

ZIRCONIA AS A BIOMATERIAL IN DENTAL PROSTHETICS

Natasha Stavreva

Faculty of Dentistry-Skopje, Department of Prosthodontics, University “St. Cyril and Methodius”-
Skopje, N. Macedonia, natasha_stavreva@yahoo.com

Abstract: As new materials and processing techniques are steadily being introduced, the technological evolution of ceramics for dental applications has been remarkable. The interest of dental research in metal-free restorations has been rising following the introduction of innovative all-ceramic materials in the daily practice. In particular, high strength ceramics and related CAD/CAM techniques have widely increased the clinical indications of metal-free prostheses, showing more favourable mechanical characteristics compared to the early ceramic materials. Zirconia has been recently introduced in prosthetic dentistry as a biomaterial for the fabrication of crowns and fixed partial dentures, in combination with CAD/CAM techniques. The aim of the present paper was to provide a brief review on some aspects of zirconia dental restorations with focus on recent scientific researches.

Keywords: Zirconia, biomaterial, dental prosthetics, CAD/CAM

1. INTRODUCTION

An ideal all-ceramic dental material should exhibit excellent esthetic characteristics, like translucency, natural tooth color, outstanding light transmission and, at the same time, optimal mechanical properties, like flexural strength, fracture toughness and limited crack propagation at the functional and parafunctional load conditions, in order to ensure long-term service. To date, zirconia has been considered a suitable choice for dental restorations due to its good mechanical properties, tooth colored and natural appearance and low plaque accumulation.[1-3] Zirconia (zirconium oxide) was introduced by Martin Heinrich Klaproth in 1789.[4]

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. [5-6] Its mechanical properties are very similar to those of metals and its colour similar to tooth color. Hence it has been called as ‘Ceramic Steel’ by Garvie. [7] The mechanical properties of zirconia are the highest ever reported for any dental ceramic.

This material is a non-cytotoxic metal oxide, is insoluble in water and has no potential of bacterial adhesion. In addition, it has radio-opacity properties and exhibits low corrosion. [8-9]

2. PHASES OF ZIRCONIA

Three crystalline shapes of this material at different temperatures are as follows: cubic (c) (from 2680°C to 2370°C); tetragonal (t) (from 2370°C to 1170°C); monoclinic (m) (from 1170°C to room temperature). Monoclinic (m) phase is a more stable phase. Incorporation of cubic oxides like MgO, CaO, Y₂O₃ and CeO₂ to zirconia can delay creation of the transformation phase. Subsequently, the zirconia crystals in their tetragonal or cubic shape at room temperature remain stable. These materials are referred to as stabilizers. [8]

One of the most important properties is a remarkable increase in fracture toughness of the material by hindering, but not preventing, the propagation of a crack; tensile stress concentration converts the transformation from (t) phase to the (m) phase. [10]

Increasing the crystal volume, constrained by the surrounding ones, leads to a favorable compressive stress. This limits growth of cracks. [11] Transformation toughening or “phase transformation toughening” (PTT) is the reported mechanism for exceptional flexural strength and fracture toughness of zirconia among all the other ceramics. [12] Heating the material at a low temperature (900–1000°C) for a short time changes the phase from monoclinic back to tetragonal form and generates a relaxation of the advantageous compressive stress at the surface, resulting in a decrease in the material toughness. [13]

The grain size influences the mechanical behavior of zirconia. It means that higher temperatures and longer sintering times produce larger grain sizes. The critical crystal size is approximately 1 μm and zirconia with larger crystals are more prone to spontaneous PTT due to lower stability, whereas a smaller grain size generates favorable properties. It is reported that with grain sizes below 0.2 μm, PTT does not increase and fracture toughness decreases. However, the sintering conditions are important because they affect the crystal size, the mechanical properties and the stability of zirconia. [14]

3. TYPES OF ZIRCONIA CERAMIC AVAILABLE OR DENTAL APPLICATION

Although, many types of zirconia-based ceramics are available, three zirconia-containing systems have been used in dentistry. Two of them are bi-phasic materials: glass-infiltrated zirconia-toughened alumina (ZTA) and the magnesium partially-stabilized zirconia (Mg-PSZ); the third type is the yttria partially-stabilized tetragonal zirconia polycrystal (3Y-TZP), a mono-phasic material which is used commonly. [15]

In-Ceram zirconia is a glass-infiltrated zirconia-toughened alumina (ZTA), in which, for the first time, zirconium oxide was used as a dental ceramic. Due to its metastable nature, zirconia is a high-performance ceramic material. High-strength cores are composed of 67 wt% of aluminum oxide and 33% of 12 mol% cerium-partially stabilized zirconium oxide; therefore, zirconia crystals (grain size $<1 \mu\text{m}$) are embedded in an alumina matrix (larger grains $<2-6 \mu\text{m}$, high elastic modulus) in such a composition that yields the highest tenacity and flexure strength inside this class of ceramics (400–800 MPa): microcracks may trigger the so-called “transformation toughening” of zirconia, so that a crack tip is more often seen to propagate through the alumina matrix surrounding the transformed crystals. [1,4] ZTA can be manufactured according to two different processes: soft machining or slip casting.

The latter presents the advantage of a more limited shrinkage but, at the same time, higher porosity and poorer mechanical properties than yttrium partially-stabilized tetragonal zirconia polycrystal (3Y-TZP), [16] the strongest and most commonly used zirconia-based ceramic. Moreover, stabilization by cerium oxide provides better thermal stability and resistance to low temperature degradation (LTD) than Y-TZP. [17,18]

The microstructure of magnesium partially-stabilized zirconia (Mg-PSZ) consists of clusters of tetragonal crystals within a cubic stabilized zirconia matrix. The added stabilizer is MgO (8–10% mol). As regards dental applications, with some exceptions (Denzir-M–Dentronic AB), such a material has not been extensively used, neither has it encountered large popularity due to its remarkable porosity, large grain size (30–60 μm), low stability, tendency to framework wear, [14] and overall poor mechanical properties, especially when compared to 3Y-TZP. [19,20]

The third common zirconia is yttrium partially-stabilized tetragonal zirconia polycrystal (3Y-TZP). This type of zirconia is made of transformable, t-shaped grains stabilized by the addition of 3 mol% yttrium-oxides (Y_2O_3). It is placed in category 4-polycrystalline solids (alumina and zirconia) and has no glassy components. All the atoms are packed into a regular pattern making it dense and stronger. Procera system is a computer-aided designing and computer-aided manufacturing system (CAD-CAM). This ceramic is the frequently used form of zirconia commercially available for dental use. [21]

4. MECHANICAL PROPERTIES

Mechanical properties of zirconia have been reported to be higher than other ceramics for dental applications. Fracture resistance of 6–10 MPa/ $\text{m}^{1/2}$, a flexural strength of 900–1200 MPa and a compression resistance of 2000 MPa have been reported for it. [22] Zirconia restorations bear an average load of 755 N. Fracture loads of 706–4100 N have been reported; all the studies have demonstrated that in dental restorations zirconia yields higher fracture loads than alumina or lithium disilicate. [23]

Zirconia ceramics yield superior wear behavior and lower antagonistic wear compared to porcelains. A trend to higher ceramic and antagonistic wear was shown after grinding treatments. [24,25] Degradation of zirconia happens in low temperatures and without mechanical load application. This condition, so-called “aging”, is a transformation of the tetragonal phase to monoclinic phase which is a stable form. Aging decreases the physical properties of the material and increases risk of failure in zirconia restorations. Presence of mechanical stresses and moisture accelerates zirconia aging. Grain size, temperature, vapor, the presence of surface defects, type, percentage and distribution of stabilizing oxides and processing techniques influence this process. Meanwhile, there is evidence in relation to the long-term evaluation of effects of aging of zirconia on dental restorations. Aging leads to changes in the behavior of the material, weakening it, and subsequently, to material degradation, with microcracks decreasing strength properties. [26]

5. MANUFACTURING

Two commonly used different techniques are available for prefabrication of zirconia frameworks: “soft machining” of pre-sintered blocks or “hard machining” of fully sintered blocks. [27]

The soft machining process is the most common manufacturing system for 3Y-TZP, based on milling of pre-sintered blocks that are fully sintered at a final stage. The process of production of these blocks consists of compacting zirconia powder in the presence of a binder through a cold, isostatic pressing process; this leads to homogeneous distribution of the components inside the block. [17] Processing at a proper pre-sintering temperature of zirconia is an important factor because this parameter influences hardness, machinability and roughness of the blocks. Hardness and machinability properties act as reverse factors; this means if hardness of block is adequate, manipulation of

blocks is performed safely, but, high hardness is unsuitable for machinability. Moreover, an increase in pre-sintering temperatures generates rougher surfaces. [1]

Usually, CAD software programs design the enlarged framework to compensate shrinkage. In CAM procedure, the framework is machined according to the designed form. After this step, the sinterization is performed. Since linear volume shrinkage of restoration is about 25%, the zirconia framework reverses previous dimensions. Performance of these steps provides cores with high stability. [1] However, a certain amount of cubic zirconia may be present due to an uneven distribution of yttrium oxide. The cubic phase has stable oxides than the tetragonal crystals which may provide an unstable material. [14] Addition of metal oxides to zirconia powder or immersing cores in metal salt solutions might yield colored cores. This coloration does not affect mechanical properties of zirconia cores. [27] Many manufacturers prefer this technique i.e. Procera Zirconia (Nobel Biocare AB, Goteborg, Sweden), Lava (3MESPE, Seefeld, Germany) and Cercon (Dentsply Degudent, Hanau, Germany).

In the hard machining technique, the so-called "hot isostatic pressing", the 3Y-TZP blocks are sintered and condensed at high temperatures (1400–1500°C) and under high pressure in inert gas medium. These blocks are very hard, dense and homogeneous. [28]

Selection of each one of these two techniques as suitable technique is a matter of controversy. Meanwhile, the most important problem in soft-machining is the difference in the sintering shrinkage of the framework and the enlargement values. [4] The major disadvantage of the hard machining technique is more time-consuming and requires very tough and wear-resistant cutting devices. Provision of these pieces of equipment renders the production procedure more costly. [11]

Milling zirconia blocks at thin sections provides various types of surface microcrack and defects. It seems that factors such as the grain size of the diamond burs or the rotation speed are effective. [29]

Surface treatments provide more roughness but decrease toughness and the strength resulting in the exposure of the processing defects to moisture. It has been reported that it induces aging potential and decreases serviceability of the restoration. [30,31]

The hard machining procedure leads to the production of monoclinic zirconia that is a weak phase in terms of aging and microcracking. [14] There is controversy about the results of studies on the surface treatments of zirconia. [1]

It appears that residual stress due to processing the restoration, especially coefficient of thermal expansion (CTE) difference between the fired zirconia and the veneering material, plays a more important role than surface treatments in aging potential. [31]

Recently, cerium oxide has been introduced as a stabilizer for dental applications. The ceria-stabilized zirconia (Ce-TZP) exhibits more suitable thermal stability and LTD resistance than Y-TZP. Ce-TZP demonstrates the highest bending strength in dental ceramics. Presence of yellow-brownish color and future discoloration of ceria-containing zirconia restorations to dark gray is a limitation for dental applications. [11,31]

Other factors such as framework thickness, connector shape and size, coefficient of thermal expansion difference between the coping and veneer affect mechanical properties of zirconia frameworks. Minimum framework thickness (0.5 mm) is necessary for copings to support veneering material and avoid core deformation. CTE of coping must be close to veneering ceramic to reduce stress in restorations. [19,32]

6. FITNESS

Various studies have reported different values for precision of fit of zirconia restorations, which is attributed to differences in experimental designs and evaluation procedures. In these studies, the marginal gaps ranged between 9.0 and 148.8 μm , with an average value of 73.8 μm . [18,33] Higher discrepancies have been detected at the internal gap (i.e. the internal distance measured between the coping and the abutment), ranging between 68.8 and 215 μm in the occlusal direction and between 52.3 and 192 μm in the axial direction. [22]

Single crowns milled with dense zirconia copings have exhibited better fit (0–74 μm). [33] Comlekoglu et al reported values of marginal gap for feather-edge, mini-chamfer, shoulder and chamfer finish lines: 87 \pm 10, 114 \pm 11, 114 \pm 16 and 144 \pm 14 μm , respectively. [34] Marginal opening is dependent on the extension and shape of zirconia frameworks. Long-span and curved zirconia frameworks have exhibited less marginal fit. [35,36] Hard-machining has been advised for complex restorations by some studies. [22]

7. 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. [37]

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. [38]

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. [39]

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. [40]

8. 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. [41]

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. [42]

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 $\mu\text{m}/\text{m K}$. [43]

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. [44]

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]

9. CONCLUSION

Zirconia-based restorations exhibit excellent esthetic characteristics and optimal mechanical properties (flexural strength, fracture toughness). Literature confirmed high success rates of these restorations.

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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