Understanding Zirconia as Restorative Material

Introduction

Zirconia made a significant appearance on the dental horizon about 5 years ago. It provided an alternative for all ceramic crowns and bridges. Today, a milling procedure is the only reliable way to create zirconia restorative components for dental use. The availability of computer numerical controlled machines (CNC) allows for highly automated end-to-end component design using computer aided design and computer aided manufacture (CAD/CAM) programs. The programs produce a computer file that is interpreted to extract the commands needed to operate a particular machine, and then loaded into the CNC machines for production of the restoration coping or framework.

There is also the possibility of producing the same results with an analogue copy-mill system.

CNC manufacturing processes still have certain limitations with regards to all the possible ways that zirconia can be used for dental restorations. However, in the near future these limitations will disappear due the advancement of digital technologies and zirconia materials.

What is Zirconia?

Zirconium dioxide ($\text{ZrO}_2$), sometimes known as zirconia, is a white crystalline oxide of zirconium and is one of the most studied ceramic materials.

Zirconium is a chemical element with the symbol $\text{Zr}$ and atomic number 40. It is a lustrous, gray-white, strong transition metal that resembles titanium.

Despite being oxide of the metal, Zirconium dioxide is in the family of the full ceramics, more specifically, the oxide ceramics, also classified as technical ceramics. Oxide ceramics are polycrystalline materials that are composed of oxides that do not degrade during sintering.

Zirconia as a pure oxide does not occur in nature. It’s most naturally occurring form, with a monoclinic crystalline structure, is the rare mineral baddeleyite. It is also found in zircon ($\text{ZrSiO}_4$). Baddeleyite and zircon form the main sources for the material. Of the two, zircon (zircon sand) is by far the most widespread but it is less pure (its purity depends on where it has been mined) and requires a significant amount of processing to yield zirconia.

The processing of zirconia involves the separation and removal of undesirable materials and impurities - silica from zircon, and iron and titanium oxides from baddeleyite. The solid mineral zircon is collected from coastal areas as sand, and is purified by spiral concentrators to remove excess sand and gravel and then by magnetic separators to remove ilmenite and rutile. The byproducts can then be
dumped back into the water safely, as they are all natural components of beach sand. The refined zircon is then purified into pure zirconia. There are several routes to the extraction of zirconia from zircon including:

- Chlorination
- Alkali oxide decomposition
- Lime fusion
- Plasma dissociation

In the form of a ceramic material, zirconium dioxide possesses a crystalline structure, i.e. the individual building blocks zircon (Zr) and oxygen (O) have short-range and long-range order. Zirconium dioxide occurs in tetragonal, monoclinic and cubic crystals, dependent upon temperature. Pure ZrO$_2$ has a monoclinic crystal structure at room temperature and transitions to tetragonal and cubic at increasing temperatures. The transformation from the monoclinic to the tetragonal phase commences at 980°C and is complete at 1173°C. The tetragonal phase changes into the cubic modification at 2370°C (as in the artificial diamond: Cubic Zirconia). Some of these phase transitions are reversible, i.e. transformation into the monoclinic phase occurs under cooling. This step is associated with a change in volume of +4.9%, inevitably resulting in high tension and cracking of the sintered product. Because of this reversibility, pure zirconium dioxide cannot be processed into solid sintered products.

In order to manufacture zirconia components, it is necessary to 'lock' the material wholly or partially into the tetragonal form by the use of additives or stabilizing agents. Several different oxides are added to zirconia to stabilize the tetragonal and/or cubic phases: magnesium oxide (MgO), yttrium oxide, (Y$_2$O$_3$), calcium oxide (CaO), and cerium (III) oxide (Ce$_2$O$_3$), amongst others. The quality of the material in the final product is dependent on homogeneous mixing-in of the stabilization component.
Fig. 1 Production of Zirconia powder

Typical properties exhibited by zirconia that are commonly utilized include:

- High strength
- High fracture toughness
- Excellent wear resistance
- High hardness
- Excellent chemical resistance
- High toughness
- Very refractory
- Good oxygen ion conductor
The properties exhibited by zirconia ceramics depend upon the degree and type of stabilization and on the processing used. Typical properties for various zirconias are given in Table 1.

**Table 1. Mechanical properties for zirconia.**

<table>
<thead>
<tr>
<th></th>
<th>Partially stabilized</th>
<th>Fully stabilized</th>
<th>Partially stabilized (plasma sprayed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g.cm$^{-3}$)</td>
<td>5.7 - 5.75</td>
<td>5.56 - 6.1</td>
<td>5.6-5.7</td>
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<tr>
<td>Hardness -Knoop (GPa)</td>
<td>10-11</td>
<td>10-15</td>
<td></td>
</tr>
<tr>
<td>Modulus of Rupture (MPa)</td>
<td>700</td>
<td>245</td>
<td>6-80</td>
</tr>
<tr>
<td>Fracture Toughness (MPa.m$^{1/2}$)</td>
<td>8</td>
<td>2.8</td>
<td>1.3-3.2</td>
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<tr>
<td>Youngs modulus (GPa)</td>
<td>205</td>
<td>100 -200</td>
<td>48</td>
</tr>
<tr>
<td>Poissons ratio</td>
<td>0.23</td>
<td>0.23-0.32</td>
<td>0.25</td>
</tr>
<tr>
<td>Thermal expansion ($10^{-6}$/°K)</td>
<td>8-10.6</td>
<td>13.5</td>
<td>7.6-10.5</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m.K)</td>
<td>1.8-2.2</td>
<td>1.7</td>
<td>0.69-2.4</td>
</tr>
<tr>
<td>Specific Heat (J/Kg.K))</td>
<td>400</td>
<td>502</td>
<td></td>
</tr>
</tbody>
</table>

**Zirconia in Dentistry**

*Polycrystalline zirconium dioxide strengthened with yttrium oxide* is the ZrO$_2$ structural ceramic that is most frequently employed in dentistry. There are a number of different abbreviations used for this material in the literature. Most frequent are 3Y-TZP, YSZ or TZ-3Y, whereby the letters have the following meaning.

- **Y** represents the stabilizing yttrium oxide, which was added at 3 mol %
- **T** represents the stabilized tetragonal crystal modification
- **Z** represents the stabilized zirconium dioxide
- **P** represents the polycrystalline nature of the structure.
A peculiarity of 3Y-TZP ceramics is its so-called *transformation strengthening*. This form consists of nearly every crystallite or grain in the material being retained in the tetragonal form to room temperature so that each grain can transform instead of only the precipitates. Local stress peaks can occur when the material is subjected to high mechanical loads, resulting in micro-cracks. A tetragonal/monoclinic phase transformation is induced by the high energy input at the apex of the crack and cannot be prevented by yttrium oxide. However, if sufficient quantities of the metastable phase are present, then an applied stress in combination with the stress concentration at a crack tip can cause the metastable (e.g. tetragonal) phase to convert to a thermodynamically stable (e.g. monoclinic) phase, with the associated volume expansion. This phase transformation can then put the crack into compression, retarding its growth, and enhancing the fracture toughness of the material. This mechanism underlies the bending resistance of 1200 Mpa and fracture toughness of approximately 8 MPa·m$^{1/2}$ that characterizes 3Y-TZ ceramics. In this case, fracture toughness describes the material's resilience against the propagation of cracks.

At the end of the 1990’s it was found that alloying Y-TZP with a small proportion of alumina improves durability, in particular at high temperatures in humid environments. The name of this material is abbreviated to TZP-A and today it is the most widely used zirconia for dental restorations. The only disadvantage of this small proportion of alumina is a slight reduction in the translucence of the zirconia. Zirconia blocks marketed as “translucent” are most likely made from Y-TZP and “opaque” blocks from TZP-A.

**From Powder to Block**

Zirconium dioxide is available to dentistry only in *ceramic block* form. The properties of the ceramic blocks are influenced both by the chosen raw material and by their manufacturing procedure.

A *variety of press-forming processes* are currently being employed to produce zirconia blocks.

First, an organic binder is added to the ceramic powder prior to pressing. It reduces internal friction during the pressing procedure. Furthermore, the binder gives the pressed block, also referred to as a *green body*, a certain inherent solidity.

Next, the powder is pressed into blocks by one of the following methods:

1. *Uniaxial pressing*
In this procedure, pressure is exerted on the powder in only one direction. The density of such a block is strongly dependent on the pourability of the powder. There is always a danger in uniaxial pressing that different densifications will result from friction between the powder and the forming tool. This can result in structural inhomogeneities. Another problem can result if the pressures used in pressing are too high. Local tensile stresses can occur during the release of the block from its form, which can lead to the formation of cracks in the green body after relaxation.

2. **CIP, Cold isostatic pressing**

In isostatic pressing, the powder is filled into an elastic mould (latex, polyurethane, or similar materials). Hydrostatic pressure is built up and exerted on this externally through a liquid. The pressing pressure is thereby equal in all directions. This method has the advantages of producing blocks that are characterized by high isotropy (direction-independent material characteristics) and even densification.

Green bodies obtained in one of these ways are pre-fired at relatively low temperature to burn out the binder. A small degree of sintering takes place, causing the zirconia powder particles to slightly fuse. The blocks are strong enough to handle and mill, but are still highly porous and lacking in strength. The porosity also allows them to soak up staining agents, permitting coloring of the frameworks prior to firing, if necessary.

The faulty behavior of ceramic work pieces is determined to a great extent by structural inhomogeneities (concept of failure of the weakest link). These inhomogeneities manifest themselves, among other ways, in different values for measured strength within the blank. The Weibull modulus best describes the variability in measured strength in ceramic materials. The higher the Weibull modulus, the more homogeneous the material, i.e. any defects are evenly distributed throughout the entire volume. Values of between 10 and 20 can now be obtained for zirconium dioxide blanks. The determination of these values is usually accomplished using the four-point bending test.

3. **HIP (Hot isostatic pressing)**

This process is different from the two described above, since it is a finishing process in which the zirconium dioxide powder is simultaneously hot-pressed and sintered. The powder is filled into a moldable, sealed container and the powder is then densified in a heatable pressure vessel under inert gas. The gas pressure thereby acts on the powder from all sides. The blanks produced in this way are extremely dense and have isotropic (direction-independent) characteristics. An extreme disadvantage of this technique is the very high finishing costs. Furthermore, the HIPed blocks are so hard that they can only be processed using specialized, costly CAD/CAM procedures.

Partially sintered zirconia block has the advantage that its chalk-like consistency makes it far simpler and faster to process without damaging the material, than in
the case for HIPed material. Depending on its density, the partially sintered ZrO₂ retains a linear sintering shrinkage of 20-25%. That corresponds to volume shrinkage of 49-57%. Dimensions of the framework must be linearly increased during milling in pre-sintered stage in accordance with the manufacturer specifications, in order to compensate for the subsequent isotropic sintering shrinkage in the oven. Frameworks then shrink to their final size and hardness during final sintering process.

The Sintering Process

Sintering is a method for making objects from powder, by heating the material in a sintering furnace below its melting point (solid state sintering) until its particles adhere to each other. Sintering is traditionally used for manufacturing ceramic objects, and has also found uses in such fields as powder metallurgy.

During the sintering process, the powder that has been densified in the pressing procedure is heated to below its melting temperature and maintained at the final temperature for some time. This is therefore a temperature-time cycle, during which the porosity and volume of the green body are substantially reduced. Densification is achieved through rearrangement of the particles and changes to their shape and size. Sintering is completed by cooling down the objects.

The characteristics that determine the quality of the sintered zirconia piece are the homogeneous distribution of grain sizes and pores. These are determined by the heating rates, hold times and the final temperature selected during the sintering process. For example, temperatures that are too high or sintering times that are too long result in so-called large grain growth. This means that individual grains grow to 100 – 1000 times their original volume (0.3-0.4 µm) at the expense of other grains. This results in extremely inhomogeneous grain size distributions with the inherent danger that the metastable, tetragonal phase will spontaneously change into the monoclinal phase. The heating rate greatly influences the even distribution of pores in the micro-structure. Areas with greatly densified ZrO₂ grains and areas with loosely packed ZrO₂ grains are the result if the heating rate is not precisely controlled. The areas with the loosely packed grains crack open further during the sintering process and often remain as structural faults and therefore as potential defective areas in the framework.

Ageing of 3Y-TZP structural ceramics

Dental work pieces made of TZP ceramics and employed for clinical purposes are exposed to factors such as moisture and continuous, dynamic loading. These conditions essentially result in a decrease in the values for measured strength and therefore in the hydrothermal ageing of the material. This decrease in strength can easily be simulated in an autoclave at 130-150°C and a water vapor pressure of 10 bars. The ageing process actually takes place far more slowly, as dental restorations are never exposed to such extreme conditions. The addition
of approx. 0.5% aluminum oxide to zirconium dioxide powders constitutes a further buffer. This substantially increases the resistance to hydrothermal ageing. Furthermore, it must be borne in mind that the framework is protected from the direct effects of water by the facing ceramic. Faulty cases as a result of hydrothermal ageing therefore appear to be highly unlikely. However, this needs to be assessed in long-term clinical studies.

**From Block to Restoration**

*Tooth Preparation*

All full ceramics require careful preparation, as the stability of ceramic restorations is dependent on the design of the tooth preparation. The physical properties of ceramics require the orientation of restorations to be such that they can resist compressive stress. Tensile stress results in cracks and splinters and is therefore to be avoided. Sharp edges as well, should be avoided.

*Cementation*

In principle, zirconium dioxide restorations can be conventionally fixed in place using any dental cement. However, it needs to be noted that zirconia does not etch, therefore for inlays and onlays, as well as for Maryland bridges, additional mechanical retention should be created in preps and in the framework.

*Framework Creation*

Sintered dental zirconia has a whiteness and translucency that very much resembles a natural tooth. There’s no need to minimize and hide the frame. Connectors in the bridge should be maximized. They should be thick and broad and can be left exposed (no need to layer them with porcelain). A minimum area of 9 mm² should be available to connectors and framework wall thickness should not be less than 0.5 mm. Copings or frameworks must be anatomically shaped to ensure even layer thicknesses of veneering ceramic. Insufficient support for the veneering ceramic on the coping or bridge framework can trigger so-called chipping fractures.

Sintered zirconia is a very dense and highly acid proof material which prevents the absorption and surface accumulation of pollutants (like plaque). Therefore in a zirconia bridge, pontics in contact with the tissue need not be veneered with porcelain.

There’s no limit to the span of a zirconia bridge or to the amount of pontics. The only condition is the right design. The larger the distance between the abutments the taller and wider the connectors should be. However, in light of the stability of this material, sound dental principles should be adhered to.

The fit of a zirconia structure should be snug, but passive. Zirconia has no flexibility and dental cements are not as rigid as zirconia. The thicker the cement
layer, the more the core will flex, increasing the potential for fracture. On the other hand, if the frame fits with resistance, internal pressure may adversely affect the restoration. Ideally, the fit of copings or frameworks should follow preparation outlines and seat passively with sealed margins.

Full contour (monolithic) zirconia restorations are becoming more popular due to the availability of more translucent formulas. The main objection to monolithic restorations comes from the perception that they are too abrasive for the opposing natural teeth. We should not confuse the strength of zirconia with abrasiveness. The surface of zirconia is very dense, smooth, stable and non-aggressive.

Zirconia dental constructions can be colored in presintered stage with special coloring liquids to obtain a sintered restoration in basic dentine color. Recently pre-colored zirconia blocks have become available. Coloring zirconia in presintered stage does not affect the strength of the material. This technique can also be used with the newer translucent blocks to customize the surface of monolithic restorations.

In porcelain-zirconia restorations, the feldspathic ceramic (porcelain) must be sufficiently supported, especially since there’s no chemical bond between the feldspathic ceramic (or any other ceramic or composite) and zirconia. For this reason the porcelain has to be baked differently on zirconia substrates, then on traditional porcelain-metal (PFM) restorations. Porcelain is maintained by compression and micro-mechanical adhesion to zirconia. Sintered zirconia is an extremely poor heat conductor, therefore different heating and cooling rates than conventional PFM restorations should be used when backing ceramic on zirconia. This is particularly sensitive in larger structures. Calculations are based on weight.

Processing

Most zirconia restorations are created from the “green state” (partially sintered). In this stage zirconia can be worked (milled and ground) freely.

However, once sintered, zirconia requires careful handling. Due to the poor heat conductivity, densely sintered zirconia should not be subjected to copious dry grinding. In such cases, there is a danger that the critical level of energy input into the framework might be exceeded (e.g., overheating, concentrated stress peaks). Possible consequences of this are phase transformations, surface tensions through distortion of the crystal lattice, fissures, and later, fissures in the facing. Densely sintered zirconia should therefore only be processed wet. The use of coarse diamonds, excessively high rpms and/or pressure must also be avoided to prevent the creation of cracks.

In the dental lab a regular sintering oven cannot “restructure” zirconia again and “heal” the cracks.
Even though the transformation strengthening compresses the crack that has been produced, which is why zirconium dioxide is also referred to as a **self-repairing material**, this so-called self-repairing only works once. If another crack is produced in the same place, it will no longer be compressed. In addition, the monoclinal phase that results from the transformation has a higher thermal expansion coefficient (TEC) than the tetragonal phase. This means that compatibility with the TEC of the facing ceramic is potentially compromised.

**Frequent reasons for fractures**

**Zirconia**

1. Non-compliance with coping or framework wall thickness (min. 0.5 mm).
2. Connecting cross-sections too small (9 mm² three sections, 12 mm² four sections).
3. Dry grinding the densely sintered framework, use of coarse diamonds, excessive rpms and/or exerting excessive pressure.

**Facing ceramic fractures and delaminations are:**

1. Insufficient support for the facing ceramic by the coping or bridge framework.
2. Copings or frameworks that are not anatomically shaped.
3. Uneven thickness of facing layers.
4. Non-compliance with the backing procedure.
5. Use of conventional ceramic heating and cooling rates.

**Summary**

Without a doubt, zirconia is a material with excellent characteristics that now occupies a permanent position in dentistry. However, the long-term success of dental restorations made from 3Y-TZP ceramics is dependent on a number of factors. Industry must supply zirconium dioxide blanks of constant high quality, based on appropriate finishing procedures. This material requires special processing techniques that all laboratories must master, as it is fundamentally different from the classically employed metallic framework materials. Therefore, factors such as preparation specific to the materials and techniques, correct methods for processing and veneering, as well as due care during use, all play a significant role in its success.
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