

Topics in Mining, Metallurgy and Materials Engineering  
*Series Editor:* Carlos P. Bergmann

Carlos P. Bergmann  
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# Dental Ceramics

Microstructure, Properties  
and Degradation

 Springer

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# Dental Ceramics

Microstructure, Properties and Degradation

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# Preface

This book contains a brief overview of dental ceramics, its microstructure, properties, and susceptibility to degradation. After the *Introduction* (Chap. 1), it presents the general context of dental ceramics, addressing special phenomena and properties as a *Biomaterial* (Chap. 2), without going too much into scientific detail of the physics and chemistry involved.

The next chapters present *Ceramic Materials for Prosthetic, and Restoration Use* (Chap. 3), and *For Orthodontic Use* (Chap. 4).

Chapter 5 presents dental ceramic focusing on microstructural characteristics in order to fulfill certain requirements such as specific flexural strength, elastic module, chemical resistance, and hardness essential for dental products. These bioceramics properties depend on their microstructure, which is determined by the phase present in the material, grain morphology and size, and grain interface.

*Mechanical Behavior of Ceramic Materials* is the subject of Chap. 6. Dental materials should withstand the forces of mastication and aggressive oral environment in which they are required to perform. Materials such as ceramic orthodontic brackets frequently fail due to the masticatory and orthodontic forces applied on them. Otherwise, the performance problems by ceramic materials are their brittleness, poor fracture resistance, and inability to absorb energy before they fracture. Therefore, as a ceramic material, dental ceramics fail due to the propagation of superficial cracks formed during their processing or due to surface impacts that occur in service. Failures of dental ceramics usually occur due to small structural defects like pores, flaws, and cracks. These defects are responsible for the loss of mechanical resistance which is especially important because of the cyclic stress and residual tension that dental ceramics are subjected to in the environment in which they are used.

Chapter 7 presents *Dental Alumina: Its Microstructure and Properties*. Alumina is the most common dental ceramic used in Dentistry. It combines inertness, good aesthetic properties, high mechanical resistance, chemical stability, corrosion, and wear resistance. The use of alumina is extending into different areas of Dentistry such as Orthodontics and Implantodontology. In Orthodontics, aesthetic brackets are made of high purity monocrystalline or polycrystalline alumina.

The *Degradation of Dental Ceramics* is discussed in Chap. 8. The aggressive intra-oral environment is a complex system. The saliva can have several pH

fluctuations in the course of a single day due to the type of food intake, the number of meals and soft drinks consumed in a day, hygiene habits, the use of fluoride solutions, the presence of orthodontic appliances, and oral microflora. The temperature in the oral environment, which varies from 0 to 55 °C according to the food intake, also exerts an influence. This temperature variation can occur with rapidity in seconds and it alters the structure of dental materials such as orthodontic wires.

We hope that the clear language and the application-oriented perspective are suitable for both materials engineers and dentists, professionals, and students who want to access major knowledge of dental ceramics materials.

Finally, we thank the staff of Springer-Verlag for their professional guidance in regard to this book.

Porto Alegre, Brazil, March 2013

C. P. Bergmann  
A. G. Stumpf

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# Chapter 1

## Introduction

The dental prosthesis (or prosthetic Dentistry) is the specialty in Dentistry where missing teeth are artificially replaced by making mobile or fixed prosthetic elements and generically from different materials. It has been almost universal that unexpected loss of tooth structure and, particularly, missing anterior teeth create physical and functional problems and often psychological and social disturbances as well.

Ancient Greek scholars Hippocrates and Aristotle wrote about Dentistry including the use of wires to stabilize tooth and fractured jaws. The replacement of missing teeth has been practiced since 700 BC in Etruria and in the Roman Empire in the first century BC (Fig. 1.1).

In the 18th century, the prosthetic materials used were human teeth themselves, animal teeth carved as human teeth, ivory and porcelain. The total prosthesis used by the first American president George Washington was carved out of hippopotamus ivory. Pierre Fauchard was the first dentist to write a dental book and to develop several dental instruments for prosthetics and orthodontics (Figs. 1.2, 1.3 and 1.4).

Europeans only managed to master the technique of making porcelain in the 1720s and the first porcelain denture was made in 1774 by the Parisian pharmacist Alexis Duchateau. Since then, the dental prosthesis was continually perfected. The first crowns and fused feldspathic porcelain inlays were made in 1886, evolving in the 1950s with the introduction of leucite (a potassium and aluminum silicate— $\text{KAlSi}_2\text{O}_6$ ), improving the properties of crowns and ceramic restorations. All-ceramic prostheses, however, have only become available on market in the 1980s.

Dentists and materials scientists have sought over time to reconcile mechanical performance with esthetics. An analysis of scientific articles published between 1981 and 1999 in *The Journal of Prosthetic Dentistry* shows that the major concern has been with the mechanical aspects of the prostheses. Since then the evolution of ceramic biomaterials as prosthetic materials is concerned with getting the most esthetic result possible, without causing damage to the opposing tooth enamel and presenting adequate mechanical performance.



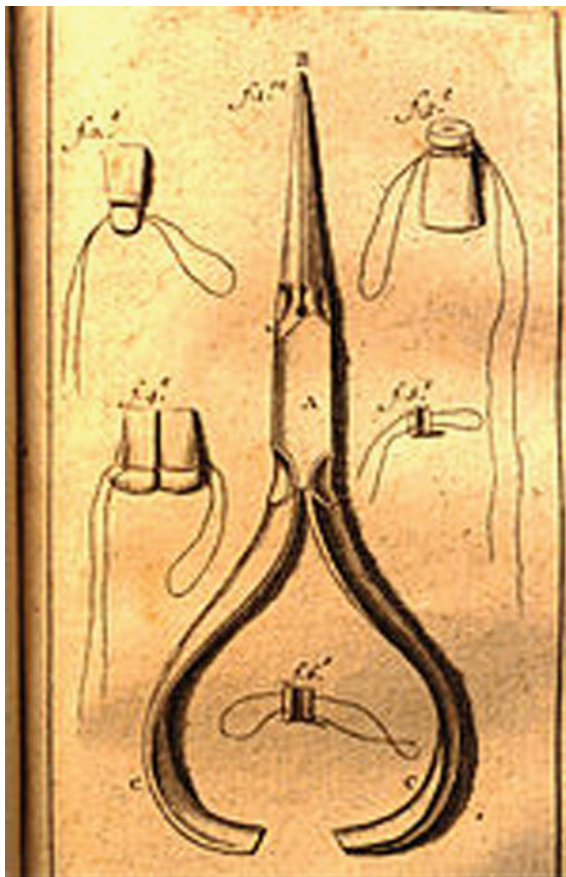
**Fig. 1.1** Image of a mandible with dental prosthetics done by Etruscans



**Fig. 1.2** Portrait of Pierre Fauchard



**Fig. 1.3** First prosthodontics plier developed by Pierre Fauchard



The use of ceramics as a prosthetic material has evolved from the metal-ceramic restorations used since the 1960s, opalescent ceramics (with the addition of oxides in the size of the wavelength of visible light), DICOR<sup>®</sup> ceramics (45 % glass and 55 % mica) to InCeram<sup>®</sup> ceramics (glass infused, partially sintered alumina).

Most of these ceramics are composed of leucite crystals dispersed in a glassy matrix. Leucite has a high coefficient of thermal expansion and raises the overall thermal expansion of the bulk porcelain leading to thermal compatibility with metal frameworks. The amount of leucite and the amount and composition of glass determine decisively the coefficient of thermal expansion of the final product.

The esthetic limitations of metal-ceramic restorations have triggered the development of new all-ceramic materials which can be used for both single restorations and short-span fixed partial dentures. Currently, many all-ceramic systems are commercially available and most offer superior esthetics, since they allow for light transmission in a manner similar to those of natural dental structures.



**Fig. 1.4** Prosthodontics tools by Pierre Fauchard

Today, the advances in the development of prosthetic materials come from the collaboration of the Ceramics Engineering and Dentistry specialists. The most notable progress includes the advent of reliable new ceramic materials and techniques, better understanding of the clinical response to the prosthesis and factors that influence clinical longevity.

Dentistry research has increasingly focused on developing new biomaterials for the various specialties such as Restorative Dentistry, Prosthodontics, Orthodontics and Surgery. The vast majority of these studies are conducted in the disciplines of Restorative Dentistry and Prosthodontics, especially regarding the study of ceramic and polymeric materials. In these investigations the focus is on developing materials that support the occlusal load and that are at the same time esthetic. In surgery, the most studied materials are those used in dental implants, coated with hydroxyapatite or not.

Orthodontics aims to correct tooth alignment and leveling, allowing adequate dental occlusion at the end of treatment. To achieve these objectives, both passive and active elements are used: among the passive elements, brackets and among the active elements the orthodontic arch. The orthodontic brackets fixed to the teeth provide a means of fitting the orthodontic arch, forming the basic components of a fixed prosthesis. The prosthesis allows the orthodontist to position the teeth in the arch in the most functional and esthetic way.

In orthodontics, the techniques and philosophy of orthodontic treatment have changed since its introduction of the specialty in 1901 by Edward Angle. Technological innovations among orthodontic materials, however, are remarkable. Before the advent of chemical adhesion to enamel developed by Buonocore (1963), the teeth were fixed with stainless steel ribbons. And until the 1970s, the only option for orthodontic devices was metal brackets. Nowadays, the professionals and patients have other options like plastic, ceramic and gold brackets and technologies such as Invisalign® (Fig. 1.5).

For the teeth to move, the arches must undergo first (inside and out), second (up and down) and third (torque) degree folds. The passive elements, the brackets, must be made so as to support the forces released by the orthodontic wires, while at the same time being biocompatible, esthetic and comfortable.

The brackets should also have good adhesion to the tooth so they remain fixed to the tooth throughout the treatment, but without causing damage to the tooth at the time of removal of the braces. For the outermost layer of the teeth, the enamel, does not regenerate and is responsible for the protection of the innervated and vascularized layers.

The most commonly used brackets in orthodontics are still made of stainless steel. However, with the growing demand for esthetics, ceramic brackets are becoming increasingly popular. These devices have appeared on the market in 1986 and have the advantage over polymeric brackets that they resist staining and discoloration and are chemically inert. They are composed of aluminum oxide, also called alumina, and can be classified as single crystal (commonly called

**Fig. 1.5** Dental orthodontic appliances Invisalign®



sapphire brackets) or polycrystalline structures according to their manufacturing process. The latter are made with sintered aluminum oxide particles, while the former contain only a single aluminum oxide crystal.

Since the production of polycrystalline brackets is simpler and less expensive, these brackets are more easily found on the market. Sapphire brackets, however, because it is made through the fusion and subsequent cooling of aluminum oxide particles, has fewer impurities and higher translucency than polycrystalline alumina, but both have similar resistance to staining. Polycrystalline brackets are more suitable for clinical use since its mechanical resistance does not fall dramatically with the scratches that can occur during their manufacture and during the connection and manipulation of the orthodontic wires.

The manufacturing process is extremely important in determining the properties of the ceramic brackets. The presence of pores, small cracks and manufacturing defects reduce the fracture resistance of these elements.

Ceramic brackets have a number of very important features that affect their clinical performance. The main problems with these accessories are their high cost, the possibility of causing damage to opposing teeth due to their high hardness, high friction, and damage to the enamel at the time of removal and fractures during their use. Their optical properties are also of great clinical importance, especially their color stability. Ceramic brackets should have good color stability. Some brands of these devices, however, do not behave this way. Another significant problem is the lack of rules for standardization of these devices. It is important to have a set of protocols and standards of minimum requirements for ceramic brackets.

The number of orthodontic treatments has increased in the last decade, especially among adults. Both the dental industry and orthodontists have been driven to develop more esthetic braces. Available on the market since 1986, ceramic devices have been widely used since then. Since their tone is similar to natural tooth enamel, it makes them more attractive esthetically.

It is therefore possible to observe that, within the field of Dentistry, ceramic materials demonstrate a wide range of applications and potential research topics. Ceramic materials stand out due to their combination of high wear resistance, good biocompatibility and low wetting angle properties, besides their high corrosion resistance and high mechanical strength. Among ceramics, alumina is one of the most researched materials.

Ceramics are normally polycrystalline materials composed of grains and grain boundaries. Grain boundaries are extremely important in the design and processing of ceramics and stress control is important to impart the desired properties to the ceramics. This can be achieved with the addition of glassy phases with the appropriate thermal expansion coefficient.

The direction of the current studies in bioceramics in Dentistry is focused on enabling the clinical use of ceramic materials, employing all their desirable properties and reducing the existing disadvantages.

The main disadvantage of dental ceramic materials compared to their metallic counterparts, is their predisposition to fracture. The brittle fracture process may



involve the formation or spread of pre-existing cracks. Under some circumstances, the fracture of ceramic materials occurs by slow crack propagation, when the tensions are static in nature. Moreover, it is known that in environments with acidic pH, the tendency to fracture increased.

The need for research to verify the mechanical behavior of ceramic materials for dental applications is required to ascertain the reliability of the material when it is put to market to be used by dentists with ease and safety for patients. A deeper understanding of behavior, however, including the performance estimation under intraoral service conditions, requires that the evaluation of ceramic materials, such as polycrystalline alumina used in dental prostheses and orthodontic brackets, be made in the light of Materials Science. That is, they should be evaluated through the association between the properties of interests and the microstructure resulting from the ceramic processing to which they were submitted.

Ceramic materials have high corrosion, wear and mechanical resistance as well as good biocompatibility and esthetics. The presence of pores, flaws and cracks reduces the mechanical resistance of these materials, where the environment is extremely aggressive. This book focuses the researches on the mechanical behavior and degradation of dental ceramics in order to develop more trustworthy materials.

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## Chapter 2

# Biomaterials

The most accepted definition of biomaterials is currently the one employed by the American National Institute of Health that describes biomaterial as “any substance or combination of substances, other than drugs, synthetic or natural in origin, which can be used for any period of time, which augments or replaces partially or totally any tissue, organ or function of the body, in order to maintain or improve the quality of life of the individual”. Such a definition, however, does not include materials such as orthodontic brackets and surgical instruments (Fig. 2.1).

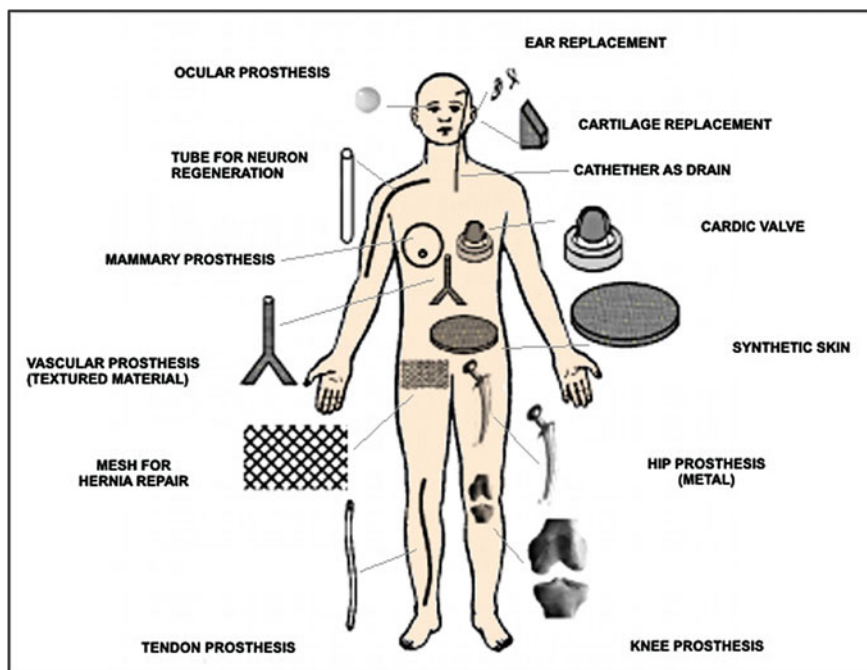
The first biomaterials used were gold and ivory for replacements of cranial defects. This was done by Egyptians and Romans. Biological materials such as placenta was used since the 1900s. Celluloid was the first man-made plastic used for cranial defects a polymethyl methacrylate (PMMA) was one of the first polymers accepted since World War II.

The Williams Dictionary of Biomaterials (Williams 1999) defined biocompatibility as “ability of a material to perform with an appropriate host response in a specific situation”. Although this definition seems vague and unhelpful at first glance, it represented a quantum leap forward at the time of its introduction. Prior to this definition, the prevailing view was that successful materials played largely inert roles the body.

A long list of ‘non-properties’ had evolved for ‘successful’ biomaterials: non-toxic, non-immunogenic, non-thrombogenic, non-carcinogenic, and so forth. The above definition required that materials not only provide some function, but also recognized that the interface created by introduction of the material will elicit a biological response. Thus, the idea that the material could be truly inert was essentially rejected with the adoption of this definition. Given today’s level of understanding of our bodies as sophisticated, complex biological environments, the idea that one could place a foreign material without some sort of response seems naïve.

Based on the reaction of the tissue to the biomaterial, these are classified into three distinct categories:

1. Biotolerant Materials: which are separated from bone tissue by a layer of fibrous tissue.



**Fig. 2.1** Examples of biomedical materials

2. Bioactive materials: which have the property of establishing chemical bonds with bone tissue, known as osseointegration. The collagen and mineral phase of the adjacent bone is deposited directly on the implant surface.
3. Bioinert Materials: in this class it is possible, under certain conditions, to have direct contact with the adjacent bone tissue. No chemical reactions shall occur between the implant and the tissue.

Recognition of an active interface between biomaterials and biological systems led to several important basic ideas about biocompatibility. These ideas persist today and comprise the essence of biocompatibility.

The first idea is that the interactions at the material–tissue interface occur for both; the material elicits a response from the body and the body elicits a response from the material. All materials will be changed at some level by their introduction into a biological environment—either via corrosion, chemical modification, deposition of substance, degradation, or other mechanism.

This exchange of responses leads to a second idea: that the material–tissue interface is dynamic. As the material and biological tissue are modified by each other, the changes themselves may suppose other changes. Thus, the interface is not static, but is changing over its lifetime. Furthermore, because the human buccal conditions are always changing—by aging, by developing systemic or local



diseases by adopting new activities, by eating differently, etc.—any equilibrium established at a material–tissue interface is subject to perturbation.

A third idea is that reactions at the material–tissue interface are a function of the tissue where the interface is created. A fourth idea about biological–tissue interfaces recognizes the nearly obvious, but often forgotten fact that the materials we use do not belong there. Biomaterials are foreign bodies, and biological responses to these materials are characterized by foreign body responses. Finally, the most recent idea about biocompatibility is that it is possible to customize interactions at the material–tissue interface.

Materials are asked to play more sophisticated, longer-term roles in tissues, customizing and optimizing the material–tissue interface to assure the best long-term clinical outcomes. We may modify the surface of a material to limit non-specific protein absorption, add peptide sequences to encourage native protein or cell interactions, or provide a three-dimensional structure to encourage matrix formation.

To accommodate the bioactive dimension of materials described above, The Williams Dictionary of Biomaterials (Williams 2008) updated his original definition of biocompatibility: “ability of a biomaterial to perform its desired function with respect to a medical 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 to that specific situation, and optimizing the clinically relevant performance of that therapy”.

Of course, in addition to biocompatibility and tissue response, other factors are important in the adaptation and longevity of a biomaterial. These factors are: material used, load applied during function, patient well-being and age, technique used. The development of new technologies is therefore essential in order to develop new biocompatible materials capable of supporting new specifications and applications.

The global market of biomaterials was estimated in 150–200 US\$ billion in 2012 including all diagnostic and therapeutic equipment. The ten largest markets are US, Japan, Germany, France, Italy, UK, Brazil, China, Canada and Spain. The growth of US market share is 9 % per year being the leading market in the world followed by Europe, with 25 % market share, and Japan. The largest market for biomaterial based products is orthopedic biomaterials followed by cardiovascular and drug delivery materials. The dental biomaterials market is around 1 US\$ billion.

## 2.1 Biomaterials in Dentistry

The market for the development of Dentistry materials has been increasing in recent years. In the United States of America, spending on Dentistry is rapidly increasing, resulting in the need for new biomaterials. The American Dental Association (ADA) reports in a 2008 survey that 94 % of the U.S. population is concerned about the rising costs of dental treatment. The ADA attributes this

increase to the higher cost of new dental materials and diagnostic tools. Therefore, the market for biomaterials and alternative materials in this field is huge.

The U.S. Food and Drug Administration (FDA) recognizes several broad types of substances that are used to promote human health; the two most common of these are drugs and devices. Most dental biomaterials are classified as devices, including filling materials, diagnostic aids, cements, bonding agents, and implants. The FDA defines a device as: “an instrument, apparatus, implement, machine, contrivance, implant, in vitro reagent, or other similar or related article, including a component part or accessory”.

Biomaterials are used in Dentistry in such restorative procedures as dental restorations, dentures, dental implants and surgical procedures, endodontic materials, in devices such as orthodontic materials (braces, elastic bands and wires) and tooth piercings.

Currently, there is pressure both from patients, who demand more esthetics, and from government agencies, which require materials that cause less environmental impact. Because of this, traditional materials such as silver amalgam are being replaced by composite resins and ceramic materials.

Restorative biomaterials are designed to recover the shape and the function of the teeth. Included in this category are materials for fillings as well as materials for the preparation of cavities. The latter can be used both to protect the pulp tissue and to create adhesion between the tooth surface and the restorative material. Dental materials should not be toxic, irritating or corrosive, and should be easy to use. The biomaterials used in Dentistry may be metals (silver amalgam, titanium and gold), ceramics (feldspar, alumina, zirconia, silica reinforced porcelain) and composites.

There are two useful concepts that help demystify dental ceramics by providing a structure within which to organize thinking. First, there are only three main divisions to the spectrum of dental ceramics: (1) predominantly glassy materials; (2) particle-filled glasses; and (3) polycrystalline ceramics. Defining characteristics are provided for each of these ceramic types. Second, virtually any ceramic within this spectrum can be considered as being a “composite”, meaning a composition of two or more distinct entities.

Many seemingly different dental ceramics can be shown to be similar or closely related to each other when reviewed within the framework of these two simplifying concepts. Additionally, the rationale behind the development of ceramics of historic and recent interest can be more easily understood. Two examples of the utility of these concepts include these statements: (1) Highly esthetic dental ceramics are predominantly glassy, and higher strength substructure ceramics are generally crystalline; and (2) the history of development of substructure. Ceramics involves an increase in crystalline content to fully polycrystalline.

Dental ceramics that best mimic the optical properties of enamel and dentin are predominantly glassy materials. Glasses are three-dimensional (3D) networks of atoms having no regular pattern to the spacing (distance and angle) between nearest or next nearest neighbors; thus, their structure is amorphous, or without form.

Glasses in dental ceramics derive principally from a group of mined minerals called feldspar and are based on silica (silicon oxide) and alumina (aluminum oxide); hence, feldspathic porcelains belong to a family called aluminosilicate glasses. Glasses based on feldspar are resistant to crystallization (devitrification) during firing, have long firing ranges (resist slumping if temperatures rise above optimal), and are biocompatible.

In feldspathic glasses, the 3D network of bridges formed by silicon-oxygen-silicon bonds is broken up occasionally by modifying cations such as sodium and potassium that provide charge balance to non-bridging oxygen atoms. Modifying cations alter important properties of the glass, for example, by lowering firing temperatures or increasing thermal expansion/contraction behavior.

Polycrystalline ceramics have no glassy components; all of the atoms are densely packed into regular arrays that are much more difficult to drive a crack through than atoms in the less dense and irregular network found in glasses. Hence, polycrystalline ceramics are generally much tougher and stronger than glassy ceramics. Polycrystalline ceramics are more difficult to process into complex shapes (e.g. prosthesis) than are glassy ceramics.

Well-fitting prostheses made from polycrystalline ceramics were not practical before the availability of computer-aided manufacturing. In general, these computer-aided systems use a 3-D data set representing the prepared tooth or a wax model of the desired substructure. This 3D data set is used to create an enlarged die upon which ceramic powder is packed (e.g. systems of PROCERA<sup>®</sup> of Nobel Biocare<sup>®</sup>) or to machine an oversized part for firing by machining blocks of partially fired ceramic powder (e.g. systems of Cercon<sup>®</sup> of Dentsply Prosthetics, Lava<sup>™</sup> of 3M<sup>™</sup>-ESPE; In-Ceram<sup>®</sup> YZ of VITA<sup>®</sup> Zahnfabrik). These approaches rely upon well-characterized ceramic powders for which firing shrinkages can be predicted accurately.

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## Chapter 3

# Ceramic Materials for Prosthetic and Restoration Use

The first uses of ceramics as dental material date from the early XVIII century. Today, ceramics are being used on a large scale as restorative materials in Dentistry. This includes materials for dental crowns, prosthesis cementation and total and partial dentures. The increase in the use of ceramic restorations has virtually removed the use of metal restorations, since they do not meet the esthetic demands of patients. Ceramic materials are best suited to replace metal, especially in erosive and corrosive environments.

Dental ceramics allow regular and diffuse transmission, as well as diffuse and specular reflectance of light, and therefore have the potential to reproduce the depth of translucency, depth of color, and texture of natural teeth. In addition, dental ceramics have a relative good resistance to degradation. The oral cavity is biologically compatible, and has a coefficient of thermal expansion that is similar to that of tooth structure.

The first dental ceramics had their use limited to the front teeth because of their low flexural strength. New technologies and manufacturing techniques have allowed the development of different ceramic systems for dental use with higher resistance, expanding the options available to dentists and allowing the manufacture of prostheses for posterior teeth.

Ceramics have been used to fabricate a wide variety of restorations including inlays, onlays, implants, crowns and fixed partial dentures on account of their biocompatibility, wear resistance and better esthetics. Due to their better esthetics, in particular, patients have become more demanding regarding the appearance of their restorations (Fig. 3.1).

The use of all-ceramic crowns has been questioned because of their lack of strength. Their counterparts, the metal-ceramic crowns, have been used successfully; the majority of all full-coverage restorations and fixed prostheses are fabricated from metal-ceramic systems that have a failure rate of only 1–3 % over 5 years. Metal-ceramic systems (MCS) have come under scrutiny, however, because of (1) potential alloy corrosion leading to toxicity and allergy concerns; (2) esthetic problems such as lack of translucency, discoloration of some ceramics from silver in the alloy, and excessive value in the cervical third; (3) the amount of

**Fig. 3.1** Dental ceramic prosthetics



tooth reduction necessary, and the associated tendency to overcontour the restoration; and (4) incompatibility between metal and ceramic, and the difficulty in establishing standard tests for bond strength and thermal compatibility.

Fixed prosthodontic treatment, whether involving complete or partial coverage and natural tooth or dental implant abutments, commonly relies on indirect fabrication of definitive prostheses in the dental laboratory. Historically, the necessity for provisional treatment has been primarily derived from this methodological process.

The importance of interim treatment, however, is more far-reaching than is portrayed by this procedural necessity and the requirements for satisfactory provisional restorations differ only slightly from the definitive treatment they precede. In the last few decades, ceramic materials for restorative dentistry have evolved significantly, and esthetic restorations, such as all-ceramic crowns and veneers, are routinely used in practice.

Different materials and production systems are available for all-ceramic dental restorations. There are two main options when using ceramics for prosthetic restorations; a single layer ceramic that is attached to the tooth structure or a two-layered structure with a high-strength ceramic core material, which supports the more fragile veneering ceramic.

Some high strength materials are designed for computerized milling techniques (CAD/CAM) where the core structure is milled from the presintered block of an oxide ceramic. A relative recent dental ceramic is yttria-stabilized zirconium oxide polycrystals. These materials are manufactured from fine particles of  $\text{ZrO}_2$  and 3–5 %  $\text{Y}_2\text{O}_3$ , which form a partly stabilized tetragonal structure at room temperature after heat treatment. Due to the optical opacity of these materials, they are covered with veneering ceramic, usually feldspathic types, with esthetic characteristics similar to the natural tooth substance.

The veneering process involves a firing procedure at high temperatures (750–900 °C) and subsequent cooling of the restoration. This process is performed at least once, usually two to five times. It is not fully known what effect this thermal history has on the properties of the core ceramic.

Patients have become more and more demanding regarding the esthetic and biocompatibility of their dental restorations, ceramic as material for inlays, onlays, crowns and bridges has become a main goal for scientific interest especially from the material point of view.

Lithium disilicate ceramic restorations became available in 2006, and can be fabricated with a heat-pressed or computer-aided manufacturing (CAD/CAM). The better translucency and shade variety makes possible anatomically contoured monolithic restorations. Lithium disilicate restorations may be fabricated in the dental office and/or dental laboratory. Improved in-office chairside milling technology allows restorations to be designed, milled, and inserted at the same appointment as tooth preparation. With the dental laboratory-based cut-back method nano-fluorapatite ceramic can be layered onto a lithium disilicate substructure at the incisal, occlusal, or facial areas to improve the optical properties and to customize the esthetic and anatomic contours.

Dental ceramics are inherently fragile in tension. While the theoretical tensile strength of porcelain is dependent upon the silicon-oxygen bond, the practical strength is 10–1,000 times less than the nominal strength.

Generally cracks may propagate in different ways in the polycrystalline ceramic material, as seen in Fig. 3.2. The crack is formed from the coalescence of microcavities inside the material, giving an appearance of acute brittle fracture (Fig. 3.2a). The crack propagates with sharp point, without any visible permanent deformation, running through the grains (transgranular fracture—Fig. 3.2b), or between grains (intergranular fracture—Fig. 3.2c).

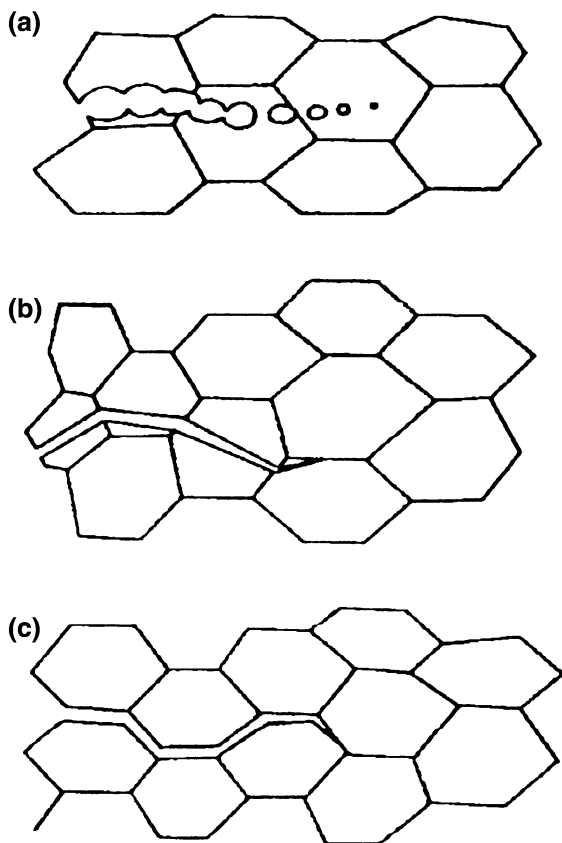
Susceptibility to fracture is the result of several factors. A volume and surface distribution of stress-raising microcracks is present in manufactured ceramics. Microcracks are caused by the condensation, melting, and sintering process; by the high contact angle of ceramics on metal; by differences in the coefficient of thermal expansion between alloy or core and veneers; by grinding and abrasion; and by tensile stresses during manufacture, function, and trauma.

Strength is most dependent upon the number and severity of these flaws. The flaws of greatest importance are located in surface areas, and are in the range of 100 pm in diameter. The largely covalent: ionic bonded structure of ceramics confers resistance to chemical degradation in the oral environment; however, it also imparts brittleness. Ductile materials, such as metallic alloys, can dissipate stress by slip and plastic deformation. Brittle materials, such as dental ceramics, have a limited capacity for distributing localized stress at nominal temperatures.

The critical strain of dental ceramics is low; the material can withstand a deformation of approximately 0.1 % before fracture. Repetitive loading, resulting in fluctuating stresses and strains, may be the most common mechanism of failure of dental ceramics.

Failure (fracture) of a ceramic crown intraorally generally occurs by a combination of bending and torsional forces, such as those produced by incisal leverage. These forces involve tensile stresses occurring as a result of comparatively light, but repeated, occlusal loading on the inner surfaces of the crown, particularly at the cervical third of anterior crowns. These low-energy flexural

**Fig. 3.2** Brittle fracture and crack propagation in the polycrystalline ceramic material: **a** coalescence of microcavities; **b** transgranular crack propagation; **c** intergranular crack propagation (Adapted of Askeland 2009)



forces place surface flaws under tension. Slow crack growth of subcritical flaws occurs as local residual stresses are relieved by the growth of existing cracks until critical dimensions are reached at the time of failure. The longer stresses are applied, the greater the chance of failure over time (Fig. 3.3).

Strengthening or toughening mechanisms are designed to resist the initiation and propagation of microcracks. In Dentistry, there are two well-known methods of

**Fig. 3.3** Fracture of dental ceramic fixed prosthetics



accomplishing this: (1) by the use of metallic substructures, and (2) by crystalline dispersions within the glass matrix.

Since the glass is the weak component, dispersion of a crystalline phase helps to manage crack growth. During firing, the glass melts and flows around the crystals, forming an ionic bond between the matrix and the crystals. Fracture lines will then pass through both phases; the high rigidity of the crystals results in the crystalline phase bearing a higher portion of the load. This results in a restricted flaw size and an increase in the toughness of the system, a function of the volume fraction of the dispersed phase. If the coefficient of thermal expansion of the dispersed phase is slightly higher than that of the matrix, the glass will be placed in compression upon cooling, thereby increasing the potential strength.

Glass-ceramics that can be sintered to conventional or fine metal frameworks have been introduced in clinical practice. They are polycrystalline solids prepared by the controlled crystallization of glasses and have been reported to present improved optical, physicochemical or mechanical properties. Glass-ceramics are made by forming special base glasses, mostly by melting, and then using controlled heat treatment (sintering) to nucleate and precipitate crystals in the glassy matrix. The number of crystals, their growth rate and thus their size are regulated by the time and temperature of the sintering process. The chemical composition and microstructure of the glass-ceramic determine its properties and main applications, while to ensure high mechanical performance it is important that the crystals are numerous and uniformly distributed throughout the glassy phase.

Kontonasaki et al. (2008) reported that low fusing feldspathic ceramic presented leucite crystals and crystals of potassium feldspar dispersed in a glassy matrix, while the low fusing glass-ceramic exhibited apart from leucite many needle-like fluorapatite crystals. The only crystal phase detected in the high fusing ceramic was leucite. The low fusing glass ceramic and the high fusing leucite based ceramic presented significantly higher fracture toughness and microhardness and lower modulus of elasticity compared to the low fusing feldspathic ceramic. The three ceramics were almost equivalent concerning their *in vitro* biological behavior and presented increased rate of cell proliferation after the 3rd day of cultivation period.

Leucite structure relies on a framework of  $\text{SiO}_4$  tetrahedrons that form rings. At room temperature, leucite crystals do have tetragonal symmetry. When heated the  $\text{SiO}_4$  structure expands slowly by untilting and untwisting the tetragonal rings until the symmetry changes to cubic at 625 °C. The phase transformation of leucite from cubic to tetragonal when cooled, in combination with the greater contraction of the leucite crystals compared to the glassy matrix due to their large thermal contraction mismatch, cause tangential compressive stresses around leucite crystals. These stresses may act either as crack deflectors or crack initiators influencing the mechanical performance of the ceramic.

The leucite content in dental ceramics is critical also due to its contribution to the flexural strength of feldspathic porcelains. It has been reported that an increase in leucite content from 10 to 30 % increased the flexural strength from 34.1 to



64.8 MPa while studies on fracture toughness ( $K_{IC}$ ) showed a direct relation of the leucite content to  $K_{IC}$ .

Nowadays, systems with higher resistance (bending strengths higher than 300 MPa) are available and include: lithium disilicate glass ceramic (e. max Press<sup>®</sup>; IVOCAR VIVADENT), glass-infiltrated composite (In-Ceram<sup>®</sup> spinell, alumina and zirconia; VITA<sup>®</sup> Zahnfabrick), pure alumina (PROCERA AllCeram<sup>®</sup>; Nobel Biocare<sup>®</sup>), yttrium stabilized tetragonal zirconia polycrystalline (abbreviated as Y-TZP) including Cercon<sup>®</sup> (Dentsply Ceramco), LAVA<sup>®</sup> (3M<sup>™</sup> ESPE) and VITA<sup>®</sup> YZ. Among these, pure alumina and especially Y-TZP, exhibit the highest fracture toughness and strength. However, e.max Press<sup>®</sup> and In-Ceram series are the only ceramics not dependent upon CAD/CAM systems and can be fabricated by dental technicians in a more traditional fashion.

It is reported in the literature that the In-Ceram<sup>®</sup> series of materials are stronger than e.max Press (formerly named Empress 2). In the In-Ceram<sup>®</sup> series of materials, In-Ceram<sup>®</sup> alumina was the first restorative system introduced for the fabrication of three-unit anterior fixed partial bridge.

In-Ceram<sup>®</sup> alumina restorations are two-layer structures in which the substrate is In-Ceram<sup>®</sup> alumina and the veneer is the conventional porcelain like one used for the metal-ceramic restorations but with coefficient of thermal expansion compatible to the In-Ceram<sup>®</sup> substrate.

Mica glass-ceramics were the first glass ceramics in Dentistry that could be mechanically processed. The precipitation of mica crystals allowed the glass-ceramics to be machined. After the centrifugal casting process had been successfully tested, glass-ceramics were developed, which could be used to mould dental restorations by employing the lost wax technique. This technique also took advantage of the viscous flow of glass-ceramics. In the meantime, intensive research has shown that leucite glass-ceramics can also be machined. This material allowed metalfree restorations to be fabricated for a patient chairside in one short appointment. The main indications included inlays and dental crowns. As this technology together with the favourable properties of leucite glass-ceramics offers many advantages, above all time savings for the dentist and patient, it is to be expected that these applications will grow in popularity until 2020.

In order to enable glass-ceramics to be used in the fabrication of dental bridges (preferably three-unit bridges) and for single crowns in the molar region, the strength and toughness of these materials had to be increased. As a significant increase in these parameters could not be achieved in leucite-based glass-ceramics, a new materials system had to be developed. Glass-ceramics of the lithium disilicate system showed a great deal of promise in this respect. These lithium disilicate glass-ceramics can be used for both the moulding and the machining technique involving CAD/CAM methods. However, neither the base glass nor the lithium disilicate end product is suitable for machining in commercial dental CAD/CAM equipment.

Although glass-ceramics allowed combining a variety of properties of glass and ceramic materials, it was not possible to achieve the highest toughness and strength parameters of ceramics. Therefore, high-strength materials came into play

for dental restoratives. As early as in the 1990s, high-strength  $\text{Y}_2\text{O}_3\text{-ZrO}_2$  sintered ceramics were used as restorative materials in Dentistry because of their high toughness. With the further development and improvement of CAD/CAM technology,  $\text{ZrO}_2$  sintered ceramics were developed for long-span dental bridges in particular. Because the strength of porcelain-fused-to-metal restoration depends on coping material, a lot of studies have been done on finding of the better coping material. In recent years, zirconia was introduced in dental area and received attention as esthetic material.

Zirconia is a crystalline dioxide of zirconium. Its mechanical properties are very similar to those of metals and its color is similar to tooth color. Fracture strength has progressively increased from glass ceramic (320 MPa) to alumina (547 MPa) to zirconia (900 MPa). Zirconia has mechanical properties similar to those of stainless steel. Its resistance to traction can be as high as 900–1,200 MPa and its compression resistance is about 2,000 MPa. This material also tolerated well with cyclic stress.

Yttria-stabilized tetragonal zirconia (Y-TZP) is gaining use in Dentistry due to its good mechanical properties. It is currently used as a core material in all-ceramic dental restorations, implant superstructures, and orthodontic brackets. Compared to other dental ceramics, its superior mechanical properties, such as higher strength and fracture toughness, are due to the transformation toughening mechanism.

$\text{ZrO}_2$  is a polymorphic material that has 3 different crystalline structures: the monoclinic phase is stable up to 1,170 °C, at which point it transforms into the tetragonal phase, which is stable up to 2,370 °C, and the cubic phase exists up to the melting point at 2,680 °C.

The introduction of osseointegrated dental implants has dramatically altered the scope of prosthodontic treatment. The availability of predictable, stable anchorage for prosthetic tooth replacement has expanded treatment options but has also increased treatment planning and technical complexity.

Despite the progress made in the last decade, due to their brittle nature, all-ceramic restorations still have lower clinical longevity compared to metal-ceramic restorations. That is why these systems were unpopular until the late 1980s.

Because of their brittle properties, however, all ceramic systems are not used in posterior region which received high occlusal force. So, all ceramic restorations were used in region which received lower force and was important in esthetic. To improve brittle properties of all ceramic systems, porcelain-fused-to-metal technique has been standard method.

Feldspar porcelains have been attractive materials in restorative Dentistry because of their approximations to the appearances and functions of human enamels. A machinable feldspar porcelain is one of the ceramic materials for dental CAD/CAM. However, this porcelain is brittle in nature and susceptible to machining-induced damage.

Studies have shown that the feldspar porcelains suffer from extensive chipping defects and microcracks in dental CAD/CAM processes, due to their high amount of glassy Phase. Also, in intraoral dental finishing of the porcelain using dental

headpieces and burs, extensive chipping damage and subsurface damage were introduced in the feldspar porcelain when using coarse grit diamond burs.

Ceramics are sensitive to stress concentrations around pre-existing cracks. The stress field at the tip of a crack can be described by the stress intensity factor ( $K_I$ ) that is controlled by the loading in Mode I (opening mode). The flaw will propagate when the stress intensity factor reaches a critical condition,  $K_{IC}$ , which is also called the critical stress intensity factor, or fracture toughness and characterizes the resistance to unstable propagation of pre-existing cracks. These flaws form during processing (i.e. pores, inclusions) or subsequent handling, finishing, or service damage.

The fracture of ceramics in service occurs with little or no plastic deformation when cracks propagate in an unstable manner under applied tensile stresses. Fracture occurs when the stress intensity factor at the crack tip ( $K_I$ ) reaches a critical level ( $K_{IC}$ ).

“Subcritical crack growth” (SCG) is a process that involves the stable growth of pre-existing flaws at stress intensity factor ( $K_I$ ) level slower than that necessary for the flaw to become unstable ( $K_{IC}$ ). In the case of stress-corrosion, this phenomenon can result from a water-assisted breakage of silicate.

Slow crack growth parameters can provide an indication of the relative susceptibility of a given material to stress corrosion phenomenon, in addition to the comparison between different materials with respect to their resistance to slow crack growth. This is of importance since the clinical longevity of ceramic restorations is often limited by lifetimes that are controlled by a slow crack growth process. Moreover, knowing these parameters can assist in understanding how the microstructure of ceramic materials can be modified to increase their lifetime in service. A wet environment combined with cyclic loading leads to crack propagation at stress levels more than 50 % below the initial strength of the material, confirming the strong susceptibility of dental ceramics to subcritical crack growth.

Microstructure significantly influenced the mechanical and slow crack growth behavior of the dental ceramics evaluated and, consequently, the strength degradation over time (lifetime). The high crystalline content and low porosity found for the polycrystalline ceramics result in high values of flexural strength, low susceptibility to slow crack growth and low strength degradation over time.

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## Chapter 4

# Ceramic Materials for Orthodontic Use

In the last three decades, great advances have been made in the mechanical properties of ceramics, reducing the presence of defects, increasing the degree of homogeneity and improving the microstructure in order to increase strength. The advent of the manufacture of laminated ceramic composites is improving the properties of ceramic materials.

The ceramic biomaterials used in Dentistry require different properties than those needed in bioceramics used in biomedical implants. While biomedical implants should be biocompatible and bioactive, the bioceramics used in Dentistry must be compatible with the oral tissues and functions, but do not necessarily need to be bioactive. Depending on the intended use, these materials must meet certain requirements for flexural and mechanical strength, modulus of elasticity, translucency, wear resistance, chemical resistance and hardness. Different chemical compositions are therefore used and the development of these materials is focused on the distinct microstructural characteristics.

Dental ceramics must withstand the intermittent forces arising from chewing, with maximum values varying between 200 and 1,000 N. When forces of this magnitude are applied to the tooth surface, mechanical stresses can occur that may compromise its integrity.

The selection of restorative ceramic materials for orthodontic use should be based on the type of clinical service that they will perform and requires careful analysis of the many physical properties, including fracture resistance.

The properties of a material are in a first instance the result of its chemical bonds at the atomic level. These bonds can be ionic in nature (when there is donation of electrons from a metal to the outer layer of a nonmetallic element, resulting in positive and negative ions that attract each other) or covalent (when electrons are shared between atoms involved in the link). The final properties, however, are also the result of interactions that occur between different phases (crystalline or not) that lead to the definition of a material's microstructure.

Among the ceramics used in Dentistry, there are a vast number of types available for clinical use. These ceramics are classified according to their type (feldspathic porcelain, porcelain reinforced with silicate, zirconia, alumina), method of manufacture (condensed, sintered, injection molded) and clinical indication.

The bioceramic materials most commonly used in Dentistry are alumina and zirconia. Alumina and zirconia are inert bioceramics that exhibit high mechanical strength, excellent corrosion resistance and good wear resistance. They are widely used in places with high stress concentrations such as joints and dental implants. They are the materials of choice for prosthetic restorations, orthodontic implants and brackets due to their excellent properties and pleasing esthetics. However, their choice as a material for dental prostheses is only viable with narrow widths, since their greater opacity makes them less esthetic than the other ceramics.

One of the most widely used types of ceramic materials for dentures and dental restorations is the system based on In-Ceram<sup>®</sup> Alumina (VITA<sup>®</sup>, Germany). This material is a 2-part structure, where the substrate is the In-Ceram<sup>®</sup> alumina and the veneer is a conventional porcelain (glassy phase). The alumina is partially sintered at 1,120 °C for 2 h, forming a skeleton of porous alumina. Then the vitreous phase is infiltrated and burned at 1,100 °C for 4–6 h, forming a composite of 65 % alumina and 35 % of glassy phase.

Although alumina is more used in dental materials, zirconia is currently being applied extensively in fixed partial dentures, implant abutments and endodontic pins due to its high mechanical strength and esthetic properties. It also presents high hardness, corrosion resistance and high tensile strength. Zirconia was in 1789 isolated from zircon by German chemist M. H. Klaproth. Among the different types of zirconia, tetragonal zirconia is the most versatile and most widely used in health care.

The problem that hinders the use of zirconia, however, is the fact that it has a less pleasing esthetic appearance than alumina and is more susceptible to aging in aqueous environments such as the intra-oral one. In current studies, there is a tendency to research alumina and zirconia composites for biomedical use, in order to combine their desirable characteristics and properties.

The use of ceramics is desirable due to its excellent chemical durability, wear resistance, excellent compressive strength, biocompatibility, esthetics and low friction when used in joints. This low friction can be explained by the hydrophilic nature of ceramics and the fact that it allows good polishing of its surfaces. However, a drawback that hinders its use is the brittle nature of ceramics and its susceptibility to fracture in areas of concentrated tension on the surface or inside of its microstructure.

Ceramics are fragile materials and unable to absorb significant amounts of energy before fracture. The stress concentration around cracks is not alleviated by plastic deformation as in ductile materials such as metals and polymers. The fragility of ceramics manifests itself when pre-existing microcracks propagate unstably until the complete rupture of the material. Hence dental ceramics fail because of the growth of surface cracks formed during their processing or impacts on its surface during use.

The sintering process makes ceramics display microscopic defects, both in its volume and on its surface. Another feature of sintered ceramics is the presence of residual stresses. The combination of microscopic defects with residual stress on

the surface, low fracture resistance and tendency for subcritical crack growth in these materials causes them to be sensitive to cracking.

Failures occur usually exactly where small structural flaws such as pores and cracks are located, because these defects are responsible for the reduction of the mechanical strength of ceramics used in Dentistry. In particular, because these ceramics are subjected to cyclic loading, residual stresses and to aggressive intraoral environment.

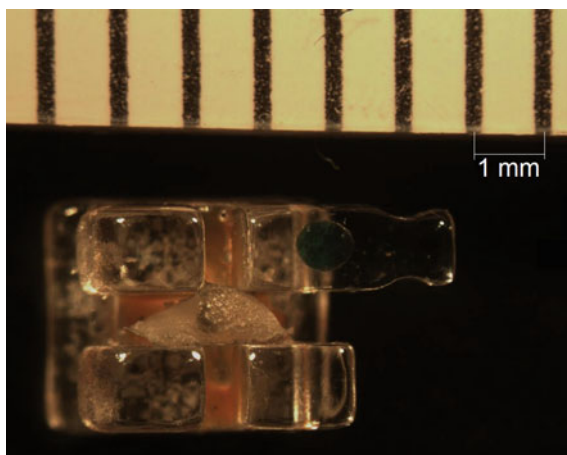
With use, ceramics are prone to fracture under light loads due to the loss of mechanical strength. In order to improve the mechanical properties and reliability of ceramics, it is therefore necessary to have a deeper understanding of how the mechanical strength is defined during the manufacturing process and what its relationship is with the microstructure, the size of the defects, besides the inherent strength of the material.

Segui et al. (1995) report that efforts to improve the resistance of dental ceramics date back over two decades, with efforts to alter their microstructure and improve their properties.

In general, the new dental ceramics have in common a considerable amount of crystalline phase within the glassy phase, which improves their physical, optical and mechanical properties. The size, distribution and nature of the crystalline phase of dental ceramics seem to be the main factor in its behavior concerning fractures.

In 1986, the first ceramic brackets became available. They were widely accepted due to their esthetic appearance. They have color stability, good torque control and higher bond strength which made them a better replacement for plastic brackets. These devices are fabricated with high purity alumina in a polycrystalline or monocrystalline form (Fig. 4.1). The polycrystalline brackets are less translucent and less esthetic, but they are cheaper and less prone to wing failure. Nowadays, most patients prefer monocrystalline orthodontic brackets once they are more discrete and look more natural.

**Fig. 4.1** Image of a polycrystalline alumina ceramic orthodontic bracket



## 4.1 Disadvantages of Ceramics in Orthodontics

### 4.1.1 Wear

Tooth wear is the phenomenon in the oral cavity characterized by the loss of original anatomical shape, which may be the result of physiological or pathological conditions. Excessive wear can damage the occlusal surfaces and cause functional alterations of chewing movements, which may result in the remodeling of the temporomandibular joint. Dental ceramics can cause damage to tooth enamel.

According to Oh et al. (2002), different factors influence the abrasive potential of ceramics on the enamel, such as physical factors (resistance to fracture, frictional resistance, hardness), microstructural factors (porosity, grain size), surface characteristics (polish, presence or absence of enamel) and environmental factors (salivary pH).

The wear of ceramics on the tooth structure occurs by fracture rather than by plastic deformation as occurs in metals. This type of failure through micro indentations is dependent on the arrangement of crystals in the glassy matrix.

A very important physical property of ceramic brackets is the extreme high hardness of aluminum oxide. It is generally thought that the harder a material is, the more it will wear an opposing material softer than itself. The Knoop hardness number (KHN) for ceramic brackets is in the range of 2,400–2,450, almost nine times as hard as stainless steel brackets (KHN approximately 280) or enamel (KHN 343).

Care should be taken when ceramic brackets are bonded to lower incisors once. In patients with deep overbite, they can become in touch with the lingual surface or incisal edge of the upper incisors leading to wear of the enamel. The same can occur with other teeth. In patients with deep overbite, metal brackets in the lower teeth can be a wise choice.

### 4.1.2 Frictional Resistance

Often, orthodontic treatments involve dental extractions to solve space issues. To close these spaces, as in other situations, the teeth are slid over the orthodontic wires. When using this technique, the surface roughness of ceramics compared to that of stainless steel, increases the frictional resistance, reducing the sliding efficiency by up to 30 % (Johnson et al. 2005). Among the ceramic brackets, those made from monocrystalline alumina seem to offer more slip resistance. The friction coefficient depends on the load and on the geometric characteristics such as surface texture, shapes and structures of the contact area.

On the market ceramic brackets can be found with metal inserts in their channels in order to minimize the effect of increased roughness of the ceramics without affecting the esthetic appeal of these devices. Authors such as Thorstenson

and Kusy (2003), however, have found no greater efficiency of esthetic brackets with metal inserts.

### ***4.1.3 Adhesion to Enamel and Removal of Orthodontic Accessories***

One of the major concerns for orthodontists who use ceramic brackets is the risk of tooth fracture at debonding. Céia et al. (2008) claim that removal of these braces can damage the enamel. Bond strengths over 14 MPa can be enough to damage the tooth surface. Lopez (1980), Reynolds (1975), suggest a value of bond strength to enamel of 7 MPa. Bond strength depends on the design of the base of the bracket, the adhesive used, the bonding technique, the thickness of the adhesive, the degree of curing of the adhesive used and the professional's experience. Removal of these devices can be done in four ways.

The first and most common one is mechanical debonding using special pliers recommended by the manufacturers (Fig. 4.2). This technique generates a large number of enamel fractures.

The second way to take off the brackets, involves heating the ceramic bracket with a rechargeable heat gun, while simultaneously tensioning the brackets (electrothermal technique). This method, however, can generate heat and pulp necrosis.

There is also a third possibility: the use of ultrasound for debonding. Despite causing little risk of tooth fracture, however, the technique is time consuming and causes wear on the tip of the devise, turning it more expensive. The last, suggested method is debonding by Laser, which would provide atraumatic, safe and fast removal.

**Fig. 4.2** Image of an orthodontic plier used to debond a ceramic bracket (Bishara et al.)





#### 4.1.4 Fracture

Clinical and experimental data show that the most frequent causes of failure in bioceramic materials are fractures, especially in ceramic brackets. Fracture resistance is an intrinsic property that depends on the intensity of the load at the crack tip in the material and the size of the crack in relation to the microstructure of the material such as crystal size, orientation and distribution of the glassy phase and porosity.

Fracture resistance therefore specifies the material's resistance against crack propagation while in use. The fracture of the material starts when a load applied to the tip of a crack or defect produces stress similar to the extrinsic resistance of the glass matrix. Since ceramic materials fracture without significant plastic deformation, the importance of  $K_{IC}$  is fundamental.

The deformation of a ceramic material before fracture is about 1 %, while for stainless steel this value is 20 %. This is because the type of crystal structure does not allow plastic deformation. Thus, the stresses caused by orthodontic treatment (binding and activation of the arch, occlusal and chewing forces) can cause cracks that lead to failures.

Braces are devices with many stress concentrators, such as fins and channels, and, just like ceramic components with structural details, they become susceptible to fracture. The manufacturing process is critical in defining fracture resistance, because a simple surface scratch will greatly reduce this property. It is common for the component to break, forcing it to be exchanged by a new bracket. The cost of each ceramic bracket unit is up to 10–15 times higher than each metal bracket unit.

While assessing polycrystalline ceramic brackets, Kusy (1988) noted that most of the fractures were intergranular and that the grains of these orthodontic accessories ranged from 25 to 125  $\mu\text{m}$ , with the outer surfaces being more porous. The same author suggested that the alumina particles should be reduced in order to decrease the number of pull-outs of grain fragments. He also suggested that the surface should be polished to reduce surface roughness and chemically and/or heat treated to increase shear strength.

The impact resistance of these devices is also affected by their composition, with polycrystalline alumina brackets being stronger than monocrystalline ones. The design of the component also influences the impact resistance, since the more compact brackets without prominent fins are more resistant. Other factors such as density and surface finishing are also important (Lawn 1993).

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## Chapter 5

# Microstructure of Ceramic Materials

The properties of ceramics depend on their microstructure, which is defined by the type, size, morphology, distribution, orientation and composition of the phases present and by the interface between the grains. In the latter case, a thick or thin layer of amorphous material may be found, originating from sintering additives. The variables involved can barely be controlled in an adequate manner, which makes it difficult to predict the final properties of a porcelain with a reasonable degree of reliability.

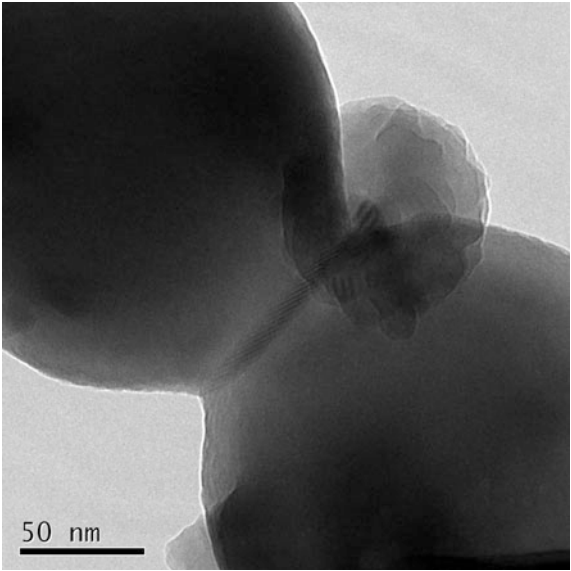
### 5.1 Formation of the Microstructure: Sintering Process

Microstructure is the name used to describe the structural characteristics found inside materials. The microstructures can be defined by the type, proportion and composition of their phases and by the form, size and distribution of their grains.

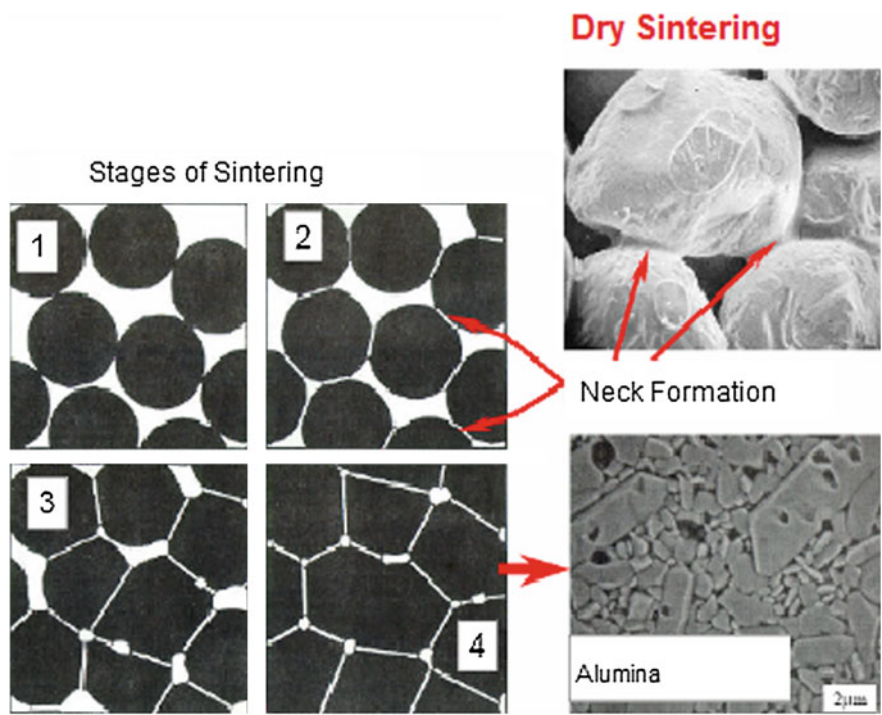
Sintering is the name of the consolidation process of ceramic powders (particles) through heating. It is the result of atomic motion stimulated by high temperatures. This movement decreases the high surface energy associated with non-sintered particles. The movement depends on whether the atoms or ions gain energy equal to or above the activation energy required to diffuse to available sites. Figure 5.1 shows an image by transmission electronic microscope of the sintering process involving hydroxyapatite particles.

The firing of porcelain promotes physical–chemical reactions responsible for the final properties of the ceramic products. In this process, it must be considered the kinetic limitations, the development of the phases, and the complexities of the microstructure. Generally, all the steps, since raw material preparation, drying conditions and firing cycle are going to have a strong influence in the product qualities. The firing cycle influence is related to the kind of furnace, firing atmosphere, maximum temperature and soaking time. All these parameters are related to quality and cost of the products.

The sintering mechanism comprises three stages: the initial, intermediate and late phase. Figure 5.2 presents schematically the sintering process stages.



**Fig. 5.1** Image by transmission electronic microscope of the sintering process involving hydroxyapatite particles



**Fig. 5.2** Sintering process stages (dry sintering)

In the initial phase, the process of sintering involves little or no densification and shrinkage and is mainly characterized by the formation of a “neck” between neighboring particles and by the decrease in surface area. In this phase, pore geometry is open and interconnected. The growth of these contact areas (neck) is responsible for changes in material properties associated with sintering.

The intermediate phase is characterized by regular and continuous pores with interconnected cylindrical structure. At this stage, the theoretical density is between 70 and 92 %, the sintering rate decreases and is very sensitive to the morphology of the pore-grain boundary region.

In the last stage of sintering, the pores are closed and spherical and grain growth is evident. The pores gradually decrease by diffusion to the grain boundary region. This densification is sensitive to grain size and the connection of pores to the grain boundary.

The sintering process is a thermally activated process. The energy required to do so is closely correlated with the diffusion mechanisms, such as the diffusion in the grain boundary. Densification can occur with the superposition of external loads combined with sintering, as occurs in pressure assisted sintering.

The transport mechanisms by which mass movement occurs can be of 2 types: by surface transportation or by material volume (bulk). The first process involves neck growth without densification and the second occurs through contraction and includes various types of diffusion, such as volume and grain boundary diffusion. During sintering, bulk transport changes the space between the particles with the growth of contact area between the grains, increasing the density and strength of the material. Sintering is more intense at higher temperatures due to the increase in active atoms and available sites.

During sintering, interaction between the pores and grain boundaries can occur in three ways: (1) the pores can slow down grain growth, (2) the pores can be moved to the grain boundary region during grain growth; and (3) the grain boundary region can move away from the pores, leaving them isolated within the grain, which lowers density. It is important to avoid this last scenario by combining small grains and pores and increasing the rate of movement of the grain boundary. Another approach to reducing pores is the elimination of gases (vacuum sintering).

The interrelationship between microstructure and sintering variables such as temperature, heating rate, sintering additives and atmosphere has been demonstrated by several authors (Kovar et al. 2000; Lawn et al. 1993 and Oh et al. 2002). For many applications, where the goal is maximizing mechanical strength, optimum sintering corresponds to maximum densification with minimal grain growth. For this to occur, as a first requirement the grain size of raw material needs to be reduced.

The sintering process performed in conventional electric ovens results in intensive grain growth, resulting in a coarse grain microstructure. Incomplete sintering leaves the material porous and recommend increasing the sintering temperature to 1,780 °C. Large pores migrate rapidly during sintering, collapsing in the grain boundaries. Small pores, however, stay trapped within the matrix.

The consequence of rapid consolidation is that gas cannot migrate to the surface of the material, staying within the materials mass. The excessive presence of porosity may therefore be due to an inadequate sintering process.

It is noted that in the presence of high porosity, defects appear to be interconnected pores and their size appears to be greater at the beginning of sintering. These authors suggest a longer sintering process. The pores appear as a result of trapped gasses from organic compounds used as compression additives.

Chinelatto et al. (2008) cite several ways to control the sintering process, obtaining ceramic materials of high density and with small grains. German (1996) indicates that controlling the heating curve is a simple and economically viable way of manipulating the microstructure. Ideally, this control is done by determining the temperature, which allows for a better rate of densification.

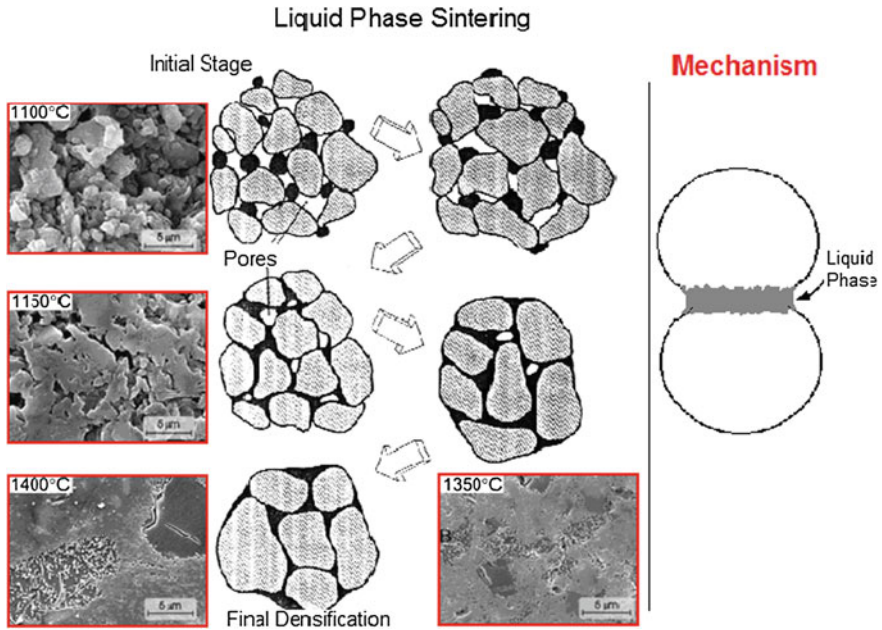
Chen and Wang (2000) have developed an effective method of  $Y_2O_3$  sintering by heating in two steps. In the first step, the material is heated at a very high temperature (T1) and then rapidly cooled to a lower temperature (T2) for a long period of time, reducing grain growth in the final stages of sintering and obtaining high densification. Wang et al. (2009) also recommend this technique for alumina, where T1 was performed between 1,400 and 1,450 °C (allowing a high rate of densification) and T2 between 1,350 and 1,400 °C for an extended period, but not longer than 24 h (avoiding surface diffusion and maintaining densification). The authors state that this sintering technique generates a density above 99 % and controlled grain size in alumina.

Han et al. (2008) have also investigated alumina concerning the relation between the increase of sintering temperature and the decrease in porosity by the rise in densification. When temperature was increased from 1,400 to 1,500 °C, porosity fell by almost 3 % and resistance doubled. Between 1,500 and 1,550 °C, there was little change in porosity, but the grains grew and had greater contact with each other, further improving the mechanical strength. These authors demonstrate, however, that too elevated temperatures (1,600 °C) leads to the excessive growth of some grains in comparison to others, leading to a reduction in mechanical strength.

To improve the properties of a material it is often necessary to increase its densification through phase stabilization (the use of another phase to prevent grain growth); active sintering (the use of an additive to increase bulk transport); reactive sintering (the use of additives to prevent loss of stoichiometry), and through liquid phase sintering.

Hence, the sintering process can be improved with sintering additives, which are used to stabilize desired crystalline structures or to form a liquid phase to assist in the increase of densification. In this sense, a glassy phase can be a sintering additive. In fact, the sintering process in presence of a glass (liquid phase sintering) can occur at lower temperature in comparison of dry sintering (sintering process without a glassy phase). Figure 5.3 presents schematically the stages of a liquid phase sintering process.

Liquid phase sintering involves the formation of liquids due to different melting temperatures of the components. The liquid phase represents 1 to 20 % of the



**Fig. 5.3** Stages of a liquid phase sintering process

volume. The liquid provides a fast means of transport. To function, certain criteria must be met:

1. the liquid must be present at the sintering temperature;
2. the liquid must form a film surrounding the solid phase;
3. the liquid must have solid solubility;
4. diffusion of atoms of the solid dissolved in the liquid needs to be fast.

The combination of wetting, liquid flow and rearrangement of particles contributes to the densification. With increasing densification the mechanism will progressively change passing through three stages: rearrangement (particles move, decreasing porosity until forming a closed structure), solution precipitation (additional densification occurs by dissolution of the solid in the grain contact); final pore size reduction or vapor phase (growth and coalescence of grains and pores occurs, dissolution of liquid into solid and phase transformation). Theoretically, materials sintered by liquid phase should have better mechanical properties because of greater densification. Some authors, however, have observed the loss in mechanical strength with the increase of the amount of glassy phase (Chu et al. 2005 and Freiman 1978).

According to Bragança and Bergmann (2003), the ideal firing temperature is associated to the moment when the glassy phase covers the entire sample surface with sufficient time to react with crystalline phases.



## 5.2 Control of the Microstructure

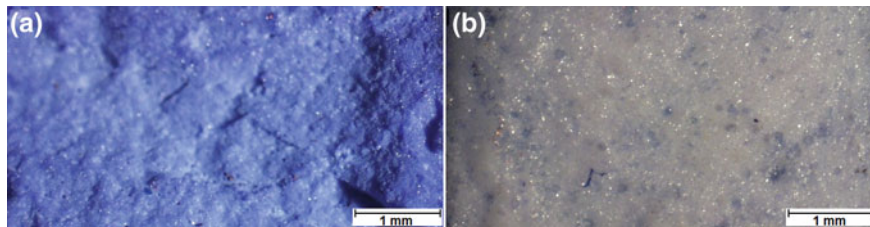
Control of the microstructure of ceramic materials is extremely important because it allows you to obtain information to estimate the performance of these materials in service. In dental ceramics, surface cracks can be detected through the fluorescent penetrant liquid method, or they can be detected through acoustic emission, both interferometrically or optically.

A red dye diluted in acetone can be used to observe the microstructure of alumina. The dye should remain in contact with the alumina for at least 24 h before analysis of the crack can be performed. The dye facilitates the observation of cracks by optical microscopy. Figure 5.4 shows optical microscopy images of two alumina-feldspar ceramic bodies stained by methylene blue.

Because the detection of cracks in dental restorations may mean that these need to be replaced, generating high costs, some authors suggest that these microscopic surface cracks in high-performance ceramics can be corrected through the glass infiltration process, improving the properties of the ceramics without causing an excessive increase in costs.

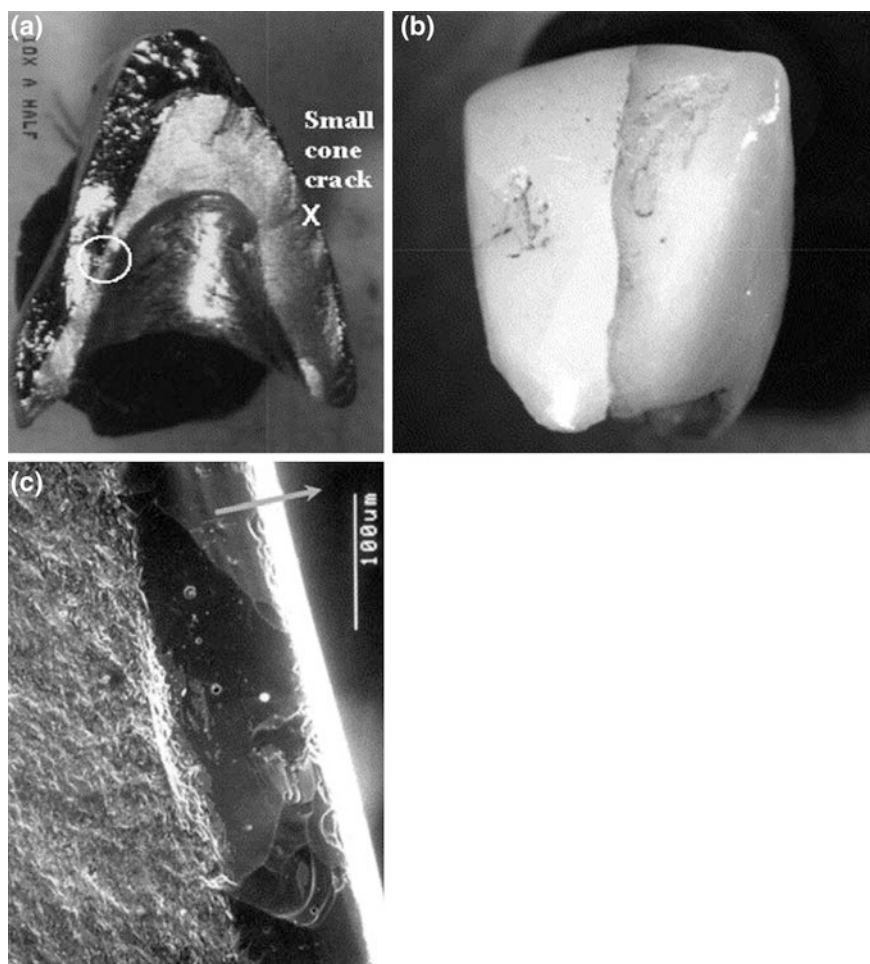
Fractography is also a commonly used method for inspecting the surface of ceramics, which can make a quantitative analysis of the fracture surface. Fractography is based on the principle that all information on the history of the fracture is contained on the surface of the material. Through Fractography it is possible to identify the location, size of the crack and the defect that caused the fracture, and to point out if there were anomalies in the process and the presence or absence of residual stresses and/or corrosive applications. Figure 5.5 shows images of fractographic analyses of three ceramic whole crown restoration failures (Quinn et al. 2005).

Acoustic Emission is also a valid technique for the inspection of ceramic materials. It consists of all manifestation of acoustic waves whose source lies within a material that is undergoing changes in its structure due to the application of mechanical stresses. When an irreversible release of energy occurs, a portion is transformed into a wave of energy that can be read by the appropriate sensors. In polycrystalline ceramic materials, subcritical crack growth is a type of acoustic emission. Due to the microstructure (inclusions, porosity, grain boundary), the



**Fig. 5.4** Optical microscopy images of two alumina-feldspar ceramic bodies stained by methylene blue



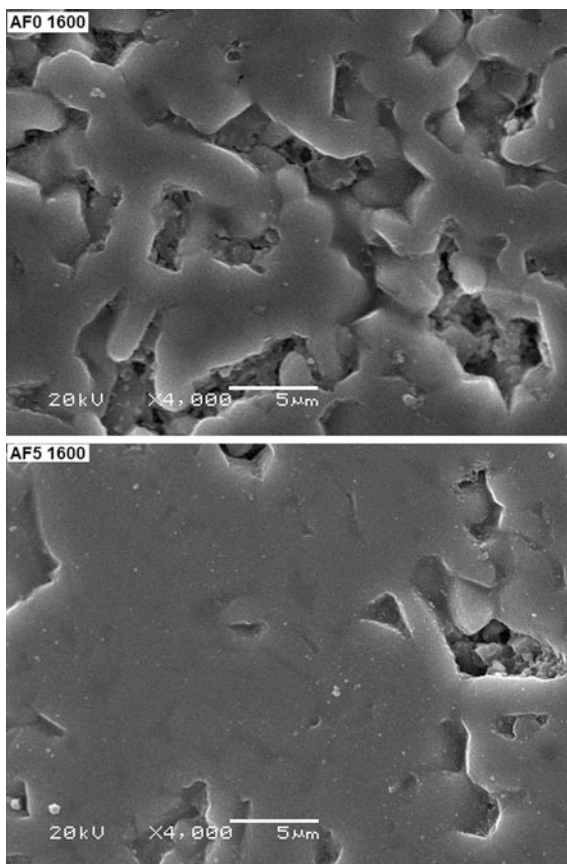


**Fig. 5.5** **a** Gold-coated optical photo of fracture surface, with a *circle* marking the area of fracture initiation. **b** Lingual view of the broken restoration, transilluminated, with most of the gold coating removed. The fragment at the *left side* of the photo is shown in **(a)**. **c** A cone crack was found in the thin veneer at the 'X' on the *right side* of the photo in **a**. The *gray arrow* in **(c)** lies amid some of the wake hackle found in the thin veneer along the side of the specimen (Quinn et al. 2005)

crack tip is irregular and growth occurs in sequential steps. The acoustic emission represents each of these steps. This technique has the advantage of being highly sensitive, locating the energy emission source and it is not necessary to locate the source before performing the test. This test also allows you to easily observe the effect of the R curve.

The ultrasound test is one of the main non-destructive test methods used because it allows the inspection of the entire volume of the part, without

**Fig. 5.6** Images by scanning electronic microscopy of two alumina-feldspar ceramic bodies

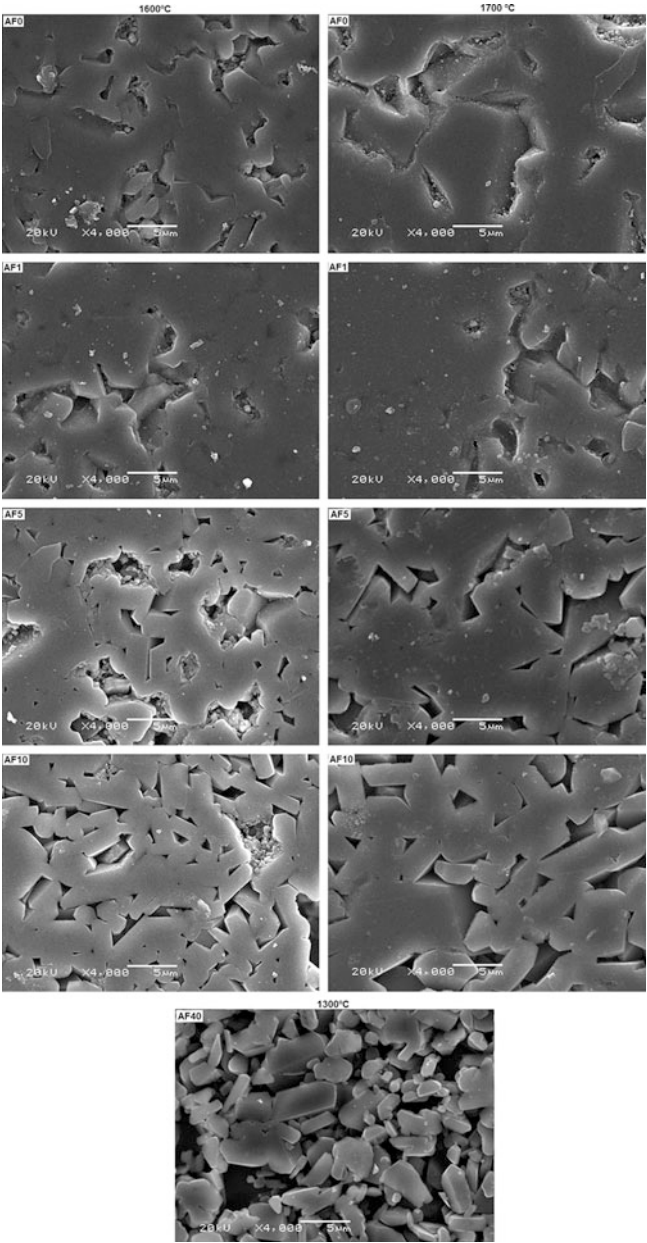


compromising its physical integrity. Ultrasound has the advantage of being able to precisely locate the discontinuities present in the parts, even those of small size. The modulus of elasticity of ceramic materials can also be determined by its resonant frequency.

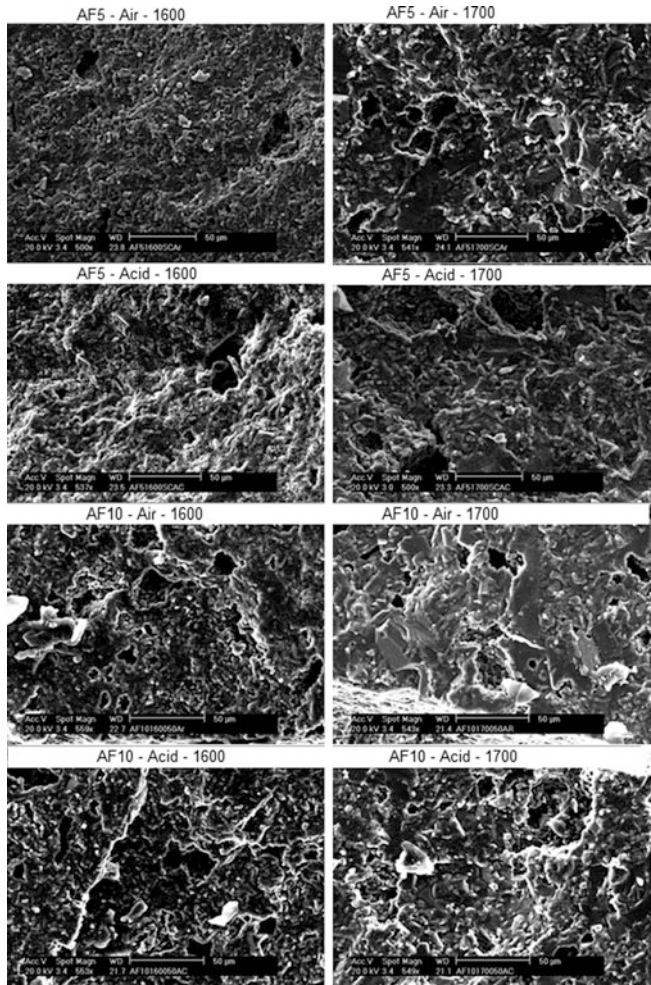
Optical microscopy allows magnifications of up to about 1,000:1. The methods for obtaining the image include: bright field, dark field, polarization contrast method, and differential Interference contrast. The images obtained can also be enhanced by electronic processing of the image to visualize more adequately the grain boundary and the material phases.

Scanning electron microscopy (SEM) is also frequently used for the observation of the microstructure of ceramic materials. It has advantages over optical microscopy because of its higher magnification and depth of focus, better contrast control, better detail localization and the possibility of microanalysis of chemical elements. Through SEM it is possible to identify the shape, size and distribution of grains.

The microscopic image is formed when an electron beam (primary electrons) hits a point in the sample, which will emit secondary electrons, backscattered

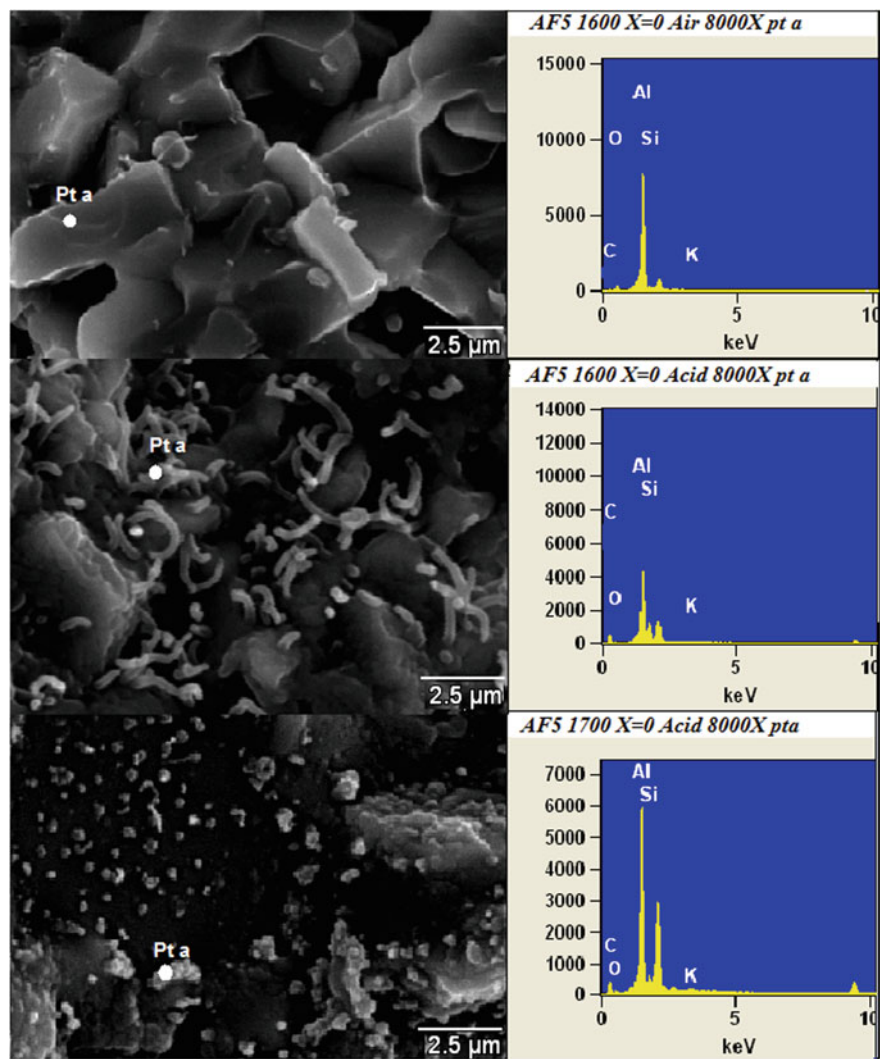


**Fig. 5.7** Images by scanning electronic microscopy of alumina-feldspar ceramic bodies exposed to hydrofluoric acid



**Fig. 5.8** Images by scanning electronic microscopy of alumina-feldspar ceramic bodies exposed to acetic acid

electrons and X rays. The secondary electrons, because they have low energy and low penetration, provide information on the material surface, such as topography and texture. The backscattered electrons provide information about regions of medium depth of the material and X-rays allow the collection of data on the chemical composition of the material (energy-dispersive X-ray spectrometry—EDS). Otherwise, the wavelength-dispersive spectrometry (WDS) operates using several crystals of different interplanar spacings (after Bragg’s law), necessary in order to cover the required wavelength range. Spectral resolution is better than for the ED type, but the latter is faster and more convenient to use. X-ray

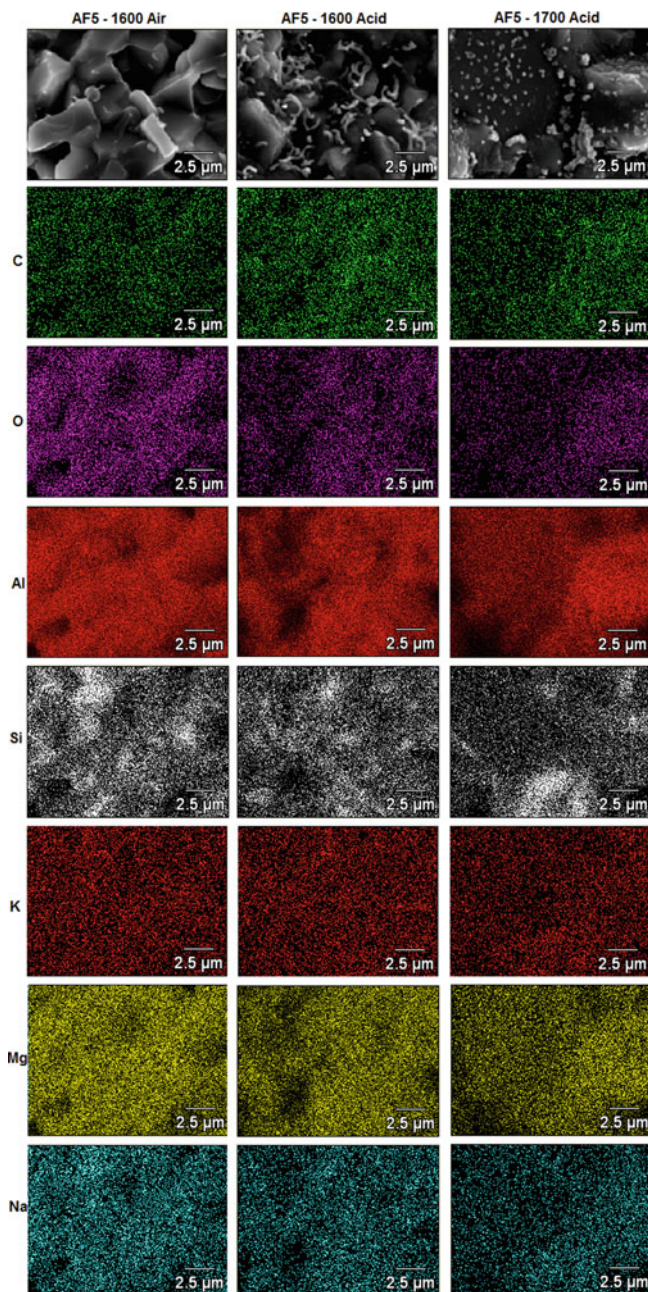


**Fig. 5.9** Scanning electronic microscopy and EDS images of alumina-feldspar ceramic bodies. *Pta* Region of EDS-analysis

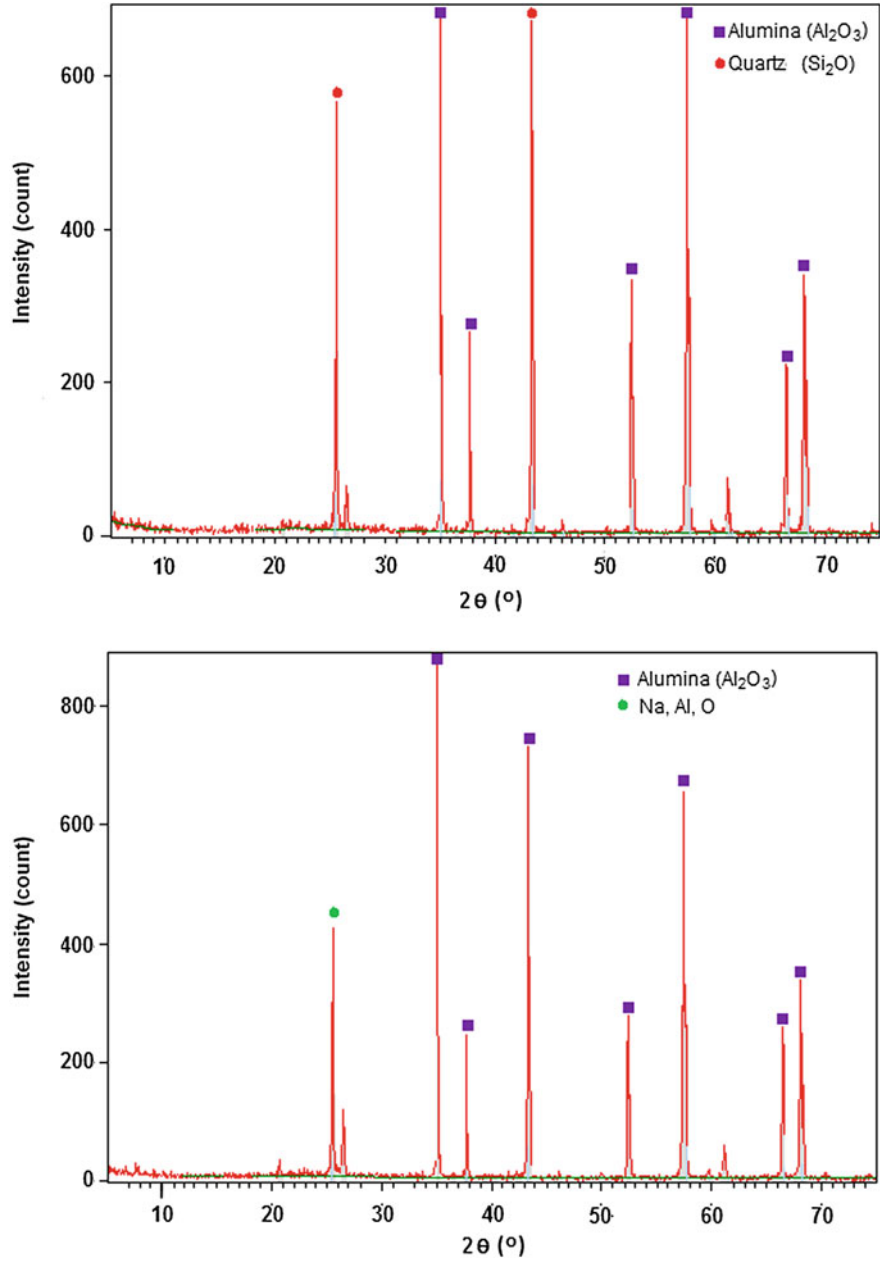
spectrometers attached to SEMs are usually of the ED type, though sometimes a single multi-crystal WD spectrometer is fitted.

It is possible use either an EDS or WDS system to produce an element map. Either way, the image is produced by progressively scanning the electron beam point by point over an area of interest. Resolution is determined by beam size, and relative response of each element is determined by how long the beam dwells on each point (and of course the actual concentration). Greater distinction can be made by longer analysis, but at the cost of time.





**Fig. 5.10** EDS-mapping of distinct chemical elements (C, O, Al, Si, K, and Mg) in an alumina-feldspar dental ceramic



**Fig. 5.11** Analysis by x-ray diffraction of an alumina ceramic body containing corundum ( $\text{Al}_2\text{O}_3$ ) and sodium aluminate ( $\text{NaAl}_{11}\text{O}_{17}$ )

Figure 5.6 shows images by scanning electronic microscopy of two alumina-feldspar ceramic bodies. Figure 5.7 presents scanning electronic microscopy and EDS images of alumina-feldspar ceramic bodies. Figure 5.8 shows EDS-mappings of distinct chemical elements (C, O, Al, Si, K, and Mg) in an alumina-feldspar dental ceramic.

X-ray diffraction is the main method used to identify crystalline phases in materials. Advances in this technique, especially in detection and counting systems and X-ray tubes, have enabled not only the identification of phases, but also quantitative analysis and the determination of crystal size and distribution. Other characteristics of ceramic materials, such as residual stresses in the cracks, can also be evaluated through X-ray. Figure 5.8 shows an analysis by x-ray diffraction of an alumina ceramic body containing corundum ( $\text{Al}_2\text{O}_3$ ) and Sodium aluminate ( $\text{NaAl}_3\text{O}_8$ ) (Figs. 5.9, 5.10 and 5.11).

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## Chapter 6

# Mechanical Behavior of Ceramic Materials

Ceramic materials are typically brittle materials, presenting very different mechanical behavior when compared to metallic and polymeric materials. Usually, the most important mechanical properties of ceramic materials concerning their mechanical behavior are tensile strength and fracture resistance, based on concepts of Fracture Mechanics.

It has been demonstrated that ceramic materials show considerable variation in strength, primarily due to their extreme sensitivity to the presence of cracks of different sizes. The unstable fracture of ceramics starts from critical flaws, and this phenomenon may be explained by the “weakest link” theory, which determines that fracture always propagates from the largest flaw favorably oriented to the tensile stress. For a given ceramic material, the distribution of crack size, shape, and orientation differs from sample to sample and its strength is statistically distributed according to the flaw size distribution.

Due to their microstructural characteristics, resulting from the ceramic processing to which they have been submitted, ceramic materials do not have a well-defined mechanical resistance. Their mechanical strength is greatly affected by the distribution of defects in their microstructure and the test methodology. Because of the random distribution of defects in the microstructure, variability is high, making comparison of materials difficult. Thus, the use of concepts of Fracture Mechanics applied to brittle materials provides scientifically sound parameters in the characterization of ceramic materials for technological applications.

Agreement exists about the cause of microcrack generation in porcelain. Due to the high thermal expansion of quartz and the low thermal expansion of the glass matrix, stresses are set up within and around the quartz particles upon cooling from the sintering temperature. Phase transformations of quartz may also be an important reason for the formations of microcracks.

On discussing the effect of the quartz particle population on  $K_{IC}$ , two findings must be considered: (1) the strong effect of the quartz size on  $K_{IC}$ , and (2) the formation of microcracks in the glass matrix. It is believed that the two effects are not independent of each other. Rather, the toughness increase is attributed to an increase in the number of microcracks. Microcracks are believed to add to the

fracture toughness due to different effects. One explanation is that microcracks modify the stress–strain characteristics of the region ahead the crack tip since they reduce the elastic modulus within this zone. This results in distributing the external stress over a larger volume, thereby shielding the tip from the applied stress. Thus, in order to initiate fracture, a higher stress must be applied which results in an enhancement of the resistance against fracture, i.e. the fracture toughness. Another kind of view is that microcracks in the highly stressed region ahead the main crack may grow by subcritical crack growth. This process contributes to absorb stored elastic energy necessary to propagate the main crack, thereby increasing the fracture toughness.

## 6.1 Mechanical, Fracture Resistance and Fatigue

Fatigue is so well recognized as a cause of fatal accidents that is now well established in the vocabulary of the mass media. Engineers have been aware of fatigue in metals for over 150 years, ever since the development of railways leads to a concern at the incidence of fractures in equipment. However, it is only within the last 30 years that a reasonable model of fatigue has been developed which can enable a designer to prevent it happening in service. The continuing incidence of fatigue induced accidents indicates that this knowledge is still either incomplete or is being imperfectly applied.

Fatigue means that (under certain loading conditions) a component may suffer a loss in strength over a period of time in service. The component appears to tire (to fatigue). There are two types of loading condition that may cause these symptoms:

- (1) Reversed (or cyclic) loading;
- (2) Steady loading, in the presence of a chemically active agent (which may be as simple as water).

Crack growth can be thought of as having three phases: nucleation, slow growth and unstable growth. In some cases nucleation is unnecessary because the component already contains a crack, from the manufacturing process, for example. If no cracks are present initially, they can be formed on initially smooth surfaces by shear deformation of the material under the action of the cyclic loading. Shears occur in both senses on planes inclined to the surface which then acquires a furrowed or wrinkled shape. The grooves or ‘intrusions’ so formed are embryonic cracks.

Mechanical resistance of ceramic materials is much lower in practice than in theory. Any kind of discontinuity produces stress concentrations in the material. This discontinuity can be a fissure, a pore, a grain boundary or even an internal sharp edge of the part. In ductile materials, these stress concentrations can be relieved by plastic deformation. In brittle materials, however, this mechanism does not occur. Instead, when stress concentrations exceed the yield strength of the material, fracture occurs. Once initiated, the fracture spreads easily under stress

because the stress concentration at the crack tip increases as the fracture progresses. For this reason, the difference between tensile and compressive strength of ceramics is also quite pronounced.

Usually, ceramic materials are much more resistant to compression than to tension, since compression forces do not have as much effect on crack propagation as tensile forces.

Because of the microstructure resulting from ceramic processing, the mechanical strength of these materials is controlled by the size of the defects that are present on the surface or volume of the parts.

Fracture-initiating defects may be any kinds of inherent irregularities on a microstructural level as for example residual pores, exaggerated grains, microscopic surface scratches, broken grain boundaries and small impurity particles. If all these defects are avoided the proper grain size, i.e. the largest grains may be the strength-limiting defects. The aim in developing a ceramic of a high strength in the brittle temperature regime therefore is to provide fracture toughness as high as possible and to avoid any microstructural inhomogeneities as far as possible.

The degradation of mechanical strength over time under load, leads to the slow growth of these defect. In general, the cracks grow in the direction where there is less energy, such as, for example, the glassy phase of ceramics. The speed of crack growth depends on the initial size of the defect, the chemical environment and the type and duration of the load, but it is independent of the geometry of the part.

Since dental ceramics present different microstructures, depending on the presence and volume fraction of a crystalline phase, mean particle size and distribution throughout the glassy matrix; and microstructure strongly affects crack propagation and the mechanical properties.

The discrepancy between theory and practice in the mechanical behavior of ceramics has been better understood since Griffith (1921), who introduced the idea of controlling (limiting) defects of the mechanical strength of brittle solids.

The basic ideas of Griffith's concept are as follows:

- (1) any real material contains defects or cracks that concentrate the applied stress;
- (2) stress concentrations at the crack tip can reach the theoretical values needed to break the bonds of the network;
- (3) atomic bonds along the fracture surface do not need to break simultaneously, instead, they can break in sequence, that is, the crack propagates through the material;
- (4) two energies are involved in the fracture process: stored elastic energy and the energy required to create the new fracture surface. These energies depend on the crack size  $c$ ;
- (5) the crack will propagate when, with an increase in the extension of the crack, the elastic energy released exceeds the energy to create the new surface.

In this context Fracture Mechanics arises in order to determine whether a crack type defect will or will not lead to the catastrophic fracture under normal service stresses. Fracture Mechanics also allows you to determine the effective degree of safety of a cracked component. For relatively brittle materials, on the lower side of

the ductile–brittle transition curve, or for structures subjected to essentially elastic tensions, fracture toughness is expressed in terms of  $K_{IC}$ . According to Tsuji et al. (1999), cracks in alumina always initiate at a distance that is equal to or lower than 0.80 times the process zone size from the notch tip that is in the vicinity of the notch front.

Fracture toughness is the ease with which a crack grows from an initial defect and is the load value at which fracture will occur. Kelly (1995) argued that flexural strength is not an interesting property when analyzing ceramic materials and suggested the use of  $K_{IC}$  because it represents the intrinsic material resistance to crack growth.

The fundamental concept of the fracture strength of ceramics has been developed mainly by Davidge and Evans. It combines the basic idea of stress concentrations around flaws which has been presented by Griffith in 1920 with the principles of Linear Elastic Fracture Mechanics developed in the 1940s.

Following Evans and Davidge, it becomes clear from the foregoing set of equations that the strength of a ceramic body is controlled by two fundamental parameters, i.e. the flaw size  $c$  and the critical stress intensity factor  $K_{IC}$ .

Based on Griffith's criteria, Eq. 6.1 was proposed for calculating the tension required to fracture a ceramic body with a defect of size  $c$ .

$$\sigma_f = \left( \frac{2E\gamma}{\pi c} \right)^{1/2} \quad (6.1)$$

where  $\sigma_f$  is the tensile strength,  $\gamma$ , the specific surface energy and  $E$ , the modulus of elasticity.

Equation 6.1 for tensile strength can be rewritten in a more general way, such as in Eq. 6.2:

$$\pi^{1/2} \cdot \sigma_f \cdot c^{1/2} = (2 \cdot E \cdot \gamma)^{1/2} \quad (6.2)$$

The term on the right is independent of the size of the defect, contains only the material parameters and can be considered constant for a given material. Consequently, the term on the left is also a material constant and is called the fracture toughness, expressed by the symbol  $K_{IC}$ .

For greater generality, the term  $\pi^{1/2}$  was replaced by a dimensionless factor  $Y$ , called the shape factor LEFM (linear-elastic fracture mechanics) (Eq. 6.3).

$$K_{IC} = Y \cdot \sigma_f \cdot c^{1/2} \quad (6.3)$$

Equation 6.3 is known as the basic equation for linear-elastic fracture mechanics. The significance of this equation is that the characteristic fracture parameter of a material is not its tensile strength  $\sigma_f$ , but the product of this term with the size of the crack defect  $c$ . That is, the mechanical strength of a material is limited by its greatest defect (the most critical in size, position or orientation). So this defect controls mechanical strength.

For tensions lower than the critical stress  $K_I = Y \cdot \sigma \cdot c^{1/2}$ , where  $K_I$  is the stress intensity factor, the shape factor  $Y$  is a function of the size of the crack. For simplicity, a relative crack size  $X$  can be defined to relate crack size  $c$  with the dimension of component  $W$ .

$$X = \frac{c}{W} \quad (6.4)$$

The function  $Y(X)$  can be calculated for many test geometries. For example, for a four point bending test, the following polynomial is a solution suggested in the literature Eq. 6.5):

$$Y = 1,99 - 2,47 \cdot X + 12,97 \cdot X^2 - 23,17 \cdot X^3 + 24,80 \cdot X^4 \quad (6.5)$$

One can therefore say that the mechanical strength of a ceramic material is a combination of an invariable parameter dependent on the material—fracture toughness—and a variable parameter—the size of the limiting defect. The variation in resistance should be attributed to the variation in the size of the limiting defect (the defect that starts the catastrophic fracture).

When applied to fatigue and stress corrosion, Fracture Mechanics allows for the estimation of the performance of components, once the size of prior defects and/or nucleated cracks in service is known. It enables you to calculate the size of allowable defects and safe operating times.

The critical value for the stress intensity factor or fracture toughness ( $K_{IC}$ ) is an intrinsic property of the material of the cracked component, for a given temperature situation, loading rate and microstructural condition. Because it is an intrinsic material property, the value of  $K_{IC}$  can be used in the analysis of any geometry, permitting the calculation of the critical size of cracks in structural designs. This parameter also allows you to observe the influence of defect size on resistance.

Segui et al. (1995), as well as Sglavo and Pancheri (1997), report that  $K_{IC}$  is a critical property that must be carefully evaluated in the selection of ceramic materials for dental use. There is, however, still a lack of research that correlates  $K_{IC}$  and the clinical performance of dental ceramics.

In the past, the focus of fatigue research was restricted to damage and crack formation processes. Since the 1960's, interest has shifted to the crack growth processes, due to the observation that:

- (1) crack growth through fatigue does not occur catastrophically (there is sub-critical crack growth) and the cracks can even be immobilized in certain circumstances;
- (2) crack nucleation can occupy only a short period of fatigue life. The cracks are formed very early in the fatigue life of a material.

Data concerning crack growth in dental ceramics are very limited. According to Thompson (2004), Morena et al. (1986) were the first to estimate the parameters of slow crack growth in dental ceramics by determining flexural strength in an

environment simulating the oral cavity. The authors assessed the influence of moisture on such materials, since water, under certain conditions, can degrade the properties of ceramic materials.

## 6.2 Tests for Determining $K_{IC}$

According to Mukhopadhyay et al. (1999), there is no single, unambiguous method to determine the fracture toughness of ceramic materials, which explains the different approaches with different methodologies addressing the issue.

Several methods have been used to evaluate the subcritical crack growth of ceramics under static or cyclic loading conditions. A dynamic fatigue test, in which the flexural strength of specimens is measured as a function of the crosshead speed in a mechanical testing machine, is often used to determine the slow crack growth (SCG) parameters in the absence of cyclic load. Statistical methods based on experimental data for the initial strength and lifetime of specimens have also been successfully applied to evaluate the subcritical crack growth of ceramics under static or cyclic load. Weibull analysis is often used to statistically describe the strength of ceramics because it takes into account the typical asymmetric distribution of strength values of brittle materials.

Several techniques, such as the double cantilever, double torsion and indentations techniques, are suggested for the determining the  $K_{IC}$  of brittle materials. One method is the test on single-edge- $v$ -notched beams. In this test bars specimens with a  $v$ -notch of finite width introduced by a saw cut and sharpened by a razor blade and oil lubricated diamond paste are load in a four-point bending test arrangement.

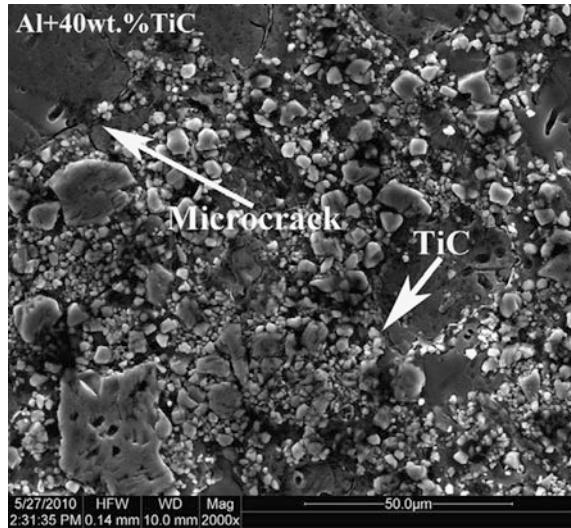
The fracture toughness can also be determined by analyzing indentation cracks. The theoretical concept supporting the indentation method is well established in the literature. According to Quinn et al. (2003), determining  $K_{IC}$  in small samples like dental prostheses cannot be done in the traditional way. Measuring the size of a crack around indentations should permit the estimation of  $K_{IC}$ . Unfortunately, the results of these tests are not accurate and standardized. These values can also vary with crack size and material homogeneity. The fracture toughness ( $K_c$ ) can be estimated for each indentation (Fig. 6.1a) according to Eq. 6.6 (Niihara et al. 1982).

$$K_c = 0.0084 \left( \frac{E}{HV} \right)^{2/5} \left( \frac{2P}{L} \right) \frac{1}{c^{1/2}}$$

where  $E$  and  $HV$  are the elastic modulus and the transition point hardness, respectively, and  $P$ ,  $L$  and  $c$  are the indentation load (kg), average diagonal length (m) and crack length (m), respectively. The crack length was measured from the tip of the indentation diagonal to the end of the crack tip (Figs. 6.2a and 6.2b).

Fischer and Marx (2002) state that the indentation method is not an adequate tool to exactly determine the fracture toughness of an unknown dental ceramic

**Fig. 6.1** Example of microcrack of the Al+40 wt.% TiC



material because the material specific, individual prefactor in the formula to calculate the  $K_{IC}$  is unknown as long no bending tests have been done.

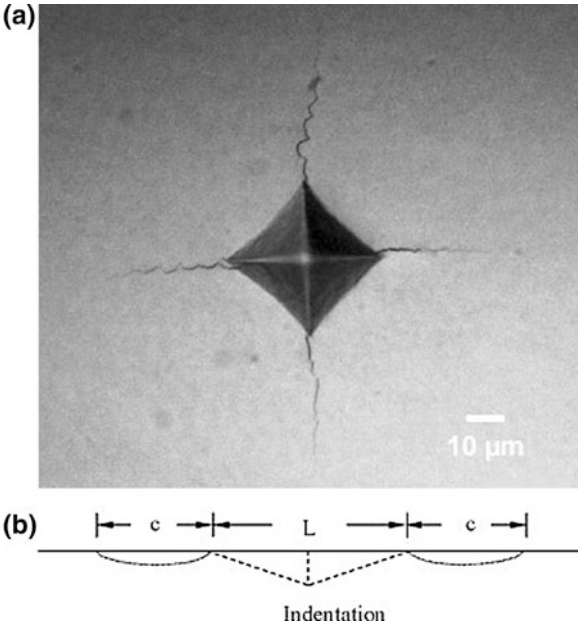
As brittle materials, ceramic materials can be tested for resistance in various ways. One of these ways is introducing a notch. This notch will act as a sharp crack. Another way is through long pre-cracks, where a well-defined crack is generated before any test is performed. The third approach is the small crack method, where a relatively small crack is introduced before fracture by indentation, as we have seen. This last category is one of the most studied because it is easy, has reduced costs and offers fast testing. Another advantage is that the created defect is usually more similar to actual defects.

Gogotsi (2003) has summarized the different methods for testing the resistance of ceramic materials and states that currently the most studied test is a variation of the single edge notched beam, called the single edge  $v$ -notched beam. Gogotsi tested the flexural strength of bars of different ceramic materials in three and four point bending tests (Fig. 6.2) with single edge notched beam and single edge  $v$ -notched beam. He concluded that the obtained results are similar, but the four points test facilitates installation of the test apparatus, since there is no need for the same level of precision in positioning the test samples as in three-point bending. Moreover, this last method allows the use of smaller specimens.

The ASTM C 1576-05 (2007) standard suggests preferably using the four-point bending test instead of the three-point bending test in advanced ceramics. The plastic region formed around the artificially produced cracks in the mechanical tests is responsible for the presence of residual stresses that facilitate crack growth.

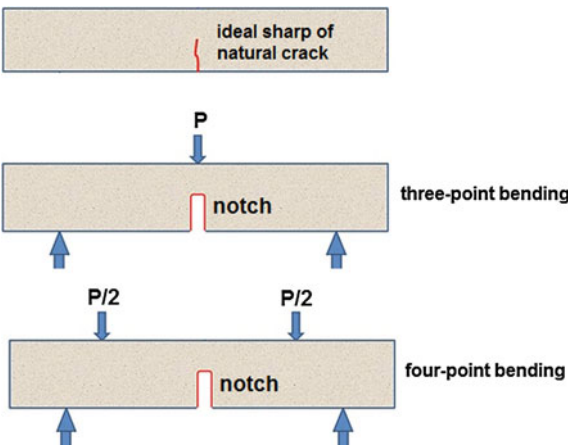
During bending the shape of cracks can be changed, often leaving the defect size equal to the component dimensions. Sglavo and Pancheri (1997) have investigated crack evolution in four-point bending tests on alumina test samples with 10 % vitreous phase. In order to observe the cracks after fracture, both

**Fig. 6.2** Indentation on enamel (occlusal surface) and the development of cracks at the indentation corners. **a** A typical indentation in young enamel. The enamel is from a 21-year-old female patient. **b** The crack configuration from a side view of a Vickers indentation (Park et al. 2008)



through a scanning electron microscope and an optical microscope, the authors used red dye diluted in acetone. They concluded that the crack can change in size and shape during the test, being more pronounced with increasing loads. The red dye was effective for the observation of the cracks, since its color contrasts with the white alumina. The observation of this region is important in order to understand the behavior of test samples when external loading is applied. These same authors showed that the cracks begin their growth steadily until they reach their critical size. (Fig. 6.3).

**Fig. 6.3** Three-point and four-point bending test using notched samples





Sherrill and O'Brien (1974) have investigated the flexural strength of alumina-feldspar ceramic test samples. They reported that when these samples are tested in an aqueous environment, mechanical strength falls by 27 % on average.

Cho et al. (2000) tested the strength of alumina at different relative air humidities and with two kinds of four-point bending tests. One of the apparatuses had inner and outer widths of 10 and 30 mm, respectively, and the other apparatus had inner and outer widths of 20 and 40 mm, respectively. The authors concluded that flexural strength decreases when the relative humidity is greater than 45 % compared with 10 % relative humidity. The resistance is also lower in the four-point bending tests on the apparatus with smaller dimensions, but this difference was not statistically significant. In another study, Cho et al. (2003) stated that the flexural strength of alumina decreases with rising temperature and humidity.

Mukhopadhyay et al. (1999) have sought to determine the fracture toughness of alumina test samples using different test methods to better understand the micromechanics at the start of the fracture. The sensitivity of experimental fracture toughness in relation to the different test methods and experimental parameters is of the utmost importance, especially because of the crack growth resistance behavior (*R* curve) of the ceramics. In conclusion of their work, the authors determined that fracture toughness values are higher in *chevron notched beam* tests than in other tests (*single edge notched beam*, fracture by indentation and fractography). The differences between the tests are more pronounced in aluminas with larger and heterogeneous grains.

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## Chapter 7

# Dental Alumina: Microstructure and Properties

Dense and polycrystalline alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) is one of the most studied bio-ceramics due to the combination of its chemical inertness and its mechanical behavior (high compression strength and wear resistance), its good biocompatibility and high corrosion resistance (Figs. 7.1 and 7.2).

### 7.1 Mechanical Behavior and Microstructure of Alumina Dental Ceramics

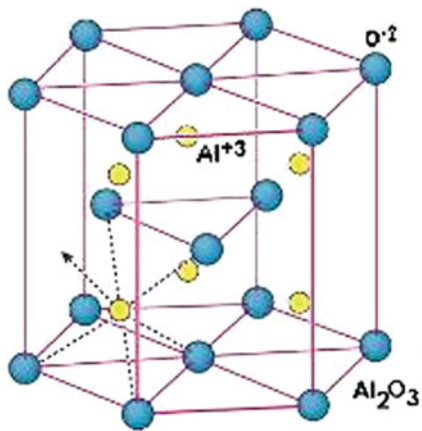
The mechanical behavior of alumina is strongly affected by its microstructure because of the propagation of cracks and secondary microcracks. The improvement of mechanical properties of alumina for use in unfavorable service situations is one of the major challenges facing researchers in recent decades.

Piconi and Maccauro (1999) state that alumina used as a biomaterial must have high purity (99.9 %), low porosity (<0.1 %), high flexural (>500 MPa) and compression strength (>4,100 MPa), a  $K_{IC}$  superior to 4 MPa.m<sup>1/2</sup> and hardness greater than 2,200 HV<sub>0.1</sub> (Figs. 7.3 and 7.4).

The U.S. National Institute of Standards and Technology predicts that at a temperature of 20 °C the properties of high purity (99.5 %) Al<sub>2</sub>O<sub>3</sub>- $\alpha$  with a grain size of 5  $\mu$ m and a density of more than 98 % should be the following: melting point of 2,050 °C, compressive strength of 3 GPa, modulus of elasticity of 450 GPa, flexural strength of 380 MPa, fracture toughness (with crack of 300  $\mu$ m in length) of 3.5 MPa.m<sup>1/2</sup>, Vickers hardness of 15 GPa, Weibull modulus of 11 and tensile strength of 267 MPa. According to Kelly (2004), the  $K_{IC}$  of alumina prostheses is around 4.5 MPa.m<sup>1/2</sup>, while for conventional metal-ceramic prostheses this indicator is around 1 MPa.m<sup>1/2</sup> and for zirconia prostheses between 8 and 12 MPa.m<sup>1/2</sup>.

Some additives may be added during the production of alumina, such as magnesium oxide (MgO), zirconium oxide (ZrO<sub>2</sub>) and chromium oxide (Cr<sub>2</sub>O<sub>3</sub>) in order to improve certain characteristics and mechanical properties. Furthermore,

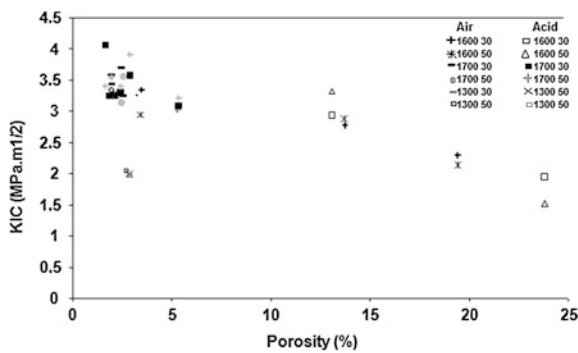
**Fig. 7.1** Crystalline structure of alumina



**Fig. 7.2** Typical alumina powder: raw material for alumina ceramic bodies

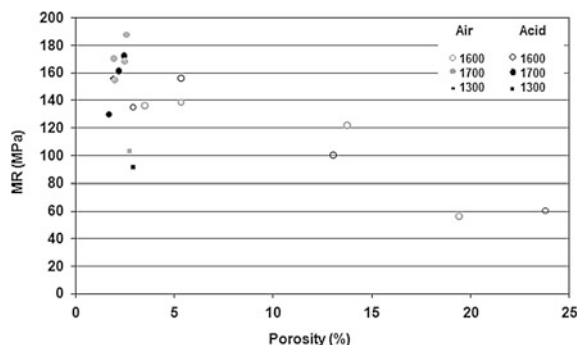


**Fig. 7.3** Relationship between porosity and  $K_{IC}$  in alumina ceramic bodies exposed or not to acetic acid



the microstructure of polycrystalline alumina as well as some of its properties depends on the additives and the residual presence of silicon and calcium oxides. These oxides are quite common and their control is critical. Many of them have

**Fig. 7.4** Relationship between porosity and mechanical resistance in alumina ceramic bodies exposed or not to acetic acid



low solubility in alumina and concentrate in the grain boundary. The segregation rate of these oxides varies with the orientation of the crystal planes of the alumina. At high concentrations, these oxides may favor the formation of the glassy phase.

The introduction of sintering additives during the processing of alumina can control grain growth and thus influence the crack growth process and consequently improve the mechanical properties of ceramic materials.

The presence of second phase or elongated grains can increase the fracture toughness of alumina, allowing the deflection of cracks. Barinov et al. (1998) state that the presence of glassy phase in alumina increases its sensitivity to crack growth, leaving the alumina less resistant to fatigue.

Teng et al. (2007) report that one of the problems with using alumina is its low flexural strength. These same authors state, however, that the mechanical properties can be improved with finer grains and by strengthening the grain boundary.

Alumina has a tendency of presenting abnormal grain growth and often the addition of dopants can avoid this. The addition of MgO and/or ZrO<sub>2</sub> can increase flexural strength of alumina between 17–27 % in three-point bending tests. The addition of these components increases the density of alumina and decreases its grain size. These researchers obtained alumina with a 40 % smaller grain size with the addition of MgO, 50 % lower with the addition of ZrO<sub>2</sub> and 80 % lower with the addition of MgO and ZrO<sub>2</sub>.

Grain boundary has a strong influence on important phenomena of the sintering process such as densification and grain growth, deformation, segregation mechanical properties and optical properties. The influence of grain boundary on the ceramic properties depends on factors such as its density and the chemical composition of its interface.

Differences in the thermal expansion coefficient between the crystalline and glassy phase may create stresses at the grain boundaries during cooling of the ceramics. These stresses can affect the mechanical properties of alumina for dental applications. The compressive forces arising from the glassy phase formed around the grains can promote crack growth. The effect of this phenomenon on fracture toughness, however, is still not well understood. Still, the authors have found that alumina with small grains is more resistant to fracture, which restates the importance of microstructure for the properties of ceramics.

Guazzato et al. (2004) state that the microstructure, strengthening mechanisms and the inter-relationships between the ceramics and these strengthening elements, as well as the mechanical properties, should be more thoroughly researched. Quinn et al. (2003) state that although microstructure is important in determining the properties of ceramics, the chemical composition should also be considered.

One of the characteristics of alumina is the  $R$  curve. The  $R$  curve represents an increase of fracture energy with the extension of the crack, indicating lower sensitivity in relation to the size of the defect in the microstructure and greater reliability of the material. This behavior can be explained by the energy consumed when crack branching, plastic deformation, and encapsulation of the crack by the damaged area during crack growth, occurs. The effect of the  $R$  curve is well observed at the beginning of the macrocrack growth and tends to saturate. However, some studies have not shown any reductions in the variability of resistance with the  $R$  curve.

Indentation tests show that alumina containing elongated and coarse grains, has an upward  $R$  curve, indicating stable crack propagation, less variability in mechanical strength. The greatest resistance is presented by alumina with a microstructure of fine and equiaxial grains and a small or even absent  $R$  curve. However, that  $R$  curve behavior and tolerance to defects are not exclusively controlled by average grain size, but by grain morphology and other factors such as grain distribution and also the mechanical strength of its boundaries.

Hotta et al. (2005) report that not only the presence, but also the size and distribution of coarse grains can be correlated with the differences in mechanical resistance between aluminas. Alumina with elongated grains can present higher fracture toughness in indentation tests of up to 80 %.

Armstrong and Cazacu (2006) have assessed the fracture toughness of alumina in indentation tests with respect to grain size and crack size. They concluded that the intensity of fracture toughness ( $K$ ) in the presence of small defects (even if these are larger than the grain size) increases with decreasing grain size. In large defects,  $K$  increases with increasing grain size.

Muchtar and Lim (1998) have studied the fracture toughness in indentation tests of high purity (99.99 %), fine-grained alumina and found that the intensity of fracture toughness ( $K_{IC}$ ) increases with decreasing grain size. The same authors assessed fracture type and concluded that in fine-grained alumina, fracture occurred intergranularly, while in alumina with dispersed grains, the fracture was a combination of intergranular and transgranular fracture. Authors such as Armstrong (2001) and Njiwa et al. (2005) also report that the mechanical resistance of alumina increases with decreasing grain size.

In recent years, different microstructure concepts have been developed to overcome the inherent brittleness of ceramics. Present studies focus on the possibility of reinforcing alumina with carbon nanotubes, improving its mechanical properties, especially fracture toughness.

## 7.2 Optical Properties of Alumina Dental Ceramics

Patients throughout the world are showing a growing interest in restorative dental materials, which enable natural teeth to be faithfully recreated with regard to their function and aesthetic appearance.

Tooth color is caused by volume reflection: the passage of incident light through the translucent enamel and dentine followed by backward emergence. This passage is concurrent with the sideward displacement of photons that, in effect, influences the result of spectrophotometric measurement of tooth color. This phenomenon would be applied similarly to shade guide tabs which were made to mimic the color and structure of natural tooth.

Optical properties of human teeth are influenced by their external configuration. Tooth dimension, shape and surface structure generate light reflection patterns, which influence the overall color. Knowing that the amount of reflected and absorbed light depends on the thickness and translucency of dentine and enamel, it is evident that the thickness of the dentine and enamel affect tooth color.

Color assessment is regarded as a complex psychophysiologic process subject to numerous variables. Dentin is considered to be the primary source of color for teeth, which is modified by the thickness and translucency of overlying enamel. The perceived color of natural teeth is a result of light reflected from the enamel surface, in addition to the effect of light scattering within enamel and dentin before it is ultimately reflected back. Clinically, it is important that ceramic restorations reproduce the translucency and color of the natural teeth.

There are several factors that affect the ability of a ceramic system to produce an acceptable match with corresponding shade guides. In addition to the opacity and shade of the ceramic that determine the definitive shade of an esthetic restoration, other factors, including porcelain brand, batches, condensation techniques, firing temperatures, dentin thickness, and number of porcelain firings, can have an effect. Studies evaluating different ceramic systems have shown that ceramics have exceptional color stability.

Ceramic restoration color is also affected by the alloy used as the substrate; thus, in metal ceramic restorations, the ceramics have greater color stability when noble metals are used. Clinically, an appropriate color combination is an important aspect for an esthetic dental restoration. According to some studies, the ability of a ceramic restoration to match the color of the surrounding dentition continues to be a matter of concern.

At present, there are 5 methods for fabricating all-ceramic crowns: condensation and sintering, cast and sintering, pressing, slip casting, and computer-aided design/computer-aided manufacturing (CAD/CAM) milling of ceramic blocks or presintered blocks. In addition to the development of advanced dental material technologies, the increased demand for esthetic restorations has resulted in the use of all-ceramic restorations in several applications. Most all-ceramic systems require the combination of 2 layers of ceramic material, such as a strong ceramic

core and veneering porcelain, with different opacity, shade, and thickness, to provide a natural appearance.

All-ceramic restorations without a metal substructure allow for greater light transmission within the restoration, thereby improving the color and translucency of the restoration; however, a perfect esthetic tooth-colored restoration cannot be ensured. If the majority of light passing through a ceramic restoration is diffusely transmitted and only part of it is scattered, the material will appear translucent. The amount of light that is absorbed, reflected, and transmitted depends on the quantity of crystals within the core matrix, their chemical nature, and the size of the particles compared to the incident light wavelength.

Kelly et al. (1996) identified core translucency as a primary factor in controlling esthetics and a critical consideration in the selection of the materials. Some all-ceramic core materials have high in vitro strength values. However, an increase in crystalline content to achieve greater strength generally results in greater opacity.

Errors associated with the duplication of dental ceramic shades are well documented in the literature. These errors are related to the metal substructure, condensation techniques, and the commercial brand of the ceramic. Other factors are known to influence color as well, including the number of firings and the firing temperature.

O'Brien et al. (1991) reported that perceivable color differences between ceramic specimens could be detected when they were fired 3 and 6 times. The first 5 ceramic firings with and without the use of vacuum have been reported to demonstrate no color differences in specimens. However, according to Barghi and Goldberg (1977), small differences were observed in subsequent firings.

The spectrum of dental restorations ranges from small restorations such as inlays and veneers to large restorations such as dental crowns and bridges. The latter are preferably secured on natural teeth. Furthermore, a trend has emerged towards implant supported restorations, particularly in the replacement of single teeth. Ceramic materials are in demand for this entire range of dental restorations.

Special attention in the development and application of glass-ceramics for dental restorations was given to the combination of properties which are typical for both ceramics and glasses. These materials gained acceptance in this field because of their exceptional translucency and appropriate strength and above all their favourable processing properties.

The exceptional properties of leucite glass-ceramics were first presented in IPS Empress®. These properties included lifelike translucency, high strength of 150–180 MPa, fracture toughness as the  $K_{IC}$  value of 1.3 MPa m<sup>1/2</sup> and good wear resistance. IPS Empress® glass-ceramics were used as 32 million units over in the fabrication of inlays and onlays (particularly for restorations in the anterior region) between 1991 and 2007.

Studies examining color changes of surface colorants after firing have demonstrated pigment breakdown at firing temperatures. Specific contributions of core and veneer thickness to the appearance of layered ceramics were determined. It was concluded that there was a significant correlation between the thickness ratio of core and veneer ceramics and the color of the restoration. Even when



adequate ceramic thickness exists, clinical shade matches are difficult to achieve because there is a wide range of translucency among the core materials of all-ceramic systems at clinically relevant core thicknesses.

Ideally, esthetic restorations would have the same reflection as the tooth, resulting in no visible difference between the restoration material and the treated tooth under all normal types of illumination. Equal reflection exists when the optical properties absorption, scattering and the anisotropy of the material are equal to those of the tooth. To get as close as possible to the ideal situation, the optical properties of both the restorative materials and native teeth should be known and matched.

Since the natural tooth with enamel and dentin comprises a layered material made up of layers with different optical properties, it is preferable to imitate this layered structure using two optically different restorative materials in order to obtain optimal color perception. However, there are no guidelines for the expected visual outcome with the materials provided by the industry and the dentist is completely free to choose and combine the appropriate materials as he sees fit.

The benefit of layer preparation to achieve a more esthetic restoration could be shown to be true, especially for teeth with a thick layer of enamel. The clinical recommendation for front teeth (e.g. a broken corner of an incisor) would be to use a dentin composite to mask the dark background of the oral cavity and have a translucent edge of about 1–2 mm at the crown of the tooth, making the reconstruction appear more natural by using the layering technique with translucent enamel shades. Since a thin enamel layer does not influence the color impression, color should be selected for the opaque shades of dentin composite to match the adjacent natural tooth material.

Optically the color perception of layered composite restorations is made up of the diffuse reflectance of the inner dentin composite and the outer translucent enamel composite, and is dependent on the thickness of each layer due to translucency of the materials.

Based on the successful long-term use of glass-ceramics and sintered ceramics, these materials show the most promise for the development of new materials up to the year 2020. Dental ceramics allow regular and diffuse transmission, as well as diffuse and specular reflectance of light, and therefore have the potential to reproduce the depth of translucency, depth of color, and texture of natural teeth.

The inclusion of small amounts of metal oxides into ceramic materials allows control of the opalescence quality of the material. Recently combined leucite-fluorapatite or fluorapatite glass-ceramics have been introduced in dental market, as fluorapatite crystals present increased chemical durability compared to that of natural teeth (hydroxyapatite), and closely resemble the crystals in natural teeth optimizing the optical properties of the material.

### 7.2.1 Controlling the Optical Parameters of Color

Dental veneering ceramics for all-ceramic restorations should allow the operator to control the optical parameters of color (hue, chroma and value) as well as the translucency. Color and translucency may be determined from the transmitted light through a material, where the light source and detector are on opposite sides of the object, or from the reflected light where the light source and detector are on the same side of the object.

Differences between the transmitted and reflected light is described as opalescence where a material is preferentially transmitting different wavelengths to those that are reflected. Enamel and dentin both exhibit opalescence resulting in the transmitted light being rich in longer wavelengths (red and orange) in comparison to the reflected light.

According to the radiation transport theory the 'optical behavior' of turbid media can be described by the optical parameters absorption coefficient  $\mu_a(\lambda)$ , scattering coefficient  $\mu_s(\lambda)$ , and the anisotropy factor  $g(\lambda)$  together with an appropriate phase function. These optical parameters are intrinsic and do not depend on sample geometry and the arrangement of light source and detector.

Intrinsic optical parameters cannot be measured directly but can be calculated from the measurable reflectance and transmission spectra, as this is the most precise theoretical model to solve the light transport equation where complex boundary conditions make analytical solutions impossible.

A spectrophotometer with an integrating sphere can operate using two different specular component modes. One mode is the specular component included (SCI) and the other mode is the specular component excluded (SCE). The specular component is the reflected light from the surface such that the angle of reflection equals the angle of incidence.

There are standards and recommendations that include the measurement geometries defined as  $d/0$  and  $t/0$ , where  $d$  represents diffuse illumination (SCE) and  $t$  represents total illumination that included diffuse and the specular component (SCI). The other character (0) represents the incident-viewing angle of the receiver optics as measured from the specimen normal.

Matte standards are required in reflectance colorimetry to simplify the problem of fully excluding or including the specular component in the measurement, as they diffusely reflect light equally in all direction, to improve the accuracy. Specularly reflected components from some surfaces (paint surfaces, glossy, semi-glossy or matte) were spread over a considerable wide range from the regular direction<sup>4</sup>. The surface of dental materials is not totally reflecting or matte. Thus, inclusion or exclusion of the specular component may be important for the color measurement of dental materials. However, limited information on the effects of the differences in the specular component mode of SCI and SCE has been reported.

One way of measuring optical properties is through the CIElab developed in 1978 by the Commission Internationale de l'Eclairage (International Commission on Illumination). This system defines color in terms of 3 coordinate values ( $L^*$ ,  $a^*$ ,

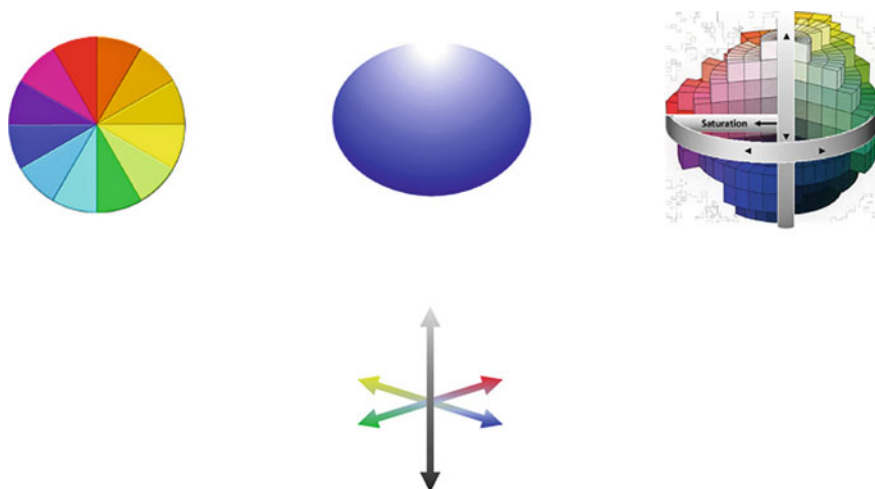
and  $b^*$ ), which locate the color of an object within a 3-dimensional color space. The  $L^*$  coordinate represents the brightness of an object represented on the  $y$  axis, the  $a^*$  value represents the red (positive  $x$  axis) or green (negative  $x$  axis) chroma, and the  $b^*$  value represents the yellow (positive  $z$  axis) or blue (negative  $z$  axis) chroma.

The color difference ( $\Delta E$ ) between 2 objects, or in the same object before and after it is subjected to particular conditions, can be determined by comparing the differences between the respective coordinate values for each object or situation. The higher the numbers, the stronger the color factors are. CIE  $a^*$  value is a measure of redness or greenness and CIE  $b^*$  value is a measure of yellowness or blueness. CIE  $a^*$  and  $b^*$  coordinates approach zero for neutral colors. For example, chroma is calculated as  $C^*_{ab} = (a^{*2} + b^{*2})^{1/2}$  (Figs. 7.5a and 7.5b).

Reflection of light from surfaces can be classified into two broad categories. The diffuse component results from light penetration to the surface, undergoing multiple reflections and refractions, and reemerging again at the surface. The specular component is a surface phenomenon, and it can be expressed as a function of the incidence angle and the refractive index of the material, the surface roughness, and a geometrical shadowing function.

Most color-measuring spectrophotometers cannot separate or compensate for several types of residual or confounded differences between instruments. The sources of these differences include specular effects, non-uniformities in integrating sphere illumination, nonlinearities in the photometric scale, and the translucent blurring effect found in translucent materials.

There are arguments on the threshold value of color difference that can be visually perceivable. The relationships between instrumentally measured color differences ( $\Delta E^*_{ab}$ ) and human observer assessment of color differences have been determined. Several studies have attempted to determine color matching tolerances.



**Fig. 7.5** **a** Creation of three-dimensional color solid. **b** CIELAB color space

Some authors reported that acceptability thresholds of color differences were 1.1 for red-varying shades and 2.1 for yellow-varying shades, and thresholds for perceptibility judgments were significantly lower than thresholds for acceptability judgements. For the perceptible limit of reflected color changes in esthetic Dentistry, a color difference value of greater than 2  $\Delta E^*ab$  units was perceived by all observers, and values between 1 and 2  $\Delta E^*ab$  units were perceived frequently. On the other hand, a clinical study of human observations and colorimetry reported that restorations judged clinically acceptable in vitro for color match had an average  $\Delta E^*ab$  of 3.715. Other clinical study found that 50 % of their observers considered that sample pairs of dental composite resins were unacceptable when  $\Delta E^*ab$  was approximately 3.3.

Segui et al. (1995) using monochromatic porcelain discs, determined that a  $\Delta E$  of 2 units was correctly detected by 100 % of observers under in vitro conditions. Some authors report that 50 % of observers consider specimens unacceptable when the  $\Delta E$  was approximately 3.3. Douglas et al. (2007) used metal ceramic crown specimens and determined that the 50 % acceptability tolerance for a group of 20 prosthodontists was between 1.7 and 2.7  $\Delta E$  units for crowns varying in yellowness and between 0.5 and 1.5  $\Delta E$  units for crowns varying in redness.

A mean color difference of 5.5  $\Delta E^*ab$  units was considered to be clinically unacceptable color match based on spectrometry measurement. As to a perceptible threshold, the average color difference of those ratings judged to be a match by the United States Public Health Service (USPHS) criteria was found to be 3.7  $\Delta E^*ab$  units based on spectrophotometer measurements, while that based on spectrometry measurement was reported as 2.6  $\Delta E^*ab$  units. Therefore, the value of 3.7 and 2.6  $\Delta E^*ab$  units as the perceptible thresholds.

An increase in the number of firings caused significant changes in the  $L^*$ ,  $a^*$ , and  $b^*$  coordinates for all-ceramic specimens, making them darker and more reddish/yellowish. For the metal ceramic specimens, the increase in number of firings did not lead to significant changes in  $L^*$ ,  $a^*$ , and  $b^*$  values.

The effect of multiple firings has been investigated in previous studies, and it has been reported that repeated firings did not noticeably affect the color of dental ceramics.

As the numbers of adults seeking orthodontic treatment has increased, tooth-colored brackets were introduced to meet the demand for more esthetic appliances. 1 Optical properties such as color stability of esthetic brackets has clinical implications for long-term color matching with the underlying teeth.

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## Chapter 8

# Degradation of Dental Ceramics

Orthodontic appliances and dental ceramics are installed within the oral cavity and this environment presents a series of external factors that can influence the mechanical and physical properties of these devices. The environment of the oral cavity aggravates the low tensile strength of dental ceramics.

Other factor is contact with air. A person inhales one cubic meter of air per day through the mouth with potential sulfur dioxide, which can affect the integrity of orthodontic wires, knots and other dental devices.

The oral microflora is one of the richest in quantity and variety of microorganisms. Both the microflora and its products can change orthodontic biomaterials. Some species metabolize the metal in the arch alloys, rings, brackets or metal channels of the ceramic brackets, while others alter salivary pH and initiate microbiological corrosion processes. Bacteria that reduce sulfate and nitrate are aggressive and inflammatory in human tissues, influencing the corrosion process of different metal alloys.

Oral temperature is also a variable. According to Iijima et al. (2004), throughout the day the intra-oral temperatures range from 0 to 55 °C, depending on ingested food. This fluctuation in temperature affects the mechanical properties of nickel-titanium orthodontic wires. Morena et al. (1986) argue that intra-oral temperatures are high in relation to ambient temperature and can be an accelerating factor in the crack growth process in ceramics.

### 8.1 Degradation of Mechanical Behavior

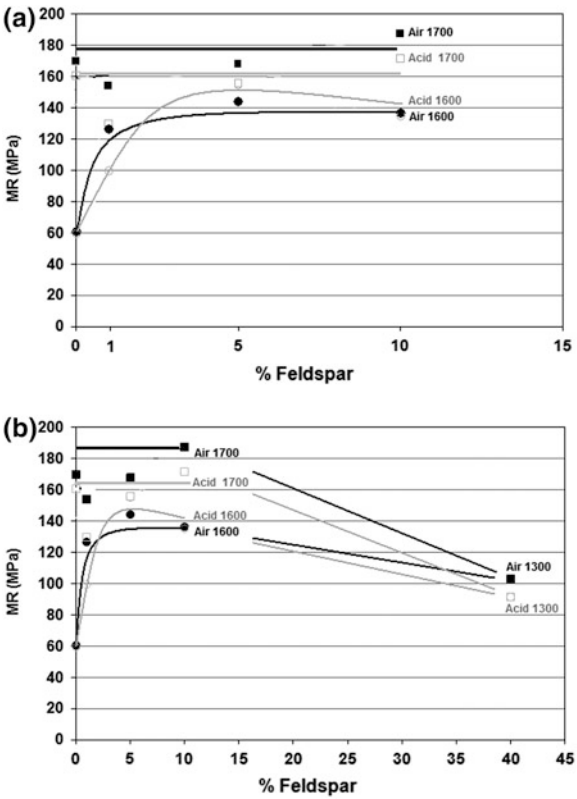
Barinov et al. (1998) have studied the environmental influence on the dynamic fatigue strength of alumina prepared with different additives, microstructures and different amounts of glassy phase. The authors concluded that the presence of glassy phase in alumina harms its strength both in air and in water. High purity alumina, however, shows lower resistance in acidic environments than aluminas containing glassy phase. The same authors also concluded that the rate of crack

growth practically does not influence the composition of the glassy phase grain boundary.

The pattern of deterioration of alumina in acidic environments is due to a chemical reaction induced by tensions between the environment and the bonds at the extremities of stress concentrators, such as microcracks, porosity and grain boundaries. pH seems to be a major factor in decreasing the resistance of high purity alumina.

Stumpf et al. (2010) studied the mechanical resistance and  $K_{IC}$  of alumina and alumina-feldspar ceramics with different amounts of feldspar addition (0, 5, 10, and 40 %) sintered at different temperatures (1,400, 1,600, and 1,700 °C) exposed to acetic acid (4 %) and air, and noticed that in general, mechanical strength is higher at higher sintering temperatures. This behavior is associated with the densification of the material at higher temperatures. Basically, there is dry sintering, which occurs in ceramic bodies without the addition of feldspar, and liquid phase sintering with the addition of feldspar. Figure 8.1 presents the mechanical resistance of alumina and alumina-feldspar ceramic bodies sintered at different temperatures when exposed or not to acetic acid. Figure 8.2 presents the fracture

**Fig. 8.1** Mechanical resistance of alumina and alumina-feldspar ceramic bodies sintered at different temperatures when exposed (b) or not to acetic acid (a)

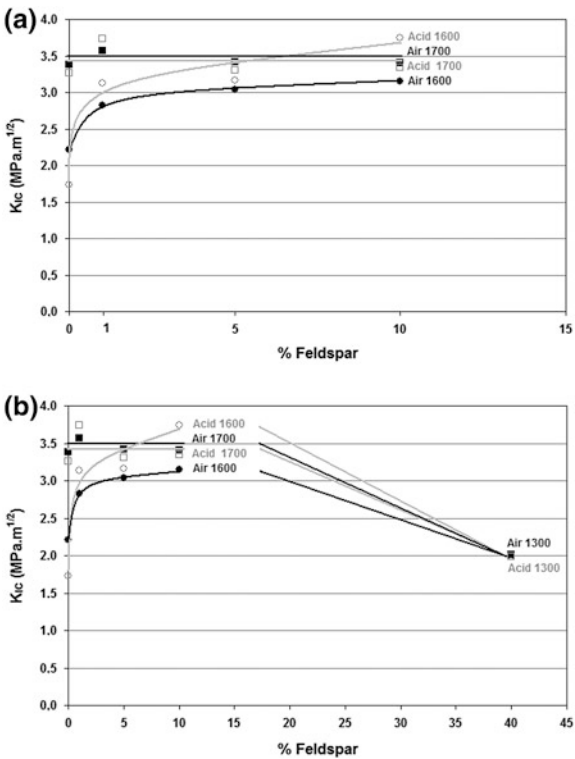


resistance of alumina and alumina-feldspar ceramic bodies sintered at different temperatures when exposed or not to acetic acid.

The results of Stumpf et al. (2010) investigation indicate that for these ceramic bodies, at a temperature of 1,700 °C sintering is nearly complete, with or without the addition of feldspar. In samples sintered at 1,600 °C it was possible to observe that the mechanical strength increases with the addition of feldspar. In these ceramic bodies such a small amount of glassy phase (between 5 and 10 %) is beneficial, since it can reduce the porosity and increase the density in ceramic bodies sintered at lower temperatures. The addition of feldspar in small amounts increases the mechanical strength of ceramic bodies heated at 1,600 °C, through the higher densification arising from more intense sintering.

In fact, the addition of feldspar to alumina acts as a glassy phase former in the sintering process. The presence of silicates in feldspar promotes a liquid phase that surrounds the alumina grains. The addition of this phase increases the rate of densification of ceramic bodies. In both cases, the surface area is effective in promoting greater contact and in intensifying the sintering phenomenon (by its effective further reduction). These phenomena lead to higher densification of ceramic bodies.

**Fig. 8.2** Fracture resistance of alumina and alumina-feldspar ceramic bodies sintered at different temperatures when exposed (b) or not to acetic acid (a)



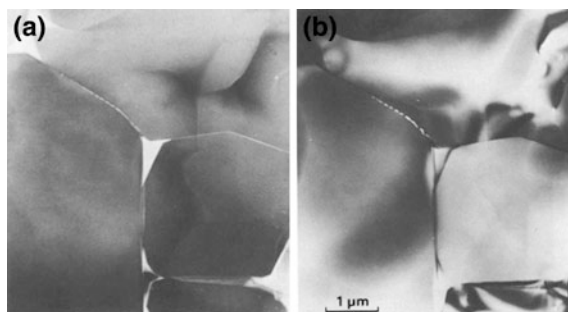


It is clear that when 40 % of feldspar is added, fracture toughness ( $K_{IC}$ ) tends to decrease in both groups (exposed or not to acetic acid). This is probably because the amount of feldspar forms glassy phase in excess. The  $K_{IC}$  values were lower for samples sintered at 1,600 °C. At this temperature, the highest value obtained for fracture toughness occurred in samples with 10 % feldspar. This way, at 1,600 °C  $K_{IC}$  increased linearly with the addition of feldspar from 0 to 10 %. This behavior shows that sintering is incomplete at the temperature of 1,600 °C in the absence of feldspar. The addition of 10 % feldspar enables liquid phase sintering, increasing the values of  $K_{IC}$ .

The variations in the  $K_{IC}$  confirm that the presence of a small amount of feldspar contributes to increase the densification of the material, when lower firing temperatures are used. Several authors agree that the grain boundary region can determine the behavior of ceramic materials and that therefore the control of this region is critical.

$K_{IC}$  has a specific value for a given material. For alumina, this value is around 3.5 MP a.m<sup>1/2</sup> (Matasa 1999).  $K_{IC}$  values obtained for the investigated ceramic samples validate the assumption that the presence of a small amount of glassy phase improves the sintering process of alumina based ceramics, through greater densification.

On the other hand, the results obtained by Stumpf et al. (2010) also confirm that an excessive amount of glassy phase causes a decrease of  $K_{IC}$ . The addition of glassy phase above this value increases the area of “vitreous cavities” that form in the contact area between three and four grains of the crystalline phase, while the film of the glassy phase that occurs between two grains does not increase much. The increase in the area of the “vitreous cavities” may therefore be a factor for reducing mechanical strength since it is a phase with lower mechanical strength (Fig. 8.3).



**Fig. 8.3** Vitreous phase accumulation in the grain's boundary area of alumina. Diffuse dark-field (a) and bright-field (b) transmission electron micrographs illustrating the continuous, intergranular nature of the glass phase along the two-grain and three-grain junctions of the alumina phase. The glass phase, appearing bright in the diffuse dark-field image, is concentrated at the three-grain junctions (Clarke 1985)

$K_{IC}$  value increases after exposure to acetic acid in ceramic bodies sintered at 1,600 °C. This effect, however, did not occur in the samples fired at higher temperatures. Jestel et al. (1998) also report that when testing a feldspathic dental ceramic (Duceram® LFC, Ducera Dental,) its mechanical strength improved after exposure to a solution of 4 % acetic acid for 16 h. The authors attributed this effect to an ion exchange mechanism that modified the surface structure.

According to Roman et al. (2008), the existence of a second phase in alumina influences the mechanical behavior of the material.

Acetic acid also had a very interesting effect on fracture toughness in samples with no feldspar, acetic acid reduced  $K_{IC}$ . This effect was also observed by Barinov et al. (1998) when comparing the mechanical strength of high purity alumina (99.5 %) and alumina with the addition of glassy phase exposed to an acidic medium (hydrochloric acid and citric acid). The authors attributed the results to the low corrosion resistance in the alumina grain boundary region.

Moreover, Stumpf et al. (2010) reported that the chemical elements that were most attacked by acetic acid, were silicon and aluminum. The chemical element that was least attacked, regardless of firing temperature, was iron. In general it is also possible to observe that the test samples sintered at 1,700 °C were attacked less than the ceramic bodies sintered at 1,600 °C, demonstrating that greater densification of these ceramic bodies improves their resistance in harsh environments.

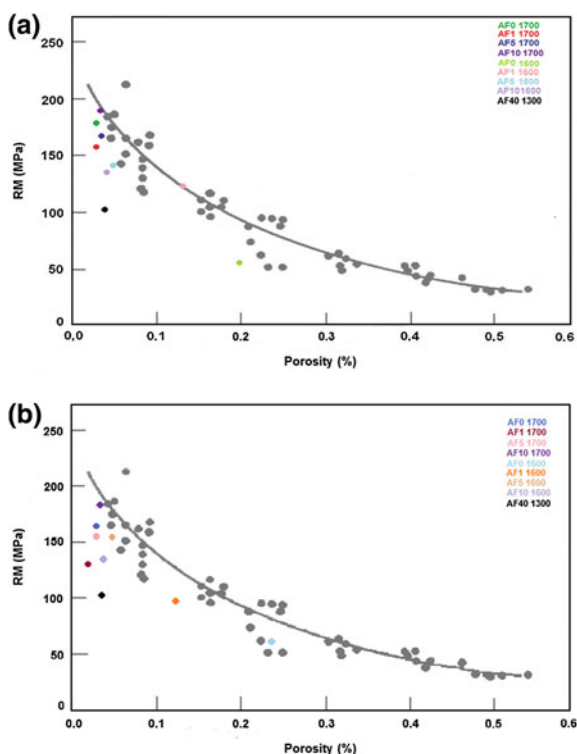
Stumpf et al. (2010) also reported that the alumina and alumina-feldspar bodies fired at lower temperatures are less dense and have a higher degree of porosity, in accord with the literature concerning the quality of the ceramic sintering process. In the same study, Stumpf et al. reported that in the ceramic bodies sintered at 1,600 °C it was possible to verify that the amount of porosity was lower in those ceramic bodies with more than 5 % of glassy phase. This behavior can be explained by the ease of sintering when there is a glassy phase present.

Cerecedo et al. (2005) have reported a similar effect in alumina ceramic bodies sintered at 1,650 °C for 6 h. The increase in strength with increasing densification reflects better sintering conditions (ASM 1991). The interdependence between the amount of porosity, sintering temperature and mechanical strength has been demonstrated by other authors (HAN et al. 2002).

Kingery (1960) has reported an exponential decrease of mechanical strength in alumina ceramics with an increasing amount of pores in the material. It is possible to observe that the addition of certain amounts of feldspar to alumina is deleterious, since the majority of test samples at the Stumpf et al. (2010) study showed mechanical strengths below the proposed curve (Fig. 8.4).

The influence of feldspar on alumina ceramic bodies is well illustrated by sample with 40 % of feldspar. Although these test samples have low porosity (less than 3 %), their strength is 40 % lower than samples with similar porosity. For the ceramic bodies exposed to acetic acid, the mechanical strength behavior was similar to those samples exposed only to air. The presence of porosity was higher in some groups, especially those fired at 1,600 °C. This could mean that acetic acid

**Fig. 8.4** Mechanical resistance and porosity's comparison in the Kingery's proposed curve for alumina's ceramics exposed (b) or not to acetic acid (a)



can better penetrate the less dense samples, increasing their porosity and reducing flexural strength.

Despite the fact that the increase in porosity was higher after exposure to acetic acid, especially in test samples sintered at lower temperatures, the decrease in strength was greater in the ceramic bodies fired at 1,700 °C. Perhaps the reduction in flexural strength was lower in samples sintered at 1,600 °C, because in these ceramic bodies some larger pore was already the largest defect and the increase in porosity after exposure to acetic acid did not make it more critical as occurred in the samples fired at higher temperatures.

Considering this behavior, it is possible to improve the formulation and firing temperature of ceramics based on the introduction of glassy phase in the microstructure of materials such as orthodontic brackets, restorations and dentures, so that these devices may face the rigors of the oral environment.

Cho et al. (2003) have evaluated the effect of temperature and humidity on alumina in four-point bending tests. The authors tested the effect of temperature variation between 10 and 55 °C and relative humidity between 20 and 80 %. They concluded that the flexural strength of alumina decreases with increasing temperature and humidity. There are few studies, however, on the influence of intra-oral temperature fluctuations on dental ceramics.

The corrosion of stainless steel orthodontic arches, for example, increases in acidic environments. When the bracket with metal channel and orthodontic arch are tested, the movement of both these elements can induce corrosion. Saliva also has a deleterious effect on the sliding performance of the arches on orthodontic braces, since it increases frictional stress.

Saliva is also subject to various pH fluctuations throughout the day, depending on the type of diet and food intake frequency of the patient. Because of this saliva can contain acids from food items, making the intraoral environment more corrosive.

The gastric contents may have a pH lower than 1. This means regurgitation can cause damage to tooth enamel and intraoral ceramic materials. It is important to point out that the presence of braces increases the retention of bacterial plaque and that this change in the quantity and quality of bacterial flora may alter salivary composition. According to Fournier et al. (1998), ceramic brackets favor the accumulation of bacterial plaque.

Patients can also use daily or weekly mouthwashes of fluoride solutions. The use of fluoride is recommended for patients with the incidence or risk of caries. Many dentists recommend regular, preventive use of fluoride solutions throughout treatment, especially for adolescent patients who do not always closely follow hygiene instructions. Daily exposure to fluoride can reduce the incidence of caries and heal existing carious lesions.

Fluoride solutions promote the formation of calcium fluoride globules that adhere to tooth enamel, stimulating its remineralization and protecting it from acid attacks. Fluorides are also present in teas, mineral water and vitamin supplements. According to Giertsenie et al. (1999), sodium fluoride mouthwash with xylitol does not alter the composition of bacterial plaque and salivary pH. Other authors, however, such as Joyston-Bechal and Hernaman (1993), believe that the plaque composition, and therefore salivary characteristics, depend on diet and exposure to fluoride.

Regardless of the possible effect of fluorides on the composition of bacterial plaque and its subsequent influence on salivary pH, these substances, especially the acidulated fluorides, alter the surface of ceramic materials. Fluoride ions in an acidic environment can chemically attack ceramics. The lower the pH of the fluoride, the greater its ability to corrode the ceramics. The pH of acidic fluoride is less than 4 (between 3.4 and 3.6), while the pH of the neutral fluoride is around 7. The low pH of acidic fluoride can result in the formation of hydrofluoric acid, attacking the surface of ceramics, especially those without surface polishing. The subsequent increase in surface roughness can increase the accumulation of bacterial plaque on the ceramic material.

Other authors also agree that acidulated fluorides, especially in high concentrations, negatively affect the surface of ceramics for dental use. Among the types of fluoride used, sodium fluoride is one of the most common.

According to Akova et al. (2007), the presence of food in the oral cavity influences dental materials. These authors state that the FDA (Federal Drug Administration) suggests the use of liquids that simulate food ingestion, such as ethanol solutions and citric acid to simulate the effects of beverages (including alcoholic ones), fruit and sweets. The authors tested the adhesion of metal brackets

to ceramic restorations, using water, 0.02 N citric acid, 0.8 % ethanol and 50 % ethanol solutions in order to test the deleterious effects of these chemicals on adherence.

The exposure of dental ceramic material to soft drinks degrades its surface, reducing its mechanical strength. The American Dental Association (ADA), as well as the ISO 6,872 standard, recommends that ceramics have their chemical resistance tested with 4 % acetic acid (ADA 69, ISO 6872). Authors like Alkhiari, Morgano and Giordano (2003), as well as Ardlin (2002), tested the changes that occur in ceramics after 16 h exposure to 4 % acetic acid at 80 °C as recommended by ISO and the ADA.

Alkhiari et al. (2003) found deleterious effects on the surface of conventional dental ceramics. Ardlin (2002), on the other hand, found no degradation when testing the aging of tetragonal zirconia with this acid, showing that this material is more stable and that it could be a promising material in Dentistry.

Rijk et al. (1985) used five test solutions: tea with tannic acid, artificial saliva, Ringer's solution, distilled water and acetic acid in a chemical stability study of five dental ceramics. They found that acetic acid was the most aggressive. One must also consider, however, that the degree of surface attack will depend on the composition of the ceramics and the type of surface finishing.

One important aspect of the critical cracks in ceramic materials is the fact that they may exhibit a slow and stable crack growth (SCG) (or static fatigue) when subjected to stresses below the critical value, especially in the presence of water or water vapor, as observed in the oral environment. Such phenomenon will eventually lead to strength degradation over time, decreasing the lifetime of dental prostheses. There is a 20–30 % reduction in strength in a moist environment.

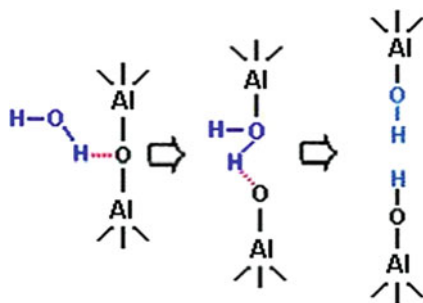
SCG process may be also influenced by the pH of the environment. The environment in which the ceramic finds itself has a strong effect on subcritical crack growth, where the aqueous environment leads to quicker crack growth and diminishes the resistance of ceramics when compared to inert environments.

Oral saliva plays a very important role in the aging and performance of intra-oral devices, since the presence of these devices in an aqueous environment makes them subject to static fatigue.

Freiman (1984), focusing on subcritical crack growth produced by environmental conditions in glass, ceramics and simple crystals, showed there is a consensus among various authors that the rate of crack growth is controlled by the chemical activity of species active in the environment as well as the stress intensity at the crack tip. The mechanism proposed by Freiman (1984) is shown in Fig. 8.5.

At the crack tip, a state of compression occurs that changes the tetrahedral symmetry of silica in such a way that the  $\text{Si}^{+4}$  atoms become highly acidic and oxygen atoms become strongly basic. Water molecules orient themselves spontaneously forming hydrogen bonds with oxygen. The electron transfer occurs, therefore, simultaneously from the oxygen of the water to the silicon, where the electrons are transferred to the oxygen of the silica. This causes the rupture of the hydrogen bond with the oxygen in the water, which is transferred to the Si–O–Si bond, giving rise to two Si–OH groups behind the crack tip. Propagation is

**Fig. 8.5** Freiman's model for subcritical crack growth for alumina in humid environments



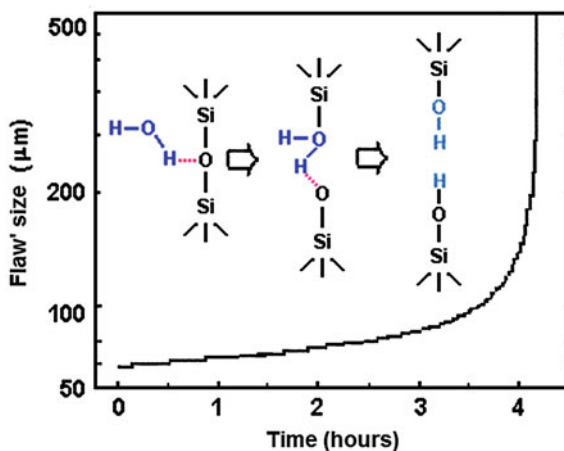
achieved through this mechanism until the supply of water to the crack tip is extinguished. Silicates, therefore, as a major component of the vitreous phase present in some compositions of alumina, make these materials more susceptible to aqueous environments.

Figure 8.6 illustrates a model of the  $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$  reaction, showing three following phases:

1. A  $\text{H}_2\text{O}$  molecule orients itself in relation to a  $\text{Al}-\text{O}-\text{Al}$  bond of the crack tip in such a way that a pair of electrons isolated from the oxygen in the water lines up with the oxygen in the alumina and a hydrogen bond occurs, connecting the oxygen in the alumina with hydrogen in the water;
2. The transfer of an electron from the oxygen in the water to the alumina occurs simultaneously with the transfer of a proton to the oxygen in the alumina. Two new  $\text{Al}-\text{O}_{\text{water}}$  and  $\text{H}-\text{O}_{\text{alumina}}$  bonds are formed;
3. Rupture of the weak link of the hydrogen, giving rise to two  $\text{Al}-\text{OH}$  groups.

Propagation is achieved through this described mechanism until the supply of water to the crack tip is extinguished. Aggressive liquids and gases can also have

**Fig. 8.6** Correlation between the SCG and the chemical mechanism proposed by Freiman for  $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$  reaction



effects similar to water, especially at high temperatures. Wiederhorn and Johnson (1973) report that the resistance of ceramics with glassy phase based on silica decreases in acidic pH when compared to alkaline pH. Alumina exhibits an ionic-covalent bond similar to silicon and has a similar model, where the silicon atom is replaced by the aluminum atom.

## 8.2 Degradation of Optical Properties

Comparing to mechanical degradation of dental ceramics little is known about color changes over time. The influence of aging or chemical substances on the color stability of esthetic brackets would be different by their composition, morphology, and surface property, all of which can influence their performance. Ceramic brackets, unlike plastic brackets, resist staining and discoloration and are chemically inert to fluids that are likely to be ingested. Although it is generally accepted that ceramic brackets have better color stability than plastic brackets, few studies have compared their color stability after aging.

Kind of material and crystal structure for dental ceramics did not influence color stability, but color stability was mainly brand-dependent. Therefore, color stability of esthetic brackets should be considered for their long-term use.

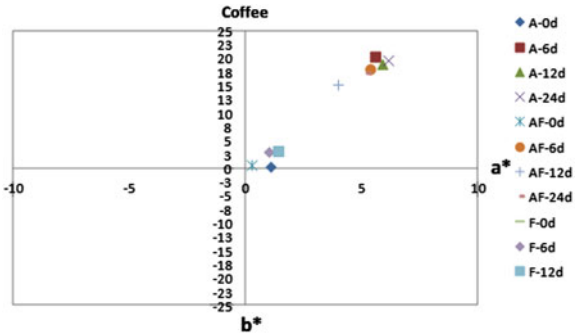
The early plastic brackets were made of polycarbonate and plastic molding powder, which take up water and change color during service. Therefore, these brackets did not last long because of discoloration, fragility, and breaking under stress. Advanced types of reinforced plastic brackets such as stainless steel slot inserts and composite resin brackets have been introduced since then.

Brackets made of polycrystalline ceramic and monocrystalline sapphire became widely available in the mid-1980s. Heat, acids, alkalis, oxygen, abrasion, enzymes, and radiation can all cause the chemical breakdown of esthetic brackets. As to the color stability of ceramic brackets, it has been reported that monocrystalline and polycrystalline ceramic brackets resist staining or discoloration from any chemical substance likely to be encountered in the mouth. However, ceramic brackets in the oral environment can be affected by color pigments in tea, coffee, and wine. Thermal cycling is generally used to accelerate the aging process to determine the color stability of esthetic restorative materials, and thermal cycling for 10,000 cycles corresponds to 1 year of clinical service.

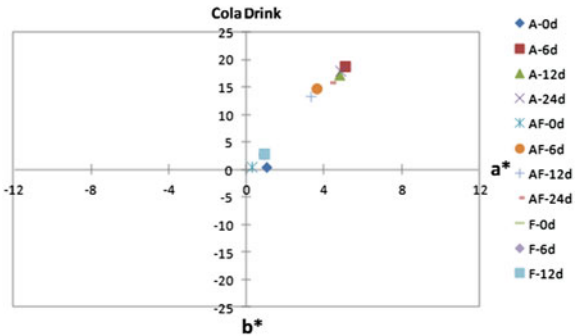
Stumpf et al. in an unpublished article studied the optical behavior of alumina, alumina-feldspar and feldspar ceramic bodies when exposed to several staining agents such as cola drink, coffee solution and grape juice during 0, 6, 12 and 24 days. This time frame was chosen because it simulates a period of 6, 12 and 24 months of orthodontic treatment.

Alumina and alumina-feldspar ceramic bodies stained in most coloring agents. The pure alumina ceramic bodies stained the most, followed by alumina-feldspar. Probably the feldspar ceramic bodies did not stain due to the lesser amount of porosities due to the presence of a glassy phase.

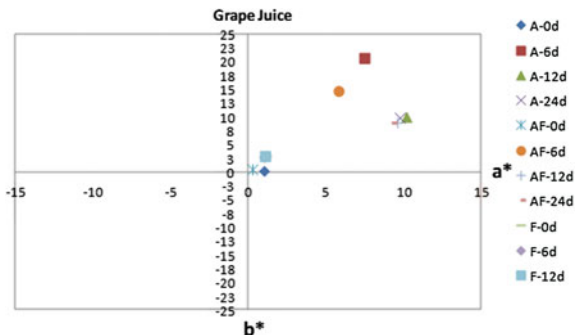
**Fig. 8.7** Alumina, alumina-feldspar and feldspar ceramic bodies exposed to coffee during 0, 6, 12 and 24 days



**Fig. 8.8** Alumina, alumina-feldspar and feldspar ceramic bodies exposed to cola drink during 0, 6, 12 and 24 days



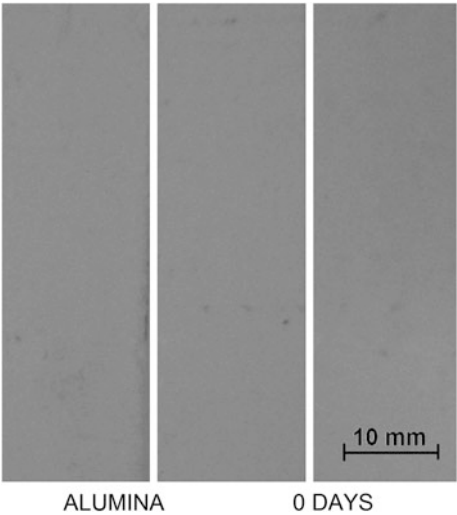
**Fig. 8.9** Alumina, alumina-feldspar and feldspar ceramic bodies exposed to grape juice during 0, 6, 12 and 24 days



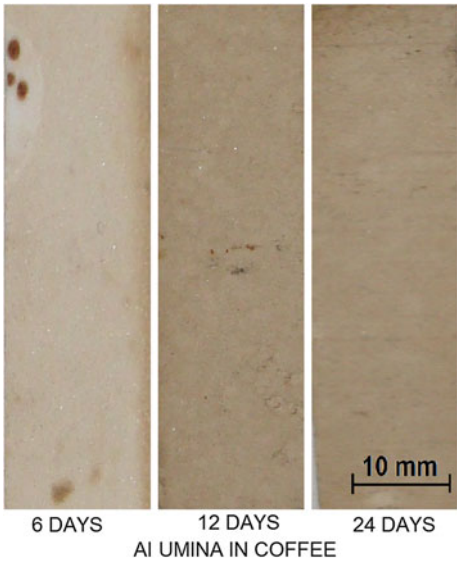
The alumina stained the most once the alumina ceramic bodies did not have any glassy phase. In the alumina ceramic bodies it was noted that the stains got worse with the increase of time. In the alumina-feldspar ceramic bodies the amount of staining was pretty much the same in cola drink in days 6 and 12 and got worse in 24 days. In the grape juice solution, the alumina-feldspar ceramic bodies stained from day 0 to 6 and remained unchanged from day 12 to 24. Figures 8.7, 8.8, 8.9 show the results. Figures 8.10, 8.11, 8.12, 8.13, 8.14, 8.15, 8.16 present images by optical microscopy of samples before and after the exposure to different stain agents (Figs. 8.17, 8.18, 8.19, 8.20).



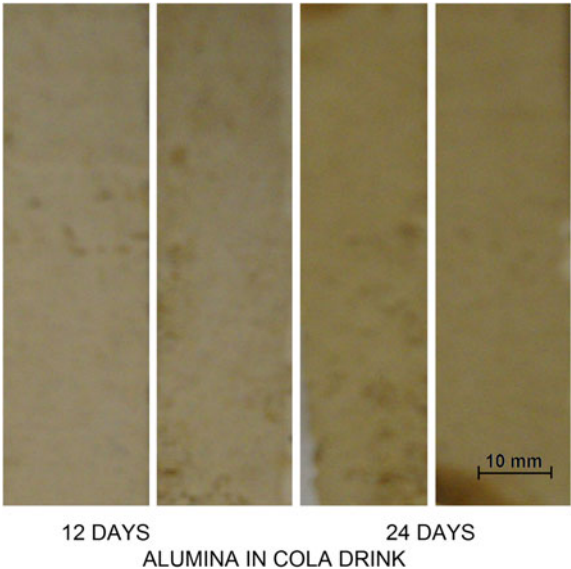
**Fig. 8.10** Image of an alumina ceramic body prior to exposure to a staining agent



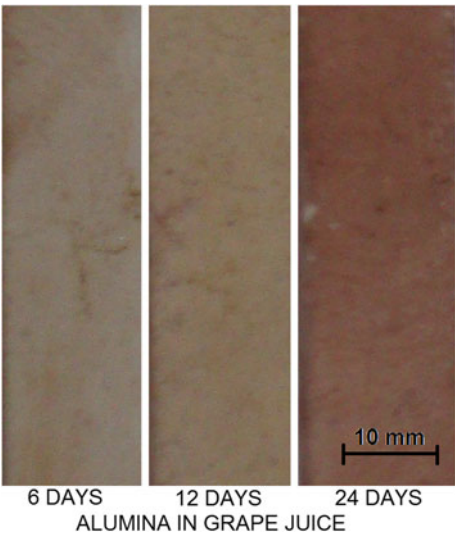
**Fig. 8.11** Comparison of alumina ceramic bodies exposed to coffee solution in 6, 12, and 24 days



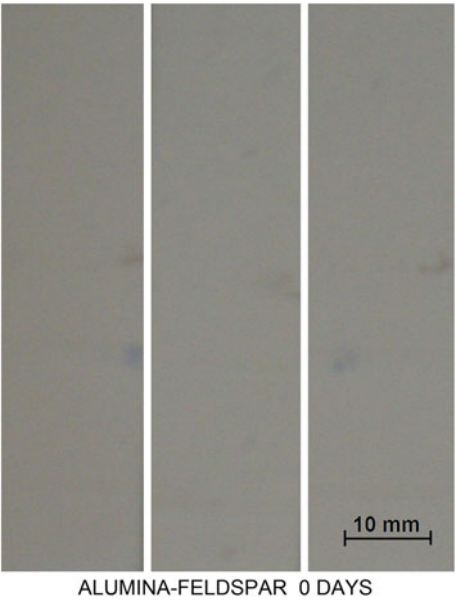
**Fig. 8.12** Comparison of alumina ceramic bodies exposed to cola drink solution in 12, and 24 days



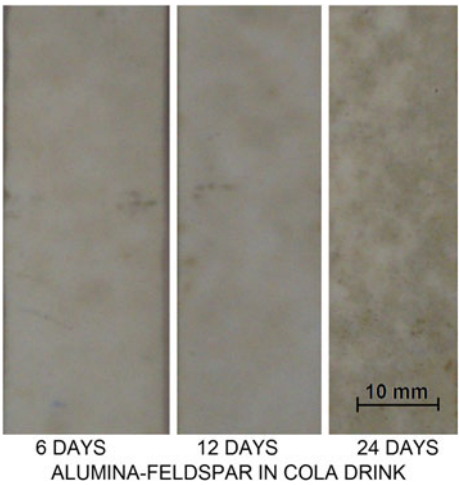
**Fig. 8.13** Comparison of alumina ceramic bodies exposed to grape juice solution in 6, 12, and 24 days



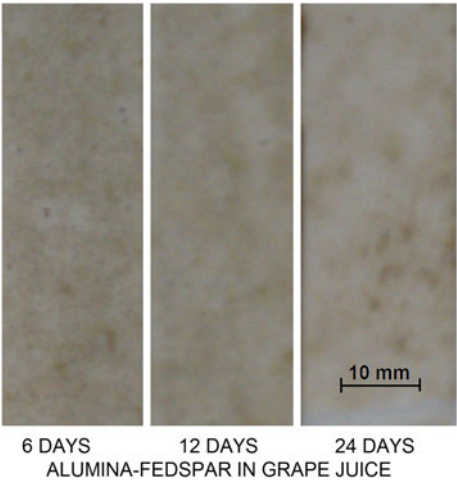
**Fig. 8.14** Image of an alumina-feldspar ceramic body prior to exposure to a staining agent



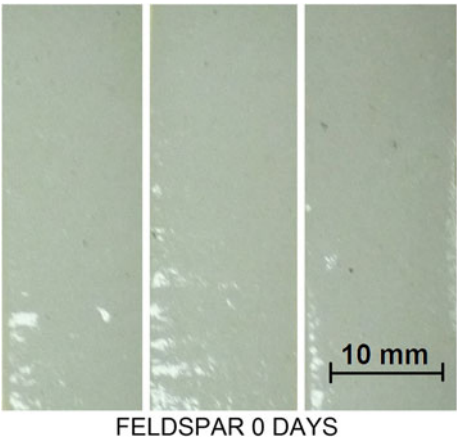
**Fig. 8.15** Comparison of alumina-feldspar ceramic bodies exposed to cola drink solution in 6, 12, and 24 days



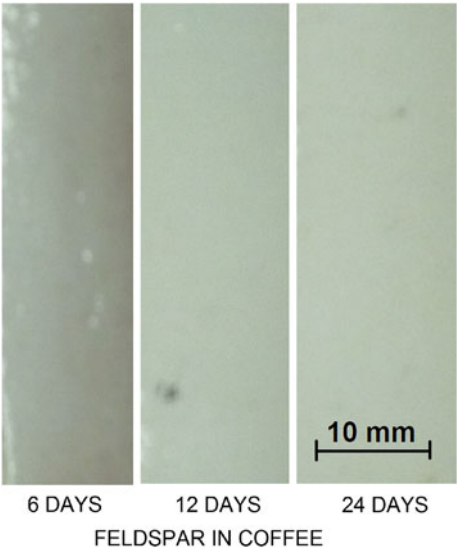
**Fig. 8.16** Comparison of alumina-feldspar ceramic bodies exposed to grape juice solution in 6, 12, and 24 days



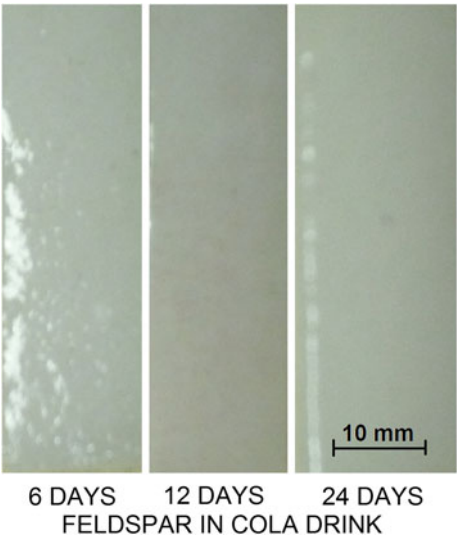
**Fig. 8.17** Image of a feldspar ceramic body prior to exposure to a staining agent



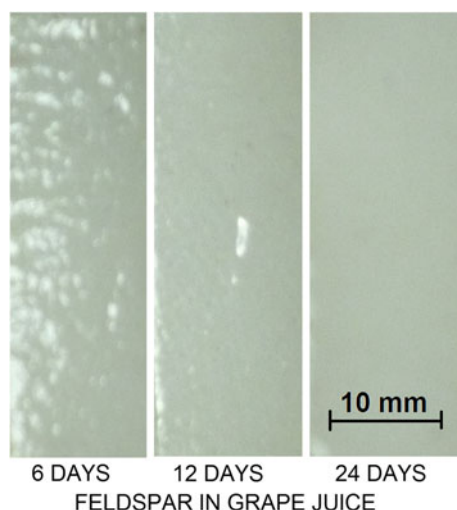
**Fig. 8.18** Comparison of feldspar ceramic bodies exposed to coffee solution in 6, 12, and 24 days



**Fig. 8.19** Comparison of feldspar ceramic bodies exposed to cola drink solution in 6, 12, and 24 days



**Fig. 8.20** Comparison of feldspar ceramic bodies exposed to grape juice solution in 6, 12, and 24 days



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