An Overview on Zirconia

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Introduction

Structural ceramics have been improved and have become increasingly more popular in dentistry with an aim to replace the infrastructure of metallic dental prosthesis. Zirconia has emerged as a versatile and promising material because of its biological, mechanical and optical properties which accelerated its use in CAD/CAM technology for different types of prosthetic treatments.1

History

“Zirconium” (Zr) is a metal and the name comes from the Arabic word “Zargon,” which means golden in colour. Zirconium dioxide (ZrO₂) was accidentally identified by the German chemist Martin Heinrich Klaproth in 1789, while he was working with the heating of some gems.2

Zirconia has been used as biomaterial since the 1970s. It has been widely used as a hip replacement material and has been used in dentistry for crown and bridge applications since 2004. The development of zirconia as an engineering material was demonstrated by Garvie et al, who showed how to make the best of tetragonal to monoclinic phase transformation of partially stabilised zirconia (PSZ) improving mechanical strength and toughness of zirconia ceramics.2

Sources

The main sources of zirconium are Zirconate (ZrO₂-SiO₂, ZrSiO₄) and Baddelyite (ZrO₂).

The Zirconate is more abundant, but less pure, requiring significant processing to get zirconia. Baddelyte already contains levels of zirconia ranging from 96.5% to 98.5% and hence known as a source of extreme purity in obtaining zirconium metal and its compounds. Zirconium dioxide (ZrO₂) resulting from Baddelyte, which is also known as ZIRCONIA, is a coarse oxide that presents a monoclinic crystal structure at room temperature. However, the powder can be purified and processed synthetically at high temperatures, forming a cubic structure called CUBIC ZIRCONIA.1 Zirconium dioxide, or Zirconia is a white crystalline oxide of zirconium which has a high tensile strength, high hardness and corrosion resistance. Dental zirconia shouldn’t be confused with cubic zirconia used as diamond simulant. It also shouldn’t be confused with zirconium, which is lustrous, gray-white, strong transition metal, or zircon (also known as zirkon), which is zirconium silicate.

Uses:1

Zirconia based ceramics are routinely used in structural applications in engineering, such as in the manufact-
ture of cutting tools, gas sensors, refractories and structural opacifiers.

1. Along with niobium, zirconium is superconductive at low temperatures and is used to make superconductive magnets, which offer hope of direct large-scale generation of electric power.

2. Zirconium oxide (zircon) has a high index of refraction and is used as a gem material.

Crystallographic forms:

- Pure zirconia exists in three crystal phases at different temperatures.
  - Monoclinic: below 1170°C (low temperature)
  - Tetragonal: 1170°C - 2370°C (Intermediate temperature)
  - Cubic: above 2370°C (very high temperature)

Noticeable changes in volume are associated with these transformations a 5% decrease in volume when heated and conversely, a 3%-5% increase in volume during cooling process.

The tetragonal to monoclinic phase transition produces cracks in bulk zirconia samples and a reduction in strength and toughness. If one modifies the composition by doping with Mg, Ca, Sc, Y or Nd, the high temperature tetragonal phase can be stabilized at room temperature. The stability of single phase tetragonal zirconia is enhanced by highly soluble trivalent stabilizers such as yttria, which induce vacancies or tetravalent stabilizers such as ceria, which are oversized or undersized with respect to zirconium. Another possibility for stabilizing tetragonal phase at room temperature is to reduce the crystal size to less than 10nm. (Fig 1)

Transformation Toughening

The structural stabilization of zirconia by yttria results in a significant proportion of metastable tetragonal phase. This metastable tetragonal phase strengthens and toughens the structure by a localized transformation to the monoclinic phase when tensile stresses develop at crack tips.

The resulting volume expansion adjacent to the crack tips produces a high local compressive stress around the crack tips, which increase the localized fracture toughness and inhibits the potential for crack propagation. Many types of crack shielding processes are possible including micro cracking, ductile zone formation and transformation zone formation. (Fig 2)

Low temperature degradation (LTD) or aging:

One property of zirconium oxide that has not been...
well studied is the phenomenon of low-temperature degradation or “aging”. Water and non-aqueous solvents are involved in formation of zirconia hydroxides along a crack. This process accelerates expansion of the fracture and can result in reduced strength, toughness, and density, leading to failure of the restoration. (Fig 3,4,5)

**Key properties of zirconium oxide:**

- Use temperatures up to 2400°C
- High density
- Low thermal conductivity (20% that of alumina)
- Chemical inertness
- Resistance to molten metals
- Ionic electrical conduction
- Wear resistance
- High fracture toughness
- High hardness

**Types of zirconia blanks**

Three main types of zirconia blanks are available for use in clinical dentistry. Though they are chemically identical, they have slightly different physical properties (e.g., porosity, density, purity, strength), which may (or may not) be clinically relevant.

- Fully sintered or HIP type of zirconia
- Partially sintered zirconia
- Non sintered or green state zirconia.

**Fully sintered or hip type zirconia**

Hot Isostatic Procedure (HIP) is the sintering procedure of the material under high temperature and high pressures. These procedures reduce the porosity of the material and ensure high values of toughness and translucency of zirconium ceramics.

Examples include:
- DC-Zirkon (DCS Dental AG)
- Everest-ZH (KaVo).

**Partially sintered or non hip type of zirconia**

Both partially sintered zirconia, and non-sintered or “green state” zirconia should be considered together (partially sintered or non-HIP zirconia) due to the similar manufacturing and fabricating processes. Blocks of these types of materials are manufactured by utilizing a spray-dried zirconia powder that is then isostatically pressed and incompletely sintered. These materials remain softer than the HIP zirconia and are easier to mill. After milling, the zirconia is then sintered completely in a furnace at 1,350°C to 1,500°C to achieve its final shape, strength, and physical properties.

Examples include
- Lava (3M ESPE),
- Cercon (DENTSPLY Ceramco)
- Vita YZ (Vident)

Nobel Biocare’s Procera system: This process utilizes a slurry of zirconia oxide that is applied to an oversized die and then sintered. (Table 1)

**Types of zirconia ceramics available for dental applications**

- magnesium cation-doped partially stabilized zirconia (Mg-PSZ)
- yttrium cation-doped tetragonal zirconia polycrystals (3Y-TZP)
- zirconia-toughened alumina (ZTA)

**Tetragonally toughened zirconia (TTZ):**

The TTZ is an MgO partially stabilized zirconia often designated MgTTZ or MgPSZ consisting of uniformly dispersed tetragonal precipitates in larger cubic phase crystals (50-100µ).

The amount of MgO in the composition of commercial materials usually ranges between 8 and 10 mol%. 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. In addition to a high sintering temperature (between 1680°C and 1800°C), the cooling cycle has to be strictly controlled, particularly in the aging stage with a preferred temperature of 1100°C. Due to the difficulty of obtaining Mg-PSZ precursors free of SiO₂, 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 and a less stable material.

Denzir-M (Dentronic AB) is an example of Mg-PSZ ceramic currently available for hard machining of dental restorations. (Table 2)

**TZP (Tetragonal Zirconia Polycrystal) ceramics**

The addition of approximately 2%-3% of molybdenum (Y₂O₃) as a stabilizing agent in zirconia allows the sintering of fully tetragonal fine-grained zirconia ceramic materials made of 100% small metastable
tetragonal grains and known as Y-TZP. The restorations are processed either by soft machining of pre-sintered blanks followed by sintering at high temperature, or by hard machining of fully sintered blocks. 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 of fully sintered 3Y-TZP blocks have been shown to contain a significant amount of monoclinic zirconia. This is usually associated with surface micro cracking, higher susceptibility to low temperature degradation and lower reliability. Several authors have reported that annealing at 900 °C for 1 hr or relatively short heat treatments in the temperature range 900–1000 °C for 1 min induce the reverse transformation from monoclinic to tetragonal. This phenomenon was accompanied by the relaxation of the compressive stresses at the surface and a decrease in strength. The firing of veneering porcelain during the fabrication of dental restorations is therefore likely to promote the reverse transformation with the consequences listed above. The mechanical properties of 3Y-TZP strongly depend on its grain size. Above a critical grain size, 3Y-TZP is less stable and more susceptible to spontaneous t - m transformation whereas smaller grain sizes (<1 µm) are associated with a lower transformation rate. Consequently, the sintering conditions have a strong impact on both stability and mechanical properties of the final product as they dictate the grain size. Higher sintering temperatures and longer sintering times lead to larger grain sizes. (Fig 6) Table 3

Glass-infiltrated zirconia-toughened alumina (ZTA)¹

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)

One commercially available dental product, In-Ceram Zirconia (Vident™, Brea, CA), was developed by adding 33 vol% of 12 mol% ceria-stabilized zirconia (12Ce-TZP) to In-Ceram Alumina. In-Ceram Zirconia can be processed by either slip-casting or soft machining. Initial sintering takes place at 1100°C for 2 h, prior to this porous ceramic composite being glass-infiltrated. The glass phase represents approximately 23% of the final product. However, the amount of porosity is greater than that of sintered 3Y-TZP and comprises between 8 and 11%. This partially explains the generally lower mechanical properties of In-Ceram Zirconia when compared to 3Y-TZP dental ceramics. In-Ceram Zirconia for machining is thought to exhibit better mechanical properties due to more consistent processing compared to the slip-cast ceramic. Conversely, Guazzato et al. reported a significantly higher flexural strength for In-Ceram Zirconia processed by slip-casting (630 ± 58 MPa) compared to the machined material (476 ± 50 MPa). There was no significant difference in fracture toughness.⁶

Soft machining of pre-sintered blanks⁹, ¹⁰, ¹¹

Briefly, the die or a wax pattern is scanned, an enlarged restoration is designed by computer software (CAD) and a pre-sintered ceramic blank is milled by computer aided machining. The restoration is then sintered at high temperature. Several variations of this process exist depending on how the scanning is performed and how the large sintering shrinkage of 3Y-TZP (25%) is compensated for. Typically the 3Y-TZP powder used in the fabrication of the blanks contains a binder that makes it suitable for pressing. The binder is later elimi-

<table>
<thead>
<tr>
<th>Table 1: Fully Sintered Versus Partially Sintered Material</th>
</tr>
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<tbody>
<tr>
<td><strong>FULLY SINTERED</strong></td>
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<tr>
<td>More denser, less porous</td>
</tr>
<tr>
<td>Milling produces more heat causing surface and structural defects</td>
</tr>
<tr>
<td>Acceptable marginal fit</td>
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<tr>
<td>Expensive manufacturing process</td>
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</table>
ated during the pre-sintering step. The powders consist of spray-dried agglomerates (about 60 μm in diameter to much smaller crystals that are about 40 nm in diameter). The blanks are manufactured by cold isostatic pressing. The mean pore size of the compacted powder is very small in the order of 20–30 nm with a very narrow pore size distribution. The binder is eliminated during a pre-sintering heat treatment. This step has to be controlled carefully by manufacturers, particularly the heating rate and the pre-sintering temperature. If the heating rate is too fast, the elimination of the binder and associated burn out products can lead to cracking of the blanks. Slow heating rates are therefore preferred. The pre-sintering temperature of the blanks affects the hardness and machinability. These two characteristics act in opposite directions: an adequate hardness is needed for the handling of the blanks but if the hardness is too high, it might be detrimental to the machinability.

The temperature of the pre-sintering heat treatment also affects the roughness of the machined blank. Overall higher pre-sintering temperatures lead to rougher surfaces. The choice of a proper pre-sintering temperature is thus critical. The density of each blank is carefully measured so that the appropriate compensating shrinkage is applied during final sintering. Machining is better accomplished in two steps. A first rough machining is done at a low feed rate while the final fine machining is performed at a higher feed rate. Restorations can be colored after machining by immersion in solutions of various metal salts such as cerium, bismuth, iron or a combination of these. The colour develops during the final sintering stage. The concentration of the solution strongly influences the final shade. Concentrations as low as 0.01 mol% are sufficient to produce a satisfactory coloration. The final sintering temperature influences the colour obtained.

Coloration with various dopants does not appear to affect the crystalline phases or mechanical properties of the final product. Alternatively, colored zirconia can be obtained by small additions of various metal oxides to the starting powder. Sintering of the machined restorations has to be carefully controlled, typically by using specifically programmed furnaces. Shrinkage starts at 1000°C and reaches 25%. Sintering conditions are product-specific. Final sintering temperatures between 1350 and 1550°C with dwell times between 2 and 5 h lead to densities greater than 99% of the theoretical density. These variations in sintering conditions are likely to be due to the initial chemical composition of the 3Y-TZP powder. For example, small additions of alumina have been shown to act as a sintering aid, allowing the use of lower sintering temperatures and times. Prior to sintering, the frameworks are placed on zirconia sintering beads to avoid deformation. The minimum thickness for the copings is 0.5 mm, below which warpage could occur. The restorations are furnace-cooled to a temperature below 200°C to minimize residual stresses.

Chevalier et al. also demonstrated that the amount of cubic phase in 3Y-TZP increases when the sintering...
The temperature reaches 1500°C with a sintering time of 5 h. The presence of larger cubic grains is detrimental to the resistance of the ceramic to low temperature aging. This points out the importance of carefully controlling the sintering step.

The restorations are finally veneered with porcelains of matching coefficient of thermal expansion. The veneering porcelain is baked at 900°C, with a hold time of 1 min.

Although diffusion processes are time-dependent, chemical reactions could occur between the two ceramic materials.

Representative systems utilizing soft machining of 3Y-TZP for dental restorations are

- Cercon® (Dentsply International),
- Lava™ (3M™ ESPE™),
- Procera® zirconia (Nobel Biocare™),
- YZ cubes for CerecInLab® (Vident™),
- IPS e.max® ZirCAD (IvoclarVivadent)

**Hard machining of 3Y-TZP and MG-PSZ**

Two systems that are available for hard machining of zirconia dental restorations.

- Denzir® (Cadesthetics AB)
- DC-Zirkon® (DCS Dental AG)

3Y-TZP blocks are prepared by pre-sintering at temperatures below 1500°C to reach a density of at least 95% of the theoretical density.

The blocks are then processed by hot isostatic pressing at temperatures between 1400 and 1500°C under high pressure in an inert gas atmosphere. This latter treatment leads to a very high density in excess of 99% of the theoretical density.

The blocks can then be machined using a specially designed milling system.

Due to the high hardness and low machinability of fully sintered Y-TZP, the milling system has to be particularly robust.

- A study by Blue et al. demonstrated that Y-TZP was significantly harder to machine than fully sintered alumina with lower material removal rates.
- Yin et al. reported that coarse diamond burs were more efficient for material removal with Y-TZP, while machining with fine burs led to a more ductile type of damage.
- Huang studied the effect of grinding speed on the type of machining damage in Y-TZP and reported both brittle and ductile removal modes at high speed with less subsurface damage. On the other hand, the fine grain size of Y-TZP leads to very smooth surfaces after machining.
- Kosmac et al. showed that sandblasting was more efficient than grinding in inducing the transformation, thereby promoting a greater increase in strength.
- Conversely, coarse grinding caused the formation of deep defects as well as a reverse transformation with elimination of the compressive stresses and a decrease in strength. These results were confirmed by Guazzato et al and Curtis et al. on Y-TZP for dental applications.
- The influence of residual stresses on the susceptibility of Y-TZP to low temperature degradation (LTD) has been thoroughly examined by Deville et al. It was concluded that the presence of residual stresses was more influential than the final roughness in promoting LTD. (Table 4)

**Contraindication:**

- Very short clinical crown that does not permit the adequate height of connector (occlusal-gingival and mesio-distal)
- In Class II Division II malocclusion patients, due to deep bite.
- Bruxism
- Participation in extreme sports
- Clinical situation wherein biomechanics is compromised.

<table>
<thead>
<tr>
<th>Type of zirconia blocks</th>
<th>Milling procedure</th>
<th>Advantages</th>
<th>Commercial example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green stage</td>
<td>Dry carbide burs</td>
<td>Less time for milling, less flaws, post milling sintering at 1500°C</td>
<td>Cercon base, Lava frame, Lava 3M ESPE</td>
</tr>
<tr>
<td>Pre-sintered</td>
<td>Carbide burs under coolant</td>
<td>Less time for milling, less flaws, post milling sintering at 1500°C</td>
<td>Zirkon Zahn, In ceram YZ Cubes, Cerec InLab</td>
</tr>
<tr>
<td>Completely sintered</td>
<td>Diamond burs under coolant</td>
<td>More time for milling, no sintering shrinkage</td>
<td>Z-blanks, Everest (KaVo Germany), Digident (Girbach Germany)</td>
</tr>
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</table>

*Table 4: Compilation of different types of commercially available Zirconia*
Tooth preparation

The tooth preparation needed to accommodate a zirconia restoration is essentially that of a porcelain-fused-to-metal crown with a few modifications. The 3M ESPE recommendations for its Lava zirconia are:
- 1.5 to 2.0 mm of incisal/occlusal reduction
- 1.5 to 2.0 mm of axial reduction.

The range of reduction is related to the aesthetic needs. The more tooth reduction, the more available space for the lab technician to appropriately layer various porcelains to achieve better aesthetics.

The axial taper should be greater than or equal to 4 degree. The horizontal angle of the margin should be greater than or equal to 5 degree. Due to the limitations of the die-scanning process and the subsequent machine milling, sharp angles in the preparation must be avoided.

A circumferential deep chamfer or rounded shoulder at the gingival margin is recommended. Ninety-degree shoulders, troughing at the margins, feather edge margins, undercuts, or sharp line angles are not acceptable. Furthermore, the technician needs to consider the final shade and select an appropriately colored zirconia that allows layering of various translucencies of porcelain to develop a restoration that demonstrates “color from within.”

Insufficient tooth preparation

Result in a restoration that is too opaque and has a monochromatic appearance due to the inherent opacity of the zirconia (opaque coping can show through).

Lack of enough room for the substructure and the porcelain layer.

Cementation techniques

Placement of zirconia restorations can be via standard cementation or by bonding.

Due to zirconia’s inherent strength, conventional cements like zinc phosphate or polycarboxylate can be used, however these cements may not be the first choice, due to their physical properties as well as their opaque nature. Opaque cements may show through the zirconia and affect the final appearance of the restoration. Glass ionomer, resin-modified glass ionomer, and self-etching resin cements have all been used with success and these have the potential to enhance aesthetics. In the case of short or extremely tapered preparations, a bonded resin cement may be best. Zirconia does not etch with hydrofluoric acid due to lack of a glass matrix, nor does it contain silica to allow silane coupling to occur.

By sandblasting the intaglio surface with aluminum oxide particles, a relatively weak bond can occur between the zirconia and the resin. The bond to zirconia can be further improved by using a chemical surface treatment with the Rocatec system (3M ESPE) prior to bonding.

Potential problems

The potential problems that can occur with zirconia can be divided into 3 categories:
- Substructure failure
- Failure of the bond at the interface between the zirconia and the layering porcelain
- Breakage and chipping of the porcelain veneer

Clinical implications

Considering zirconia’s high strength, this material enables the clinician to place a ceramic restoration almost anywhere in the mouth. Single crowns, implant abutments, and bridges can be fabricated from zirconia.

Manufacturers suggest that:
- 2 abutment bridges can have a 38-mm span
- Multiple abutment bridges can have a span of 47 mm

Zirconia is a semi translucent substance that is only slightly more opaque than dentin. By varying the thickness of the coping, the amount of opacity can be controlled. In addition, Lava (3M ESPE) and inVizion (Vident) allow the lab to shade the substructure in the “greenstate”. This allows the color to penetrate the material, as opposed to surface stain, giving the final restoration a natural appearance (“chroma from within”).

Zirconia is radiopaque, enabling the clinician to detect more easily improper fit and marginal caries.

It has been shown to be biocompatible, without any reported cases of toxicity, patient allergy, or sensitivity. For clinical success, the layering porcelain ideally should have the same coefficient of thermal expansion as the zirconia substructure. On average, manufacturers recommend that the minimal thickness for a zirconia coping should be 0.3 mm for anterior teeth and 0.5 mm for posterior teeth. For a fixed prosthesis fabricated with zirconia, the cross-sectional dimension for a connector should be 9 mm², this is much smaller than the 16mm² connector recommended for conventional glass ceramics. This decrease in connector dimension is due to zirconia’s greater strength, allowing for a smaller connector and thus resulting in a more aesthetic appearance.
Zirconia in implant dentistry

Ceramics from aluminum, titanium, and zirconium oxides have been used for root form, endosteal plate form, and pin-type dental implants. The compressive, tensile, and bending strengths exceed the strength of compact bone by 3 to 5 times. The aluminum, titanium and zirconium oxide ceramics have a clear, white, cream or light grey color, which is beneficial for applications such as anterior root form devices. Minimal thermal and electrical conductivity, minimal biodegradation, and minimal reactions with bone, soft tissue, and the oral environment are also recognized as beneficial when compared with other types of synthetic biomaterials. Although initial testing showed adequate mechanical strengths for these polycrystalline alumina materials, the long-term clinical results clearly demonstrated a functional design-related and material-related limitation. The established chemical biocompatibilities, improved strength and roughness capabilities of sapphire and zirconia, and the basic property characteristics of high ceramics continue to make them excellent candidates for dental implants.

Conclusion

Use of zirconia-based all ceramic crowns and fixed prostheses is rapidly growing. Zirconia-based crowns and fixed prostheses have undergone only a few years of basic science research and laboratory clinical observation. To date, the research results are promising. However, significantly more clinical research is needed regarding this concept. Overall, the potential for zirconia-based all ceramic restorations appears to be very good.

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