Zirconium Oxide Ceramics in Prosthodontics

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Summary

Dental ceramics justifies more frequent use in prosthetic restoration of damaged dental status. Inlays, crowns and three-unit bridges have been made of all-ceramic system. Zirconia dioxide is a well- known polymorph. The addition of stabilising oxides like MgO, Y_2O_3 to pure zirconia, makes it completely or partially stabilized zirconia which enables use in prosthodontics. Tetragonal Zirconia Polycrystals (TZP) stabilized with 3mol % yttria, has excellent mechanical and esthetical properties. Fixed prosthetic appliances of this ceramic have been made using CAD/CAM techniques. It can be expected that zirconium oxide ceramics will replace metal-ceramics in restorations that require high strength.

Key words: *Zirconia, mechanical properties, Tetragonal Zirconia Polycrystals (TZP), partially stabilized zirconia (PSZ), In-Ceram Zirconia.*

Introduction

Zircon has been known as a gem since ancient times. The name of metal zirconium, comes from the Arabic Zargon, which means golden colour. Zirconia, the metal dioxide (ZrO_2) ,was identified in 1789 by the German chemist Klaproth (1). The development of zirconia as an engineering material was demonstrated by Garvie et al, who showed how to make the best of T-M phase transformation of Partially Stabilized Zirconia (PSZ) improving mechanical strength and toughness of zirconia ceramics (2). ZrO_2 exists in several modifications and shapes and it is known a lot of different kinds of processing from cold to warm. Pure ZrO_2 is of limited use for industrial applications because of the phase transformations that occur.

Zirconia is stable in oxidizing and poor reducing atmospheres. It is inert to acids and bases at room temperature (RT) with the exception of HF. It reacts with carbon, nitrogen and hydrogen at temperatures above 2200°C and does not react with the refractory metals up to 1400°C. However, its reactivity is strongly dependent upon the type and quantity of the stabilizer used in the ceramic (3).

Structure and properties of zirconium dioxide

Zirconium dioxide appears as a monoclinic, cubic or tetragonal polymorph. At room temperature only the monoclinic ZrO_2 exists. This phase is stable up to 1170°C when it inverts to a tetragonal, metastable phase, whereas above 2370°C it turns into a cubic

phase. Cooling enables allotropic changes below 1070°C, when the tetragonal phase is transformed into monoclinic. It occurs in the temperature range of about 100°C. By the mentioned transformation of ZrO_2, its volume increases by 3 - 4 % and its form is changed. Stress caused by volume increase forms cracks in pure zirconia ceramics, which simply disintegrates at RT after sintering at temperatures between 1500 and 1700°C. To stabilise ZrO_2, several oxides have been added (ZrO_2-CaO, ZrO_2--MgO, ZrO_2-Y_2O_3) (1, 4-6). Stabilisation primarily means decreasing the temperature of T- to M-phase transformation. Oxide as a stabiliser, partially or wholly prevents transformation and is a factor of the transformational strengthening of the zirconia-based ceramic structure. By the addition of stabilising oxides such as CaO, MgO, CeO_2 or Y_2O_3 to pure zirconium dioxide, a multiphase material is obtained, known as partially stabilised zirconia (PSZ). At RT the PSZ matrix is of cubic structure, with monoclinic and tetragonal precipitates. Garvie and Nicholson demonstrated how PSZ's mechanical properties can be enhanced by the homogenous and uniform distribution of the monoclinic phase in a cubic matrix (7). Ruff et al. proved in 1929. that the stabilisation of the cubic C-phase is possible at RT if a small amount of CaO is added to ZrO_2 (quot. from Piconi and Maccauro, 1). The addition of large amounts of a stabiliser such as MgO will induce a cubic crystal structure during firing, which does not revert to the monoclinic phase upon cooling (3).

The addition of less than 10wt% of stabilisers results in high-density of the ceramic particles, yielding thus transformation toughened zirconia or tetragonal zirconia polycrystals (TZP) (3, 8, 9). Extremely fine crystals inhibit T M phase transformation during cooling. Transformation toughened zirconia exhibits superior strength and fracture toughness (10, 11). Due to these properties, the load of this material can induce the phase transition of tetragonal to monoclinic crystals, with a corresponding change in volume. TZP exhibits optimal characteristics below 500°C.

Depending on the stabiliser, MgO or Y_2O_3, there are two different microstructures. The addition of MgO yields relatively coarse-grained (50-100μ) microstructure, known as Mg-PSZ.

The grains are predominantly cubic morphology with fine precipitates of tetragonal phase. Garvie et al. observed that tetragonal metastable precipitates uniformly dispersed within the cubic matrix can transform into the monoclinic phase when the matrix pressure decreases. This occurs at the formation and growth of cracks within the matrix which is thereby deformed (2). The stress induced by volume increase, caused by crystal transformation, acts in opposition to the strain, which accelerates crack propagation. The material becomes more resistant due to the lack of energy lost in suppressing compressive forces through volume increase. This is related to crack propagation during the TõM phase transformation. Such tetragonal metastable precipitates can be formed by adding 8mol% MgO to ZrO_2. Tetragonal metastable phase can also be formed in the matrix during controlled cooling.

There are two basic types of Mg-PSZ. One (MS) exhibits superior fracture toughness, high mechanical strength and average thermal shock resistance. Application is optimal at temperature below 800°C, with minimal thermal cycling. The other type (TS) exhibits excellent thermal shock resistance, lower strength but higher toughness. TS can be optimally processed at a temperature above 600°C.

The addition of Y_2O_3 enhanced the characteristics of ZrO_2 in applications. The main characteristic of yttria-zirconia ceramics is a fine-grained (<1 μ) microstructure known as Y-PSZ or tetragonal zirconia polycrystals (TZP). If we consider PSZ, the material is multiphase. On the other hand, TZP is a monophase or almost monophase material. In the TZP material with approximately 2-3mol% Y_2O_3 particles are tetragonal. The tetragonal TZP phase at RT depends on the amount of yttrium oxide, the grain size, and the matrix pressure. Lin et al. observed that the aluminium-silicate matrix in TZP destroys yttrium ions on grain boundaries, causing the loss of tetragonal phase stability (12). Zirconium dioxide with a higher Y_2O_3 concentration is completely stabilised, less flexible and deformable than the partially stabilised (13). It is less resistant to thermal shock than Mg-PSZ. Optimal temperature for its applications is below 500°C.

At high temperatures (>900°C) yttria-stabilised zirconia is prone to deformations due to the suspension of insoluble particles and high degree of oxygen permeability, which results in creep (3, 12, 14, 15). Rieth et al. (10) and Gupta et al. (11) first reported obtaining this ceramic.

The successful ZrO_2 application required a new component that would retain cubic phase resistance at high temperatures. The mixing of ZrO_2 and 5mol% Er_2O_3 stabilises the zirconia microstructure and increases deformation and creep resistance at high temperatures. The ZrO_2-Er_2O_3 microstructure consists of stable and metastable tetragonal precipitates. They convert to a nanosized tetragonal lamellar structure during thermal treatment. Stabilised or partially stabilised zirconia act as surface thermal barriers (16).

There are several ceramic materials toughened by lanthanum phosphate or zirconium dioxide (17, 18). Zirconia toughened alumina (ZTA) is increasingly applied in dental restoration (14, 19-22). The addition of ZrO_2 makes glass-infiltrated In-Ceram ceramics tougher. In-Ceram Zirconia (ICZ) contains 33wt% of partially stabilised zirconium dioxide, which increases tensile strength and fracture toughness. This material also contains 16wt% CeO_2 (23).

Zirconia ceramics have superior mechanical properties to other biomaterials, e.g. aluminium oxide ceramics (9, 23-27). It has by far the highest fracture strength values (x = 913 - 1000 MPa) and also the Weibull module (m = 18.4) (9, 26-33), which ensures its higher clinical durability compared with In-Ceram ceramics. In spite of high strength before fracture In-Ceram has a lower value of the Weibull module. This means that fractures in In-Ceram ceramics could also occur at smaller loads. The Young's module of ZrO_2 ceramics is in the same order as the one of base metal alloys (33).

ZrO_2 ceramic is extremely hard (HV 1200), its flexural strength is 1000-1300 MPa (three-point flexure test), and fracture toughness 9-10 MPa. Optimal mechanical properties are a result of ZrO_2 powder purity, the specific size and distribution of particles, industrial sintering, hot isostatic pressing (HIP), and fine-grained metastable microstructure (34). HIP toughened ZrO_2 is resistant to bite forces up to 1000 N. External load causes phase transformation and volume increase of up to 4%. This dimensional change caused by pressure, stops crack propagation and thereby toughness the material. The so-called transformation toughening is another reason for the excellent mechanical properties of TZP (9, 35). Sandblasting has the same positive effect. Electroplating of metal surfaces by zirconium dioxide reduces the release of metal ions (36). Thermal cycling enhances the bond between the composite and zirconia's ceramics (37).

ZrO_2 biocompatibility is similar to that of titanium (23). Y-PSZ as implants exhibit the same osseo integration percentage as titanium (34). As the first layer around the wax object, zirconium dioxide reduces the reaction of titanium with investment material. At the same time it reduces the thickness of the surface reaction layer on titanium cast (38).

Processing and application of zirconium dioxide

Zirconium dioxide as a biomaterial has been used in medicine as ball heads for Total Hip Replacements. ZrO_2 is mostly used for inlays, crowns, onlays, bridges, implants, commercial posts and attachments because of its good esthetical, chemical, mechanical properties and dimensional stability. (9, 20, 25, 31, 39-45).

Silver-grey colours of tooth structure are an esthetical problem in reconstruction of anterior teeth because of metallic posts. Non-metallic posts in combination with all-ceramic crowns are aesthetically preferable for the restoration of anterior teeth (9, 20, 35, 42-45). Industrially made ceramic material in the form of a blanket or ingots have better fracture strength than those made in the dental laboratory (27). They are more suitable for clinical usage, although CAM/CAD machining may cause surface and subsurface cracks (46). Zirconium dioxide is known as a white, black and green one, with regard to its processing (47). Zirconia-based ceramic can be obtained by sintering procedure or in heat-pressed reaction (48). During sintering intermetal phases oxidise first ($ZrSi_2$). It appears $ZrSiO_2$ and SiO_2 as amorphous matrix. By sintering of ZrO_2 and SiO_2, ingots of black zirconium dioxide are formed. Oxidation causes growth and expansion of particles which compensates contraction as a consequence of sintering. HIP procedure is the sintering procedure of material under high pressure and at high temperature. These procedures reduce porosity of the material and ensure high values of toughness and translucency of zirconium ceramics. There is no additional sintering or infiltration.

Ingots prefabricated by HIP are formed by Computer-Aided-Design/Computer-Aided-manufactur-

ing (CAD-CAM) techniques. The tooth should be conusly prepared with 5-15-degree taper. An optical impression is made and the basic colour and colour of tooth checked. Ingots are milled within one hour with accuracy of 1 nm in detail reproduction. Veneering can be obtained with one of the dental ceramics. It may be cemented like any other ceramic crown. Zirconium ceramic does not react to protein in saliva. Plaque does not remain on the surface of these crowns (49).

White ZrO_2 can be processed by basic procedure. Enlarging crowns or bridge skeletons are milled from porous, presintered blanks. The objects will later be sintered. Shrinkage is 20-30%, which enables optimal dimension of restorations. This process is called the Cercon system (13).

Dimensional stability of core made by the Cercon system is also retained during the fusing ceramic layers and glazing.

Clinical application of Y-TZP ZrO_2 in dentistry started more than ten years ago.

Prosthetic appliances can be shaped by hard procedure. Because of dimensional stability, sintered ceramic blanket may be milled in proportion 1:1. It can be coated with ceramic material and glazed.

Infiltration type zirconium ceramic is based on AlO_3/ZrO_2. The white ingots are milled by white procedure and infiltrated with lanthalium glass.

There are few literature data on the success of zirconium as construction and veneer material. Y--TZP ZrO_2 have less thermal coefficient than conventional feldspathic ceramic. It is necessary to find ceramic material with adjusted thermal coefficient. Today, zirconium ceramic has indication for crowns and three-unit bridges.

Zirconium ceramics is one of the many materials which can ensure optimum aesthetics and functional permeability in restorations of long duration.