



Zirconia Ceramics

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ABSTRACT

Zirconia ceramics have become popular among other dental ceramics thanks to their biological, mechanical, optical, and aesthetic properties. CAD/CAM (computer-aided design/ computer-aided manufacturing) technology improvement has played a vital role in the increased popularity of zirconia ceramics; easy computer manipulation significantly expanded the possibility of using different types of restorations. Zirconia ceramics have a broad spectrum of indications in prosthetic dentistry, from simple restorations to complex structures supported by dental implants. A good orientation in the classification, features, and manipulation of zirconia ceramics is the main key to success.

KEYWORDS

zirconia ceramics; adhesion; biocompatibility; production of zirconia

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Received: 19 June 2024

Accepted: 25 August 2024

Published online: 22 October 2024

Acta Medica (Hradec Králové) 2024; 67(2): 39–45

<https://doi.org/10.14712/18059694.2024.18>

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INTRODUCTION

Prosthetic dentistry is undergoing a paradigm shift from metal-ceramic restorations to all-ceramic restorations (1). In order to replace metal-ceramic restorations, all ceramic restorations have been developed. Zirconia has differentiated itself among all dental ceramics as a versatile and promising material due to its biological, mechanical, and optical properties. CAD/CAM (computer-aided design / computer-aided manufacturing) technology has played a significant role in producing zirconia restorations (1, 2).

The name of the metal, Zirconium, originates from the Arabic and Persian origin, "Zargon", meaning "golden in color" (3, 4). Zirconia, the metal oxide ZrO_2 , was first discovered in 1789 by German chemist Martin Heinrich Klaproth. In 1824, Swedish chemist Jöns Jakob Berzelius managed to isolate it for the first time (2–6). In 1975, Gravier et al. proposed a model to rationalize the desirable mechanical properties of zirconia, which has been called "ceramic steel" (7).

PHASES OF ZIRCONIA

Zirconia has a feature known as polymorphism, characterized by the atoms' geometric arrangement in different ways and different crystallographic structures. Zirconium oxide crystals are organized in crystalline structures, which can be divided into three crystallographic phases. The cubic (C) is in the form of a straight prism with square sides, the tetragonal (T) is in the form of a straight prism with rectangular sides, and the monoclinic (M) is in the form of a deformed prism with parallel sides (2, 5, 8).

Pure zirconia is in the monoclinic phase, which is stable at room temperature up to 1170 °C. Between 1170 °C and 2370 °C, tetragonal zirconia is formed, while cubic zirconia occurs above the temperature of 2370 °C until the melting point of 2716 °C (9, 10). Moreover, there are noticeable alterations in volume, which are related to this phase transformation. A significant volume increase of about 4.5% occurs along with the transformation from the tetragonal phase to the monoclinic phase during cooling, which creates a surface compressive stress within the material; thereby, flexural strength is increased (11). Moreover, phase change affects the integrity of the material. As a result, aging becomes more likely. (11, 12, 13).

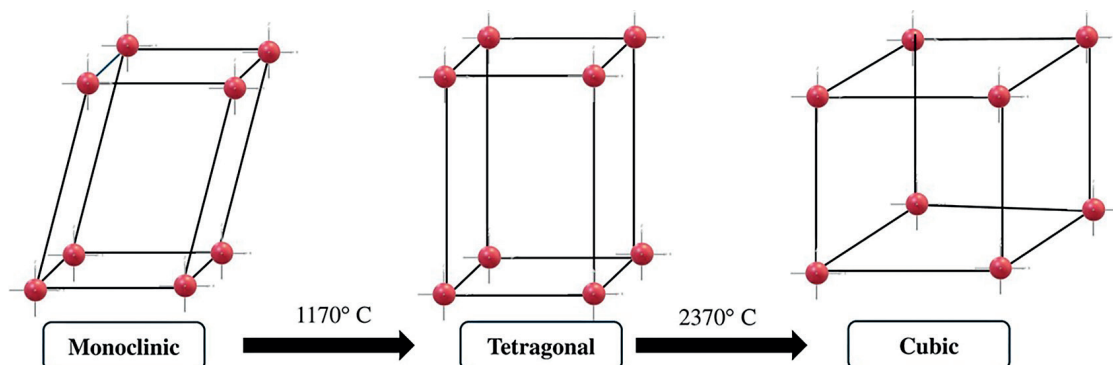


Fig. 1 Phases of zirconia.

STABILIZED ZIRCONIA

Stabilized zirconia is a combination of zirconia polymorphs obtained at room temperature by adding stabilizers (4). Passerini et al. (14) and Ruff et al. (15) found that the tetragonal and cubic phase could be stabilized at room temperature thanks to alloying zirconia with metal oxides such as CaO, MgO, Y_2O_3 , CeO_2 , Er_2O_3 , Eu_2O_3 , Gd_2O_3 , Sc_2O_3 , La_2O_3 and Yb_2O_3 (16). Amongst them, yttrium oxide (Y_2O_3) is the primary stabilizer used in general medicine and dentistry. The stabilization principle is based on replacing Zr^{4+} cations with Y^{3+} cations in the ZrO_2 crystal structure. Zr^{4+} is a tetravalent ion, while Y^{3+} is a trivalent ion. Replacing a tetravalent ion with a trivalent ion will cause one oxygen anion to remain free in the crystal structure. This free oxygen anion is called an oxygen vacancy, and it subsequently prevents the phase transformation (8, 17).

The amount of yttrium oxide has an influence on stabilization (17, 18). When the amount of yttrium oxide is over 8 mol%, the cubic phase becomes stable at room temperature, and it is called cubic stabilized zirconia (CSZ). When yttrium oxide is 3 to 8 mol%, both cubic and tetragonal phases are mixed at room temperature; it is called partially stabilized zirconia (PSZ). When the yttrium oxide is about 3 mol%, tetragonal phases are almost 100% at room temperatures. In this case, it is called tetragonal zirconia polycrystal (TZP) (18).

BIOCOMPATIBILITY

Zirconia's biocompatibility has been thoroughly assessed, and studies have proven its biocompatibility (12, 19, 20). No study found a difference or identified any modifications in the biological health of the soft and hard tissues around the zirconia-based restorations (13, 21–25).

PHASE TRANSFORMATION TOUGHENING (PTT)

The adsorbed energy can break some of the atomic bonds in a polycrystalline structure under the influence of mechanical, thermal, or combined stresses, leading to tetragonal crystals changing into a more stable monoclinic phase (metastability). Phase Transformation Toughening is the term used to describe this spontaneous and irreversible

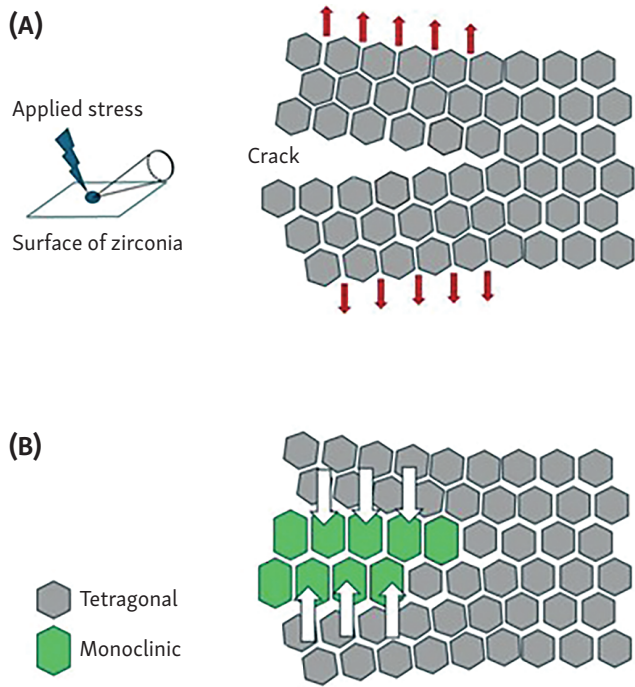


Fig. 2 Crack propagation and phase transformation toughening.

change. A crack can occur on the surface of a material if there is enough force. At that moment, the forces from the initial impulse act perpendicular to the crack surface, and the crack is spread until the forces causing crack expansion are no longer sufficient. In metastable tetragonal zirconia, these forces lead to local destabilization of the tetragonal phase, which results in tetragonal to monoclinic phase transformation. This creates a zone with a mixture of tetragonal and monoclinic phases. This phase transformation is related to volume expansion, which causes the crack to tighten and close (13, 17, 26).

From a technological point of view, PTT has been promoted as a significant improvement since it enables zirconia’s self-repairability within the material (13, 26, 27).

LOW-TEMPERATURE DEGRADATION (LTD)

Low-temperature degradation (aging) is characterized by spontaneous irreversible transformation change from tetragonal to monoclinic phase, which occurs along the

time at room temperature. LTD is a multifactorial phenomenon influenced by several variables, such as temperature, crystal dimension, surface defects, percentage and distribution of stabilizing oxide, wetness, and mechanical stress. Explicitly, the last two factors are the common causes of zirconia aging. LTD is known to cause worsening of zirconia’s mechanical properties, contributing to the onset of microcracks and toughness reduction (13, 26, 28–30).

THE MANUFACTURING PROCEDURE FOR ZIRCONIA

Zirconia restorations can be fabricated by CAD/CAM milling based on two different production methods: soft machining of pre-sintered or hard machining of fully sintered zirconia or additive manufacturing (13, 32).

Soft machining is the most used method based on the milling of pre-sintered zirconia blanks (Green state) made by cold isostatic pressing, a mixture of zirconia powder, stabilizing oxides, and a binding agent (13). With this method, zirconia is very homogenous, and the milling procedure is easier. Production time, machinery wear, and the number of surface defects are decreased. However, 20–30% of oversizing is required for this milling process due to sintering shrinkage (11, 13, 31).

Hard machining is done by milling fully sintered zirconia produced by hot isostatic pressing at 1400–1500 °C (2, 4). This method eradicates the shrinkage problem after milling since there is no need for oversizing (11, 31). Due to the high hardness and low machinability of fully sintered zirconia, a longer milling time is required. Moreover, zirconia may undergo monolithic phase change after the hard machining process because of mechanical stress, working burs friction, and overheating, which can affect the mechanical properties of zirconia (11–13, 31).

Additive manufacturing is a technique that describes successive adding and joining materials, whether in powder or liquid form, layer by layer of fabricate prosthesis using a 3D printer. This approach comes in many different forms such as material extrusion, powder bed fusion, plaster-based 3D printing, laminated item production, stereolithography, and polyjet 3D printing. The advantages of this technology are extensive, offering almost limitless design possibilities, the ability to create complex structures in a single production cycle, user-friendly operation, and the flexibility to customize colors and materials for

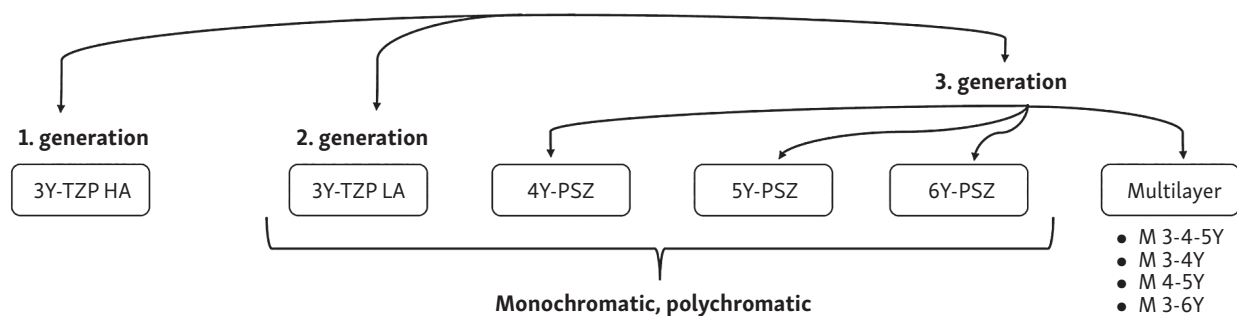


Fig. 3 Zirconia classification.

different sections of the print. However there are challenges related to this method such as the high costs of the required machines and software, limitations on the types of materials that can be used, and high sensitivity to inconsistencies in the input data (32–35).

ZIRCONIA CLASSIFICATION

1. First generation of zirconia ceramics 3 mol% yttria-stabilized tetragonal zirconia polycrystalline with high alumina content (3Y-TZP HA)

The first zirconia ceramics used for dental applications was 3Y-TZP HA, conventional zirconia, which contains 0.25–0.5 wt% alumina and 3 mol% Y_2O_3 (1) and 100% tetragonal crystals. These types of ceramics began to be used for their high toughness and flexural strength, which is bigger than 1GPa (2, 5, 37). Their indications are limited due to a lack of aesthetics (10). They display considerable opacity due to their natural birefringence of noncubic zirconia, which leads to light scattering from grain boundaries and pores (10). As a result, they are mainly indicated as a framework for porcelain-veneered crowns and fixed dental prostheses in the posterior region (10, 36, 37).

2. Second generation of zirconia ceramics 3 mol% yttria-stabilized tetragonal zirconia polycrystalline with less alumina content (3Y-TZP LA)

The composition of these types of zirconia has been changed to enhance translucency. Alumina content was decreased to less than 0.05 wt%, and the sintering temperature was increased (10, 31, 37). In this way, porosity was eliminated, and alumina grains were reduced, and within the zirconia, the latter were repositioned, which occurs on grain boundaries of zirconia (31). Therefore, high light transmittance and high strength were achieved together (31). On the contrary, this type of zirconia ceramic contains metastable tetragonal zirconia, which limits translucency (17). Due to esthetic reasons, they are not used in the anterior region. However, they are used for single crowns for posterior regions and long-span bridges (17, 38).

3. Third generation of zirconia ceramics (4Y-PSZ, 5Y-PSZ, 6Y-PSZ)

The desire for more translucent zirconia ceramic emerged because of the esthetic inadequacy of the second generation of zirconia ceramic compared to glass ceramics in terms of translucency (31, 33). This led to the development of the third generation of zirconia ceramic by increasing yttria content up to 4 mol%, 5 mol%, or 6 mol% (10, 18, 31, 37). This zirconia, when compared to the first and second generation, contains not only a tetragonal phase but also a cubic phase in the proportion of up to 50 % (31). This significantly enhanced translucency; on the contrary, strength and toughness were reduced since cubic zirconia is not capable of transformation toughening (10, 18, 39). However, the volume of cubic crystals is bigger than that of tetragonal ones, which indicates that light scattering is less intense at the grain boundaries and porosity, which makes zirconia more translucent (31). Because of high

translucency and lack of toughness, their indications are limited to anterior crowns and veneers (18).

Although the translucency of zirconia ceramics has improved over the years, they are monochromatic. So as to produce restorations that mimic the natural tooth appearance, polychromatic and multi-layered zirconia ceramics were developed (40). In polychromatic zirconia, among the different layers, the same amount of yttria content and cubic phase is observed (40). The main difference is pigment composition, which makes the difference in shade, not in translucency (41). A different approach has been used to produce multi-layered zirconia, where the same material contains different compositions of yttria and microstructures. The incisal layer is more translucent because it has more yttria content. However, increased yttria concentration reduces mechanical properties. The cervical layer is not as translucent as the incisal layer due to a lower concentration of yttria, but due to this, the cervical layer has higher mechanical strength than the incisal region. Between those two layers, there is a transition layer, which is a mixture of various types of yttrium oxide (40–43). Thanks to the unique property of transmission of shade and translucency, they have a broad spectrum of indications, including anterior crowns and veneer, with high esthetic expectations (18, 40).

ADHESION TO ZIRCONIA AND CEMENT SELECTION

Zirconia lacks an amorphous glassy matrix; because of this, it cannot be pre-conditioned by using hydrofluoric acid etching (13, 44). In order to achieve good adhesion to zirconia ceramics, several methods were suggested (44, 45). However, the first step for adhesion is to create a contaminant-free surface (45). This is carried out by polishing with papers, sprays, milling cutters of silicon carbide ranging between 220 to 4000 grit, ultrasonic cleaning, or using different solutions such as water, alcohol, acetone, ethanol, and isopropanol with a usage time between 1 to 10 minutes (44, 45). Special cleaning agents are recommended to use in order to eliminate surface contamination in the oral cavity after try-in (46, 47). Two commercial brands

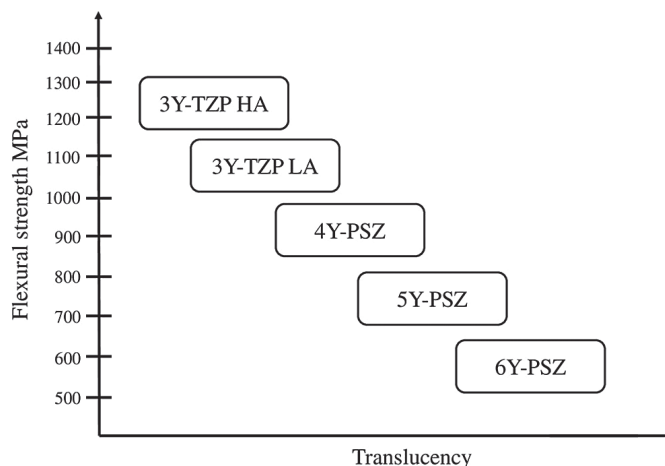


Fig. 4 Flexural strength and translucency.

are mostly used: Ivoclean and Katana cleaner. According to the manufacturer's scientific information, the effect of Ivoclean in removing saliva contaminants might be explained by the balance of chemical reactions, in which the direction of the solution balance relies on the concentration of the reaction partner. With a higher amount of one reactant, binding to that reactant is much more likely than to any other less common reactant. This material is composed of an alkaline suspension of zirconia particles; because of this, Ivoclean can be applied only extraorally before cementation. Phosphate contaminants from saliva on the surface of ceramic restoration will bind based on the size and concentration of these zirconia particles in Ivoclean, thus supporting the cleaning action on the zirconia surface (46, 47–49). Katana Cleaner is an acidic solution composed of 10-MDP (10-methacryloyloxydecyl dihydrogen phosphate) salts. Thanks to 10-MDP salts, Katana Cleaner can be used intraorally and extraorally. This chemical can neutralize fatty acids, adjust and buffer pH, and dissolve oils and other components that are not water-soluble. The hydrophobic part of the 10-MDP salt forms a bond with contaminants. In contrast, the hydrophilic part of the 10-MDP salt does not form bonds; thus, the contaminants can be removed by rinsing with water (46, 47, 50).

Sandblasting is a process that uses the energy discharged by the bounce of alumina particles that are generated by a high-speed source (45, 51). With this method, surface energy, roughness, wettability, and appearance of a hydroxyl group, which will create a bond between primer and cement, are increased (44). On the contrary, sandblasting can cause surface deformation, defects, and cracks; consequently, the mechanical properties of zirconia might be jeopardized (52). For this reason, it is essential to carry out this process based on adequate parameters regarding pressure, distance from the source, and particle size (44, 45, 53). These parameters vary in particle size from 30 to 110 μm , pressure from 0.5 to 4 bar, and distance from the source from 10 to 20 mm (44). However, 2 bar pressure and 50 μm particle size are recommended (54, 55–57).

Tribochemical silica coating is another approach to increase adhesion to zirconia (44, 45). It is a sandblasting process done by blasting alumina particles covered by silica onto the zirconia surface. (44, 45, 58). This process creates an uneven surface while fusing silica into a zirconia structure, allowing the application of silane as a coupling agent (44, 45, 59). This leads to the appearance of chemical chains of siloxane between cement and residual silica, increasing adhesion and improving the wettability and surface energy of zirconia (44). Tribochemical silica coating is done by two methods: the Rocatec system is based on the traditional sandblasting process followed by the use of silica-coated alumina particles (110 μm). Another system is the Cojet system, which uses alumina particles (50 μm) covered by silica, and the Cojet system can be performed at chair side (60). The pressure used with these systems ranges from 0.8 to 4 bar. However, crack propagation is observed when used at high pressure because a pressure of 1.8–2.8 bar is recommended to achieve a significant increase in adhesion (44, 51, 56).

Fusion sputtering, as described by Aboushelib (61), is a technique for creating a rough zirconia surface by spraying an air-water jet carrying microscopic zirconia particles (4–12 μm) on non-sintered zirconia (61, 62). After the sintering process, these microscopic non-sintered particles fuse to underlying zirconia. Therefore, surface area and surface roughness is increased (61–63). 3 bar, 7–12 μm particle size, 20 mm distance from a target, and 5-second application time were advised to obtain adequate adhesion to zirconia (62, 64).

Selective infiltration etching is another method to modify the zirconia surface (44, 45). Zirconia is covered by silica-based material, which diffuses within the zirconia structure at 960°C. Afterward, hydrofluoric acid is applied for about 10 minutes to dissolve the glass component. In this way, the zirconia surface becomes roughened (64, 65, 67, 68).

Lasers were also used to alter the surface of zirconia (44, 45, 63). The goal of laser application is to create a rough surface and increase wettability, which will allow micromechanical interconnection with the resin (69). Several types of lasers (Er: YAG, Nd: YAG, Yb: YAG, CO₂) have been used with different parameters of power, energy intensity, distance, and duration (70–72).

The hot acid etching method relies on a controlled corrosion process and the metallic character of zirconium (60). Acid selectively etches zirconia, and it creates micro-retention areas on the surface by removing less arranged atoms (63, 72). Various acidic solutions have been suggested, such as phosphoric acid, nitric acid, and hydrofluoric acid (68–70).

Functional monomers are those that show reactive side-chain groups whose purpose is to synthesize more complex compounds (75). They contain at least one polymerizable and functional group (76). However, 10-MDP (10-Methacryloyloxydecyl dihydrogen phosphate), 4-META (4-methacryloyloxy ethyl trimellitate anhydride), 6-MHPA (6-methacryloyloxy ethyl phosphonacetate), 3-TMSPMA (3-(Trimethoxysilyl) propyl methacrylate), MAC-10 (11-methacryloyloxy-1,1-undecane dicarboxylic acid) are used. 10-MDP is currently the most popular functional monomer since it provides long-term reliable adhesion (44, 45, 76). 10-MDP has two terminal groups. In one terminal, there is phosphoric acid, which gives a reaction with zirconia and creates a phosphate – oxygen – zirconium bond. At the other end of the molecule, there is a vinyl group that has a role in copolymerization with resin. Between these two groups, a carbon chain, which is responsible for viscosity, rigidity, hydrophobicity, and solubility, stands (44).

For zirconia cementation, conventional and adhesive resin cements are indicated (77, 78). Conventional cements are indicated for full coverage zirconia restorations, considering the simple and less demanding procedure (77). Adhesive cements are used to achieve better marginal seals and improve retention and fracture resistance (77).

CONCLUSION

Zirconia ceramics have shown significant technological development over the past ten years, which has led to a

wide range of applications. Zirconia ceramics are the ideal choice of material for demanding restorations and highly aesthetic constructions thanks to the unique features of zirconia ceramics, such as strength, resistance to wear, resistance to corrosion, and aesthetic features.

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