Transformation-toughened zirconia: An overview

Binita Pathak[1], Brijesh Maskey[2], Amar Bhochhibhoya[3], Dibya Devkota[4]

[1]Assistant Professor, Department of Prosthodontics, Nepal Medical College, Kathmandu, Nepal

[2]Associate Professor. Department of Prosthodontics and Maxillofacial Prosthetics, People's Dental College and Hospital, Kathmandu, Nepal

[3]Assistanr Professor, Department of Prosthodontics, T.U Teaching Hospital, Maharajgunj Medical Campus, Institute of Medicine, Maharajgunj, Kathmandu, Nepal

[4]Lecturer, Department of Prosthodontics, Nepal Medical College, Kathmandu, Nepal

Abstract

Zirconia is a "metastable" ceramic, consisting of monoclinic, tetragonal, and cubic phases. Partially stabilized zirconia is preferred choice for dental use since they offer the opportunity to fabricate prosthesis which is not available with other ceramic materials. Phase transformation in zirconia ceramics represents one of the most remarkable innovations in the ceramic field. This phase transformation can have desirable consequences, increase in crack growth resistance which is referred to as "phase transformation toughening". However, the phase-induced volumetric transformation can also have disastrous consequences, if not properly controlled. This article provides information on crystallography of zirconia and the main characteristics of the tetragonal to monoclinic transformation and also discusses the positive (transformation toughening) and negative aspects (ageing/LTD) of the tetragonal to monoclinic transformation.

Key words: Degradation; Phase Transformation; Toughened Ceramics; Zirconia

Introduction

In recent times, both social pressure and the interests of the dentistry profession has driven the prosthodontic procedures to achieve the highest level of esthetics. Ceramic restorations, specifically porcelain restorations made without any metal, are referred to as "esthetic restorations".[1] The search for high-resistance ceramics to replace the metal in metal-ceramic restorations started at the close of the twentieth century and has not yet come to a conclusion. Since 1960, zirconia ceramics have been in use. Dental researchers have been interested in its promising in vitro qualities since the beginning, and its usage has significantly expanded during the past ten years. Its mechanical resilience, chemical and dimensional stability, toughness, and an elastic modulus on par with stainless steel are its main advantages for usage as a biomaterial.[2] The outstanding mechanical qualities of transformation-toughened zirconia (TTZ), in combination with the CAD/CAM fabrication process, which enabled the production of large and complex restorations with high accuracy and success rates, are the primary reasons for their clinical success and popularity.[3] As zirconia is becoming increasingly popular, it should be remembered that some forms of zirconia may be susceptible to aging and that processing conditions can play a crucial role in the low temperature degradation (LTD) of zirconia. Dental zirconia haven't yet shown any clinical evidence of LTD, but the mixture of lower-grade powders, high sintering temperatures, and close

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***Corresponding Author**

Dr Binita Pathak, Assistant Professor
Department of Prosthodontics, Nepal Medical College, Jorpati, Kathmandu, Nepal
Email: drbinitapathak@gmail.com
Phone No.:9851186112

contact with mouth fluids has the ability to start this slow yet autocatalytic phenomena.[4]

Crystallography and phase transformation in zirconia ceramics

At standard conditions of pressure and temperature, zirconia is monoclinic (m). The material changes structure as the temperature rises, first becoming tetragonal (t) above 1170 °C and then becoming cubic (c) over 2370 °C.[5,6] Bulk zirconia develops cracks as a result of the reversible tetragonal-to-monoclinic (t-m) phase transformation, which is followed by an increase in volume (3-5%) upon cooling. The considerable volume changes brought on by these transformations upon cooling render the pure material unsuitable for applications requiring a solid structure. By alloying tetragonal zirconia with different oxides including CaO, MgO, Y_2O_3, it is possible to stabilize tetragonal zirconia at normal temperature and prevent this reversible t-m transformation. With * denoting metastability, these low valence oxides encouraged the creation of more symmetric c* and t* lattice structures.[5] By doing this, the beneficial mechanical properties of the tetragonal phase are maintained and the stresses associated with the t-m phase transformation are reduced. It is possible to create a microstructure during cooling that includes lens-shaped "precipitates" of tetragonal Zirconia in cubic grains of zirconia with carefully controlled chemical additives and heat treatments.[7]

Forms of transformation toughened zirconia

Three different types of materials are developed as a result of the t-m transformation in zirconia (Table 1). These three toughened microstructures have different origins and specifics for stabilizing the t phase. All three materials undergo t stabilization, and the martensitic t-m transformation contributes to toughness.[5,8]

1. **Dispersion-toughened ceramics**

   This group of ceramics involve zirconia particles dispersed in another matrix. For instance, ZrO_2 are dispersed in alumina (Al_2O_3) and mullite ($3Al_2O_3.2SiO_2$) to form ZrO_2-toughened alumina (ZTA)and ZrO_2-toughend mullite (ZTM).[9] Here, the t phase's stability at room temperature is primarily achieved by particle size, particle shape, and particle position. In-Ceram Zirconia (Vita Zahnfabrik), which is an interpenetrating composite of 30% glass and 70% polycrystalline ceramic composed

Table 1: Forms of transformation-toughened zirconia.

Transformation-Toughened Zirconia
1. Zirconia (dispersed phase) toughened ceramics; e.g., ZTA (alumina), ZTM (mullite) • Dental example: In-Ceram zirconia (Vita Zahnfabrik)
2. Partially stabilized zirconia (PSZ; e.g. Ca-PSZ, Mg-PSZ, Y-PSZ) • Lenticular (lens shaped) tetragonal precipitates in a cubic matrix • Dental example: Denzir-M (Dentronic AB)
3. Tetragonal zirconia polycrystals (TZP; e.g. Y-TZP, Ce-TZP • Nominally 98% tetragonal, fine grain size • Dental examples: DC Zirkon (DCS Precident, Schreuder & Co) Cercon (Dentsply Prosthetics) Lava (3M ESPE) In-Ceram YZ (Vita Zahnfabrik)

of Al_2O_3:ZrO_2 in a vol.% ratio of roughly 70:30, is the only commercial example of a dispersion-toughened ceramic in dental material.

2. **Partially stabilized zirconia (PSZ)**

   These materials are among the toughest of the TTZ with a complex microstructure. These ceramics contain stable c-ZrO_2 in a matrix with intra-granular t-ZrO_2 precipitates. Dopants such as CaO, MgO etc are used but in lower concentration than required for full stabilization of c-ZrO_2. Due to the materials' deliberate lack of full stabilization, it is termed "partially stabilized zirconia" (PSZ).[9] Commercial example is Mg-PSZ appears to be available as a dental ceramic (Denzir-M, Dentronic AB, Sweden).[10]

3. **Single-phase, polycrystalline (t-ZrO2)**

   Fine grain zirconium oxides with low concentrations of stabilizing Y_2O_3 could retain up to 98% of the metastable t phase. To allow each grain to change instead of just the precipitates, every crystallite or grain in the material is kept in this state in tetragonal form until room temperature. This material is referred to as tetragonal Zirconia polycrystal (TZP).[11] By changing the yttria dopant concentration in yttrium cation-doped tetragonal zirconia polycrystals, the trend toward enhanced phase stability with smaller t-ZrO_2 particle size may be reversed (3Y-TZP). One commercial example is nano-scale Ce-TZP with 20% Al_2O_3 (Nanozir), is investigated as a dental ceramic.[12]

Despite the fact that there are numerous varieties of toughened zirconia systems currently available, only three have been employed in dentistry. They are zirconia-toughened alumina (ZTA), magnesium cation-doped partly stabilized zirconia (Mg-PSZ), and yttrium cation-doped tetragonal zirconia polycrystals (3Y-TZP).[13] Yttrium-stabilized zirconia polycrystals make up the majority of the zirconia-based ceramic systems now utilized in dentistry (3Y-TZP).[8] These restorations are either processed through hard machining of fully sintered blocks or through soft machining of presintered blanks employing CAD-CAM technology and high temperature (1350–1550°C) sintering.[14]

Consequences of Transformation

Transformation toughening

Excellent mechanical characteristics are added to stabilized tetragonal zirconia by the stress-induced t-m transformation, which is also accompanied by a 4.5% volume increase.[5] This distinct characteristic causes the establishment of a transition zone that successfully increases toughness by concealing the crack tip and preventing further crack propagation. As a result of transformation, there are two main phenomena that occur: (1) enhanced resistance to the propagation of both small and long fractures; and (2) toughness that increases with crack length (referred to as R-curve behavior). The phrase "R-curve behavior" refers to a rise in toughness—a measure of resistance to crack growth during fracture extension.[8] A transformation zone that is initially connected to the crack tip and later transforms into a crack wake feature. Size of this zone and zone microstructure characteristics regulate toughening (grain size and microcracking, in particular).[15]

When compared to other all-ceramic core materials, this material's high fracture resistance is demonstrated by greater flexural strength (900–1000 MPa) and fracture toughness (5.5–7.4 MPa).[16]

The stable tetragonal phase of zirconia by any means strengthens and toughens the structure by a localised transformation to the m phase when tensile stresses develop at crack tips. The resulting volume expansion adjacent to crack tips produces a high local compressive stress around crack tips, which increases fracture toughness and inhibits the potential crack propagation.[5] This phenomenon of transformation toughening increases the flexural and tensile fracture resistance of stabilized zirconia and presumably the survival probabilities of zirconia based restorations. Although toughened ceramics are far less tough than metals (40–65 range for steels), they represent a vast improvement over conventional ceramics and glass. In comparison, conventional ceramics have relative fracture toughness in the 3–4 range and are therefore brittle like glass and transformation-toughened ceramics fall in the 6–15 range.[17] For linearly elastic brittle materials, the highest strength and highest toughness occur in the same material; this is not the case for transforming ceramics. As cracks grow from an initial size, transformation events create an incrementally increasing toughness.[18]Most of the highest toughness ceramics (especially high Mg-PSZ) demonstrate non-linear, non-elastic yielding prior to failure.[19]

The expense of production of toughened ceramics is high. Despite their excellent qualities (high strength, toughness, and reduced brittleness), they have not found widespread use. Hence, they won't replace their metallic equivalents until they exhibit performance characteristics that save money, such as improved operating temperature or much longer lifetime.

Another difficulty is creating strong ceramic microstructures that can only remain stable at high temperatures. The force that propels the phase shift in TTZ lessens and eventually vanishes as temperature rises. This material consequently loses its toughness.[17]

Cyclic fatigue of TTZ

During cyclic loading, TTZ lifetimes are found to be less than they would be under equivalent static loading. Crack growth rates under cyclic conditions can be 7 orders of magnitude higher than for chemically assisted (water-enhanced) crack growth at equivalent crack-tip stress intensities.[5,20] It is also found that for small crack i.e. natural flaw size range (1) crack growth rates are more than that of long cracks at equivalent applied stress intensities and (2) that crack extension occurs at stress intensities below the threshold for long-crack growth.[5,21]

Low temperature degradation of 3Y-TZP

The less desirable quality of zirconia, its vulnerability to low temperature degradation (LTD) is a result of questionable stability of toughened zirconia at elevated temperatures. Kobayashi was the one who first noted this occurrence.[22] On the other hand, due to this metastability, zirconia is prone to ageing in the presence of water.[23] The metastable tetragonal phase to the more stable monoclinic phase is shown to slowly change in surface grains in a humid environment at relatively low temperatures (150-400 °C). On the surface of polycrystalline zirconia, isolated grains often serve as the initial sites of LTD, which later advance toward the bulk of the material.[5] Factors that influences tetragonal zirconia's stability is likely to encourage low temperature deterioration. These factors include grain size,[5] stabilizer content,[24] residual stress levels,[25] and even the presence of cubic phase.[26] Every step of the fabrication process of zirconia ceramics (sintering temperature and duration determine grain size, amount of cubic phase, and yttrium segregation) has to be carefully controlled to prevent LTD.[27] The effects of the LTD process on zirconia's long-term performance or aging are related to (a) roughening, which will result in increased wear, and (b) microcracking, which will result in grain pull-out and generation of particle debris as well as potentially premature failure when the microcracked, damaged zone reaches the critical size for slow crack growth to proceed.[5] For the first time, Haraguchi et al. reported on two instances of phase transformation-related surface degradation (roughening and microcracking).[28] Since the late 1980s, 3Y-TZP has been used to create the femoral heads for total hip replacement prostheses, but since then, its use in orthopedic surgery has decreased by more than 90%, largely because of a string of failures that started in 2001.[29] The 400 failure examples in 2001 have also demonstrated that the ISO standard has to be changed, at the very least to account for the aging issue.[30]

Conclusion

The well-known "transformation toughening" phenomenon in zirconia, which results in a significant increase in mechanical characteristics particularly fracture toughness is caused by the change under stress of metastable tetragonal zirconia into monoclinic phase (PSZ, TZP). Zirconia has some degrading restrictions, though. The fundamental reason for degradation is the phase transformation that the physiological medium of the human body causes. Till now clinical evidence of LTD is not evident in dental zirconia, but the mixture of lower-grade powders, high sintering temperatures, and close contact with mouth fluids increases the chance of LTD. Therefore, zirconia ceramics must be carefully fabricated, with each step of the process (sintering temperature and duration influence grain size, amount of cubic phase, and yttrium segregation). In light of how zirconia femoral heads performed in orthopedics in the past, further study and careful monitoring of in vivo zirconia use are required.

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