



Zirconia based ceramics, some clinical and biological aspects: Review



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ABSTRACT

Improved material strength, enhanced esthetic and high biocompatibility give Zirconia ceramic a great possibility to be used for a wide range of promising clinical applications. This review presents the different types of zirconia materials available for dental application, the effect of machining procedures on these materials, the esthetic of zirconia ceramics and bonding of the veneering ceramics in addition to the biologic properties of these new materials.

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1. Introduction

The Stone Age and Bronze Age were named for the materials that dominated these major historical periods. Consequently, the modern era, which is encountering an ever-increasing assortment of ceramic materials for industrial or biomedical use, could be characterized as the “Ceramic Age”. Ceramic materials that specially developed for medical and dental use are termed bio-ceramics. Over the last decade, zirconia technology has encouraged a rapid development of metal free dentistry that may provide high biocompatibility, enhanced esthetics and improved strength [1].

The name “Zirconium” comes from Arabic word “Zargon” which means “golden in color” which in turn comes from the two Persian words Zar (gold) and Gun (color). Zirconium dioxide (ZrO_2) was accidentally discovered by a German chemist his name is Martin Heinrich Klaproth in 1789 while he was working with certain procedures that involved the heating of some gems [2]. Subsequently, Zirconium dioxide was used as rare pigment for a long time. In late sixties the progress of research, the use of zirconium as biomaterials was refined. The first use of zirconium oxide (ZrO_2) for medical purposes was made in 1969 in orthopedic as a new material for hip head replacement instead of titanium or alumina prostheses [3].

Zirconium (symbol Zr) is a transition metal element, atomic number 40, atomic weight 91.22, density of 6.49 g/cm³, a melting point of 2,128 K (1855 °C or 3371 °F) and a boiling of 4,682 K (4409 °C or 7968 °F) and lustrous with exceptional corrosion resistance. Pure zirconium exists in crystalline form as a white and ductile metal and in an amorphous form as a blue black powder. Zirconium is ranked 18th in abundance among the element in earth’s crust, however, this element does not occur in nature in a pure state but only in conjugation with silicate oxides ($ZrO_2 \cdot xSiO_2$) or as a free oxide (ZrO_2) [4-7]. Zirconium Dioxide (ZrO_2) is a white crystalline oxide of zirconium found in the minerals baddeleyite (ZrO_2) and zircon (ZrO_2).

Zirconium oxide crystals can be categorized into three crystallographic phases: the cubic phase (C) in the form of straight prism with square side, the tetragonal phase (T) in the form of a straight prism with rectangular sides, and the monoclinic phase (M) in the form of a deformed prism with parallelepiped sides. The cubic phase is stable above 2370 °C and with moderate mechanical properties, the tetragonal phase is stable between 1170 °C and 2370 °C with improved mechanical properties, and the monoclinic phase, which is stable at room temperature up to 1170 °C, with lower mechanical properties and may contribute to a reduction of the ceramic particles cohesion [8-10].

These lattice transformations are martensitic, characterized by being diffusionless (i.e. involving only coordinated shifts in lattice positions versus transport of atoms), occurring athermally implying the need for a temperature change over a range rather than at a specific temperature and, involving a shape deformation [4]. This

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transformation range is bounded by the martensitic start (Ms) and martensitic finish temperatures. Volume changes on cooling associated with these transformations are very crucial and substantial so it results in a pure material that is unsuitable for any applications requiring an intact solid structure. This change is about 2.31% in case of C→T transformation and approximately 4.5% on cooling from T to M [5].

1.1. Phase transformation

At ambient pressure, unalloyed zirconia can be found in three crystallographic forms depending on the temperature. At room temperature and upon heating up to 1170 °C, it is monoclinic. At temperature between 1170 and 2370 °C it is tetragonal and above 2370 °C and up to the melting point it is cubic.

Upon cooling, the transformation from the tetragonal (t) phase to the monoclinic (m) phase is characterized by a substantial increase in volume (about 4.5%), sufficient to lead to catastrophic failure, sufficient to lead to catastrophic failure. This transformation begins at 950 °C and is reversible [11].

Garvie et al. in their important paper "Ceramic Steel" explained the best method to use phase transformation of zirconia to improve the mechanical strength and toughness of this type of ceramics. They stated that tetragonal phase precipitates that are finely dispersed within the cubic matrix were able to be transformed into the monoclinic phase when the constraint exerted on them by the matrix was relieved by a crack propagated within the matrix. The stresses resulted from this phase transformation (into a larger size phase) will act in opposite direction to the stress fields that initiate and promotes crack propagation. Such mechanism will result in enhancement in fracture toughness as the energy associated with crack propagation is dissipated both in both phase transformation and in overcoming stresses due to the volume expansion. This process is known as transformation toughening [6].

It was discovered that such strong ceramic could result from alloying of pure zirconia with lower valance oxides, such as MgO, La₂O₃, CaO and Y₂O₃, and this decreased the amount of strained (m) phase at room temperature and favored more symmetric (c) and (t) lattice structures. These (c) and (t) phases are analogous to those in pure zirconia but have dopant ions substituted on Zr⁴⁺ sites and have a fraction of oxygen sites vacant to retain charge neutrality [7].

2. Different types of zirconia ceramics materials available for dental applications

2.1. Yttrium tetragonal zirconia polycrystals (3Y-TZP)

Since the late eighties, biomedical grade zirconia usually contains 3mol% yttria (Y₂O₃) as a stabilizer (3Y-TZP) [8]. 3Y-TZP has been used to manufacture femoral heads in total hip replacement prostheses, but its use in orthopedic surgery has been reduced by more than 90%, mostly due to a series of failures that occurred in 2001 [2]. Also 3Y-TZP is available in dentistry for the fabrication of dental crowns and fixed partial dentures. It has superior mechanical properties as its flexural strength reaches 900–1200 MPa and fracture strength about 9–10 MPa(m)^{1/2} [12–13].

The restorations are processed either by soft machining of presintered blanks or by hard machining of fully sintered blocks. The mechanical properties of 3Y-TZP are strongly affected by its grain size [9]. Above a critical grain size, 3Y-TZP is less stable and more susceptible to spontaneous t→m transformation (grain sizes (<1 μm) are associated with a lower transformation rate). In the same time, below a certain grain size about 0.2 μm, the transformation is not possible, leading to reduced fracture toughness [10]. Consequently, the sintering conditions (through which the

grain size is controlled) have a strong impact on both stability and mechanical properties of the final product. Higher sintering temperatures and longer sintering times lead to larger grain sizes [11]. Currently available 3Y-TZP for soft machining of dental restorations utilizes final sintering temperatures between 1350 °C and 1550 °C depending on the manufacturer.

Restorations produced by soft machining are sintered at a later stage (i.e. following the forming steps), this process prevents the stress-induced transformation from tetragonal to monoclinic and leads to a final surface virtually free of monoclinic phase unless grinding adjustments are needed or sandblasting is performed. Most manufacturers of 3Y-TZP blanks for dental applications do not recommend grinding or sandblasting to avoid both the t→m transformation and the formation of surface flaws that could be detrimental to the long-term performance, despite the apparent increase in strength due to the transformation-induced compressive stresses. In contrast, restorations produced by hard machining have been shown to contain a significant amount of monoclinic zirconia. This is usually associated with surface microcracks, higher susceptibility to low temperature degradation (LTD) and lower reliability [14].

2.2. Glass-infiltrated zirconia-toughened alumina (ZTA)

Another approach to advantageously utilize the stress induced transformation capability of zirconia is to combine it with an alumina matrix, leading to a Zirconia-Toughened Alumina (ZTA) [15]. One commercially available dental product, In-Ceram Zirconia (Vident™, Brea, CA), was developed by adding 33 vol% of 12mol% ceria stabilized zirconia (12Ce-TZP) to In-Ceram Alumina [16]. In-Ceram Zirconia can be processed by either slip casting or soft machining. Initial sintering takes place at 1100 °C for 2 h, followed by glass infiltration of this porous ceramic composite.

One of the main advantages of the slip-cast technique is the very limited amount of shrinkage. However, the amount of porosity is greater than that of sintered 3Y-TZP and comprises between 8 and 11% [17]. This explains the lower mechanical properties of In-Ceram Zirconia when compared to 3Y-TZP dental ceramics [12]. On the other hand Ce-TZP ceramics usually exhibit better thermal stability and more resistance to low temperature degradation than Y-TZP under similar aging conditions [18].

In-Ceram Zirconia for soft machining is thought to exhibit better mechanical properties compared to slip-cast ceramic due to more consistent processing. Conversely, Guazzato et al. reported a significantly higher flexural strength for In-Ceram Zirconia processed by slip-casting (630 ± 58 MPa) compared to the soft machined material (476 ± 50 MPa) [19]. Also the fracture toughness varied between 3.1 and 4.61 MPa(m)^{1/2} for both materials [20]. The two materials exhibited similar microstructure characterized by large alumina grains (6 μm long, 2 μm wide) together with clusters of small zirconia grains (less than 1 μm in diameter). The crack patterns were consistently transgranular for ZrO₂ and intragranular for Al₂O₃. An advancing crack results in the tetragonal to monoclinic transformation. The associated increase in volume creates microcracks in the alumina matrix surrounding the transformed particle. The toughness is therefore enhanced by microcracking [21].

2.3. Magnesia partially stabilized zirconia (Mg-PSZ)

Although a considerable amount of research has been focused on magnesia partially stabilized zirconia (Mg-PSZ) for possible biomedical applications, this material has not been successful. This mainly due to many causes as the presence of porosity, the large grain size (30–60 μm) that can cause wear of the opposing

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