Zirconia in dentistry: Part 1. Discovering the nature of an upcoming bioceramic.

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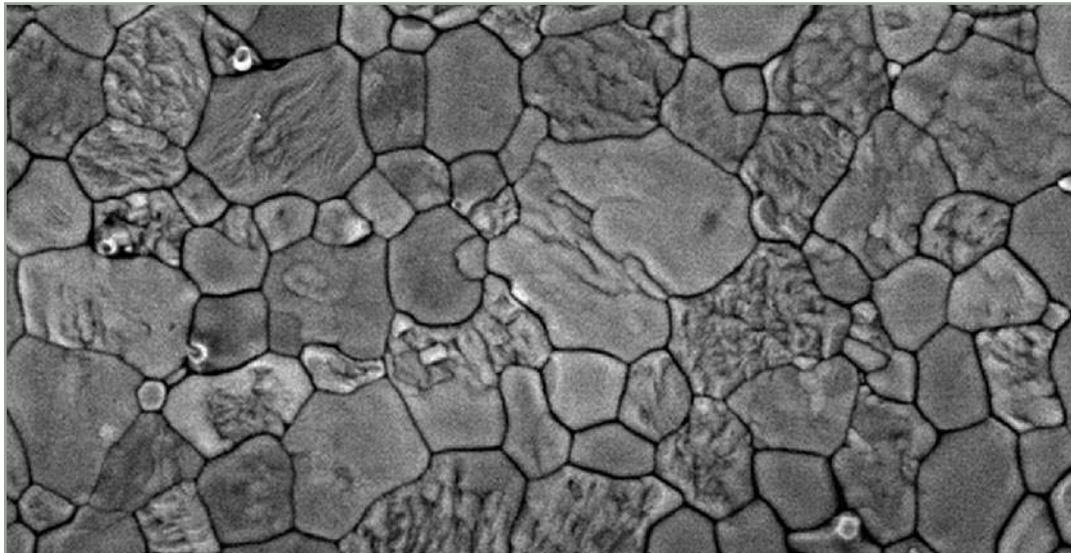
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Abstract

Advanced ceramic materials such as zirconia have great potential as substitutes for traditional materials in many biomedical applications. Since the end of the 1990s, the form of partially stabilized zirconia has been promoted as suitable for dental use due to its excellent strength and superior fracture resistance as result of an inherent transformation toughening mechanism. In addition, zirconia bioceramic presents enhanced biocompatibility, low radioactivity, and interesting optical properties. The introduction of computer-aided design/computer-aided manufacturing (CAD/CAM) techniques has increased the general acceptance of zirconia in dentistry. However, some fabrication procedures such as grinding, polishing, sandblasting, heat treatment, and veneering of the fine-grained metastable zirconia microstructures may affect the long-term stability and success of the material by influencing its aging sensitivity.

The purpose of this review is to address the evolution of zirconia as a biomaterial; to explore the material's physical, chemical, biological, and optical properties; to describe strengthening procedures; and finally to examine aging, processing, and core/veneer interfacial effects.
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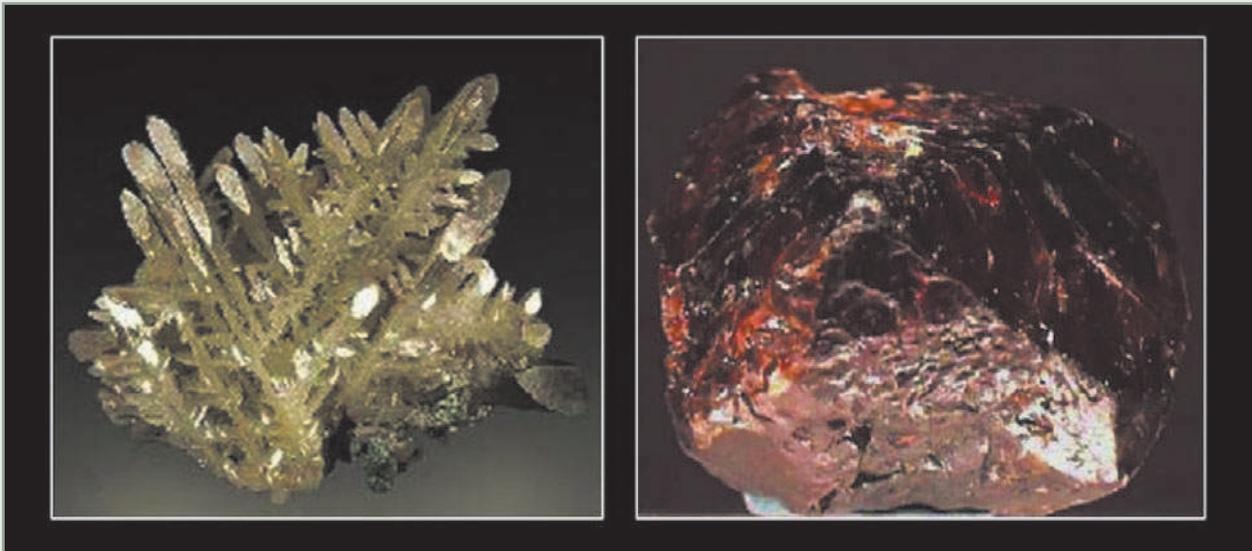
Introduction

The Stone Age and Bronze Age were named for the materials that dominated these major historical periods. Consequently, the modern era, which is encountering an ever-increasing assortment of ceramic materials for industrial or biomedical use, could be characterized as the "Ceramic Age."

Ceramic materials that are specially developed for medical and dental use are termed bioceramics. Over the last decade, zirconia technology has propelled a rapid development of metal-free dentistry that may provide high biocompatibility, enhanced esthetics, and improved material strength. The extensive knowledge gained with regard to zirconia ceramic chemistry, crystallography, and the production of these engineered ceramics led to promising and advanced dental applications.

Techniques previously applied to metals are now considered applicable to different ceramic systems. Phase transformations, alloying, quenching, and tempering techniques are currently applied to a range of zirconia ceramic systems. Significant improvements to the fracture toughness, ductility, and impact resistance have minimized the gap between the physical properties of ceramics and metals. Moreover, recent developments in non-oxide and tougher ceramics (eg, nitride ceramics) and massive investments in dental industry (eg, CAD/CAM systems) have also created great hope that ceramic materials have potential application in clinical dentistry. From the technological point of view, zirconia seems to present short-term excellent performance; however, no long-term data regarding intra-oral longevity exists, and for this reason its future is still unknown.

The purpose of this review is to define the evolution and development of zirconia as a biomaterial. More specifically, it will address the physical, chemical, and optical properties; material chemistry within the different crystallographic phases and strengthening procedures; tissue response regarding biocompatibility; and to describe aging and surface effects during processing techniques.

Historical developments

Zirconium minerals were discovered decades ago but are still referred to as *jargon, jacinth,* and *hyacinth*. The metal zirconium (Zr) comes from the Arabic word *zargon* (golden in color), which in turn derives from two Persian words: *zar* (gold) and *gun* (color). The metal dioxide zirconia was discovered by the German chemist Martin Heinrich Klaproth in 1789 and was isolated by the Swedish chemist Jöns Jakob Berzelius, in 1824.

Nowadays, zirconia is used extensively for industrial purposes; most of these applications are listed in Table 1. Research and development on zirconia as a biomaterial were started in the late sixties of last century when Helmer and Driskell published the first paper concerning different zirconia biomedical applications.[1] Since then, research based on the work of Garvie and Nicholson,[2] has focused on yttrium-oxide partially stabilized zirconia (Y-PSZ) ceramics, also known as yttrium-tetragonal zirconia polycrystals (Y-TZP) that both exhibit high biocompatibility[3,4] and improved fracture toughness.[3,5] In general, modern zirconia biomaterials and products used as surgical (implant) materials should meet the requirements de-

Table 1   Y-TZP

Applications and typical uses of zirconia in industry	
Tube and rod mill rolls	Thermal insulator
Pump and valve parts	Hot metal extrusion dies
Precision fixtures	Thread and wire guides
Stamping, drawing, and extrusion dies	Fuel cell membranes
Precision ganging products	Fiber optic components
Wire guides	Precision ball valve balls and seats
Cutting tools	Grinding and dispersing media
Deep well down-hole valves and seats	Powder compacting dies
Oxygen sensors	Marine pump seals and shaft guides
Rollers and guides for metal tube forming	High density ball and pebble mill grinding media
Electric furnace heaters over 2,000°C in oxidizing atmospheres	High temperature induction furnace susceptors

Table 2   Y-TZP

Medical applications	Dental applications
Surgical tools	Composites
Blood handling	Extracoronal attachments
Instrumentation	Full and partial coverage crowns
Surgical implants	Fixed partial coverage crowns
Orthopedics (TZP ball heads)	Veneers
	Posts and cores
	Primary telescopic crowns
	Orthodontic brackets
	Implant abutments
	Implants

scribed by the International Organisation for Standardisation (ISO) 13556. Zirconia ceramics have different applications in contemporary medicine, however, the most widespread application is the manufacturing of Y-TZP ball heads for total hip replacements (THR) or total hip arthroplasty (THA), first introduced by Christel.[3]

Moreover, with the continuing development of the current CAD/CAM systems, dentistry also became proficient with different zirconia based applications (eg, high-strength frameworks, endodontic posts, implants, brackets, etc.) (Table 2).

Definitions

Zirconium (pronounced /zər-ˈkō-nē-əm/): symbol Zr, transition metal element, atomic no. 40, weight of 91.22, lustrous and exceptionally corrosion resistant. Pure zirconium exists in a crystalline form as a white and ductile metal and in an amorphous form as a blue-black powder. Zirconium has a density of 6.49 g/cm^3, a melting point of 2,128 K (1,855°C or 3,371°F) and a boiling point of 4,682 K (4,409°C or 7,968°F). Among the elements in earth's crust zirconium is ranked 18th in abundance, however, this particular element does not occur in nature in a pure state but only in conjunction with silicate oxides (ZrO_2 x SiO_2) or as a free oxide (ZrO_2).[6,7,8]

Zirconium dioxide (ZrO_2), known as *zirconia*, is a white crystalline oxide of zirconium. Although pure zirconium oxide does not occur in nature, it is found in the minerals baddeleyite and zircon ($ZrSiO_4$) (Fig 1). At ordinary temperatures, it has a hexagonal close-packed crystalline structure and forms a number of compounds such as zirconate ($ZrO3^{-2}$) and zirconyl (ZrO^{+2}) salts. Zirconia is obtained as a white powder and possesses both acidic and basic properties. Zirconium oxide crystals are arranged in crystalline cells (mesh) which can be categorized in three crystallographic phases: *1)* the cubic (C) in the form of a straight prism with square sides *2)* the tetragonal (T) in the form of a straight prism with rectangular sides and *3)* the monoclinic (M) in the form of a deformed prism with parallelepiped sides (Fig 2). The cubic phase is stable above 2,370°C and has moderate mechanical properties, the tetragonal phase is stable between 1,170°C and 2,370°C and allows a ceramic with improved mechanical properties to be obtained, while the monoclinic phase, which is stable at room temperatures up to 1,170°C, presents reduced mechanical performance and may contribute to a reduction in the cohesion of the ceramic particles and thus of the density.

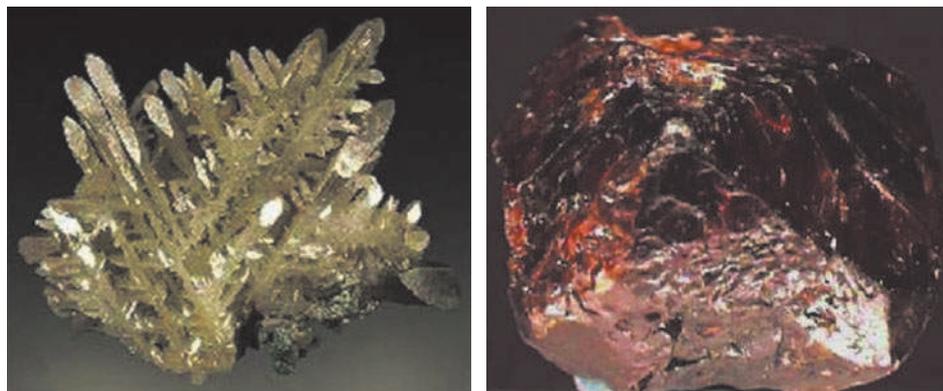**Stabilized zirconia.** This is a mixture of zir-

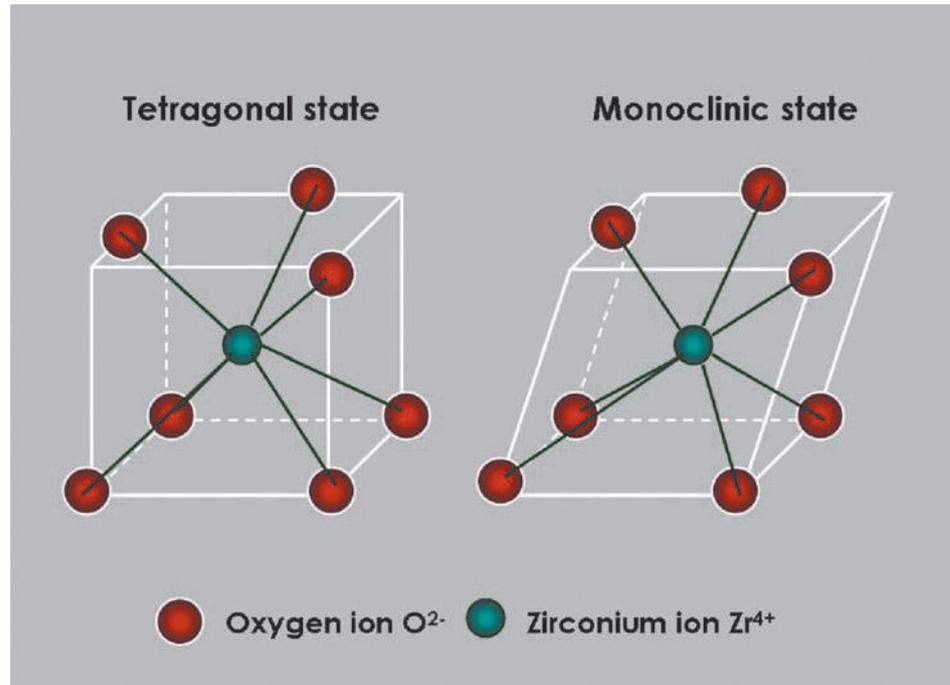**Fig 1** The minerals **(a)** Baddeleyite (ZrO_2) and **(b)** Zircon ($ZrSiO_4$).

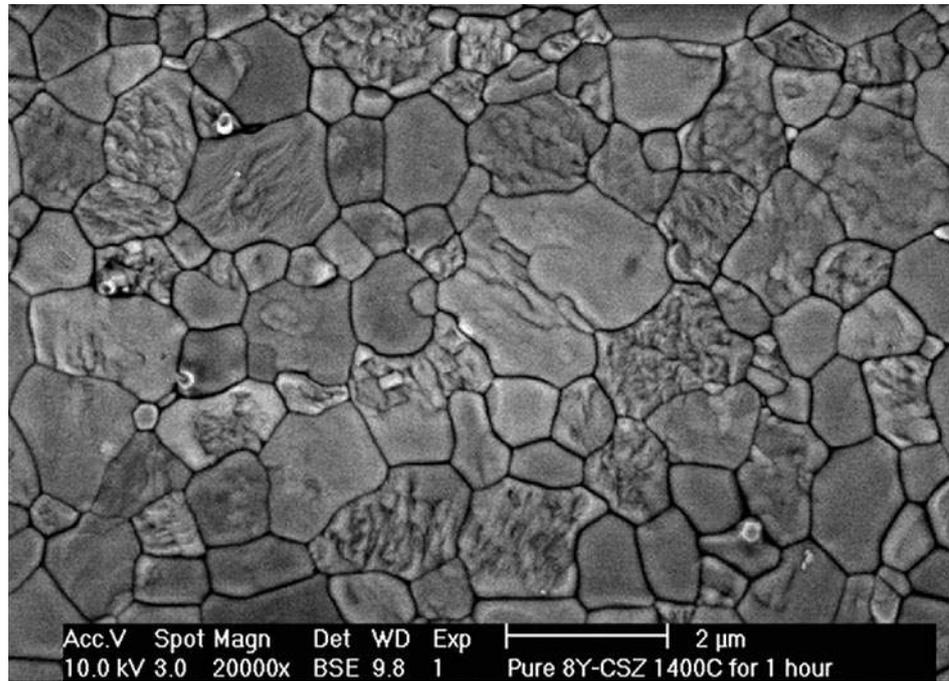**Fig 2** Tetragonal (left) and monoclinic (right) crystallographic phases of zirconium oxide.

Fig 3 Microscopic image of fully yttria-stabilized cubic zirconia (13.75 wt% 8 mol% Y_2O_3-ZrO_2).

conia polymorphs, because insufficient cubic phase-forming oxide (stabilizer) has been added and a cubic plus metastable tetragonal ZrO_2 mixture is obtained. A smaller addition of stabilizer to the pure zirconia will bring its structure into a tetragonal phase at a temperature higher than 1,000°C and a mixture of cubic phase and monoclinic (or tetragonal) phase at a lower temperature. This partially stabilized zirconia is also called tetragonal zirconia polycrystal (TZP). Several different oxides, eg, magnesium oxide (MgO), yttrium oxide, (Y_2O_3), calcium oxide (CaO), and cerium oxide (Ce_2O_3), can be added to zirconia to stabilize the tetragonal and/or cubic phases. The addition of stabilizing oxides allows for the generation of a multi-phase material at room temperature. Fully stabilized zirconia is produced when more than 16 mol% CaO (7.9 wt%), 16 mol% MgO (5.86 wt%) or 8 mol% Y_2O_3 (13.75 wt%) is added to ZrO_2, and it has a cubic form (Fig 3). With the addition of smaller amounts of stabilizing oxides, zirconia can also be partially stabilized in a multiphase form, known as partially stabilized zirconia (PSZ). PSZ microstructure at room temperature generally consists of cubic zirconia, as the major phase, and monoclinic and tetragonal zirconia precipitates, as the minor phase. These precipitates may exist at grain boundaries or within the cubic matrix grains.[7]

Yttrium–oxide partially stabilised zirconia (Y–PSZ). A fully tetragonal fine-grained zirconia ceramic material made of 100% small metastable tetragonal grains (Y-TZP) after the addition of approximately 2 to 3 mol% yttrium oxide (Y_2O_3) as a stabilizing agent.[3,8] The fraction of the T-phase retained at room temperature depends on the processing temperature, the yttrium content, the grain size, and the grade of constraint exerted on them by the matrix.

Above a critical grain size, which is primarily related to the yttrium oxide concentration, spontaneous T-M transformation of the grains can be take place, whereas this transformation would be inhibited in a finely grained structure. Reduction in grain size and/or increase in concentration of the stabilizing oxide(s) can reduce the transformation rate. Particularly, vast reduction of the grain size leads to loss of their metastability while the increase in concentration of the stabilizing oxide(s) above 3.5% may allow the nucleation of significant amounts of stable cubic phase. Therefore, to obtain a tetragonal metastable pase at room temperature, the grain size must be less than 0.8 mm and the amount of stabilizing oxide not more than 3 mol%.[10] Y-TZP ceramics can be produced with the co-precipitation of Y_2O_3 with ZrO_2 salts or by coating of the ZrO_2 grains with Y_2O_3.[7] An interesting characteristic of the Y-TZP ceramics is the formation of compressive layers on their surface. Surface tetragonal grains are not constrained by the matrix and for that reason can spontaneously transform to monoclinic grains leading to improved mechanical and wear properties of this material.

Y-TZP exhibits exceptional fundamental properties of great interest to bio-medical engineering, such as high strength, fracture toughness, hardness, wear resistance, good frictional and non-magnetic behavior, electrical insulation, low thermal conductivity, corrosion resistance in acids and alkalis, modulus of elasticity similar to steel, and coefficient of thermal expansion similar to iron. However, Y-TZP materials and/or devices (eg, implants) employed for clinical applications should meet the criteria of ISO 13356 and the American Society for Testing and Materials (ASTM) F1873.

Table 3   Chemical composition, physical, mechanical, and thermal properties of Y-TZP

Property	Y-TZP	ISO 13356 requirements	ASTM F1873 requirements
Chemical composition (wt %)			
$ZRO_2+HfO_2+Y_2O_3$	> 99.0	> 99.0	≥ 99.0
Y_2O_3	4.5–5.4	4.5–5.4	4.5–5.4
Al_2O_3	< 0.5	< 0.5	≤ 0.5
Other total oxides	< 0.5	< 0.5	≤ 0.5
Physical properties			
Bulk density (g/cm^3)	6.05	≥ 6.00	≥ 6.00
Grain size (μm)	0.2	≤ 0.6	≤ 0.6
Monoclinic phase (%)	1	-	≤ 5
Porosity	< 0.1%	< 0.1%	< 0.1%
Mechanical properties			
Flexural strength (4 point) (MPa)	1,666.0	≥ 800	> 800
Elastic modulus (GPa)	201	-	≥ 200
Vickers hardness (HV)	1,270.0	-	> 1,200.0
Fracture toughness (Kgf/mm$^{2/3}$)	16.8	-	-
Fracture toughness K_{IC} (MPa m^{-1})	7–10	-	-
Compressive strength (MPa)	4,900.0	-	-
Impact strength (MPa)	137.0	-	-
Thermal properties			
Thermal expansion coefficient (x10^{-6}/°C)	11x10^{-6} K^{-1}	-	-
Thermal conductivity (W/m°K)	2	-	-
Specific heat J/kg°K)	500	-	-

The chemical compositions, and the physical, mechanical, and thermal properties of Y-TZP are listed in Table 3 according the above criteria.

Phase diagrams and transformation strengthening

As mentioned before, the monoclinic form is stable at room temperatures and up to 1,170°C; above this temperature it transforms into the denser tetragonal phase with a volume decrease of 5%.[3] The tetragonal phase is stable between 1,170 and 2,370°C and above this temperature it acquires a cubic crystal form (Fig 4). During cooling, a T-M transformation occurs in a temperature range from 670 to 1,070°C, followed by a volume expansion of approximately 3 to 4%.[7] This phase transformation generates stresses that result in crack formation.[3]

In the presence of a small amount of stabilizing oxide additives (eg, CaO, MgO, Y_2O_3), the tetragonal particles provided are small enough and can therefore be maintained in a metastable state at temperatures below the tetragonal to monoclinic transformation temperature. At room temperature, tetragonal metastable zirconia exists only in particles of less than 30 nm. This stability is due to the lower surface energy of the tetragonal phase compared to the monoclinic, or due to the con-
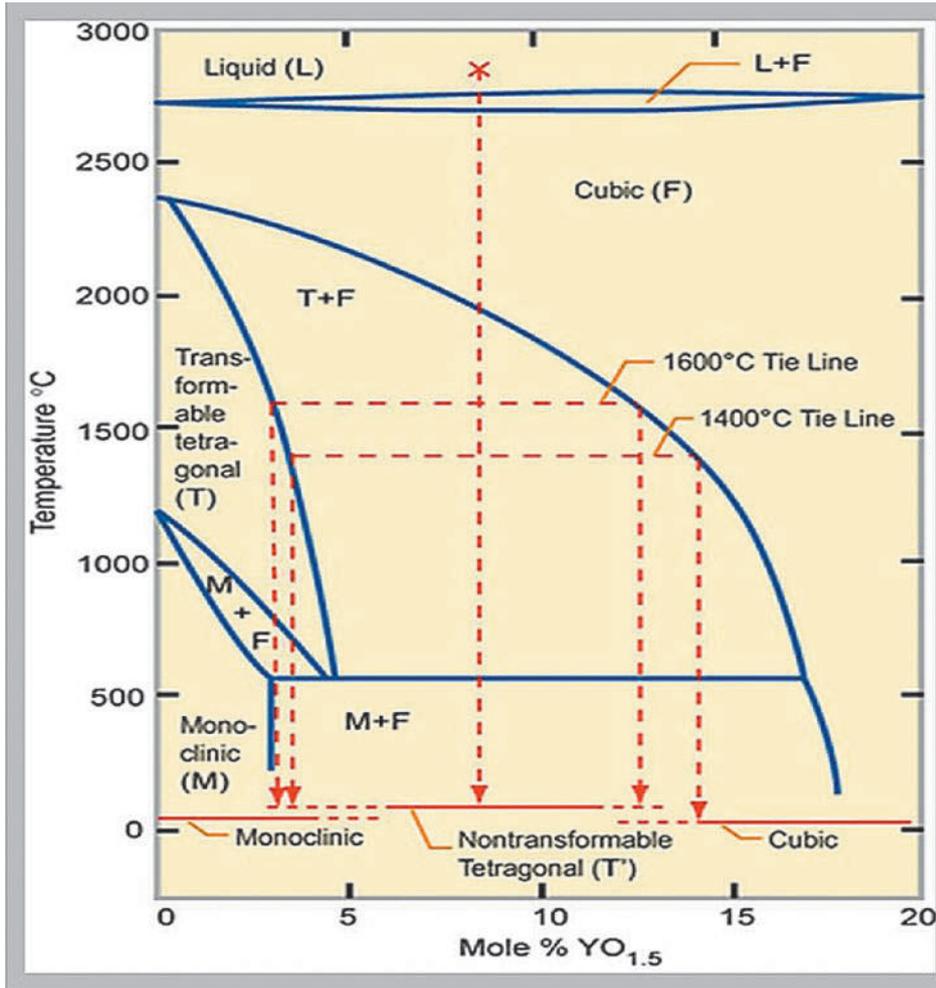
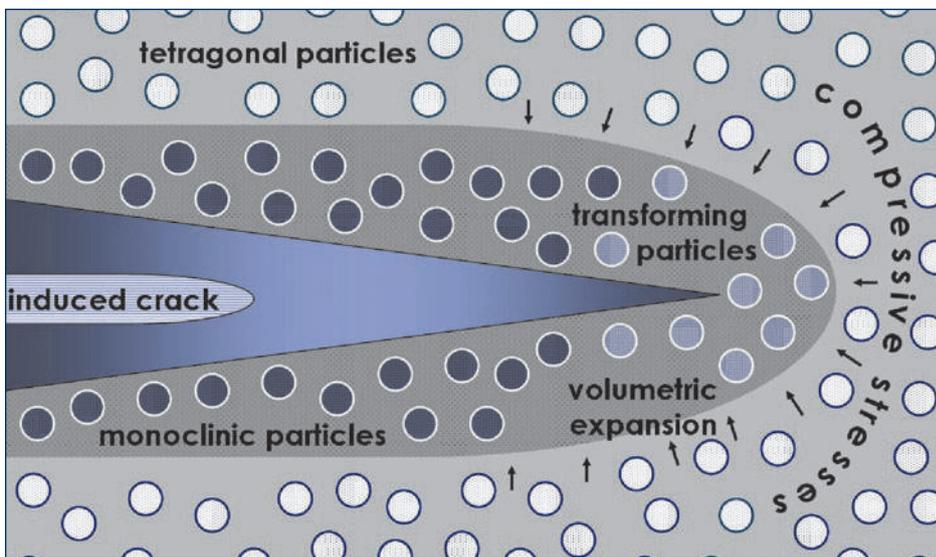**Fig 4** Phase diagram of partially stabilized zirconia (PSZ).

Fig 5 Schematic drawing of zirconia martensitic-like phase transformation occurring at the crack tip.

straint of the rigid matrix on the tetragonal grains that opposes transformation to the less dense monoclinic form.[2]

Under stresses by the neighbour grains, ie, when a crack propagates within the material mass, the tetragonal grains can be transformed to monoclinic.[7] This particular transformation is associated with a volume expansion of 3 to 5% of the grains, which ultimately leads to compressive stresses at the edge of the induced crack front. For this reason, extra energy is required in order for the crack to propagate further. This energy absorbing mechanism is due to the martensitic-like transformation occurring at the crack tip (Fig 5). The toughness of the ceramic is based on such dissipative mechanisms operating at microscopical level.[3,7] The enhancement in toughness is obtained, because the energy associated with crack propagation is dissipated both in the T-M transformation and in the overcoming of the compression stresses due to volume expansion. This mechanism is also known as transformation toughening and is considered as the basis for the very high strength of Y-TZP.[9,11–15]

Radioactivity

Zirconia powder contains small amounts of radionuclides from the uranium-radium (^{226}Ra) and thorium (^{228}Th) actinide series.[13,16,17] Because of these radioactive impurities, different concerns were raised in the early 1990´s about the use of zirconia ceramics for medical and dental applications. However, after purifying procedures, zirconia powders with low radioactivity (< 100 Gyh^{-1}) can be achieved.[18,19] These values are below the European ra-

diation limits for human body external exposure or for local internal exposure of organs and tissues and comparable to those of alumina ceramics and Co-Cr alloys.[20] After purifying, uranium concentration in zirconia powders ranges between 0.001 and 0.007 Bq/g, (max: 1.0 Bq/g according to ISO 6872). Therefore, the radiation levels of the commercially available zirconia powders conform to the recommendations of the International Commission for Radiation Protection (ICRP) and are generally found lower than the normal ambient radioactivity induced by natural radiations.[13,19]

Moreover, the International Standards Organisation (ISO 13356) and the American Society for Testing and Materials Standards (F1873) recommended that the mass activity of zirconia powders used for surgical grade ceramics should be lower than 200 Bq/kg.[21] The mass activity of the current zirconia powders is much lower than the human bone mass activity (20–50 Bq/kg), which roughly corresponds to a radionuclide content of 1 ppm (0.0001%) or less.[22]

In conclusion, since the radioactivity of Y-TZP ceramics can be effectively managed by purification procedures following appropriate standards, Y-TZP can be considered suitable for biomedical applications. However, it is highly recommended that each zirconia powder be validated before use for biologic applications and regularly controlled.[13,18]

Biocompatibility

Both in vitro and in vivo studies have confirmed the superior biocompatibility of high purity Y-TZP powders especially when they

are totally purified from radioactive contents. Zirconia ceramics are chemically inert materials and no local or systemic adverse reactions have been reported. *In vitro* tests showed that zirconia ceramics have similar cytotoxicity to alumina (both lower than TiO_2). No cytotoxic, oncogenic, or mutagenic effects on fibroblasts or blood cells were observed[7,23] and no stochastic effect or chromosomal aberrations induced by Y-TZP ceramics doped with 0.5 ppm of UO_2 could be found.[24]

The *in vivo* behavior of Y-TZP compared with alumina did not allow the demonstration of any differences regarding tissue reaction.[2,3,25,26] In different animal studies, it was demonstrated that zirconia implants osseointegrate as well as titanium ones.[27–29] One-stage partially stabilized zirconia implants could achieve long-term stability of osseointegration without any biomechanical problems.[29,30] The enhanced biocompatibility of zirconia implants was also confirmed by the strong bone tissue response to a modified surface achieved after six weeks of healing in rabbits.[31] Bacterial colonization of zirconia surfaces was found to be lower than that of titanium ones.[32,33]

Aging

Y-TZP ceramics suffer from a low temperature degradation phenomenon (LTD) known as aging. Progressive, spontaneous transformation of the tetragonal phase into monoclinic results in the degradation of the mechanical properties of Y-TZP.[7] A slow T-M transformation occurs when Y-TZP is in contact with water or vapor,[34] body fluid or during steam sterilization,[7] which leads to surface damage. Non-aqueous solutions with a single-pair electron orbital opposite

to a proton donor site can also destabilize Y-TZP, causing strength degradation.[34,35] This, rapid low temperature degradation mechanism was described by several models.[36,37] Sato et al. postulated that the reaction of water with the Zr-O-Zr at the crack tip and the formation of Zirconium hydroxides (Zr-OH), accelerates crack growth of pre-existing flaws and promotes the T-M phase transition.[34]

The main steps of TZP aging were summarized by Swab.[38]

1. The most critical temperature range for the development of aging is 200 to 300°C.
2. The effects of aging are the reduction in strength, toughness and density, and an increase in monoclinic phase content.
3. The degradation of mechanical properties, due to the T-M transition, takes place with micro and macro cracking of the material.[39]
4. T-M transition starts on the surface and progresses into the material's mass.
5. The reduction in grain size and/or the increase in concentration of stabilizing oxide reduce the transformation rate.
6. T-M transformation is enhanced in water or in vapor.

Surface degradation of the material during low temperature aging involves roughening, increased wear and microcracking, grain pullout, generation of particle debris, and possible premature failure.[40] Surface elevations take place most likely because of the more voluminous M-phase transformed particles.[35] Craters have also been observed as a result of worn out monoclinic spots on the degraded surface of the material.[40] The strength degradation level varies between TZP ceramics because aging behavior is related to the differences in

equilibrium within the microstructural parameters, such as yttrium concentration and distribution, grain size, flaw population, duration of exposure to aging medium, loading of the ceramic restoration, and manufacturing processes.[7,35,40]

Optical properties

Yttria-stabilized zirconia (YSZ) has been proven suitable for optical applications due to its high refractive index, low absorption coefficient, and high opacity in the visible and infrared spectrum.[41] Zirconia is a good white pigment and a good opacifier due to its total opacity to visible light and its high refractive index (2.1 to 2.2). The maximal opaque effect of zirconium oxide is attributed to dispersed particles slightly greater in size than the wavelength of light and to the different refractive index of its matrix. The increased opacity of zirconia ceramics can be very useful in esthetically demanding clinical situations, as for example in cases of masking dischromatic abutment teeth or metal posts and cores.[42] Regarding its relative translucency, Heffernan et al. evaluated several ceramic materials and found that zirconia ceramics posses the highest amount of relative translucency, comparable to that of metal.[42,43] Different grades of zirconium have different levels of translucency—the higher the grade the more translucent the material. The grain size, distribution of the various grain sizes, pressing method and conditions, and different additives can affect the translucency of a restoration. The light transmission of yttrium-stabilized zirconia (LAVA, 3M ESPE, St. Paul, MN, USA) determined in a spectrophotometer analysis by direct transmission coefficient for wavelengths from 400 to 700 nm, was found to be lower than that of densely sintered Al_2O_3, and $MgAl_2O_4$ infiltrated and lithium disilicate ceramics, but higher than Al_2O_3 or Al_2O_3/ZrO_2 infiltrated materials.[44]

Currently, coilared zirconia cores are offered by some manufacturers to enhance esthetic outcomes. Different coloring agents are introduced for a better esthetic performance of the white shade zirconia frameworks. These frameworks can be further customized in terms of form and esthetics by veneering with porcelain, through the layering or pressing technique.[45] Dentin-like coloring of the framework facilitates the veneering process, and has no influence on the frameworks' flexural strength.[46] Individual characterization of the monochromatic zirconia cores provides esthetically comparable results to the common layering techniques and multi-shade block systems, but no long-term follow-up data on the color stability exists.[45,47]

Zirconia frameworks, due to their high density (residual porosity $< 0.05\%$) and homogeneity even with limited core thickness (0.5 mm), provide an adequate level of opacity, which offers adequate masking of underlying discolored abutments and permits a controlled depth of translucency after veneering.[42,43]

The effect of zirconia ceramics with or without veneering on the color of the mucosa, was evaluated by Jung et al. The authors concluded that zirconia did not induce visible color changes in 2 mm- and 3 mm-thick mucosa, regardless of the application of a veneering material. Visually perceivable color changes were accessed by 1.5 mm mucosa thickness or less. The shift of the chroma in these cases is along the yellow-blue axis, but no explanation for this shift has been proposed.[48]

The high radiopacity of zirconia ceramics, comparable to that of metal alloys, enhances the radiographic evaluation of marginal integrity, removal of cement excess, and recurrent decay.

Processing

The mechanical properties of Y-TZP ceramics depend not only on the microstructure, but also on defects present in the starting powders or defects induced during manufacturing. The use of high purity ZrO_2 starting powders contributes to the hydrothermal stability that is a prerequisite for the T-phase. The presence of impurities in grain boundaries, due to milling bodies used in powder processing or as sintering aids, can alter the stability of the T-phase.[7] Similarly, components added to ZrO_2 for other purposes (eg, shade adjustment) can also alter the stability of the T-phase.[35] Differences in zirconia processing (eg, temperature and time) can affect the microstructure of the material and therefore its resistance to aging.[40] Research has focused on the effect of different surface treatments on the strength of zirconia-based materials. A strong correlation was found between flexure strength and the severity of surface and subsurface damage as indicated by surface roughness.[49,50] In daily use, zirconia is subjected to different types of surface damage as a result of the CAD/CAM milling processes and other laboratory procedures. As a consequence the mechanical properties and the long-term stability of treated restorations can be quite different than those of the starting material.

Grinding

Grinding generally increases the strength of metastable TZP due to the T–M transformation at several microns depth under the material's surface and the development of compressive strains as a result of the transformation-related volumetric increase.[2] These compressive stresses prevent the formation or the propagation of superficial microcracks, but still surface and subsurface damage is promoted. The mechanism responsible for this damage is the grain pullout due to the volumetric increase and the formation of microcraters after the phase transformation.[51] The latter leads to surface roughness and porosity, which influence the wear resistance of the material.[7]

Extensive heat that is locally generated during severe machining may exceed the T-M transformation temperature and for this reason promote a reverse (M-T) transformation.[52] The rhombohedral zirconia phase found after grinding, which presents similar behavior as the T-phase, could also explain the increase in mean flexural strength and the enhanced resistance to crack propagation.[51]

Fine machining using a 25 µm diamond wheel provides a noticeable improvement in strength of Y-TZP whereas coarse grinding resulted in strength reduction. Manual grinding performed with less stress under water spray coolant can promote the T-M transformation, decrease the critical flow size, and increase the surface compressive layer.[35,53,54] Grinding with coarse grinding tools may introduce deep surface flaws which act as stress concentrators and may determine the strength of the zirconia restoration.[35,49,53]

Grinding of the inner surface of crowns during CAD/CAM machining is the most critical procedure since those areas concentrate maximal tensile stresses. In order to avoid damage during clinical loading, microcrack concentration at those areas should be minimized. Strength degradation can be reduced by using a ductile grinding mode and by using a suitable grinding instrument. During machining, the direction of tool rotation, the sharpness, and the number of active grains in the diamond tool appear to be very important determinants of surface properties of the material.[49]

After sintering, fine-grained Y-TZP exhibits high strength but is less damage tolerant than the tougher coarse-grained Y-TZP, as the grinding-induced cracks extend deeper into its mass.[54,55] The perpendicular flaws to the grinding orientation are of greater importance since they could initiate fracture upon loading.[56]

The effect of grinding on strength values is mainly dependent on the amount of the transformed M-phase, the metastability of the T-M transformation, the grinding severity, and the locally generated temperatures.[56] Improvements that reduce flaws during processing may improve the material's stability. Alternatively, methods such as the machining of partially sintered ceramics or non-grinding profiling procedures can also enhance the strength of zirconia restorations.[7]

Polishing

The polishing process produces surface scratches that induce residual stresses in the material. According to the type and the amount of these stresses, polishing may lead to the development of a compressive surface stress layer, which is beneficial for aging resistance.[57] Fine polishing after grinding can remove the compressive layer of M-phase from the surface and reduce the severity and amount of surface defects and flows to a degree where the internal strength of the material becomes the dominant factor determining its mechanical performance.[58] Eventually the flexural strength increases.[56]

Sandblasting

Sandblasting zirconia ceramics promotes adhesion of the luting cement to the framework and provides a strengthening technique for Y-TZP at the expense of reduced stability.[59] Microscopy of the sandblasted surfaces showed a uniformly damaged and rough surface with plastically displaced material and cracks randomly oriented. However, a thin compressive layer of transformed M-phase counteracts strength degradation, which is caused by the sandblasting-induced flaws, and effectively increases the strength. The lower temperatures and stresses developed by sandblasting in comparison with grinding induce T-M transformation and allow the maintenance of the resulting M-phase.[48,56,60] Sandblasting after grinding removes some larger grinding-induced cracks and weakly attached surface grains, and simultaneously produces surface compressive stresses that strengthen the material.[53] According to Zhang et al., no immediately apparent damage from airborne-particle abrasion (50 μm aluminum oxide for 5 seconds at 276 KPa) has been shown to compromise the fatigue strength of zirconia-based ceramics.[50,61] Hang Wang et al. indicated that particle abrasion with 50 μm aluminum oxide particles at 0.35 MPa pressure for 5 s/cm^2 at a distance of 2.0 cm resulted in an increase in the strength

of CAD/CAM and ground bars, while sandblasting with 120 µm aluminum oxide resulted in significant weakening of the bars and increased surface roughness.[62] Despite the increase in strength values after abrasion with 50 µm aluminum oxide particles, the authors noted that the long-term effect of this induced damage still has to be considered as a potentially weakening factor.[62]

In contrast with the above studies, other investigations demonstrated that airborne particle abrasion mechanically assists the growth of pre-existing surface flows and defects and reduces strength and long-term survival.[50] Crack growth of zirconia starts at a threshold intensity factor (K_{IC} = 3.1 MPa m$^{1/2}$), which is much lower compared to its critical crack intensity factor (K_{IC} = 7.4 MPa m$^{1/2}$) and as a result even the smallest surface defect could be large enough to act as an effective stress concentration site, finally increasing the fracture probability and deteriorating the fatigue life of the restorations.[63] The effective length of surface flows introduced by sandblasting does not seem to exceed significantly the thickness of the compressive surface layer, and thus the strength of the material can be increased.[54]

Surface and heat treatment

Surface and heat treatments have a counteracting effect on the flexural strength of Y-TZP ceramics.[56] In general, the strength of Y-TZP can be increased by wet grinding or sandblasting, while it is reduced when followed by heat treatment. Regardless of the holding time, heat initiates the reverse (M-T) transformation, eliminates the M-phase from the material surface, relieves the created compressive fields, and decreases the strength of the material.[56] Under clini-

cal conditions, a greater amount of M-phase on the surface provides improved flexural strength and therefore may be desirable. An excessive amount of M-phase can lead to microcracking and predispose the material to a more rapid moisture-assisted transformation over time, under dynamic loading in the acidic and aqueous oral environment.[56,64] In the work of Hang Wang and colleagues, thermal firing had no influence on the flexure strength, whether performed before or after particle abrasion.[62] The effect of heat treatment, through reverse transformation or relief of any pre-stresses present, remains a point to be further investigated.[56]

Veneering

Preliminary clinical results showed that delamination (or chipping) of the veneering porcelain from the underlying core was detected as one of the most common complications.[65] In retrieved failed clinical restorations or laboratory testing specimens, the interface between the zirconia core and the veneering material has been determined as the origin of the failure.[66–68]

The following factors have been identified to decrease the core-veneer bond strength: *(1)* pre-stresses, due to differences in thermal expansion coefficients (TEC) of the core and veneering materials, *(2)* poor wetting of the core by the veneering ceramic, *(3)* firing shrinkage of the veneering layer, *(4)* phase transformation of the zirconia crystals at the core-veneer interface due to thermal influences or loading stresses, and *(5)* inherent flaw formation during processing.[69]

The TEC of the veneering ceramic (9.1–9.7 x 10^{-6} K^{-1}) should be slightly less than that of the zirconia core (10.8 x 10^{-6} K^{-1}). TECs of the current Y-TZP ceramics

range from 10 to 10.5 x 10^{-6} K^{-1} and therefore compatible veneering materials are already available from the manufacturers. During cooling to room temperature, this difference leads to pressure tensions within the veneering mass and thus enhances the bonding strength between the two materials.[70] This TEC mismatch leaves the veneering porcelain in residual compression, which also provides additional strength to the restoration.[71] Since the core is subjected to tensile stresses, both relative high flexural strength and thickness of the core are important to achieve a durable bond.[72] Moreover, special attention must be paid in the designing of the core for an occlusal and/or connector shape that provides sufficient support for the veneering porcelain.[65]

Bonding of the veneering ceramic on a zirconia surface is primarily caused by micromechanical interactions between the core and the veneering layer; therefore, their mechanical properties should match, to a certain extent, in order to achieve a durable bond.[73,74] Furthermore, microstructural defects in the porcelain, including areas of porosities, agglomerates, inclusions, and large grain zones are other possible reasons for the delamination of the veneering material. The difficulties in building up the green porcelain densely and homogenously over the core surface prior to firing without trapping air bubbles, and the structural flaws existing in the interface because of wettability factors, can promote laminate fractures.[75] Current studies demonstrated that sandblasting of the restoration prior to veneering has a negative effect on the interface due to remaining alumina particles in the zirconia outer surface, which lead to a change of the TEC of the core to be veneered.[10]
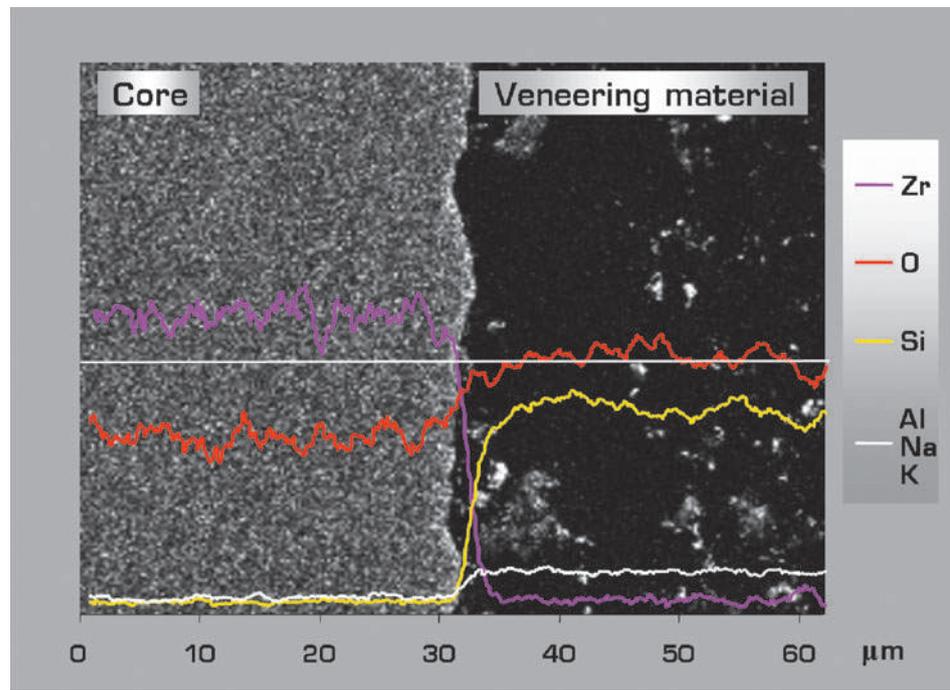

Fig 6 Backscattered electron image (SSD) and line scans of elements Zr, O, Si, Al, Na, and K of the zirconia core/veneering interface (Cercon, Degussa). The white line represents the direction of the elemental distribution assessment (courtesy of Dr Alexandros Tagmatarchis, Athens, Greece).

Besides the conventional veneering ceramics used with a standardized layering technique, new veneering ceramics were developed for a new manufacturing method where the veneering material is heated up to its melting temperature and then pressed onto the zirconia core. Due to the applied external pressure, deformation and cooling stresses of these pressable veneering materials are limited and a better surface contact to the zirconia core is attained.

The use of liner materials can provide a tooth color shade to the zirconia framework. The application of liner material simultaneously with veneering is recommended for some veneering ceramics as it improves the core/veneering bonding strength and thus to reduces the interfacial failure rates. Liners enhance the core-veneer bond and reduce interfacial failure of pressable veneering materials as well.[76]

The elemental composition and interfacial distribution of the zirconia core and the veneering materials were determined by backscattered scanning electron microscopy and image analysis. The analysis identified no transitional interface zone or distinct ionic presentation (Fig 6).[77]

Discussion

For the past several years, extensive research has focused on new promising ceramic materials and the improvement of their mechanical properties, such as strength and toughness. Among the various toughening mechanisms, those related to the phase transformations of zirconium oxide particles have appeared particularly efficient and attractive. Good chemical and dimensional stability and mechanical strength and toughness, coupled with a Young´s modulus of the same order of magnitude of stainless steel alloys, was the origin of interest in using zirconia as a ceramic biomaterial. In the late 1970s, Zr_2O-TZP was introduced into the market of technical ceramics. Though at first only applied for technical purposes such as machined parts for heavy duty use and wear resistance, it was soon recognized that zirconia also showed great potential for application in bioceramics. More recently, several publications have demonstrated the potential interest of partially stabilized zirconia as a candidate biomaterial. In 1990, the biocompatibility of zirconia was evaluated and the ISO standard (13356) was established.[21] Although biomedical grade zirconia was introduced as a biomaterial just 20 years ago, today more than 600,000 zirconia femolar heads have been implanted worldwide. The zirconia market for dental applications also increases more than 12% per year.[40]

Despite the extended use of zirconia in many different technical and biomedical applications, some questions concerning its properties have not yet been fully answered and a large controversy exists among scientists, clinicians, and industry. As emphasized recently by Clarke et al., the reason for misleading interpretations and confusion is mainly the absence of rigorous scientific clarification of the mechanism of low-temperature degradation (LTD) or aging.[14] After more than 20 years of research, aging still remains a key for zirconia components. The failures that have occurred in orthopedic implants are a striking example of the negative impact of LTD in the presence of water on the long-term performance of zirconia devices. It seems that the LTD aging process is attrib-

uted to a cascade of energy-originated phenomena. The T-phase achieved at high temperatures with stabilizing additives, tends in the presence of water to be slowly transformed to M-phase, which is the most stable structure at room temperature. According to Yoshimura et al., the phase transformation is accompanied by an increase in the crystal lattice size. The reversible expansion and contraction of the monoclinic lattice seems to be caused by the inclusion and exclusion of OH⁻ in the lattice and formation of Zr-OH and/or Y-OH bonds[35] through the chemical adsorption of H_2O at the surface.[37] The process is favored due to the high ionic conductivity of Y-TZP.[78] This structural transition, related with finite atomic displacements and energy acceleration, leads to phase nucleation and growth, which results in volume increase associated with lattice invariant strains and stresses concentration.[79] The accumulation of strain by the migration of OH-ions at the surface and in the lattice produce nucleating defects.[39] Though transformation starts first in isolated grains on the surface by a stress-corrosion type mechanism, the volume increase stresses the neighboring grains and initiates microcracking, offering a path for water to penetrate further down into the specimen.[44,80] Eventually, a crack-corrosion mechanism leads to disintegration and mass exfoliation, which limits the predictable long-term use of existing compositions and procedures.[81]

With the increasing use of Y-TZP in other applications (dental, coatings, solid oxide fuel cells), a careful understanding and control of aging in different thermochemical conditions is necessary. It is difficult to characterize zirconia as aging free since the transformation occurring upon aging is a "natural" return back to the monoclinic equilibrium state. However, the transformation kinetics can be much affected by micro-structural issues, and some solutions have been proposed in the literature.

Studies on zirconia as a ceramic biomaterial are now being concentrated on the improvement of its performance, and several promising models have been proposed. Among them, the addition of small amounts of silica or the use of yttria coating instead of co-precipitated powders, seem to have a clear benefit for preventing aging, while preserving good toughness and strength. Ceria-doped zirconia ceramics have also been considered, since they exhibit superior toughness and almost no aging. Perhaps the most promising future of zirconia as a biomaterial is through its use as reinforcement in zirconia-toughened alumina (ZTA), which may offer an exceptional balance between slow crack growth and aging resistance. The addition of alumina to zirconia clearly hinders aging or at least reduces its kinetics drastically, and the composite materials have outstanding mechanical and tribological properties. This may be the way to benefit from zirconia transformation without the major drawback associated with its transformation under steam or body fluid conditions. In order to obtain the bone bonding properties of hydroxyapatite and an enhanced toughness, composites formed by hydroxyapatite ceramic as matrix and zirconia as a second phase have also been proposed.[82–84] Since aging degradation starts as a surface phenomenon, surface treatments (cementation and nitridation) can slow down the aging process and maintain good mechanical properties.

All of the alternative zirconia-based materials mentioned above have been successfully developed on the laboratory

scale, but there is still a need for a more detailed understanding of aging related issues and in vivo studies that can confirm their superiority over Y-TZP.[40]

Conclusions

Purification processes, new processing methods (CAD-CAM, hot isotactic pressing), identification and test-proof procedures allow the large-scale use of zirconia in technical and biological applications.

The biocompatibility of zirconia has been well documented and in vitro and in vivo tests on Y-TZP have revealed good biocompatibility with no adverse reactions with cells or tissues.[85]

There is a need for advanced specifications for ISO standards. According to Deville et al., the actual ISO requirements concerning the long-term stability and surface state of Y-TZP specimens should be updated with regard to the actual knowledge of the aging phenomenon. Advanced specifications are required to ensure the long-term stability and success of Y-TZP biomedical components.[57]

As many new trends and applications for zirconia are being discovered, the future of this biomaterial appears to be very promising.

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