

KEY POINTS

- First-generation zirconias are today materials that can be used with great confidence for many clinical situations.
- Recently developed translucent and high-translucent zirconia materials are promising, but long-term follow-up studies are still lacking and the gain in esthetic properties could include the loss in mechanical properties.
- The choice of material should be done with great care, using materials only that are well known for the clinician.

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This paper has been peer reviewed.

Hjerppe J, von Steyern PV. Two decades of zirconia as a dental biomaterial – what have we learned? *Nor Tannlegeforen Tid*. 2019; 129: 22–28

Two decades of zirconia as a dental biomaterial – what have we learned?

Jenni Hjerppe and Per Vult von Steyern

Yttrium oxide stabilized tetragonal zirconium-dioxide polycrystal (referred to as yttria-stabilized zirconia, Y-TZP or briefly zirconia) is a durable dental ceramic material that has exceptional biocompatibility. These properties make it an excellent material for use in the oral cavity. Zirconia was first introduced as a framework material (first generation) for tooth-supported single crowns and fixed dental prostheses (FDPs). The survival rates of these constructions are high, and the only drawback has been the exposition to superficial porcelain chipping, so called chip-off fractures. This was leading to learning curve in veneering techniques as well as development of new more translucent zirconia materials that can be used as monolithic structures without veneering porcelain or cut-back structures where only the labial facades are veneered.

The purpose of this article is to describe the material properties of different zirconia materials as well as some clinical indications.

A strive for aesthetic dental reconstructions led to the development of material combinations with porcelain as the main aesthetic component supported by a strong, tough framework material. The materials often considered to be the gold standard for dental reconstructions were specially developed high-gold alloys used with compatible porcelains, combinations that emerged in dentistry in the late 1950s under the name porcelain fused to metal or later metal ceramics (MC). After a long period when MC was the dominating material combination for fixed dental prosthesis (FDPs) there was a growing demand for even more aesthetic and less expensive metal-free materials (1).

That led to the development of densely sintered oxide ceramics, like aluminum oxide (Al_2O_3 , often referred to as alumina) and later yttrium oxide stabilized tetragonal zirconium-dioxide polycrystal (referred to as yttria-stabilized zirconia, Y-TZP or briefly zirconia). Alumina was the dominating oxide ceramic material under the 1990s, either glass infiltrated (as a hybrid ceramic) or densely sintered, but in both cases in combination with veneering porcelain. The clinical outcome of crowns made of those materials was promising, but studies showed that the strength and toughness of alumina was somewhat limited when used for FDPs (2).

First-generation zirconia-based materials, on the other hand, have been used since the mid 1990s with results showing that they can be used for almost all types of FDPs, tooth-supported and implant-supported ones, as long as the dimensions are sufficient. The survival rates are high and the only draw back has been that FDPs are prone to superficial porcelain chipping, so called chip-off fractures (3). Regarding cores and frameworks, however, zirconia has shown to have superior mechanical properties compared to alumina and is nowadays widely used clinically for routine treatments (4).

The focus of the development of zirconia-based reconstructions has been in two main directions during the last decade. One direction was to learn how to veneer the first-generation zirconia without creating detrimental residual stresses in the veneering porcelain, thus reducing the risk for chip-off fractures. The other direction was to develop zirconia materials with optical properties closer to the natural tooth structures, in order to make them feasible for use monolithically (in full anatomy). Then aesthetically acceptable reconstructions might be produced without the need of comparably weak veneering porcelain. This offers a possibility to combine strength with sufficient optical properties in one and the same material. By changing the microstructure of zirconia, it is possible to increase translucency and to decrease the light scattering properties of the material, with the intention to at the same time preserve the unique mechanical properties of zirconia (5).

Many different zirconia materials are available today and both mechanical and optical properties differ to such an extent, that it is important for the clinician to be able to distinguish between the different materials when deciding what material to use in a specific clinical situation. The purpose of this article is therefore to enlighten the material properties of different zirconia materials as well as some clinical indications.

Properties of stabilized zirconia

Zirconia is a polymorphic material that occurs in three crystal phases depending on temperature: monoclinic (m , $< 1170^\circ\text{C}$), tetragonal (t , $1170\text{--}2370^\circ\text{C}$) and cubic (c , $> 2370^\circ\text{C}$). During the fabrication process, zirconia reconstructions are sintered at temperatures well above 1170°C , which results in a tetragonal material structure. During cooling, when the temperature passes approximately 1170°C , phase transformation occurs in grains where tetragonal crystals transform into monoclinic ones. Since the monoclinic grain is 3–5 % larger in volume compared to the tetragonal ones, volumetric expansion occurs which leaves the material with high residual stresses, very brittle and prone to spontaneous crack growth within the material. Zirconia grains are microscopically visible but vary in size from 0.2 to 0.8 μm depending on production history (6).

In order to avoid zirconia turning into monoclinic phase during cooling, small amounts (2–3 mol %) of stabilizing oxides, like yttrium oxide (Y_2O_3 , yttria) are added to the material. The yttria-doped material is then stabilized in the tetragonal phase also at room temperature (7).

Favorable mechanical properties are achieved in the material using stabilizing oxides in a process described as transformation toughening. When a crack is formed in the surface of the material, it tends to grow and expand into the bulk of the material. Local tensile stresses at the crack tip area mediate a t-m transformation of the zirconia grains in the area under stress, leading to a volumetric expansion of 3–5 % in the crack tip area, thus resulting in a local residual compressive stress. For the continuing growth of the crack, loading forces first need to neutralize the residual compressive stress in the crack tip area, before tensile stresses can start to build up. Consequently, higher loads are needed for continuing crack growth, which practically means that the residual compression prevents further crack propagation (7). (Figure 1).

Zirconia has been shown to be an excellent material for use in the oral cavity. It is highly chemically stable and the thermal conductivity is extremely low (7). In vitro and in vivo studies have shown that zirconia has relatively low tendency to adhesion and colonization of bacteria on the surface of the material and it is chemically

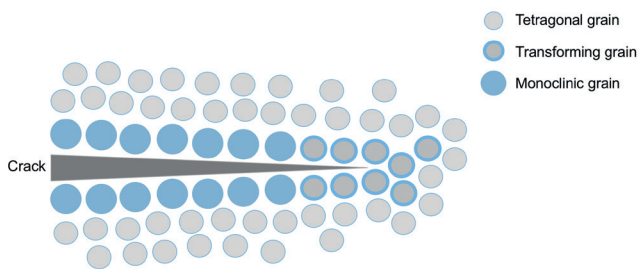


Figure 1. Local tensile stresses at the crack tip area mediate a t-m transformation of the zirconia grains in the area under stress, leading to a volumetric expansion of 3–5 % in the crack tip area. This is resulting in a local residual compressive stress at the crack tip preventing the crack propagation. The grain size is varying from 0.2 to 0.8 μm . The figure is modified from Piconi and Maccauro (1999).

very close to titanium-oxide (8–10). First-generation zirconia has more favorable mechanical properties than all the other dental ceramic materials. Both flexural strength and fracture toughness are high, ranging from 800 to 1500 MPa and 9.4 to 11.5 MPa $\text{m}^{1/2}$ respectively (7, 11, 12). (Table 1) The fracture toughness is an important property for evaluating the fracture behavior and crack propagation of a ceramic material. The fracture toughness value could help to evaluate the damage tolerance and long-term clinical success of the material.

Phase transformation from t-m has also been seen on the surface of zirconia material in *in vitro* studies due to environmental stresses like presence of water, body fluids (saliva) and especially hot water vapor (autoclave) (13, 14). Chevalier and co-workers showed that in a humid atmosphere the tetragonal grains on material surface might transform into monoclinic ones. As the monoclinic grains are 3–5 % larger, this sudden volume expansion leads to swelling on the material surface and enables water to penetrate through grain boundaries resulting micro- and macro-cracking of zirconia (14). This phenomenon is called low temperature degradation (LTD) and it was first thought to be detrimental for zirconia constructions in oral cavity. However, in 7 to 10 years clinical follow-up studies almost no signs of low temperature degradation of the frameworks have been seen and the survival rates of zirconia frameworks have been excellent (3, 15). But spontaneous t-m phase transformation can occur on the material surface due to mechanical stress induced by surface treatments like grinding (16).

First-generation zirconia has a regular polycrystalline structure without any amorphous phase (glass). Compared to glass-ceramics this difference in microstructure makes zirconia mechanically more durable, but with optical properties such as high surface reflection, low translucency and an extreme light scattering property that give the material an opaque appearance. It is important, however, to remember that first-generation zirconia is not opaque but

have unfavorable optical properties regarding potential for tooth resemblance (17).

The polycrystalline structure of zirconia cannot be etched with hydrofluoric acid (HF) and the bond strength is not as high as the one that can be achieved to HF etched porcelain or glass ceramics (18). In clinical studies loss of retention and secondary caries are typical complications (19, 20). One of the reasons for this could be poor bond strength, especially since it's known that long-term water storage is decreasing the bond strength (21). Other possible reasons for loss of retention might be related to surface properties and precision as a result of milling, or choice of cement. Zirconia can be milled either in pre-sintered stage (soft machining) or fully sintered stage (hard machining, e.g. Hot Isostatic Pressing, HIP zirconia) and the milling of zirconia, especially in fully sintered stage, often results in a glossy surface with low surface roughness. Since the material is highly inert, a chemical reaction with some bonding products and cements is unlikely to occur, which is detrimental to micromechanical retention. If production (milling) is done with a 3-axis milling unit, or if the geometry of the preparation doesn't allow for precise milling (if drill compensation is needed), then the ferrule or cement gap might be insufficient, again making the reconstruction susceptible for loss of retention (22). Finally, zinc phosphate cement was previously recommended frequently for zirconia, with properties (brittle, water-soluble, a low retentive cement) that are unsuitable for some cases with respect to the aspects mentioned above, should not be recommended at all. This was confirmed and concluded in a study by Larson et al (23). Kern et al (24) have described a method for bonding to zirconia, and this and other bonding procedures for zirconia will be discussed in another paper in this series of articles.

Chipping

Due to the unfavorable optical properties of the framework material and the potential risk for low temperature degradation, zirconia was first introduced as a framework material that had to be veneered for acceptable aesthetic result. However, clinical investigations showed that superficial chip-off fractures of the veneering material turned out to be the most commonly seen technical complication. In previous studies chipping rates of 15–32 % have been reported during follow-up times from 9 to 10 years (3, 25).

There have been many attempts to solve the chipping problem. Anatomical framework design has always been considered important to assure sufficient support for veneering porcelains, which is congruent with the demands for other veneered prosthetic constructions as MC for instance. Early CAD/CAM-produced reconstructions did not, however, always meet up with those demands since

many CAD-software had technical design limitations. It was not always possible to consider opposing arch when using the CAD. In those cases, the dental technician had to estimate how much space was needed for the porcelain and sometimes the porcelain layer became too thick and thereby unsupported (26). The effect of insufficient porcelain thickness was confirmed in a recent study where fracture strength of veneering porcelains was shown to be reduced with almost 50 % if the veneer thickness was increased from 1 mm to 2 mm. That study confirmed that anatomical shape of a zirconia crown is an important factor in avoiding chipping (27).

Another reason for the chipping is that the thermal conductivity of zirconia is extremely low. After firing porcelain on zirconia, during cooling, the porcelain is cooled from the surface only and not through the coping as it is the case with a metal coping with high thermal conductivity. Thus, the zirconia coping isolates the porcelain since no heat dissipation takes place through the core, only from the porcelain surface. The outer layer of the porcelain is then cooled first and already rigid when the bulk material continues to shrink during the continued solidification phase. In room temperature, residual stresses remain between the surface layer of the porcelain and the bulk porcelain, leaving residual stresses in the bulk porcelain, close to the surface. Later, during function in the oral cavity, shear loads initiate the growth of sub-surface crack, and subsequently superficial chip-off fractures (28). It was shown in a recent study that the thicker the zirconia core, the higher the risk for residual stresses and chip off fractures (29). Hence, using slow cooling protocols during porcelain firing, better matching the coefficient of thermal expansion of zirconia and the veneering porcelain and careful polishing of the veneer surface after occlusal adjustments are considerations that might lead to less chipping (27, 30–32).

Translucent and high translucent zirconias

Clinical failures with porcelain chipping have lead to development of more translucent zirconia materials that can be used as monolithic structures without veneering porcelain or cut-back structures where only the labial facades are veneered. The final esthetic result can be achieved with material translucency, coloring with infiltration liquids, zirconia powder colors and surface staining with glazes. The translucency depends on the thickness of the material, the darkness of coloring pigments if present, grain size and the zirconia material's phase distribution (33). Glass-additives are another way to achieve translucency, but then a wider definition is used for what should be considered a zirconia material.

Gaining translucency

When the light strikes the surface of the material, some of it will be reflected from the surface and some will pass into the bulk of the material. Part of the light in the bulk will be absorbed and part of it will be scattered at grain boundaries or transmitted through the material. Increased translucency of zirconia can be gained by increasing the sintering time and/or temperature, which leads to grain growth (6, 33). With larger grain sizes the number of grain boundaries decreases and consequently since light scattering takes place at grain boundaries, scattering decreases. Scattering disperse the light diffusely back to the surface, giving the material a whitish opaque appearance in contrast to when the light can pass through the material with few disturbing grain boundary passages; hence being transmitted with less diffraction through the material. The latter material appears more translucent.

Other way to produce more translucent zirconia is to add more stabilizing oxides (Y_2O_3), up to 8 mol %. During the sintering process fully-stabilized zirconia is formed and there is more cubic phase present, i.e. the material is more translucent. However, cubic grains are yttrium rich and the surrounding tetragonal grains do not have sufficient amount of stabilizing oxides, which makes the grains unstable and prone to t-m phase transformation (34). This will lead to decreased mechanical properties of fully stabilized zirconia materials. In a recent in vitro study Sulaiman and co-workers showed flexural strength of 734 MPa for fully stabilized zirconia, when flexural strength of partially yttrium stabilized zirconia was in the same study 1108 MPa (35). Development of nanocrystalline zirconia might provide durable and translucent material in the future (6). By reducing the grain-size to nanometer-level high translucency is achieved by high in-line transmission of the light.

The studies of translucency have shown that translucent zirconias have better optical properties than first-generation zirconia material for frameworks (36). The translucency is however not as good as the translucency of enamel and dentine (37) or lithium-disilicate reinforced glass ceramic (38). There are some differences in mechanical and optical properties between the different commercial brands. (Table 1)

Clinical indications

Zirconia can be used as a framework material for tooth- and implant-borne single crowns and FDPs veneered with porcelain or as monolithic structures. (Figure 2) It should be noted, however, that the indications for FDPs made of the new translucent and high translucent zirconia materials are limited. Many of the new translucent materials have low flexural strength and fracture toughness. Since it has been suggested that 800 MPa in flexural strength and 3.5 MPa

Table 1. Properties of different zirconia materials. (The values are from references 7, 11, 12, 35 and limited data sheet information)

	Some commercial examples	Flexural strength (MPa)	Fracture toughness (MPa m ^{1/2})	Translucency parameter (TP) after polishing*	Clinical indications
First-generation zirconia	ICE-Zircon (Zirkonzahn) IPS e.max ZirCAD (Ivoclar Vivadent) Procera Zirconia (Nobel Biocare)	≈ 800–1500	9–12	10.4–11.5	Frameworks for single crowns and multiple-unit for FDPs on teeth and implants, implant abutments, implants
Translucent zirconia	Prettau (Zirkonzahn) Bruxzir Zirconia (Gledewell Laboratories) Wieland Zenostar translucent (Ivoclar Vivadent)	≈ 750–1200	4–9	11.1–13.0	Monolithic single-crowns or FDPs on teeth and implants with or without veneering of labial facades
High-translucent zirconia	Prettau Anterior (Zirkonzahn) Katana High translucent (Kuraray Noritake INC)	≈ 650–750	3–5	13.4–15.0	Monolithic single-crowns or FDPs on teeth and implants with or without veneering of labial facades

*The translucency parameter is measured from 1 mm thick specimens.



Figure 2. A monolithic (full contour), high translucent, multi-shaded, implant-supported zirconia dental reconstruction 11 21 22.

m1/2 in fracture toughness, is the lower limit for recommending a material for FPDs in the posterior region (ISO 6872) (39), high translucent zirconia might be restricted to small (up to 3-unit) anterior FPDs and single-crowns in moderately loaded situations. The clinical outcome of tooth-borne constructions will be discussed in more detail in another paper of this series of articles.

Zirconia is also a material for implant abutments with direct connection to implants or through cemented titanium bases, but for the same reasons as mentioned above, only first-generation zirconia with sufficient strength and toughness should be considered for abutments until clinical data proves otherwise.

The clinical advantage of zirconia abutments over titanium ones is the light color. Dark titanium abutments can shine through peri-mucosal tissues causing esthetic problems especially with patients who have thin gingival biotype. The load-bearing capacity of zirconia abutments has shown to be on the range of 412N to 624N (40, 41) and this seems to be sufficient to bear the maximal occlusal forces in the anterior area. In the clinical study of Zembic and co-workers, cumulative success rate for zirconia implant abutments connected on implants with external connection was 96.3 % during eleven-year follow-up time (42). Connection type influences the clinical longevity of constructions on zirconia abutments. In a retrospective multi-center clinical study there was a significant difference in survival rates for abutments with external (99.7 %) and internal (93.1 %) connection with a mean 6-year follow-up time (43).

There is only little clinical evidence available of monolithic implant-supported zirconia FDPs. In a recent systematic review, it was shown that monolithic zirconia seems to work well as a material for complete-arch implant-supported FDPs, short-term prosthetic cumulative survival rate being 96.8 % (44). More studies and longer follow-up times are needed to confirm these results and to give information about shorter implant-supported FDPs as well. When the facades of the monolithic FDPs are veneered, problematic chipping of the veneering porcelain might still occur (45). Different core designs have been proposed to overcome this problem (46).

Zirconia as an implant material

Over the years zirconia has also been introduced as a dental implant material. In vitro and in vivo studies have shown that zirconia implant material seem to have desirable osseointegration, cell metabolism and soft tissue response (47, 48). One-piece zirconia implants seem to bear high fatigue loads in laboratory conditions (49). A recent prospective multi-center study was showing high survival rate of 98.5 % and a low marginal bone loss of single- and three-unit FPDs supported by one-piece zirconia implants after 3 years in function (50). However, these constructions are not yet recommended for clinical use since there is no long-term clinical data available.

Wear

When the monolithic materials were introduced, concern was raised about the wear of the antagonist, as zirconia is a hard material. However, recent studies have shown that monolithic zirconia with glazed surface is causing similar wear to antagonist enamel surface as other ceramic materials (51, 52). In vitro wear simulation has shown that less hard ceramics like glass ceramics cause more wear on antagonist enamel because of the increased ceramic surface roughness during the wear procedure. Well-polished monolithic zirconia surface is causing less wear because of slighter surface roughness (52). Furthermore, the wear-pattern differs since unglazed zirconia surfaces tends to be more polished during wear, causing less abrasion to the antagonists, while glass ceramics and porcelain gets rougher over time, becoming more and more abrasive.

There is some clinical and in vitro evidence that zirconia framework material used in implant-borne constructions can cause

wear of titanium counterparts i.e. abutments and implant shoulders when the framework is directly connected to abutments or implants with occlusal screws (53, 54, 55). Care should be taken when treating patients with implant-borne zirconia constructions. It would be advisable to check the torque of the occlusal screws regularly.

The wear of the titanium implant parts could be avoided by, cementing or mechanically connecting the zirconia construction on titanium bases. In the laboratory studies the mechanical strength of zirconia – titanium base combinations have been reported higher than plain zirconia abutments (55–57). Some clinical evidence is available about these constructions and the results are promising (43, 58). The weakest link could be the resin cement interface between titanium base and zirconia abutment/crown.

Conclusions

The following can be concluded from the development of zirconia materials within the last two decades. First-generation zirconias are today materials that can be used with great confidence for many clinical situations. Earlier problems with chip-off fractures might be solved, but more clinical studies are needed to confirm this.

Recently developed translucent and high-translucent zirconia materials are promising, but long-term follow-up studies are still lacking and the gain in esthetic properties could include the loss in mechanical properties. There are, furthermore, many different brands of translucent and high translucent materials available on the market, employing different techniques for achieving translucency. Hence, it is recommended that choice of material should be done with great care, using only materials that are well known for the clinician.

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