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DENTAL ZIRCONIA: FROM MATERIAL SCIENCE TO CLINICAL ASPECT – A REVIEW

Dentistry

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ABSTRACT

Zirconia is a restorative material known for its esthetics and metal free nature. Zirconia has occupied an increasingly important role due to its excellent mechanical and bio compatible characteristics. Initially, this material was used only for all-ceramic frameworks. Later, the introduction of translucent zirconia with improved aesthetic properties, paved way for the realization of monolithic prosthetic products with various advantages like elimination of chipping risk, good mechanical properties (superior to monolithic lithium disilicate products), the possibility of processing by a CAD-CAM technique (greater standardization and quality of results, with cost reduction), manufacturing of smaller thicknesses, and a more conservative dental preparation. Although improved mechanical properties are important for long term success, zirconia, unlike glass ceramics, is not susceptible to etching and this makes it impossible to realize the adhesive procedures. To improve the bonding of zirconia to the tooth structure, various surface treatments are available. This article discusses on properties of zirconia, its manufacturing process, luting protocol and its applications in prosthodontics

KEYWORDS

zirconia, biocompatible, esthetics, ceramic steel

INTRODUCTION

Dental restorations and prostheses such as inlays, onlays, crowns, fixed partial dentures (FPDs), and removable dentures are used to restore the form, function and esthetics for the patient. During the 20th century, both dental materials and dental devices progressed remarkably. Owing to the increased demand for safe and esthetically pleasing dental materials, new high strength Metal free materials have been recently introduced. Biomaterials for dental use are classified into metal, ceramics, synthetic polymer and composite materials. For dental prosthesis, previous ceramics and resin were brittle, and the use of these alone for restoration and dental prosthesis preparation was limited due to the problem of the material's strength. Thus, metal has been frequently used, prioritising mechanical strength over esthetics but demands for metal-free restoration has recently increased due to esthetic problems of metal colour penetration through the marginal gingiva and gingival staining by metal, a problem of metal allergy, and environmental protection concerning rare metals.

Zirconia

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 (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***'. Zirconia was discovered by the German chemist Martin Heinrich Klaproth in 1789. Its mechanical properties are very similar to those of metals, and its colour is similar to tooth colour. Hence, it has been called as '***Ceramic Steel***' by Garvie[2].

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 1170ºC. From 1170ºC to 2370ºC, tetragonal zirconia is formed, while cubic zirconia is formed at temperatures above 2370ºC up to the melting point (2680ºC). 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". With the addition of stabilising 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).

Types Of Zirconia:

- 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 3 mol% yttrium oxide (Y_2O_3). 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.

In *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 ZrO_2 intragranular precipitates within a matrix of stabilized cubic ZrO_2. Due to the difficulty of obtaining Mg-PSZ precursors free of SiO_2, 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.

In *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 dop - ants but is controlled instead by particle size, particle morphology and location (intra- or intergranular)[2,13].

Properties Of Zirconia:

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 m1/2, which is almost twice as high all that of Aluminium 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.

Biocompatibility:

They are chemically inert materials, allowing good cell adhesion and while no local or systemic adverse reactions have been associated with it. 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 similar to 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.

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.

Optical Characteristics:

Yttria-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 possess 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. 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.

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 favourable 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".(Fig.1)

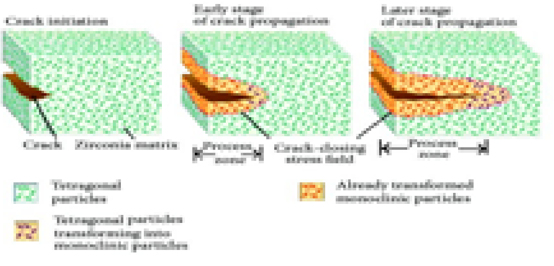

Fig: 1 *Phase Transformation toughening*

Aging:

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. 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 aging reduces mechanical features of zirconia, the decrease falls into clinically acceptable values[2].

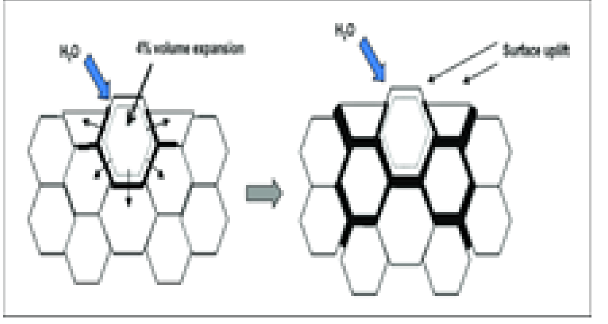

Fig.2: *Aging*

Manufacturing Procedures

CAD/CAM zirconia dental frameworks can be produced according to two different techniques: "soft machining" of pre-sintered blanks or "hard machining" of fully sintered blanks. 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.

In ***hard machining***, fully-sintered 3y-TZP blocks are used. They are prepared by pre-sintering at temperatures below 1500ºC to reach a density of atleast 95% of the theoretical density. The blocks are then processed by "hot isostatic pressing" at high temperatures (1400-1500ºC) 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.

Luting Of Zirconia:

As zirconia does not contain glassy matrix, it is free of silica. Hence, it cannot be etched by conventional etching technique. 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. Various surface conditioning includes mechanical conditioning, laser conditioning, chemical conditioning, coupling agents and silica coating.

In *Acid etching*, Hydrofluoric acid is used. HF removes the glassy matrix of ceramics and creates microporosities which enables a micromechanical retention of resin composites. However, this was not effective with zirconia as it lacks glassy matrix. During *sandblasting,* the inner surface of zirconia crown is abraded by alumina particles at a microscopic level. This enables the resin luting cements to flow into the micro undercuts and increase the retention *mechanically.* However, the use of air borne particle abrasion may lead to sharp scratches, cracks and grain pull out. Damage to the surface of the ceramics and loss of material may occur. These sharp and deep defects lead to increased stress developing at the tip of the crack which turns them into crack initiation sites. In *laser conditioning*, when *CO_2 laser* is focused on ceramic surfaces, the temperature of the surface increases due to the induction of heat. As a result, conchoidal tears appear. These surface irregularities provide micro undercuts and improves the retention.

Silane coupling agents are hybrid inorganic – organic bifunctional molecules. Water reacts with the silane molecule's alkoxy groups (RO_3Si-) to form a silanol group (SiOH). The hydroxyl group (OH) reacts with available Si and O on the ceramic surface to form siloxane (-Si-O-Si-O-) covalent bond. The methacrylate groups of resin luting agents combine with monomeric end of silane molecules resulting in the formation of a series of siloxane covalent bond between resin and the ceramic surface. As siloxane bonds are sensitive to hydrolytic degradation, it affects the stability of the adhesive interface. No significant effectiveness was seen in the surfaces with absent or reduced Si content[19].

To increase the adhesion between the zirconia crown and resin luting agents, *primers* containing 6-methacryloxyhexyl phosphonoacetae (6MPHA),10-methacryloyloxydecyl dihydrogen phosphate (10 MDP) etc are used. The hydroxyl group of zirconia reacts with the phosphate group to form a stable Z- O- P between the primer and zirconia surface. The surface of zirconia becomes an organic – inorganic hybrid composite which reacts with polymerizable groups of methacrylate resin composites resulting in increased bond strength and durability The most used primer was 10MDP. *Kern and Wegner (1998)* suggested that a durable resin bond to YPSZ was achieved only after sandblasting the ceramic and using one of two resin composites containing a special phosphate monomer[9]. *Kitayama.S* (2010) stated that bond strength was improved by using primer containing silane coupling agent for silica- based ceramic and primer with a phosphonic acid monomer or a phosphate ester for zirconia ceramic[10]. *Atsu et al (2006)* stated that tribochemical silica coating and the application of an MDP–containing bonding/silane coupling agent mixture increased the shear bond strength between zirconium-oxide ceramic and resin luting agent[6]. 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.

Applications Of Zirconia

Bilayer veneers:

The inherent opacity of the zirconia core allows clinical application of high strength veneer restoration with better masking ability for the colourmanagement of discoloured teeth. The modified core may be fabricated with 0.2 mm to 0.4 mm thickness.

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 4º- 6º 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 4º- 6º taper. Tooth preparation can be realized with various finishing lines, although chamfer and rounded shoulder are recommended. 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.

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 mm^2. 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. Height of abutment is fundamental to obtain ZrO2 frameworks with correct shape and dimension in order to ensure mechanical resistance of restoration.

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. 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.

Zirconia Implant:

Y-TZP as an 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. Zirconia implants have shown to present a lower inflammation rate compared to titanium implants due to lower bacterial attachment. These are now being considered as a valuable alternative treatment, particularly in subjects with a thin gingival phenotype. With an aesthetic complication rate close to 0%, these implants are the obvious choice for anterior aesthetic rehabilitations. Y-TZP implants can successfully osseointegrate under loading conditions similar to titanium implants. *Sennerby et al*. (2005) reported that Y-TZP implants with a moderately roughened surface showed a four- to fivefold increase in resistance to removal torque compared with machined Y-TZP implants and a direct bone formation could only be observed on implants with a modified surface[15].

Commercial zirconia implants were initially available only as one-piece implants. However, they displayed various limitations such as the lack of angled abutments to correct misalignment and the fact that cementation was the only option for connecting prosthodontic elements to one-piece implants, with the risk of leaving excess luting cement in the submucosal area, particularly when inserting the implants deeper in the aesthetic zone. This led to the introduction of two-piece zirconia implants, where the fixtures and abutments are separated. Previous systematic reviews have concluded that one- and two-piece zirconia and titanium implants demonstrate no significant difference in terms of bone-to-implant contact, removal torque or implant survival. Survival rates ranged from 67.6 to 93.3% for zirconia implants (67.6 to 90.9% for one-piece zirconia implants; 85.7 to 93.3% for two-piece zirconia implants). Marginal bone loss for zirconia implants ranged from 0.42 ± 0.4 mm to 1.51 ± 0.68 mm. Amongst zirconia implants, one-piece systems seem to have a lower survival and success rate than two-piece systems[9].

Despite of various advantages with zirconia implants, the scientific clinical data for ceramic implants in general and for zirconia implants in particular are not sufficient to recommend ceramic implants for routine clinical use.

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 greyish 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[2].

CONCLUSION

Zirconia has become the keystone material in the field of prosthodontics due to its excellent mechanical and biocompatible properties. Improvement in cementation of zirconia restorations to the tooth structure using primers and surface treatment have reduced the bonding failure and improved the longevity of the prosthesis. In implant dentistry, zirconia implants seem to be reliable due to low inflammation rate and superior esthetics. Altogether makes Zirconia a noteworthy and emerging material in prosthodontics.

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