REVIEW ARTICLE

ZIRCONIA IN DENTISTRY - AN OVER VIEW

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ABSTRACT

The interest of dental research in metal-free restorations has been rising in the last 20 years following the introduction of innovative allceramic materials in the daily practice. In particular, high-strength ceramics and related CAD/CAM techniques have widely increased the clinical indications of metal-free restorations, showing more favorable mechanical characteristics compared to the early ceramic materials. Zirconia has been recently introduced in prosthetic dentistry 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.

Keywords: Zirconia, Biocompatibility, Fixed partial dentures, Implant abutment.

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INTRODUCTION

Zirconium (Zr) is a metal with the atomic number 40.It was first discovered in 1789 by the chemist MartinKlaproth¹. Zirconia (ZrO_2) is a white crystalline oxide of zirconium. 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'². The material has a density of 6.49 g/cm³, a melting point of 1852 and a boiling point of 3580.

It has a hexagonal crystal structure and is gravish in color. Zr does not occur in nature in a pure state. It can be found in conjunction with silicate oxide with the mineral name Zircon $(ZrO_2 \times SiO_2)$ or as a free oxide (ZrO₂) with the mineral name Baddeleyite³. These minerals cannot be used as primary materials in dentistry because of impurities of various metal elements that affect color and because of natural radionuclides like urania and thoria, which make them radioactive⁴. Complex and timeconsuming processes that result in an effective separation of these elements are necessary in order to produce pure zirconia powders. After purification the material produced can be used as a ceramic biomaterial. 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.

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. 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 "stabilizers⁵".

STABILIZED ZIRCONIA

Stabilized zirconia is a mixture of zirconia polymorphs obtained at room temperature, by the addition 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. Several different oxides are added to zirconia to stabilize the tetragonal and/or cubic phases. Magnesia (MgO), Yttria (Y₂O₃), Calcia (CaO), and Ceria (CeO), amongst others, allow the generation of Partially Stabilized Zirconia (PSZ)^{6,7}. Partially stabilised zirconia displays high resistance to temperature changes which makes it suitable for use in an environment subject to high temperatures. When the whole material is constituted by transformable t-zirconia grains it is called Tetragonal zirconia polycrystals (TZP).

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)

• Zirconia-toughened alumina (ZTA).

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). 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. 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 ($30-60\mu m$) 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.⁵

BIOLOGICAL CHARACTERISTICS

Biocompatibily

In vitro and in vivo studies have confirmed a high biocompatibility of zirconia, especially when it is completely purified of its radioactive contents. Generally, ceramics are inert materials, which have no adverse local or general tissue reactions. As the ceramic prostheses are made with highly polished surface, they can contact the gum tissue and assist in the maintenance of gingival architecture. Depending on the smoothness, the ceramics prevent the buildup of plaque, creating a favorable surface for the gingival tissues. Zirconia based ceramics are chemically inert materials, allowing good cell adhesion, and while no adverse systemic reactions have been associated with it. However, particles from the degradation of zirconia at low temperature (LTD) or from the manufacturing process can be released, promoting an immune localized inflammatory reaction⁸.

Degree of toxicity

In vitro tests have shown that zirconia has a lower toxicity than titanium oxide and similar to alumina. Cytotoxicity, carcinogenicity, mutagenic or chromosomal alterations in fibroblasts or blood cells has not been observed⁹.

Radioactivity

Zirconia is often accompanied by radioactive elements of long half-life, such as thorium (Th) and uranium (U). The separation of these elements is difficult and costly. Two types of radiation are correlated with zirconia: alpha and gamma. Significant amounts of alpha radiation have been observed in zirconia based ceramics used in the manufacture of surgical implants, because, due to their high ionization, the alpha particles destroy cells of hard and soft tissues. As for gamma radiation, the literature suggests that the radiation level is not worrisome in zirconia⁹.

MECHANICAL PROPERTIES

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'. Fracture toughness of Zirconia is between 6 and 10 MPa, which is almost twice as high as that of aluminium oxide ceramics. This is due to transformational toughening, which gives zirconia its unique mechanical properties. Its resistance to traction can be as high as 900-1200 MPa and its compression resistance is about 2000 MPa^{10,11}. Cyclical load stresses are also tolerated well by this material. Surface treatments can also modify the physical properties of zirconia. 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^{12,13}.

Ageing

Aging occurs through a slow surface transformation to the monoclinic stable phase. This transformation begins in individual particles on the surface through a mechanism of stress corrosion. The initial transformation of specific particles can be related to a state of imbalance: greater particle size, lower yttria content, specific guidance from the surface, the presence of residual stress, or even the presence of a cubic phase. The transformation occurs through nucleation and growth processes¹⁴. This phenomenon leads to a cascade of events occurring in neighboring particles, leading to an increase in volume that stresses the particles and results in subcritical crack growth (SCG), offering a way for water to penetrate inside the material.

MANUFACTURING PROCEDURES

CAD/CAM technology is commonly used for fabrication of zirconia dental frameworks. 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, framework is designed by sophisticated computer softwares (CAD). Then, through a CAM milling procedure, a framework with, accurately controlled dimension is machined out of the blank. For milling two different techniques can be used. "soft machining" of presintered blanks which employs milling of pre-sintered blanks that are then fully sintered at a final stage or "hard machining" which employs milling of fully sintered blanks¹⁴.

For systems employing pre-sintered blocks, they seem less machine influenced, because the blocks are more porous. The subsequent sintering of presintered machined infrastructure increases the hardness and fracture toughness. However, repeated heat treatments, to those parts which are subjected to application of feldspathic or glass porcelain, seem to have a negative effect on fracture resistance of the material¹⁵.

On the other hand, the fully sintered blocks present high hardness, requiring robust devices that will generate more power and thus greater compressive tension on the outer surface of the block, enabling the transformation of the tetragonal to monoclinic phase $(t \rightarrow m)$.

APPLICATION

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 auxillary components like cutting burs, surgical drills, extracoronal attachments and orthodontic brackets.

Zirconia implant.

The principal disadvantage of titanium is its dark grayish color, which often is visible through the peri-implant mucosa, therefore impairing esthetic outcomes in the presence of a thin mucosal biotype. Unfavorable soft tissue conditions or recision of the gingival may lead to compromised esthetics. Furthermore, reports suggest that metals are able to induce a nonspecific immunomodulation and autoimmunity. Galvanic side effects after contact with saliva and fluoride are also described. Although

allergic reactions to titanium are very rare, cellular sensitization has been demonstrated. Because of these disadvantages, novel implant technologies that produce ceramic implants are being developed. However, ceramics are known to be sensitive to shear and tensile loading, and surface flaws may lead to early failure. These realities imply a high risk for fracture. In recent years, high strength zirconia ceramics have become attractive as new materials for dental implants. The inflammatory response and bone resorption induced by ceramic particles are less than those induced by titanium particles, suggesting the biocompatibility of ceramics¹⁶. The clinical use of zirconia dental implants is limited because fabrication of surface modifications is difficult, and smooth implant surfaces are not beneficial for osseointegration because of poor interaction with tissues. Although zirconia may be used as an implant material by itself, zirconia particles are also used as a coating material of titanium dental implants. A sandblasting process with round zirconia particles may be an alternative surface treatment to enhance the osseointegration of titanium implants^{17,18,19}

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. 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. 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 canal²⁰.

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

thickness²¹.

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. Tooth preparation can be realized with various finishing lines, although chamfer and rounded shoulder are recommended^{22,23.}

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 mm²⁴. Height of abutment is fundamental to obtain ZrO₂ frameworks with correct shape and dimension in order to ensure mechanical resistance of restoration.

Contraindications ■ As cantilever pontic ■ In class II div II malocclusions patients, due to deep bite there will be insufficient space for labo-lingual connector width. ■ Mesial tilting of abutment tooth with supra erupted teeth, which cannot be corrected with minimal enameloplasty. ■ Very short clinical crown that does not permit height of connector (occlusal-gingival).

SURVIVAL RATES AND COMPLICATIONS OF ZIRCONIA BASED RESTORATIONS

Many studies have been performed on survival rates of zirconia restorations. The bulk of data available for zirconia posterior FPDs indicate the best clinical results (93.3%) with all-ceramic systems. Complications of zirconia FPDs have been reported as cracking or chipping of veneering ceramic, whereas other all-ceramic restorations have exhibited some framework fractures. A study retrospectively reported that the success rate of 26 CAD/CAM cross arch zirconia implant bridges was 98.6% at the unit level after 5 years of service. Successful soft tissue parameters were found around all the implants. After 4 years of service, the reported failure rates were 4-6%²⁵. Routine mechanical complications of such restorations have been reported as framework fractures, chipping of veneering ceramic and loss of retention or deboning. Bulk fracture is a rare occurrence and usually such fractures occur in long-span FPDs²⁶. Range of the incidence of chipping reported in zirconia-based restorations was different. In non-load-bearing areas, these unsuitable factors can result in failures such as chipping^{27,28}. However, areas under loading such as connectors are susceptible to chipping with a higher incidence rate. It is clear that ceramic veneer cracking is a multifactorial phenomenon and that only some of its possible causes have been distinctly highlighted: differences in CTEs between framework and ceramic, firing shrinkage of porcelain, areas of porosities, flaws on veneering, poor wetting by veneering material on core, improper framework support, overloading and fatigue²⁹. Because of differences in the material composition of ceramic systems (composed of metal, alumina or zirconia, glass-ceramics and feldspathic ceramics), different treatments are required for the exposed material surfaces after chipping³⁰.

BONDING TO ZIRCONIA

One problem of zirconia application is its adhesion to different substrates. Routine methods for bonding of restorations to hard tooth structures and restorative materials do not provide desired bond strength for ZrO_2 components. Surface treatment of zirconia produces an activated surface in different applications.

Conventional surface treatment techniques are (1) acid etching (typically HF), (2) abrasion with diamond (or other) rotary instruments, (3) air abrasion with alumina (or other) particles, (4), application of different laser types and (5) a combination of these techniques that actually roughen surfaces^{31,33}. Since zirconia is resistant to aggressive chemical treatment, very aggressive mechanical abrasion methods must be used to provide sufficient surface roughness. Zandparsa et al³⁴ compared the effect of airborne particle abrasion, acid etching (Piranha solu-

tion), and application of an alloy primer on shear bond strength of zirconia to enamel and concluded that airborne particle abrasion in combination with the application of a zirconia primer provides a durable bond strength. Surface grinding is a commonly used alternative for roughening the surface of ZrO₂ to improve mechanical bonding. There are several methods used for surface roughening: roughening with abrasive paper or wheels (SiC or Al₂O₃), particle air-abrasion using Al₂O₃ or other abrasive particles ranging in size from 50 to 250 µm and grinding with a diamond bur. A novel surface roughening technique that has been explored for ZrO₂ is selective infiltration etching (SIE). SIE uses a heat-induced maturation process to prestress surface grain boundaries in ZrO₂ to allow infiltration of boundaries with molten glass. The glass is then etched out using HF, creating a network of inter-granular porosity that allows nanomechanical interlocking of resin cement. The advantage of SIE is that it only involves grains that are exposed to molten glass, allowing control of the area to be etched. The use of SIE improved nano-mechanical retention of zirconia by increasing the surface area available for bonding). Recently, it was reported that the experimental hot etching solution could be considered an alternative treatment modality to sandblasting for zirconia cores to avoid phase transition at the surface from tetragonal to monoclinic that may be detrimental for the longevity of the zirconia-veneering ceramic restoration³⁵. Recently, use of lasers is a method for roughening of surface of zirconia restorations. Results of laserbased studies are controversial. Akyl et al reported that roughening of the surface of Y-TZP ceramic by Er:YAG laser increased the shear bond strengths of ceramic to dentin and reduced microleakage scores³⁶. Resin cement is a standard material for luting a ceramic prosthetic to tooth structures. Resin-based composite cements have compositions and characteristics similar to conventional restorative composite resins and consist of inorganic fillers embedded in an organic matrix (e.g. Bis-GMA, TEGDMA, UDMA). The use of phosphate monomer luting cements on freshly air-abraded zirconia is the simplest and most effective way for zirconia cementation procedure. These resin cements have shown good mechanical retention. MDP-containing

resin cement continues to be a popular choice for luting ZrO₂ prosthetics in clinical applications due to its low failure rate and loss of retention.

CONCLUSION

Although clinical long-term evaluations are a critical requirement to conclude that zirconia has good reliability for dental use, biological, mechanical, and clinical studies published to date seem to indicate that ZrO₂ restorations are both well tolerated and sufficiently resistant. Ceramic bonding, luting procedures, ageing and wear of zirconia abutment should be evaluated in order to guide adequate use of zirconia as prosthetic restorative material. Patient selection, coupled with adequate clinical and technical protocols, are imperative in order to obtain good performance of these restorations. 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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