will continue well into the future. The choice of biomaterials for a given clinical situation will continue to be based on a comparative analysis of cost, benefits, and risks.

One should expect dentistry to continue its dependence on developments in materials science and technology, with a focus on the preservation and enhancement of oral health through the prevention of caries and periodontal disease and the rehabilitation of missing, damaged, and destroyed hard and soft tissues. New dental biomaterials must satisfy the following perennial, requirments. They must: (1) be nontoxic to human cells; (2) be toxic to microbes and fungi; (3) be able to form an excellent seal between the oral cavity and underlying tooth structure; (4) be sufficiently **bioactive** to stimulate in vivo repair of tissues that have been damaged by disease, trauma, or dental treatment; (5) have properties similar to the tissue that is to be repaired or replaced; (6) exhibit handling properties that allow ease of manipulation and promote optimal clinical performance; and (7) exhibit an esthetically pleasing appearance.

Over the past 30 years technology has advanced tremendously and has benefited dental materials science in a variety of ways, including laser applications, imaging technologies, composites technology, "smarter" and stronger ceramics, and minimally invasive dental procedures (Garcia and Tabak, 2009). **CAD-CAM** technology has reduced the need for impression materials and has also reduced the time required for fabricating and delivering both fixed and removable devices (Strub et al., 2006). At the time of this writing it has been almost 12 years since Feitas (2000) predicted that the first micron-sized dental nanorobots would be constructed within 10 to 20 years. Such advances are very futuristic and may still not be realized for many decades. However, some of the other technologies foreseen at that time have made substantial progress, including those involving the use of **nanomaterials**, **biomimetics**, tissue engineering, biotechnology, and regenerative dentistry. This chapter reviews technologies that have demonstrated their proof-of-concept potential and have either been **recently** introduced but not yet clinically proven for the long-term or are not far beyond the immediate time horizon. Several new materials that are certain to expand in use are also included.

In the following sections and subsections several technologies are discussed under various headings (**Nanotechnology**, Resin Restorative Materials, Tissue Engineering, Regenerative Dentistry and so on). However, substantial overlap exists among these approaches to various oral health–related problems; therefore any subcategorization is to a greater or lesser extent arbitrary. In the following discussions, the reader will often find that one subject area is necessarily intertwined with another. For example, a major thrust in developing restorative resin composites is to utilize ever smaller reinforcing filler particles. As explained in Chapter 13, this has led to the development of nanoparticle fillers, which overlaps with the field of nanotechnology. In another example, one of the major dental applications of regenerative dentistry uses stem cell biology to promote periodontal wound healing and tissue regeneration, which are also objectives of both biological delivery systems and tissue engineering. So, although tissue engineering does not always involve biological delivery systems or vice versa, it often does and is therefore, categorized separately.

Shown in Figure 21-1 is a flowchart of basic, translational, and clinical research links representing stages in the development and evaluation of emerging technologies and products. The farther to the right of the chart a technology or material is seen, the higher the probability that it will have a desirable clinical outcome.

BIOMATERIALS

Any matter, surface, or construct that interacts with biological systems is considered to be a biomaterial. In the present context only synthetically derived or highly processed nonsynthetic materials are discussed. In dentistry, these are also called dental materials.

NANOTECHNOLOGY

The introduction of microfill restoratives in the early 1970s ushered in the era of dental nanotechnology. As discussed in Chapter 13, microfilled composites contain silicon dioxide (SiO_2) reinforcing particles about 40 nm in diameter that are dispersed in prepolymerized resins that have been ground to form so-called organic filler particles in the micron size

Research stage	Basic research	Applied/transitional research		Clinical trials		Applicability to dental practices	
Technology classification	Emerging technology concepts	Nanotechnology advances	Nanotechnology validation	Established nanotechnology	Integrated nanotechnology and microtechnology	Spin-off technology	Cost-benefit demonstrated
Testing stage	Hypothesis testing	Product evaluation	Bridge between basic/applied and clinical practice	Pilot and retrospective studies	Randomized controlled trials	Performance appraisal	Refinement of technologies
Outcomes	Preliminary data	Comparative performance	Preliminary evidence	Validation of evidence	Promising treatment outcomes	Optimum treatment outcomes	Adoption by clinical practices or dental labs
Stage of technology development	Technologies are feasible		Technologies are imminent or validated		Further refinement needed	Technologies applied to health care tasks	Oral health care goals fully achieved
Level of evidence	Clinical simulation	Proof of concept	Probability of specific outcomes	Limited applicability of technology	Application of refined technology	Demonstrated benefits in lab and clinic tasks	Fully documented and well-established evidence
Level of success	Desirable technologies, materials and devices		Possible future technologies, materials, and devices		Probable future technologies, materials and devices	Likely future technologies, materials and devices	Proven future technologies, materials, and devices

FIGURE 21-1 Flow chart of basic, translational, and clinical research links to develop and evaluate emerging technologies and products.

range. Current microhybrid and nanofilled composites contain filler particles range from about 20 to 600 nm. This use of nanoparticle technology allows the formulation of dental materials with high translucency, excellent initial polish, and retention of gloss while maintaining mechanical properties and wear resistance equivalent to those of current clinically proven hybrid composites. Several 2- to 3-year clinical trials have investigated the nanohybrids performance in a variety of oral restorations and found that the nanohybrids show great promise for extending survival beyond the current 5 to 10 years. Currently, a variety of approaches designed to overcome the deficiencies of nanoparticle composites are in progress. None of these is likely to result in a breakthrough that will lead to a universal esthetic composite that can rival the durability of amalgam. However, there is a high likelihood that many will contribute incremental advantages that, when combined and optimized, will result in such a material by the next decade.

? CRITICAL QUESTION

In which ways will nanotechnology provide products or processes that can improve oral health outcomes?

Other recent applications of nanotechnology in dentistry have focused on the delivery of molecules that promote hard tissue remineralization by noninvasive techniques. In this context, the most promising technology for the nanorestoration of tooth structure is *biomimetics*, the study and use of processes that mimic those that occur in nature, particularly those that involve self-assembly of components to form, replace, or repair oral tissues (Saunders, 2009). These concepts are discussed further later in this chapter.

For dental biomaterials, nanoparticulates have been shown to strongly influence the host response at both cellular and tissue levels, making their use particularly attractive for modifying dental implant surfaces. Electrophoretic, sol-gel and pulsed laser deposition, sputter coating, and ion beam–assisted deposition, among others, are approaches that have been utilized to develop nanotextured thin-film biocompatible coatings for implant surfaces. These technologies reduce the thickness and particle size of the coating layer and thereby increase its specific surface area and reactivity, thus improving the interaction with the surrounding living tissue. See, for example, Bayne (2005) and (Subramani and Ahmed, 2012).

These technologies are at an advanced stage and their use to develop nanosized preparations of various components in dental materials and improve both performance properties and durability in the near future is quite likely. However, it should be noted that nanosized particles and surface features with very high surface area–to-volume ratios are usually different in their bioactivity, solubility, and antimicrobial effects compared with larger particles. Thus, these changes in

properties cannot be extrapolated by an inverse linear analysis of particle size, but must be determined through in vitro and in vivo testing of the nanomaterials. Potentially important nanoparticles will range from metals, such as silver, to ceramic powders, such as titanium dioxide. For example, in situ–generated silver nanoparticles have been reported to be highly effective in restorative resins, bonding resins, and prosthetic resins for inhibiting a variety of biofilm-forming bacteria while not interfering with manipulation, curing, mechanical properties, or other performance properties (see Fan et al., 2011, and Oei et al., 2012).

Several of the emerging materials and technologies described later in this chapter rely on nanotechnology.

RESIN RESTORATIVE MATERIALS

Prolonging the service life of dental restorations is of great public health importance because it delays or avoids the need for repair or replacement of the restorations. The frontier for resin restorative materials continues to be the reduction of composite shrinkage, reduced porosity, improving the composite-dentin interface, reducing wear and attrition, and increasing the degree of conversion of resin monomers. Improvements in these characteristics are needed in order to increase the service life of resin-based restorations and thereby reduce the need to retreat the original restored teeth.

Longevity and survival studies have shown that dental resin composites available during the past 10 years or so have an average replacement time of 5.7 years. The failures were mainly caused by three primary factors: (1) surface loss due to two- and three-body wear; (2) marginal deficiencies due to breakdown and/or gap formation and (3) secondary marginal caries (secondary caries). Whereas the relatively recent innovations discussed earlier ("Innovations in Dental Composites" in Chapter 13) have likely increased the service life of currently marketed resin composites, there is still an incomplete understanding of all factors that lead to failures. For example, there remains significant uncertainty on the interactions among several variables including bacterial biofilms, such as dental plaque and the mechanisms of wear, fatigue, fracture, and secondary caries. Current ongoing research is making progress to gain better insights into how interactions among physical and oral environmental factors and the composition of composites initiate and influence failure mechanisms (Petrovic et al., 2010). Future research should lead to developments that further extend durability and survivability, possibly rivaling that of amalgam.

Another factor that influences longevity is operator error. Materials that present difficult handling, curing, and other technique-related problems are inherently prone to mistakes that often lead to material defects (e.g., air inclusions and low degree of cure), which in turn hasten the onset of fatigue and other failure mechanisms. Here, too, substantial research and development effort is in progress that can be expected to lead to a series of ever more "technique insensitive" (forgiving), operator-friendly, resin-based materials that also maintain a balance of other required properties such as strength, wear resistance, and esthetics.

Two recently introduced novel flowable composites, G-aenial Universal Flo (GC America, Alsip, IL) and Surefil-SDR flow (DENTSPLY International, York, PA), among others, exemplify such operator-friendly materials. Both are highly translucent and offer flowable rheologies (i.e., consistencies) and easy handling together with a large depth and degree of conversion; they are marketed as bulk fill, universal restorative resins with exceptional ease of placement. Both exhibit low shrinkage and low shrinkage stress when tested in vitro, and early clinical trial results show that they have early-stage wear resistance and durability similar to those of current posterior resins.

G-aenial Universal Flo is based on 4,8-di(methacryloxy methylene)-tricyclodecane (TCDDMA), a bulky, space-filling dimethacrylate monomer (see Figure 13-22 in Chapter 13). TCDDMA has a tricyclodecane three-ring central group that prevents monomers from aligning and thus offsets polymerization shrinkage. This "steric hindrance" effect slows the rate of polymerization and lengthens the time needed for the curing reaction to reach the point of solidification. This facilitates the ability of adjacent polymer chain segments to slip among themselves and relax stresses that develop before the resin paste solidifies.

Surefil-SDR flow utilizes what the company describes as a "polymerization modulator" in the backbone of the SDR resin monomer. A schematic of a dimethacrylate monomer—which appears to have a bulky, space-filling central group similar to that of TCDDMA—is shown in the company literature. Whatever the chemical structure, published results show that the material has flow and other handling characteristics, together with a high translucency, that promote a high degree and depth of cure. These features place it in the category of technique insensitive.

These two highly flowable composite products also contain a reinforcement filler loading on a par with highly loaded, nonflowable, even "packable" hybrids such as those described in Chapter 13. This high loading, together with low curing stress and a high level and depth of cure, account in large part for the expectation of their high durability and long service life. At this time the means whereby this combination of high filler loading and a flowable working consistency are achieved have not been disclosed. However, given the intensity of research and development, other products of this type can be expected and, with further improvements, significant progress toward the goal of ensuring reliably placed restorative resins with the durability and forgiveness of amalgam combined with the esthetics of porcelain can be expected in the near future.

ANTIMICROBIAL MATERIALS

Although the clinical performance of dental resins has improved remarkably in terms of durability, bond strength, and esthetics, most resins lack antimicrobial properties. Consequently, the inclusion of bacteriostatic or bactericidal properties is greatly needed, especially since synthetic materials of all types readily facilitate bacterial colonization and biofilm formation. Such new, improved materials may be derived

from formulas with better nanofiller or improved interphase bonding agents for the ceramic fillers and resins. Future composite restoratives may also arise from (1) new fluoride-containing monomers for the prevention of secondary caries (such as fluoride-releasing dimethacrylate monomer containing a ternary zirconium fluoride chelate), (2) antibacterial monomers (such as methacryloyloxydodecylpyridinium bromide (MDPB), (3) antibacterial and fluoride-releasing monomers, (4) the use of a higher filler percentage with nanoparticles, and (5) **matrix metalloproteinase (MMP)**–inhibiting components incorporated in the composite. Continual fluoride uptake (recharging from food or periodic treatments) and release are desirable in restoratives to inhibit or prevent caries. Antimicrobial characteristics are desirable, but they must be sustained after polymerization. Silver and titanium particles continue to be considered for antimicrobial effects, alone or attached to polymers. Silica nanoparticles are already used in composites to improve polishability and translucency, but new nanoparticles may exhibit enhanced penetration into etched dentin to improve mechanical and adhesive properties. The MMP-inhibiting materials may deter degradation of the etched dentin that interfaces with a dental composite in the hybrid layer. Suppression of MMP by agents other than ethylenediaminetetraacetatic acid (EDT) and chlorhexidine can also inhibit remineralization, which is a likely area of improvement for dentin bonding agents.

The treatment and management of dental caries have always been fundamental parts of dentistry. Early discovery of the disease's demineralization process facilitates the ability to inhibit or arrest the caries process or to remineralize the lesion's tissue, which is of significant value to the patient. New non-fluoride-containing, antimicrobial monomers such as MDPB, may help to prevent secondary caries, whereas other more effective fluoride-containing/releasing resins may be invented for this purpose. Antibiotics are being used as endodontic irrigation rinses, especially when they are combined with various acids or chemicals that quickly dissolve the dentinal smear layer created by endodontic instruments in a root canal. Combination devices containing a drug, BMP, or amino acids are envisioned for endodontic and periodontal uses. Antimicrobial materials are needed for restoratives and other dental materials that have novel and improved properties compared with those that are now available. For instance, future materials may use the antimicrobial properties of the calcium silicates or calcium aluminates for enhanced endodontic and pulpal procedures necessitated by the adverse effects of bacterial action. Silver zeolite, triclosan, and modified (chlorinated) polyethylene or other polymers may satisfy applications where an antimicrobial material is needed.

Preventing and removing biofilms is especially important for periodontics and endodontics. Adjunctive liquids are needed that can quickly kill and remove bacterial colonies in biofilms during periodontal scaling. In endodontics, new irrigants are needed to better remove and deactivate smear layers containing remnant bacteria after root canal preparation. As with acid etching, the frontier for smear layer removal or biofilm dissolution continues to advance with faster, more effective treatment regimens.

? CRITICAL QUESTION

What are the stages of research that will lead to the adoption of new remineralizing materials and processes for dental practices?

REMINERALIZING AGENTS AND MATERIALS

The remineralization of tooth surfaces with incipient lesions, prevention of secondary caries, and durable bonding to etched dentin are key areas of research for future dental materials (Donly et al., 1994 and Lippert et al., 2004) because of their great public health importance in preventing sustained enamel demineralization and prolonging the service life of composite restorations without repair or replacement. In the future, nanoparticles of hydroxyapatite may be helpful for remineralization because they are on the same crystalline scale as naturally occurring hydroxyapatite crystals in teeth. A promising example of this approach was reported by (Li et al., 2008) who found that 20-nm nanohydroxyapatite particles provided an anticaries repair effect while larger hydroxyapatite particles did not.

New remineralizing dentin bonding agents should ensure wetting and flow and preferably completely fill the demineralized zone created by etching prior to or simultaneous with bonding to the restorative material. For instance, new MTA-type* products have been tested in the lab with polyacrylic acid and sodium tripolyphosphate as a dentin-bonding layer. When it was applied under a restorative material, the combined material infiltrated the demineralized collagen fibrils with precursors that restored the calcium phosphate at the interfaces of the dentin and the restorative material. These and other remineralizing materials are needed to move forward from the laboratory to clinical trials of new dental adhesives for composites. Incorporation of some of these technologies into primers and dentin bonding agents are expected to both inhibit caries activity and increase the service life of composite restorations.

Low concentrations of fluoride are known to promote enamel and dentin remineralization (Gelhard and Arends, 1985). However, after treatments with topical fluoride gels, rinses, or dentifrices, salivary fluoride concentrations decrease exponentially to low concentrations within a few hours.

The appearance of secondary (recurrent) caries denotes a state of demineralization of the tooth tissues at the margin of a restoration. In today's dental practices, the margins of restorations are often placed in subgingival areas for the sake of enhanced esthetics, but this situation predisposes to increased plaque retention and secondary caries.

The clinical diagnosis of secondary caries is the most common reason for the replacement of restorations in general practice; this includes all types of restorations, such as those produced with amalgam, composite, and glass ionomer

*Mineral trioxide aggregate (MTA) is a mixture of calcium silicates and a radiopacifier such as and bismuth oxide; See Chapter 14 on cements.

cement. Typically 50% to 60% of all replacements of directly placed restorations in general practice are associated with the diagnosis of secondary caries. Since 50% to 75% of all restorations in adults are replacements of previously inserted restorations, the clinical diagnosis of secondary caries leads to billions of dollars of costs for patients. Therefore, it is important, in this context, to assess the scientific basis for the clinical diagnosis and prevention of secondary caries and to enhance the potential to remineralize previously demineralized enamel adjacent to restorations.

The dental literature reflects a strong demand for preventive and "healing" therapies for individuals at moderate risk for caries to prevent a shift to a high level of risk. For some of these individuals, the daily ingestion of fluoride from toothpaste, well water, and other fluoridated sources may be inadequate to prevent caries, especially when other risk factors are present. These factors include a reduced saliva flow rate, increased consumption of foods and beverages that contain fermentable carbohydrate (that is, cariogenic substances), and reduced tooth cleaning ability. Saliva analyses indicate that residual fluoride concentrations in the mouth after long periods between tooth brushing decrease from 1 ppm or more to a range between 0.02 and 0.08 ppm. Because of this reduction in fluoride, remineralization may not be possible, since the transfer of calcium and phosphate ions into enamel depends on a sufficient and sustainable supply of fluoride ions. Furthermore, because the concentration of calcium ions in saliva is also very low in healthy individuals (a maximum of approximately 60 ppm), remineralization may be further retarded without an additional source of calcium.

It is well known that low concentrations of fluoride have a beneficial effect on enamel and dentin remineralization. For treatments to be effective over periods longer than the brushing time and the subsequent time for salivary clearance, fluoride must be deposited and slowly released. Calcium fluoride or similar deposits act in such a way because of a surface covering of phosphate and/or proteins, which make the CaF_2 less soluble under in vivo conditions than the pure form in inorganic solutions. Subsequently, in the presence of phosphate groups on the surface of calcium fluoride globules, fluoride is released with decreasing pH when the phosphate groups are protonated in dental plaque. Saliva alone has the ability to increase plaque pH with bicarbonates, although typically this process may take up to 2 hours. The susceptibility of apatite in enamel surface layers makes it critical to control the acidity of the plaque fluid and Ca^{2+} and PO_4^{3-} concentrations in saliva. The subsequent remineralization process is characterized by the reverse of this process. When the oral pH is restored to approximately 7, Ca^{2+} and PO_4^{3-} ions are incorporated into the depleted mineral layers of enamel as new apatite. The demineralized zones in the crystal lattice act as nucleation sites for new mineral deposition. In the presence of fluoride (at high concentrations), the original carbonated apatite (CAP) loses its remaining carbonate and is replaced by a hybrid of hydroxyapatite (HAP) and fluorapatite (FAP). This cycle is fundamentally dependent on enamel solubility and ion gradients. Essentially, the sudden drop in pH produces an undersaturation of these essential ions (Ca^{2+} and PO_4^{3-}) in plaque fluid with respect to tooth mineral following meals. This promotes the dissolution of enamel. At neutral pH, the ion supersaturation of plaque produces a reverse shift in the equilibrium, causing a mineral deposition within the tooth surface.

Emerging technologies and materials that promote remineralization at early and moderately advanced stages of caries will be developed more rapidly as soon as the primary factors that dominate the remineralization process can be controlled effectively. In addition, more sensitive imaging or measurement processes are needed to validate early stages of remineralization and to more effectively determine whether or not preventive therapies produce optimal outcomes.

BONE-GRAFTING MATERIALS

In addition to remineralizing small lesions, gross remineralizing treatments and bone grafts are increasingly needed for dentistry. Bone-grafting materials are necessary for various oral surgeries, such as alveolar ridge augmentation and sinus augmentation and for the placement of implants or to improve mandibular denture stability. Extraction socket grafting materials are gaining popularity to prevent the collapse of cortical bone and enable the placement of an implant. Also, patients prefer faster treatment with fewer surgeries, which is driving research toward single-stage implant procedures with immediate functional loading (IFL). Implants with nanotechnology coatings may increase the success and acceptability of the single-stage and IFL procedures, but before implant placement, grafts are often needed.

Graft materials are available containing allogeneic, xenogeneic, or synthetic hydroxyapatite particles to act as a scaffold for gradual replacement by the patient's bone. These current bone grafts slowly resorb and the replacement bone densifies over months until a restorative denture or implant can be made. More rapid resorption and bone-growth-stimulating materials are needed to meet the demand for faster implant placement after tooth extraction, even immediate placement. Some available grafting materials are designed for faster resorption and bone growth. For instance, PepGen P-15 (DENTSPLY Friadent, Mannheim Germany), a hydroxyapatite product with an amino acid, is available for accelerating natural bone regeneration. Infuse (Medtronic, Minneapolis, MN) , a collagen sponge with recombinant human bone morphogenetic protein-2 (rhBMP-2), is indicated for sinus augmentation and localized alveolar ridge augmentation. Bone morphogenetic proteins, also known as cytokines, represent a group of growth factors that can affect cell interactions and cell behavior. Perioglas and NovaBone Dental Putty (NovaBone Products, Jacksonville, FL) contain coarse (greater than 100 μm) bioglass particles for implantation as a resorbable scaffold for bone growth and periodontal grafting. Ostim-Paste (aap Biomaterials GmbH, Dieburg, Germany) is a nanocrystalline hydroxyapatite paste that can be used to repair the intraoral bony defects that may result from cystectomies (a surgical procedure to remove a cyst), root tip resections, extractions, and surgical tooth removal

and for augmentations in the areas of the alveolar processes and maxillary sinuses (sinus lift) as well as to fill periodontal defects. Clinical trials are needed to determine the success of each of these approaches and guide the development of future products.

New bioactive glasses are under development that contain more boron and silica than the original formulas of 45S5 bioglass (45 wt% SiO_2 and a 5:1 ratio of CaO to P_2O_5) for **osteogenesis**, and the new formulas may be resorbed more quickly with faster bone replacement. Copper or silver in these glasses may also enhance soft tissue deposition in other applications. Powders, fibers, or foams of the bioactive glasses may be used as scaffolds for use in the rapid replacement of bone or soft tissue. Scaffolds of bioactive glass are used for **osteoconductivity**, and they may also initiate **chondrogenesis**. The latter could be useful for **temporomandibular joint (TMJ)** treatments. Combinations of biodegradable polymers with bioactive glass particles may also enhance tissue replacement and serve as the basis for new grafting materials.

? CRITICAL QUESTION

In which ways does the use of smart materials lead to improvement in the quality of oral health care?

STIMULUS-RESPONSIVE "SMART" MATERIALS

"Smart" materials are designed for interaction with external stimuli such as light, temperature change, stress, moisture, pH, or electric/magnetic fields (McCabe et al., 2009). Currently, these dental materials include (1) zirconia ceramics that transform from a tetragonal to monoclinic crystal form when tensile stress is induced at crack tips, leading to an increase in crystal volume and compressive stress that tends to prevent propagation of the cracks; (2) composites designed for initiation of curing by irradiation with particular wavelengths of blue light or composite cements that change color when irradiated (for use in orthodontics); (3) glass ionomer cement that when desicccated, weakens the cement to make it easier to remove orthodontic bands; and (4) glass ionomer restoratives that increase the release of fluoride when the pH in plaque fluid decreases (ten Cate et al., 1995).Nickel-titanium wires that soften when chilled below body temperature for bending are "smart" and very useful for threading together orthodontic brackets at the earliest treatment stages with the most misaligned teeth. Future smart materials may include cements that can be triggered to soften and allow debonding by a temperature change or irradiation process. Cements such as this would be very attractive for use with temporary crowns, orthodontics, and some implant restorations.

Emerging technologies and materials may also include smart hydrophilic resins that effectively seal moist microscopic crevices adjacent to defective restorations and release fluoride and/or other mineralizing agents when the pH of oral fluids decreases to a range of 4.0 to 5.5—that is, when enamel demineralization often occurs.

The use of sealants, varnishes, and composites that release fluoride is not new. However, most of the studies on these materials were based on commercial products whose compositions were not known precisely and whose ages at placement were unknown or not identified. In addition, few studies have analyzed the influence of particle composition, particle size, and particle size distribution, nor have they demonstrated the on-demand nature of "smart sealing materials."

Secondary caries and the unnecessary replacement of defective restorations can be prevented and adjacent enamel remineralized through one of the following preservative treatments: (1) sealing of marginal crevices adjacent to defective restorations with a hydrophilic resin; (2) sealing crevices with a smart resin capable of the controlled release of chlorhexidine or other antibacterial agent; (3) sealing crevices with a smart resin capable of the controlled release of fluoride; and (4) applying a sealing resin or varnish that can release xylitol or other caries management agents at specified concentrations over a specific period of time.

The rapid induction of anesthesia may be another future application for smart materials. For instance, particles or substances could be applied in the sulcus and an external trigger could start or stop the anesthetic reaction. Smart material concepts provide the clinician with better control, which will certainly suggest approaches for new products.

SELF-ASSEMBLING MATERIALS

Self-assembling material systems automatically construct prespecified assemblies.[7] Viruses, cells, tissues, and whole organisms are examples of biological assemblies, whereas crystals are an example of nonbiological assemblies; both can be derived from polymers, metals, ceramics, or be composites of several types of components. Self-assembly occurs by orchestrated stages of initiation, propagation, and termination. Control systems for initiation and/or propagation may be templates (e.g., template polymerization of proteins, patterning of silica templates for electrical circuits), or they might depend simply on natural rules corresponding to energetically favorable physical, chemical, mechanical, and/or biological events (e.g., capillary forces, heterogeneous nucleation of crystallization, surface energy reduction, phase separation, micelle formation, and steric probabilities for molecular folding).

The bone or soft tissue scaffolding of graft materials can be considered to be self-assembling. The coarse particulate or spongy bone graft materials are designed to encourage biological tissue to respond and replace the structure where the scaffolding is placed. Future materials may include templates of proteins to encourage biological events, such as specific tissue (Fan et al., 2007). For example, the Stupp laboratory (Palmer et al., 2008; Webber et al., 2010) has developed a broad class of self-assembling peptide derivatives that offer exciting novel therapies of broad potential impact in regenerative medicine. These peptide amphiphiles (PAs) incorporate a short hydrophobic domain on one end of a hydrophilic oligopeptide sequence that also contains bioactive signaling sequences. Nanostructures can be designed from these peptides that, through self-assembly strategies and

supramolecular chemistry, have the potential to combine biocompatibility with bioactivity and also offer broad engineering design flexibility for the development of multiple biomedical and biomaterials applications. This type of research has shown early-stage proof-of-concept results for some applications and is close to translation into clinical applications for others. However, for most applications (e.g., the regeneration of teeth), translation remains a distant but likely achievable target. Several of these possibilities also involve tissue engineering, biomimetics, and stem cell biology, which are discussed in greater detail below.

SELF-HEALING (SELF-REPAIRING) MATERIALS

Self-healing is an *autonomically* initiated response to damage or failure. In order to achieve this function, a self-healing material must be capable of (1) identifying and (2) repairing failures (Fischer, 2010).

Composite materials for restorations are subject to aging in situ, and all biomaterials typically have a limited lifetime; they gradually degrade because of physical, chemical, and/or biological phenomena such as creep, fatigue, unresolved internal stresses, corrosion, dissolution, erosion, or biodegradation. As a result, the material eventually fails at some stage, such as leakage at the resin-dentin bonded interface, fracture of resin composites, chipping of porcelain, or corrosion of amalgam. Nature manages to renew many biological materials. For example, bone continually remodels and can heal itself (self-repair) even after a major fracture. Nature's approach has inspired efforts to develop self-healing capabilities for synthetic materials. One of the first such materials, an epoxy system, is similar to resin-based dental materials. The self-healing system consists of microencapsulated dicyclopentadiene and Grubb's metathesis catalyst. If a crack occurs in the epoxy composite, some of the microcapsules are ruptured near the crack and release dicyclopentadiene, which subsequently fills the crack and reacts with the catalyst, resulting in polymerization of the dicyclopentadiene and repair of the crack. Such materials have been observed in laboratory tests to improve the recovery of composite fracture toughness after stress. Similar systems have exhibited a significantly longer service life under mechanical stress in situ compared with those without the potential for self-repair.

Another approach under investigation is a self-healing material that operates on the basis of a pH increase experienced by proteins during the maturation of a mussel byssus secretion to control catechol-Fe^{3+} interpolymer cross linking via pH changes.

Although no biomaterials with such properties have been commercialized as yet, self-healing systems would be extremely useful for dental resins, as they would have significantly longer life cycles and improved clinical performance. They may very well perform better than those repaired with conventional macroscopic repair approaches, some of which have been shown *not* to lead to satisfactory mechanical properties of the repaired composite (Jandt and Sigusch, 2009).

These technologies are being intensively investigated at present and may well appear in dental products within a few years (Fischer, 2010).

BIOACTIVE MATERIALS

Generally, present-day dental materials do not induce dental tissue responses and are not **bioactive**. However, bioactive biomaterials with novel and improved properties are needed. For example, a bioactive material that promotes the formation of hydroxyapatite mineral would have numerous benefits, including remineralization of adjacent tooth substance, the potential to close gaps between restoration and tooth, improved bond strength durability associated with reduced bond degradation, and enhanced bone integration with implant surfaces. New bioactive materials are under development that, in general, will create a biomimetic "presence" in vivo that induces healing by processes that are superior to those of many present-day dental materials.

Such new bioactive materials that have either been recently introduced or that are expected to soon become available include novel formulas of hydraulic (water-setting) ceramic powders. For instance, calcium–silicate-containing powders (predominantly tri- and dicalcium silicate powders, also known as mineral trioxide aggregate or MTA-type) are now considered the gold standard for endodontic surgical procedures and have gained increasing acceptance for pulp capping, pulpotomy, and apexification procedures. Calcium aluminate–based powders, being more acid-resistant, are being used with glass ionomers to make supragingival cement for prosthodontics and have found limited use for restorative applications. Their acid resistance makes them useful for infected sites, which are generally acidic; as such, the aluminates may be used for the same indications as MTA-type materials (Darvell and Wu, 2011). Calcium phosphate cements are generally slower-setting than the hydraulic cements but are being used for scaffolding purposes where the formation of hydroxyapatite is necessary and porosity is acceptable.

A novel approach has recently been reported that uses dental resins containing bioactive TiO_2 nanoparticles. These particles promote hydroxyapatite formation, enhance mechanical strength as reinforcing fillers, and can also act as photocatalytic bactericidals (Welch et al., 2010). For example, a dentin bonding adhesive with TiO_2 nanoparticles can provide on-demand, photoinduced microbial inhibition and at the same time can fill (i.e., "heal") marginal gaps via remineralization of adjacent dentin and enamel. This technology has the potential to reduce the incidence of secondary caries, improve tissue integration with implant surfaces, and prevent **peri-implantitis** and other infections at the tissue/implant interface. These results are intriguing and highly promising, but they have not yet been tested clinically.

Often it is the surface of materials that makes them bioactive. Titanium as an implant material is an example. Like chromium, titanium spontaneously reacts with oxygen to form a self-repairing, protective oxide layer (TiO_2), which makes it largely corrosion-resistant, inert, and biocompatible. However, surface roughness and other aspects of surface

topography, together with surface chemistry, are also known to strongly influence the early events in healing and osseointegration that follow implant placement. Interactions between proteins, cells, tissues, and implant surfaces play a role in this process and help determine the eventual success or failure of all implanted materials and devices.

The surface chemistry and topography-related mechanisms that control these events are poorly understood. Nevertheless, substantial research effort in dental implantology is currently directed at developing surfaces with controlled topography and chemistry at the nanoscale level to optimally promote protein adsorption and cell adhesion. On other fronts, the use of biomimetic calcium phosphate coatings to enhance **osteoconductivity** and the incorporation of biological agents to accelerate bone healing in the peri-implant area are also areas where rapid progress is being made.

Overall, these efforts to understand and control surfaces are showing great promise, and some are likely to lead to materials, processes, and/or procedures in the near future that will greatly enhance the reliability of placement, indications for use, and the success rate of dental implants (Le Guéhennec et al., 2007).

BIOLOGICAL MATERIALS

Biomaterials science is exploring new technologies and is increasingly shifting from materials science and engineering and replacement therapies to bioengineering and natural tissue repair or replacement therapies. Biological biomaterials lead to natural tissue restoration and rely heavily on tissue engineering, biomimetics, self-assembling systems, cell biology, regenerative dentistry, and other technologies.

BIOMIMETICS

This field of research involves the study of the formation, structure, and function of biologically produced substances and materials (such as silk and conch shells) and biological mechanisms and processes (such as protein synthesis) for the purpose of synthesizing similar products by artificial mechanisms that mimic natural ones. Of particular interest here are those that involve self-assembly of components to form, replace, or repair oral tissues (Saunders, 2009; Fan et al. 2007).

An intriguing prospect for this approach is the use of self-assembling peptide amphiphiles (PAs) that contain both a photopolymerizable group and the arginine-glycine-aspartic acid-serine (RGDS) cell adhesion sequence. The self-assembling nature of the PAs causes the formation of networks of prealigned nanofibers, mimicking natural fibers. These nanofibers can be formed into tissue-engineering scaffolds and used as substrates for mesenchymal stem cell (**MSC**) cultures. Topographical patterns produced from the aligned PA nanofibers were found to promote alignment of MSCs, which indicate that the cells sensed and responded to the nanoscale features of the scaffold surfaces. The aligned MSCs then differentiate to form bonelike tissue (Welch et al., 2010).

These technologies are under intensive investigation and development and will very likely be translated into clinically useful materials and treatments in the not too distant future. These and other biomimetic approaches and uses of tissues engineering scaffolds are discussed further in the sections headed "Tissue Engineering" and "Regenerative Dentistry," below.

TISSUE ENGINEERING

According to the National Institutes of Health, tissue engineering is an emerging multidisciplinary field involving biology, medicine, and engineering that is likely to revolutionize health care and the quality of life for millions of people worldwide by restoring, maintaining, and enhancing tissue and organ function. The main requirements for producing an engineered tissue are the appropriate levels and sequencing of regulatory signals, the presence of responsive progenitor cells, an appropriate extracellular matrix or carrier construct (i.e., scaffold), and an adequate blood supply for oxygen and nutrients. Either biological or synthetic polymers are used to form the tissue engineering scaffolds. Recent advances in understanding growth factors and biodegradable polymer scaffolds have made possible the successful tissue engineering of cartilage, bone, and related tissues (Slavkin and Bartold, 2006). Nakashiwa and Reddi (2003) have summarized the remaining achievements required to develop the clinical techniques needed for the creation, substitution, and/or replacement of dental tissues. Among the many potential applications are fracture repair, dentin and periodontal ligament replacement, alveolar ridge augmentation, temporomandibular joint reconstruction, preosseointegration of dental implants, and partial or whole tooth regeneration.

Tooth loss is the most common organ failure. The regeneration of a tooth can include not only regrowth of the entire tooth complex as a complete biological organ but also regeneration of individual components, including enamel, dentin, pulp, cementum, and periodontal tissues (Yuan et al., 2011; Sonoyama et al., 2006). Currently there are two main lines of investigation regarding this possibility. The first deals with restoration of partial tooth damage and focuses on using the existing reparative capacities of the tooth and/or use of tooth-related **stem cells** for the repair of damaged tooth parts (Petrovic and Stefanovic. 2009). The second line of investigation focuses on whole-tooth regeneration by using stem cells and/or conventional tissue engineering techniques.[32,32a] The first successful bioengineering of entire tooth structures was reported in 2002 using cells from dissociated porcine third molar tooth buds seeded on biodegradable polymer scaffolds that were implanted in rat hosts for 20 to 30 weeks (Young et al., 2002).

Osteonecrosis is a new and serious dental disease that arises from bisphophonates received intravenously or orally related to other medical conditions. More effective osteonecrosis treatments are also needed and biological solutions to this end may be found. Conventional debridement is ineffective; therefore other treatment modalities are needed, to treat the condition, and to avoid the onset by dental events such as surgeries or extractions.

In periodontics, tissue engineering is being used to develop new therapies beyond those based solely on infection control. Chronic periodontitis is one of the most common oral diseases worldwide, after caries. Tissue engineering strategies are currently being developed to serve as periodontal regenerative therapies for the restoration of lost alveolar bone, periodontal ligament, and root cementum. These strategies are based on the growth of new functional tissue rather than replacement of the periodontium. These studies have shown that regeneration of small- to moderate-sized periodontal defects using cell-scaffold constructs is feasible and that this technology may well evolve and become available for selected clinical scenarios in the near future (Chen and Jin, 2009; Chen et al, 2012). Yet even though tissue engineering has created the means for eventual predictable and optimal periodontal tissue regeneration, progress toward clinical studies and routine clinical periodontal regenerative medicine and clinical use remains in an early stage (Hollister and Murphy, 2011; Rosa et al., 2012).

A still greater challenge is major bone reconstruction after trauma or cancer, as well as augmentation following implants. There are formidable challenges for regenerating normal structure and restoring the functionality of tooth-supporting tissues. Future possibilities depend on a better understanding of the cellular and molecular mechanisms involved in periodontal tissue regeneration, the differentiation potential of stem cells, and the interactions among stem cells, scaffolds, and host tissues. Given the recent progress and intense research and development activities in these areas, it should soon be possible to place implants even under adverse anatomic or biological circumstances. Current findings also offer promise that tissue engineering will soon lead to the ability to reconstruct lost bone in bone deformities in a more effective and less traumatic way than that offered by the traditional autogenous bone transplantation approaches (Rosa et al., 2012).

At this time it is difficult to predict the full impact of tissue engineering on the future of dentistry. However, it offers the ability to bring together advances in such disparate areas as materials science, genetics, molecular biology, and cell biology to develop new alternatives for the regeneration of both bone and soft tissues (Park et al., 2010) and for new restorative procedures to regenerate enamel.[18,38,39] An important consideration will be the cost of these procedures, at least initially. Not only is the cost of treatment important but also to be considered are the costs required to fully develop the technology, demonstrate clinical efficacy, overcome regulatory hurdles (Hollister and Murphy, 2011), and train clinicians[36] in the use of these innovative techniques.

DELIVERY SYSTEMS FOR BIOLOGICALS

Tissue engineering approaches that combine biomaterials with such biologicals as proteins (growth factors, etc.), genes, and cells (both differentiated and stem cells) are promising routes to the therapies discussed above. Thus they are a source of active ongoing research directed in part toward developing competent scaffolding materials capable of fulfilling application-specific requirements for biodegradation, biocompatibility, mechanical stability, biofunctionality, and processability (Hubbell, 2003; Lia et al., 2008).

The key attributes of any biological delivery system are controlled, sustained, and targeted release. Each of these attributes is fundamentally dependent on the ability to predictably generate a functionalized material (Tayalia and Mooney, 2009).

An example of a promising biological delivery strategy is to increase osseointegration of titanium implants by coating them with extracellular matrix components such as collagen, bone morphogenic proteins (BMP), and other proteins known to improve healing, induce peri-implant bone formation, and enhance osseointegration. For this technology to advance, further development is required to learn how to orchestrate the release pattern, optimize the time that the active components remain bioactive, control degradation, optimize the extracellular matrix that forms on the implant surfaces, and achieve maximum bone formation at minimal concentrations. As these and other questions remain unanswered at present, this appears to be a viable approach but one likely to require 10 years or more before a version is available for general use in dental practice.

CRITICAL QUESTION

Why are engineered tooth roots more likely to have a greater impact on dentistry than the engineered whole teeth now under development?

REGENERATIVE DENTISTRY

Restorative dentistry is only very gradually transitioning away from replacement therapies using synthetic materials toward biology-driven repair, replacement, and regenerative medicine therapies. As currently envisioned, regenerative dental treatments have three key requirements: (1) a scaffold structure (either biological or synthetic), (2) progenitor/stem cells, and (3) the presence of inductive morphogenetic signals. For these approaches, the mouth has special advantages compared with other locations owing to its minimally invasive access and ease of observation (Bayne, 2005).

For tooth regeneration, two major approaches have been taken, both of which utilize stem cells, the building blocks that can develop into various types of specialized cells. One approach uses scaffolds seeded with stem cells; the other uses stem cells without scaffolds. Significant progress has been made with both of these approaches (Zivkovic et al., 2010). The main characteristics of dental stem cells are their potential for multilineage differentiation and self-renewal.

Stem cells have been isolated from many tissues and organs, including dental tissues. Five types of dental stem cells have been established: (1) dental pulp stem cells, (2) stem cells from exfoliated deciduous teeth (SHEDs), (3) stem cells from apical papillae (SCAPs), (4) periodontal ligament stem cells (PDLSCs), and (5) dental follicle progenitor cells. Dental stem cells can differentiate into odontoblasts, adipocytes, neuron-like cells, glial cells, osteoblasts, chondrocytes, melanocytes, myotubes, and endothelial cells. Possible

application of these cells in various fields of medicine makes them good candidates for future research as a new, powerful tool for a variety of therapies, including those related to oral health (Petrovic and Stefanovic, 2009).

Although stem cells will eventually be used to grow replacement human teeth, the signaling processes that control the development of discrete dental morphologies for incisors, canines, premolars, and molars must be clearly understood before whole-tooth regeneration will become a practical goal. Although this goal remains speculative, substantial progress has been made in developing an understanding of the mechanisms and challenges involved, and several proof-of-concept investigations are leading the way (Koussoulakou et al., 2009; Yildirim et al., 2011; Duailibi et al., 2004; Galler et al., 2010).

The repair and regeneration of dental *tissues*, rather than whole-tooth regeneration, offer possibilities for earlier realization. Thus, intensive investigations are being directed toward the development of techniques and materials to regenerate dentin, pulp, periodontal ligaments, and even whole root structures.

The dentin-pulp complex offers a particularly attractive target for regeneration because the pulp chamber has a nearly ideal environment, and such an achievement would lay the foundation for eventual whole-tooth replacement (Sloan and Smith, 2007). For example, Huang et al. (2009) discovered that stem cells retrieved from dental pulp produce pulp-like tissue in an emptied human root canal, together with the deposition of dentin-like mineralized tissue on the canal walls. Yet another step toward regenerative endodontics was taken when cells from human exfoliated deciduous teeth were observed to generate a dental pulp tissue when blended with nanofiber peptides as scaffold materials and injected into root canals. A similar approach by (Galler et al., 2008) using the self-assembling peptide amphiphiles (PAs, discussed above) as scaffolds to encapsulate stem cells, taken from deciduous teeth, revealed that they proliferate and secrete a soft collagen matrix. Similarly, dental pulp stem cells differentiate into an osteoblast-like phenotype and deposit mineral when encapsulated. In addition to pulp and dentin, such a PA/dental stem cell biological delivery system also has potential as a treatment for dental caries by promoting the regeneration of mineralized as well as soft tissue. These examples demonstrate the feasibility of clinical regeneration of the dentin-pulp complex. At this time many challenges remain, and regeneration may never be applicable for all clinical circumstances. However, it is foreseeable in the relatively near term that stem cell/tissue engineering therapies will become available to stimulate pulp to deposit dentin and continue the natural developmental root growth of noninfected, accidentally injured immature teeth.

Regeneration of the tooth root represents yet another feasible near-term goal rather than the regeneration of the whole tooth. Arguably the adult tooth owes more of its biological vitality to the root than to the crown. This possibility was demonstrated by transplantation of a root-shaped calcium phosphate mineral block loaded with swine stem cells from apical papillae (SCAPs), which was coated with a resorbable gelatin containing periodontal ligament stem cells (PDLSCs); it was placed into the extraction socket of a minipig lower incisor. This approach successfully generated a root/periodontal structure adequate for use in place of titanium or other implant material to attach a ceramic crown (Nakahara and Ide, 2007). SCAPs are easily accessible, since they can be isolated from human third molars. The development of a combination of SCAPs and PDLSCs encapsulated in a resorbable scaffold offers a relatively near-term means of clinically inducing a root form and connective tissue in alveolar bone for the attachment of an artificial crown.[30,43]

Both biomaterials and biological materials are playing an indispensable role in progress toward regeneration of a tooth root, crown, pulp, dentin, enamel, or entire tooth. Repair occurs by the use of metals, ceramics, or synthetic resin materials, whereas regeneration is controlled by biological restoration. Tooth regeneration is an extension of concepts in the broad field of regenerative medicine to restore a tissue to its original form and function by biological mechanisms. Whereas substantial progress has been and is being made, whole-tooth regeneration remains a distant but achievable goal—one that would cause dentistry to undergo a paradigm shift from repair and replacement to regeneration.

? CRITICAL QUESTION

In what ways do emerging diagnostic tests and processes improve the quality of dental treatment?

INSTRUMENTS AND PROCESSES

DIAGNOSTIC DEVICES AND TECHNIQUES

A variety of new and evolving modern diagnostic techniques have been introduced in recent years for caries, periodontal disease, oral cancer, herpes simplex infection, and candidiasis as well as for incipient fractures and various other traumatic conditions. Several promising alternatives are also either in development or under investigation. Some are based on instruments that produce images directly from the patient, while others utilize saliva or other biological specimens taken from the patient and analyzed separately. Those that are based on diagnostic instruments include radiographic, optical, laser fluorescence, ultrasound imaging, and electrical conductance technologies. A selected group of those that appear to be the more promising in the near term are discussed below.

Cone-Beam Computed Tomography (CBCT)

Digital x-ray imaging systems are evolving to use more CBCT. In dentistry CBCT provides high resolution, low distortion, and digital imaging of the hard tissues of the head. Instead of pixels, the resolution is measured in **voxels**, and the images are often sharper than conventional CT images. The term *cone-beam* refers to the cone shape of the x-ray beam, unlike conventional CT, which uses a fan-shaped beam to create multiple thin slices. CBCT produces Panorex and cephalometric projections, which become three-dimensional images when the data are reformatted in a volume. The

images that result can be manipulated with the instrument's visualization software from any point of view (e.g., in the axial, coronal, sagittal, and cross-sectional planes). Layers can be "peeled away" to show hidden underlying anatomical structures and defects. The slice thickness can be changed, and the structures can be tilted, zoomed, and highlighted. These are views that most dentists have not seen previously. Treatment decisions can change drastically with the advent of such advanced views.

Swept-Source Optical Coherence Tomography (SS-OCT)

This CBCT-related technology uses infrared laser optics rather than x-rays and can generate high-resolution cross-sectional images of microstructures in biological systems. It has been under development for many years for various medical imaging tasks, including examination of the oral cavity (Otis et al., 2000). but has recently shown significant progress such that development of a practical device may well be available for dental applications within a few years (Shimada et al., 2010). This nonionizing real-time tomographic technology is capable of detecting structural flaws and variations at a submicron scale and has shown promise for a variety of dental diagnostic tasks. For example, it may prove useful in monitoring the accuracy of composite restoration placement, the development of polymerization contraction gaps, detection of vascular lesions, and detection of occlusal caries.

Laser-Induced Fluorescence

"Quantitative light-induced fluorescence" (QLF; Inspektor Research Systems, Amsterdam, The Netherlands) is a well-advanced technology but still not widely used in routine dental practice. The QLF method is based on the autofluorescence of teeth and of certain plaque microorganisms. When teeth are illuminated with high-intensity blue light, they emit light in the green part of the spectrum, which diminishes when less mineral content is present in the enamel. Bacterial metabolic activity and plaque formation produce porphyrin-type biological pigments, which fluoresce bright red. Thus QLF-based instrumentation detects and quantifies de- and remineralization of dental tissue as well as bacterial activity. It is a simple yet effective way to reveal lesions in teeth well before they become frank lesions or cavities. White spot lesions (early dental caries) are detected and quantified as well as bacterial metabolic activity on and in the teeth. When lesions are identified at an early stage, the teeth will repair themselves if good oral hygiene practices are followed. The technique provides a measure of the degree of existing enamel demineralization via a small video sensor. Thus, it is possible to collect a digital image of each tooth, which can then be visualized on the screen and analyzed for the amount of enamel loss. It allows either the dentist or oral hygienist to provide the patient with immediate information and a direct incentive to monitor the quality of oral care procedures.

A recent addition to QLF instrumentation (QLF-D BiLuminator) allows ordinary white light images to be collected simultaneously with fluorescent images. The image pairs aid direct visual assessment and provide a comparison that highlights such features as leaking restoration margins and secondary caries, occlusal and interproximal caries, sealant integrity and cariogenic activity under sealants, as well as calculus and gingivitis (de Josselin de Jong, 2009).

Laser Photothermal Radiometry (PTR)

PTR detects modulated thermal infrared (black-body) radiation emitted from hard dental tissue that results from absorption of laser light and its nonradiative energy conversion into heat, creating a small temperature rise. In translucent materials such as enamel and dentin, depth information is obtained following optical-to-thermal energy conversion and transport of the incident laser power in two distinct modes: (1) conductively from a near-surface distance (50 to 500 μm) controlled by the thermal diffusivity of enamel and radiatively through black-body emissions from several-millimeter depths owing to optical penetration of the diffusely scattered laser-induced optical field and (2) partial infrared transparency (infrared "spectral windows") of the hard dental tissue, which allows the thermal photons to exit the enamel and register on the detector.

Two variations on this emerging nondestructive technology for exploiting the optothermophysical properties of teeth have recently been reported in a series of papers (Amaechi, 2009; Helen et al., 2011; Tabatabaei et al., 2011). Both take advantage of the effects that changes in porosity and the crystalline status of enamel have on thermal and optical properties of hard tissues, caused by cariogenic demineralization and formation of subsurface lesions. As demineralized lesions grow, optical scattering increases, optical absorption also increases, and thermal conductivity and diffusivity decrease. The two distinct detection modalities are:

1. Infrared photothermal radiometry and modulated luminescence (PTR-LUM). PTR-LUM (Quantum Dental Technologies, Inc., Toronto, Canada) scans a tooth with a low-power pulsating (modulated) laser light. The light is scattered and absorbed by the tooth and two phenomena are observed: the laser light is absorbed and re-emitted at a longer wavelength as luminescence and heat is generated (less than 1 °C). Simultaneous measurement of the two phenomena, heat (mid-IR) and light (near-IR) provides information on the presence and extent of decay up to a depth of a few millimeters below the surface.
2. Thermophotonic lock-in imaging (TPLI) using a spread laser beam illuminating the whole tooth and a midinfrared camera in the lock-in mode, producing images at a fixed frequency.

TPLI is an extension of PTR into a full imaging modality. It uses the same physical photothermal wave principles as PTR: increased light scattering and absorption by a carious lesion increases the thermal-wave amplitude and shifts the thermal-wave centroid closer to the surface, producing contrast between a carious lesion and intact enamel in both amplitude and phase images. TPLI phase images are

emissivity-normalized (just as PTR phases are) and therefore are insensitive to the presence of surface stains. Amplitude images provide integrated information from deeper enamel regions due to the radiative contributions that overlap conductive heat transfer. TPLI imaging is noncontacting and is reported to have higher sensitivity to very early demineralization than do dental radiographs (Tabatabaei et al. 2011).

Ultrasound Imaging

Better termed *ultrasonography*, this well-established medical diagnostic imaging technique has recently shown promise for high-resolution imaging with enhanced specificity and sensitivity for the early detection and monitoring of several oral pathologies. Ultrasonography is nonionizing and noninvasive and, with further development, it seems likely that handheld devices will become available within a few years for the detection of enamel and dentin demineralization caused by caries under and around existing restorations and on occlusal and interproximal surfaces as well as for the detection of cracks, calculus, and periapical lesions (Ghorayeb et al., 2008; Hinders et al., 2010).

Infrared Spectroscopy for Multiple Inflammatory Parameters

An optical spectroscopy instrument is under development to enhance the early detection and monitoring of peri-implant inflammation and thereby reduce the number of implant failures (Nogueira-Filho et al., 2011). The instrument uses visible, near-infrared spectroscopy to measure alterations in regional tissue hemodynamics in periodontal tissue. Tissue oxygenation at peri-implantitis sites is substantially reduced compared with healthy sites owing to increases in deoxyhemoglobin and a decrease in oxyhemoglobin at the peri-implantitis sites. To diagnose these changes, the instrument simultaneously measures tissue oxygenation, total tissue hemoglobin, deoxyhemoglobin, oxygenated hemoglobin, and tissue edema.

Salivary Genetic Testing

This technology is emerging as a molecular biology–based analytical test for use with periodontal disease and oral cancer. Easily administered, chair-side salivary assessments such as those performed by OralDNA Labs (Brentwood, TN) can identify patients whose genetic susceptibility to periodontal disease may put them at increased risk. This genetic testing for the interleukin-1 (IL-1) gene cluster, a significant inflammatory mediator, complements other periodontal screening procedures and other salivary bacterial DNA tests for specific oral pathogens. Saliva analysis is used to screen for oral human papillomavirus (HPV), especially the variants HPV-16 and HPV-18 as potential etiologic agents in the development of squamous cell carcinoma of the head and neck. Diagnostic testing will continue to expand and enhance treatment modalities. The use of this type of testing can also assist in achieving patient acceptance of needed treatment and cooperation with the clinician to improve periodontal health (McGlennon, 2011).

Liquid-Based Cytology

This is a relatively new, FDA-approved screening technique for oral infections. It is based on the minimally invasive collection of transepithelial mucosal cells and other microbiological aspects for processing and evaluation. With liquid **cytology**, the clinician can request tests for several generalized oral conditions such as herpes simplex infection and candidiasis, or suspicious areas of leukoplakia or erythroplakia (OralCDx, CDx Laboratories, Suffern, NY). Cytology provides the evidence needed to determine if an immediate invasive full-thickness biopsy procedure should be performed (Scheifele et al., 2004).

Acceptance and utilization of such diagnostic technologies as CBCT, QLF, and salivary genetic testing are already at hand and growing. The use of these and many of the others is expected to increase in the near future, with positive benefits for both the dental profession and its patients.[50,53,55,57] Each technique varies in its mode of action and capability as a diagnostic aid. For most dental diagnostic tasks, differences in presentation and behavior among anatomic sites make it unlikely that any one diagnostic modality will have adequate sensitivity and specificity for all circumstances. Thus, a combination of diagnostic tools will continue to be needed to reliably diagnose oral diseases and conditions earlier, and to provide corrective or preventive treatment at a stage where it can be more effective.

? CRITICAL QUESTION

How does CAD-CAM production of dental prostheses differ from the processes of stereolithography, robocasting, powder-bed ink-jet printing, and laser scanning?

COMPUTER-DRIVEN FABRICATION SYSTEMS

Existing dental CAD/CAM systems vary dramatically in their capabilities. None can yet acquire data directly in the mouth and produce the full spectrum of restoration types that can be created by traditional dental laboratory techniques, although materials and indications continue to expand. Both copy milling and true CAD-CAM systems have been developed. Ceramic and metal crowns and metal superstructures (overdenture bars) have been made using subtractive (machining) of blocks of zirconia, leucite-containing porcelain, filled resins, cobalt-chromium alloy, and titanium. Temporary crowns can be made in the lab using CAD-CAM systems that are either "additive" or "subtractive." The additive systems use the free-form buildup of a design from a resin that is cured "voxel by voxel" to create the device, using a resin that is cured in special computer-controlled lab equipment and cured with ultraviolet light. Refinements and esthetic improvements are expected for all of the present systems (Beuer et al., 2008).

Three-dimensional printing techniques are being developed for the formation of ceramic or resin composite restoratives. Printing techniques will be a fruitful area where more sophisticated equipment and technologies can enable the use of enhanced dental materials, especially for fixed prosthodontics.

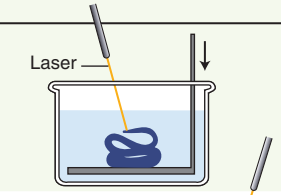
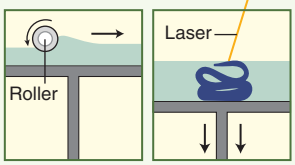
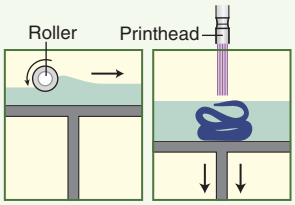
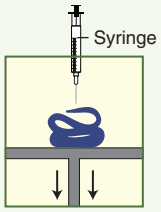
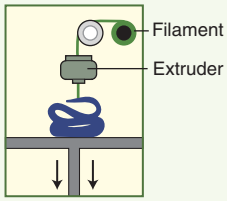
TECHNIQUE	SMALLEST PRINTABLE FEATURE	MATERIALS
Stereolithography Laser cures photopolymer as platform lowers into liquid vat. 	1–70 μm	Photopolymers
Laser sintering Laser melts powder rolled onto platform. Platform lowers with each layer printed. 	45–100 μm	Metals Polymers
Powder-bed ink-jet printing Printhead sprays liquid binder onto powder to fuse layers. Platform lowers with each layer printed. 	350–500 μm	Ceramics Metals Polymers
Robocasting Syringes extrude fluid materials that harden on lowering platform. 	200–400 μm	Biopolymers Some metals Food
Fused deposition modeling Heated extruder melts plastic filament, which cools on lowering platform. 	260–700 μm	Thermoplastics

FIGURE 21-2 The technologies available for three-dimensional printing. A variety of techniques can use various materials to build solid objects with different resolutions. (Adapted from Butscher A, Bohner, M Hofmann S, Gauckler L, R. Müller R: Structural and material approaches to bone tissue engineering in powder-based three-dimensional printing, Acta Biomaterialia Mar;7(3):907–920, 2011.)

Optical scanning of teeth will become the norm. The use of optical scanners will reduce the demand for impression materials and dental stone for fabrication of restorative crowns and other prostheses. Optical scanning of full arches is changing the methods of generating orthodontic treatment plans as well as complex restorative cases.

Three-dimensional printing techniques are beginning to be used to fabricate the metal framework of dental crowns and bridges. Other techniques are being developed in three-dimensional printing for more advanced dental applications, including the creation of bone-graft scaffolds (Vorndran et al., 2010). As noted above, a variety of techniques can be used to build solid objects with different resolutions and materials. Those developed to date are summarized in Figure 21-2 (Wolf, 2010).

Emerging technologies may expand the capabilities of future systems dramatically, but they will require a different type of dentistry skill or laboratory technical training to enable their use to full effect.

COMPUTER-AIDED EDUCATIONAL SYSTEMS

Haptic Technology

Dental education may add haptic technology to reduce the risk to patients during training and to enhance the learning experience. **Haptics** involves the electromechanical

stimulation of interactions with virtual objects—that is, those existing only in a computer simulation. This process has been described as "doing for the sense of touch what computer graphics does for vision."[62] Although haptic devices are capable of measuring bulk or reactive forces applied by the user, they should not be confused with touch or tactile sensors that measure the pressure or force exerted by the user on the interface.

Haptic technology has made it possible to investigate in detail how the human sense of touch works by allowing the creation of carefully controlled haptic virtual objects. These objects are used to systematically probe human haptic capabilities, which would otherwise be difficult to achieve. These new research tools contribute to our understanding of how touch and its underlying brain functions work.

Just-in-Time Learning

One of the most serious challenges facing health professionals is the explosion of new biomedical information and products. The "just-in-time learning" approach entails learning skills that allow the clinician to quickly find new knowledge related to a patient's specific problem, when needed, at the point of care. This is in contrast to passively reading professional journal articles, attending continuing education courses, and attempting to assimilate large quantities of information some of which may never be used.

To provide dental professionals with a means of keeping up-to-date after graduation, a program for teaching the just-in-time approach as well as for acquiring evidence-based practice (EBP) information has recently been developed (Rugh et al., 2010; Rugh et al., 2011) based on a model in which dental students are taught four EBP skills that enable them to:

1. Ask focused questions (in a PICO format, where "P" stands for the patient or problem; I, the intervention; C, the comparison intervention; and O, the outcome). That is, "For a patient with (problem A), how does (intervention B) compare with (comparison C) with regard to outcome D)?"
2. Use a systematic PubMed search strategy to find the highest level of evidence.
3. Critically evaluate the evidence.
4. Make clinical judgments about the applicability of the evidence for the patients.

A searchable online critically appraised topics (CATs) library related to clinical dental problems has been established and currently includes over 400 CATs developed by students, residents, and faculty. The library is available online at https://cats.uthscsa.edu/ for not only practicing dentists, but also educators, researchers, and the general public. The CATs Library provides key word–searchable topics. Each topic is presented as a structured one-page summary and critique of the best available evidence on a focused question. The library serves as a rapidly accessible source of evidence-based information for use in making on-the-spot clinical dental decisions. The library also includes a feedback mechanism for faculty and practitioners to comment on specific CATs.

ENVIRONMENTAL CONSIDERATIONS

GREEN DENTISTRY

Dental offices in the United States flush an estimated 25 million gallons of clean drinking water down the drain every day, generate some 5000 pounds of mercury-laden amalgam waste, and somehow get rid of huge amounts of other chemicals and disposable plastics. The Eco-Dentistry Association (EDA) is leading a movement to "green" America's 125,000-plus dental offices. As of 2008, dental offices in 45 states and 13 other countries have joined the organization and pledged to reduce their impact on the environment. Such initiatives include installing amalgam separators, using digital x-ray imaging in place of photographic images, replacing disposable lab coats with washable coats, using suppliers that offer environmentally sound products and services, and installing energy-efficient lamps and other equipment. These changes have been found not only to substantially reduce environmental impact but also to lead to substantial cost savings and other benefits. Micrylium Laboratories of Toronto is one example of a dental products supplier that specifically focuses on green products. For example, the company provides disinfectants for surfaces, immersion, and dental water lines that are not only environmentally safe but also have fast, clinically relevant kill times. Another example is an evacuation system detergent that both disinfects the tubing and also chelates mercury to enhance amalgam separation. Such products and other environmental initiatives are gaining acceptance and will quite likely become the standard of practice in the near future.

SUMMARY

This chapter has focused on technologies that have been developed but that have not yet been fully implemented as well as those that have not yet passed the proof-of-concept stage shown in the "level of evidence" section of Figure 21-1. Dental school educators and practicing dentists whose focus is on disease prevention, minimally invasive dentistry, and improved methods for extending the survivability of restorations will seek technologies that relate to processes promoting remineralization, and they will continue their search for improved technologies in these areas for years to come. More importantly, they will continue to search also for more sensitive and specific means of detecting the early stages of lesion development, and for three-dimensional imaging of remineralization. To be successful, these technologies must be more sensitive than current diagnostic methods. Thus, improved monitoring of early caries lesions will be essential to judge whether or not proposed methods and materials of disease management can be successful in ensuring remineralization and avoiding surgical intervention. If judged to be successful, these technologies and diagnostic methods would satisfy the "proven technologies, materials, and devices" outcome of Figure 21-1.

For product developers, laboratory technologists, oral surgeons, and prosthodontists, innovative technologies related to oral and maxillofacial reconstruction methods offer several pathways to improved oral health care. Although several innovative methods for prosthesis construction in lab settings have already emerged and others are emerging, the search will continue for biological technologies that will allow "natural" regeneration of lost or diseased tissues.

Finally, for materials scientists, implantologists, molecular biologists, cell biologists, and geneticists, this chapter will hopefully serve as a platform from which further innovative technologies for oral and maxillofacial applications can evolve. What is perfectly clear from this overview of emerging technologies is that sustained collaboration among specialists in the various areas of research and clinical practice will be essential to expedite the development of these technologies and for fully evaluating their effectiveness in solving clinical problems and for improving oral health outcomes overall.

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SELECTED READINGS

Useful Websites (accessed February 2012)

The Inside Scoop. Interviews with Oral Health Researchers. A variety of subjects and technologies under development are reviewed via interviews with key scientists supported by the NIH National Institute of Dental and Craniofacial Research. Recent subjects include biomimetics, building a tooth, craniofacial research, dental composites, dental practice-based research networks, diagnostics, genes/genetics, head and neck cancer, health disparities, pain/inflammation, periodontal disease, research training experiences, salivary disorders/dry mouth and TMJ disorders. http://www.nidcr.nih.gov/Research/ResearchResults/InterviewsOHR/

Library of critically appraised topics related to clinical dental problems. The "CAT" library provides key word–searchable topics. Each topic is presented as a structured one-page summary and critique of the best available evidence on a focused question. The library is designed as a rapidly accessible source of evidence-based information for use in making clinical dental decisions. https://cats.uthscsa.edu/

The Eco-Dentistry Association. Information about the association and resources to develop "green" dental practices. http://www.ecodentistry.org/?page=AboutGreenDentistry

Dental Restorative Materials—A Pollution Prevention Perspective. Information regarding the health, safety, and environmental issues arising from the chemical ingredients used in dental restorative materials. http://wsppn.org/studies/dental-chemical-use/fact-sheets/restorative-materials/

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Zivkovic P, Petrovic V, Najman S, et al: Stem cell–based dental tissue engineering. *Sci World J: TSW Dev Embryol* 10:901–916, 2010. DOI 10.1100tsw.2010.81
This review focuses on the use of tissue engineering strategies in tooth regeneration using stem cells and stem cells/scaffold constructs. The authors point out that although whole tooth regeneration is still not possible, there are promising results.

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