

ZIRCONIA: PROPERTIES AND APPLICATION — A REVIEW

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ABSTRACT

Over the last decade, zirconia has propelled a rapid development of metal-free dentistry with improved material strength, enhanced esthetic and high biocompatibility for a wide range of promising clinical applications. It holds a unique place amongst the oxide ceramics due to its excellent mechanical properties owing to the phase transformation toughening mechanism. Like other side of the same coin, this mechanism is also responsible for its low temperature degradation which is the main limiting factor in the extensive use of zirconia.

Zirconia is an inert material and presents reduced bond strength with the conventional ceramic cementation procedures. Bonding to traditional silica based ceramics is a predicta.

A high percentage of clinical failures of zirconia-based restorations are attributed to debonding and or fracture of veneering ceramic. This review presents the properties, types of zirconia for dental application, the manufacturing procedures, the various application and its guidelines, luting of zirconia and bonding of the veneering ceramics.

INTRODUCTION

Recently zirconia has emerged as a versatile and promising material among dental ceramics, due to its excellent mechanical properties owing to the transformation toughening mechanism. Zirconia (ZrO₂) is a white crystalline oxide of zirconium.¹ Zirconia is a polycrystalline ceramic without a glassy phase and exists in several forms. The name 'zirconium' comes from the Arabic word 'Zargon' which means 'golden in colour'. Zirconia was discovered by the German chemist Martin Heinrich Klaproth in 1789.²

Its mechanical properties are very similar to those of metals and its colour similar to tooth colour. Hence it has been called as 'Ceramic Steel' by Garvie.³ The mechanical properties of zirconia are the highest ever reported for any dental ceramic. This may allow the realization of posterior fixed partial dentures and permit a substantial reduction in core thickness. These

capabilities are highly attractive in prosthetic dentistry, where strength and esthetics are paramount.⁴

PHASES OF ZIRCONIA

Zirconia is polymorphic in nature, and displays different crystal structure at different temperatures with no change in chemistry. It exists in three crystalline forms: monoclinic (m), tetragonal (t) and cubic (c). Pure zirconia has a monoclinic structure at room temperature, which is stable up to 1170°C. From 1170°C to 2370°C, tetragonal zirconia is formed, while cubic zirconia is formed at temperatures above 2370°C up to the melting point (2680°C). Upon cooling spontaneous reversal of transformation occurs.¹ The transformation is a thermal and diffusionless ("martensitic").⁶ Furthermore, the t-m transformation occurs with a volume expansion of about 4-5% inducing high compressive stresses in the material.¹

Passerini and Ruff et al, discovered that the tetragonal, or even the cubic form could be retained metastably at room temperatures by alloying zirconia with other cubic oxides termed as "stabilizers".⁴

STABILIZED ZIRCONIA

Stabilized zirconia is a mixture of zirconia polymorphs obtained at room temperature, by the addition

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of stabilizer. With the addition of stabilizing oxides in concentrations less than those required for complete stabilization, zirconia can also be partially stabilized in a multiphase form, known as partially stabilized zirconia (PSZ). It consists of cubic zirconia, as the major phase, and monoclinic and tetragonal zirconia precipitates, as the minor phase. When the whole material is constituted by transformable t-zirconia grains it is called Tetragonal zirconia polycrystals (TZP). To date, Zirconia stabilized with Y₂O₃ has the best properties for dental applications.

Yttrium-Oxide Partially Stabilised Zirconia (Y-PSZ) is 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 (Y₂O₃) as a stabilizing agent.¹

PHASE TRANSFORMATION TOUGHENING

When a crack develops on zirconia surface containing metastable t-ZrO₂, it is subjected to a remote macroscopic tensile stress. This tensile stress concentration at the crack tip causes the transformation of metastable t-ZrO₂ to the monoclinic crystalline phase. The consequent volume increase of the crystals, constrained by the surrounding ones, results in a favorable compressive stress which acts on the surfaces of the crack, and thus hinders its propagation. Such a mechanism has been defined “transformation toughening” or “phase transformation toughening”.^{5,1}

PROPERTIES

Mechanical Properties: Mechanical properties of zirconia were proved to be higher than those of all other ceramics for dental use and similar to those of stainless steel. Fracture toughness Zirconia is between 6 and 10 MPa m^{1/2}, which is almost twice as high all that of aluminum oxide ceramics. This is due to transformational toughening, which gives zirconia its unique mechanical properties. It has a flexural strength of 900–1200MPa and a compression resistance of 2000MPa. An average load-bearing capacity of 755N was reported for zirconia restorations. Fracture loads ranging between 706N, 2000N and 4100N were reported; all of the studies demonstrated that in dental restorations zirconia yields higher fracture loads than alumina or lithium disilicate.¹

Biocompatibility: Both in vitro and in vivo studies have confirmed the superior biocompatibility of high purity Y-TZP powders. They are chemically inert ma-

terials, allowing good cell adhesion and while no local or systemic adverse reactions have been associated with it.¹ Zirconia ceramics have similar cytotoxicity to alumina (both lower than tiO₂). No oncogenic, or mutagenic effects on fibroblasts or blood cells were observed. Zirconia implants osseointegrate as well as titanium ones. Zirconia creates less flogistic reaction in tissue and lesser bacterial colonization than titanium. However, particles from the degradation of zirconia at low temperature (LTD) or from the manufacturing process can be released, promoting an immune localized inflammatory reaction.⁹

Radioactivity: Zirconia powder contains small amounts of radionuclides from the uranium-radium (226Ra) and thorium (228Th) actinide series. However, after purifying procedures, zirconia powders with low radioactivity (< 100 Gyh⁻¹) can be achieved which were below the European radiation limits for human body external exposure of organs and tissues and comparable to those of alumina ceramics and Co-Cr alloys.¹

Optical Characteristics: Ytria-stabilized zirconia (YSZ) shows high refractive index (2.1 to 2.2), low absorption coefficient, and high opacity in the visible and infrared spectrum. The increased opacity of zirconia is very useful in esthetically demanding clinical situations to mask polychromatic substrates like blackened teeth, pins and metal cores. Because of its opacity, it must be covered with translucent ceramics to yield natural tooth-like appearance. Zirconia ceramics posses the highest amount of relative translucency, comparable to that of metal. The use of CAD/CAM has allowed the construction of a thinner infrastructure (0.5mm), creating more space for the application of a ceramic layer.⁹ The high radiopacity of zirconia ceramics, comparable to that of metal alloys, enhance the radiographic evaluation of marginal integrity, removal of cement excess and recurrent decay.¹

AGEING

Aging or low temperature degradation is the spontaneous, slow transformation of the metastable tetragonal phase to the more stable monoclinic phase, in the absence of any mechanical stress, occurring over time at low temperatures. It is exacerbated in the presence of water, steam or fluids. LTD is based upon the same mechanism as PTT; that is, it requires the presence of t-ZrO₂ grains in thermodynamic metastability which can undergo t-m transformation.

The slow transformation of tetragonal crystals to the stable monoclinic phase starts at the surface in

isolated grains by a stress corrosion type mechanism and later progresses inwards to the bulk of the material. The transformation of one grain is accompanied by an increase in volume that induces stresses on the surrounding grains. This causes a surface uplift and microcracks which offers a path for the water to penetrate down into the specimen. Water penetration then exacerbates the process of surface degradation and the transformation progresses from neighbour to neighbour.

Ageing is associated to roughening which will lead to increased wear and microcracking which will lead to grain pull-out and generation of particle debris and slow crack growth leading to premature failure. Apart from these drawbacks, the zirconia crystals once already transformed to the m-polymorph cannot exhibit PTT, just like a used match cannot be lit again.⁷ This phenomenon can have detrimental effects on the mechanical properties of zirconia. The main factors affecting the aging phenomenon are the grain size, the type and the amount of stabilizer and the presence of residual stress. Although ageing reduces mechanical features of zirconia, the decrease falls into clinically acceptable values.⁸

DIFFERENT TYPES OF ZIRCONIA CERAMICS AVAILABLE FOR DENTAL APPLICATIONS

Although many types of zirconia-containing ceramic systems are currently available, to date only three types are used for dental application. These are:

- Yttrium tetragonal zirconia polycrystals (3Y-TZP)
- Magnesium partially stabilized zirconia (Mg-PSZ) and
- Zirconia-toughened alumina (ZTA).

ZTA and Mg-PSZ are by-phasic materials with t- phases as a minor phase; whereas “yttria partially stabilized tetragonal zirconia polycrystal” (3Y-TZP), is a mono-phasic material.

3Y-TZP: Yttria partially stabilized tetragonal zirconia polycrystal (3Y-TZP) is the most popular and frequently used form of zirconia commercially available for dental applications. It consists of an array of transformable t-Zr grains stabilized by the addition of 3mol% yttrium-oxide (Y₂O₃). 3Y-TZP is fabricated with microstructures containing small grains (0.2 to 0.5 mm in diameter) depending on the sintering temperature, which avoids the phenomenon of structural

deterioration or destabilization in the presence of saliva, slowing the growth of subcritical cracks. It exhibits low porosity and high density.

Partially stabilized zirconia (Mg-PSZ): The stabilizer added is MgO in concentrations lower than that required for full c-ZrO₂ stabilization. In commercial materials the amount of MgO usually ranges between 8 and 10 mol%. The microstructure of Mg-PSZ consists of tetragonal ZrO₂ intragranular precipitates within a matrix of stabilized cubic ZrO₂. Due to the difficulty of obtaining Mg-PSZ precursors free of SiO₂, magnesium silicates can form that lower the Mg content in the grains and promote the t-m transformation. This can result in lower mechanical properties. This material has not been successful due to the presence of porosity, associated with a large grain size (30-60µm) that can induce wear, low stability, and overall poor mechanical properties, especially when compared to 3Y-TZP.

Glass-infiltrated zirconia-toughened alumina (ZTA): Zirconia particles are combined with a matrix of alumina forming a structure known as zirconia-toughened alumina (ZTA). The zirconia-toughened materials utilize the stress-induced transformation capability of the dispersed zirconia. In contrast with the other two classes, stability of the tetragonal phase to room temperature does not primarily involve the use of dopants but is controlled instead by particle size, particle morphology and location (intra- or intergranular).^{4,5}

MANUFACTURING PROCEDURES

CAD/CAM zirconia dental frameworks can be produced according to two different techniques: “soft machining” of presintered blanks or “hard machining” of fully sintered blanks.⁵

Soft machining: The soft machining process is the most diffused manufacturing system for 3Y-TZP, based on milling of pre-sintered blanks that are then fully sintered at a final stage. The pre-sintered blanks, at the so-called “green state”, are produced by compacting zirconia powders along with a binder through a cold, isostatic pressing process.

The die of the supporting abutments or directly the wax patterns of the crown/FPD are scanned. Both contact scanners and non-contact scanners are available. After scanning, a virtual, enlarged framework is designed by sophisticated computer softwares (CAD). Then, through a CAM milling procedure, a framework with enlarged, accurately controlled dimension is machined out of the blank. The sinterization of the

framework is completed at high temperature. During sinterization the framework regains its proper dimensions as it undergoes a linear volume shrinkage.

Hard machining: Fully-sintered 3Y-TZP blocks are used. They are prepared by presintering at temperatures below 1500°C to reach a density of at least 95% of the theoretical density. The blocks are then processed by “hot isostatic pressing” at high temperatures (1400-1500°C) under high pressure in an inert gas atmosphere to produce very hard, dense (99% of the theoretical density) and homogeneous blocks of fully sintered zirconia. The blocks can then be machined using a specially designed milling system to shape the framework to the proper, desired form and to the right, final dimension. Due to the high hardness and low machinability of fully sintered Y-TZP, the milling system has to be particularly robust.^{4,5}

APPLICATION AND GUIDELINES FOR ZIRCONIA IN DENTISTRY

The spectrum of clinical application of zirconia includes the fabrication of veneers, full and partial coverage crowns, fixed partial dentures, posts and/or cores, primary double crowns, implants, implant abutments and various other dental auxiliary components like cutting burs, surgical drills, extra-coronal attachments and orthodontic brackets.

Bilayer veneers – the inherent opacity of the zirconia core allows clinical application of high-strength veneer restoration with better masking ability for the colour management of discoloured teeth. The modified core may be fabricated with 0.2 mm to 0.4 mm thickness.¹⁰

Zirconia crowns – Tooth preparation for zirconia crowns is comparable to those for metal-ceramic restorations. The abutment should be adequately prepared to allow enough space for both the substructure and the veneering material and the favourable distribution of the functional stresses. Preparation in anterior teeth must have a reduction of at least 1.5 mm incisal and 1.0 mm axial on margin with a 4°6° taper; axial reduction in aesthetical areas can be extended up to 1.5 mm. Posterior teeth should be prepared with 1.5 mm of occlusal reduction and with 1.0mm of axial reduction on marginal region with a 4°6° taper. Tooth preparation can be realized with various finishing lines, although chamfer and rounded shoulder are recommended.³ After milling, a 0.5 mm-thick uniform zirconia core should be fabricated for single posterior crowns. Particularly in the anterior region, strength and esthetic requirements

may allow the fabrication of 0.3 mm thick copings, however, reduction of the coping thickness from 0.5 mm to 0.3mm can negatively influence the fracture loading capacity (35% decrease) of zirconia single crowns.¹⁰

Fixed partial dentures – Exceptional mechanical properties of zirconia like high flexural strength and fracture resistance allows realization of fabrication of all-ceramic FPDs in both anterior and posterior sites. For a good long-term prognosis for zirconia FPDs, the connectors should be properly designed and fabricated. Connecting surface area of the FPD must be at least 6.25 mm². For this reason, ceramic FPDs should only be used when the distance between the interproximal papilla and the marginal ridge is close to 4 mm. In a comparison between 3-, 4- and 5-unit zirconia fixed partial dentures and minimal connecting surface resulted, respectively, 2.7mm², 4.0 mm² and 4.9mm². Height of abutment is fundamental to obtain ZrO₂ frameworks with correct shape and dimension in order to ensure mechanical resistance of restoration. Although some manufacturer allows obtaining also full arch restorations, 5 units-FPDs are reported to be as maximal possible.³ Maximum tensile stress concentrates on the gingival surface of the connector and the veneering porcelain may control the failure. Hence the ultimate strength can be achieved by omitting porcelain veneering in that region.¹⁰

Zirconia posts – The main advantage of zirconia posts lies in its translucency and tooth-colored shade, thereby rendering the material usable with all-ceramic crowns in the anterior region. Zirconia posts are also indicated for teeth with severe coronal destruction, as they offer better strength than composite materials. Post space preparation principles for zirconia posts are similar to other post systems. Care should be rendered to preserve tooth structure during root canal preparation. Maintenance of both appropriate ferrule effect (minimum 2mm in height) and the periphery of the root canal dentin (minimum 1 mm in width) are essential for achieving clinical longevity. Zirconia posts can be placed in conjunction with hybrid composites or special built-up composites.¹⁰ The main disadvantage of zirconia posts is that its higher rigidity results in more of root fractures than fracture of posts which is undesirable. Besides, it is almost impossible to retreat teeth restored with zirconia posts as it is very difficult to remove it from the root canal.¹¹

Zirconia implant – Y-TZP as endosseous dental implant material presents enhanced biocompatibility, improved mechanical properties, high radiopacity, and

easy handling during abutment preparation. Zirconia ceramic is well-tolerated by bone and soft tissues. Y-TZP implants can successfully osseointegrate under loading conditions similar to titanium implants. Nevertheless, clinical and laboratory research data were scarce on safe recommendations for a widespread clinical application of Y-TZP implants.

Zirconia abutments – Conventional metal (titanium) abutments do shimmer, especially through all-ceramic crowns with increased semi-translucency and, subsequently, through thin peri-implant mucosa, resulting in a grayish appearance of the entire restoration. These esthetic problems or the possible exposure of the underlying metal abutment can be accommodated by the clinical application of zirconia abutments. Y-TZP abutments are available as prefabricated and custom-made. Further customization can be achieved by either extra-oral or intra-oral preparation. A pronounced chamfer or a shoulder preparation with rounded inner line angles are the most recommended finish lines.¹⁰

LUTING OF ZIRCONIA

A major clinical problem associated with use of zirconia-based components is the difficulty in achieving suitable adhesion with intended synthetic substrates or natural tissues. Resin-based composite cements are the standard material used in luting a ceramic prosthetic to tooth structures. The non-silica composition of zirconia makes it difficult to bond zirconia to tooth structures using traditional resin composite cements. In some instances, high strength ceramic restorations with ideal retention can be placed using conventional cements which rely only on micromechanical retention. However, a resin bonding is desirable in many clinical situations such as short or tapered prepared tooth structure. Strong resin bonding relies on micromechanical interlocking and adhesive chemical bonding between the cement and the ceramic surface.

Retention of zirconia-based ceramic restorations depends on mechanical roughening of the surface and chemical bonding with adhesive monomer in special primers or resin cements. An acidic adhesive monomer such as MDP bonds to zirconia-based ceramics. The phosphate ester group of the acidic monomer results in chemical bonding to metal oxides, zirconia-based ceramics and other ceramics. Therefore it is recommended to use self-adhesive or adhesive resin cement containing an adhesive monomer (MDP) or application of ceramic primer containing an acidic adhesive monomer as pre-treatment before cementation of zirconia.

Chemical-cured phosphate monomer-containing resin-based cements, Panavia Ex (10-methacryloyloxydecyl-dihydrogenphosphate or MDP) and Panavia 21 Ex, exhibited high bond strength. They showed no significant difference in bond strength after artificial aging as they formed a water-resistant chemical bond with zirconia.

The addition of a MDP-containing bonding/silane coupling agent to enhance bonding of MDP resin cements has produced positive results. It was shown that particle air-abrasion or tribochemical coating, followed by the application of MDP-containing bonding/silane coupling agent, resulted in increased bond strength compared to MDP-containing cements alone.

BONDING OF VENEERING MATERIAL TO ZIRCONIA

Zirconia copings for crowns or multi-unit frameworks require application of veneering ceramic, usually specialized porcelain, to achieve suitable esthetics. A high percentage of clinical failures of zirconia-based restorations are attributed to debonding and/or fracture of veneering ceramic.

The bond strength between zirconia and veneering ceramics is influenced by many factors. Bonding mechanisms include chemical bonding, mechanical fitting, and shear stress based on the difference in the coefficient of thermal expansion between the TZP and the veneering ceramics. However no conclusion has been reached regarding the bonding mechanism itself. Factors influencing the bond strength include surface roughness, heat treatment of the TZP and the use of liner porcelain.

Since ceramics are extremely susceptible to tensile stresses, achieving a slight compressive stress in the veneering ceramic is preferred, as in metal-ceramic (PFM) restorations. For this to occur, the veneering material must have a thermal expansion coefficient lower than the core material. Zirconia ceramics have coefficients of thermal expansion (CTE) ranging from approximately 9 to 11 $\mu\text{m}/\text{m K}$ while specialty porcelains can have CTE values ranging from 7 to 13 $\mu\text{m}/\text{m K}$.

The use of zirconia surface modifiers to achieve strong primary bonding between coping and veneering ceramic could improve the clinical failure rates observed to date. Application of a silicate intermediate layer, applied on the zirconia surface via a tribochemical approach has been studied. A vapour deposition approach could also enable conformal silicate surface modification

without use of an aggressive physical process, which might result in damage to the coping surface.

The application of a liner, used to modify the colour of white zirconia for esthetics, has shown mixed results in bond strength when used on veneers. Aboushelib et al. showed that addition of a liner increased bond strength in Cercon Base/Ceram S core-veneer system but decreased bond strength when used in the Cercon Express core-veneer system.

The bond strength of veneer to Zirconia is comparable to that of veneer to metal and is thought to be sufficient for dental applications.¹²

CONCLUSION

Zirconia applications seem to consolidate a well-established position in clinical dentistry, due to the improvements in CAD/CAM technology and to the material's exceptional physical properties. 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. Existing clinical studies demonstrated a promising survival potential regarding tooth-supported restorations but also revealed significant complications such as high incidence of early fractures of either the veneering or the core materials. Longitudinal studies will help to determine the degree of clinical benefit or severity of complications. Basic research should be conducted in the fields of aging, veneering, framework design, bonding, surface modification and esthetic performance to further illuminate the observed complications and provide solutions that will accelerate expected clinical outcomes. 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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