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Chapter

Zirconia in Restorative Dentistry

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Abstract

Advancements in dental material science and technology have improved over the past decade tremendously. The demand for tissue-friendly esthetic materials has been fulfilled to a certain extent on account of the development of new materials. Most materials meet the requirements of esthetics, function and biocompatibility. They exhibit the properties of color stability, improved resistance to wear, dimensional stability and they are tissue-friendly. These new materials are able to provide desirable and optimum treatment outcomes on a long-term basis on account of their nature and advances in manufacturing and fabrication. Reinforced ceramic restorations are now completed within a very short time from start to finish—from digital impression to bonding of the restoration. Zirconia-reinforced ceramics share the top choice in materials along with lithium disilicate. The most recent zirconia has improved optical properties and has the potential to overcome its problem of increased opacity. These zirconia-based ceramics have successfully replaced even precious metal alloys and porcelain-fused-to-metal prostheses due to the above-mentioned qualities. This chapter throws light on zirconia and the different types used in dentistry, applications, methods of fabrication and clinically relevant properties.

Keywords: zirconia, yttria stabilized tetragonal zirconia, zirconia-based ceramics, dental porcelain, CAD-CAM

1. Introduction

Ceramics are inorganic substances produced by firing metallic and non-metallic constituents at a high temperature [1]. Ceramics have been widely used in dentistry for more than 100 years [2], and have since been advancing in terms of their physical, mechanical and optical properties [3]. As described by Kelly and Benetti [4], ceramics have been classified into three groups based on the glass content.

- i. Predominantly glassy materials derived from feldspar (silica and alumina) and best reproduce the optical properties of enamel and dentin
- ii. Particle-filled glasses to improve mechanical properties. For example, leucite was the first crystalline filler to be incorporated into feldspathic porcelain. Lithium disilicate and mica are other such fillers

- iii. Polycrystalline ceramics: no glass is present and is much stronger than glass-based ceramics. They can either be pressed into oversized molds (compensates for shrinkage during firing) under pressure or blocks may be processed into restorations using CAD-CAM (Computer-Aided-Designing Computer-Aided-Machining).

The drawback is that there is no quantifying the amount of glass phase required for the ceramic to be included in either the predominantly glassy or the particle-filled glasses category. Also, polycrystalline ceramics do not contain glass, hence the classification lacks clarity. Another classification was outlined by Gracis et al. [5] who proposed a new grouping based on the formulation of the ceramics.

- i. Glass-matrix ceramics: include feldspathic ceramics, synthetic ceramics, glass-infiltrated ceramics
- ii. Polycrystalline ceramics: include alumina, stabilized zirconia, zirconia-toughened alumina, alumina-toughened zirconia
- iii. Resin-matrix ceramics: include resin nano-ceramics, glass ceramic in a resin interpenetrating matrix, zirconia-silica ceramic in a resin interpenetrating matrix.

Zirconia is presently the most studied and researched dental material. The name “zirconium” originates from the Arabic term “Zarcon”, which translates to “golden in colour.” The dioxide form of zirconium (ZrO_2), known as zirconia, was first identified by a German chemist Martin Heinrich Klaproth in 1789 in a reaction product of heating some gems [6]. It was used along with other rare earth oxides as pigments in ceramics. Zirconia was first used as a biomaterial in 1969 for hip head replacement in orthopedics [3]. Crystalline zirconia occurs in three forms: monoclinic (M), tetragonal (T) and cubic (C). At room temperature, pure zirconia is monoclinic and remains stable in this phase up to 1170°C. Monoclinic zirconia is usually associated with surface microcracks, higher susceptibility to low temperature degradation (LTD) and lower reliability for use in dentistry [7]. Above this temperature, it transforms first into a tetragonal and then into the cubic phase. They transform from one phase into another, induced by a combination of different factors such as, temperature, humidity and stress [8].

It is crucial to know that all three phases differ in their properties. One that is useful in dentistry is tetragonal zirconia. The tetragonal form is stable between temperatures 1170° and 2370°C. The transformation from tetragonal to the monoclinic occurs upon cooling, and results in a volumetric *increase* of 4%. Pure unalloyed zirconia is unstable at room temperature and would shatter spontaneously and catastrophically on cooling due to $t \rightarrow m$. Hence, the tetragonal form must be stabilized to room temperature to overcome stress cracks and transformation volumetric changes on cooling [1, 7, 9]. For this reason, zirconia is doped with various oxides, such as yttrium oxide (Y_2O_3) or cerium oxide (CeO_2) or other metallic oxides such as magnesium oxide (MgO) and calcium oxide (CaO). Significant molecular stability can be obtained with ZrO_2 doped with Y_2O_3 . It has superior mechanical properties than other combinations; although sintering is much more difficult, this is the main kind of zirconia considered for biomedical use (**Figure 1**) [9].

The concept of fracture toughness and tensile stress is central to the excellent mechanical properties of yttria-stabilized zirconia. Ceramics are fired at such high

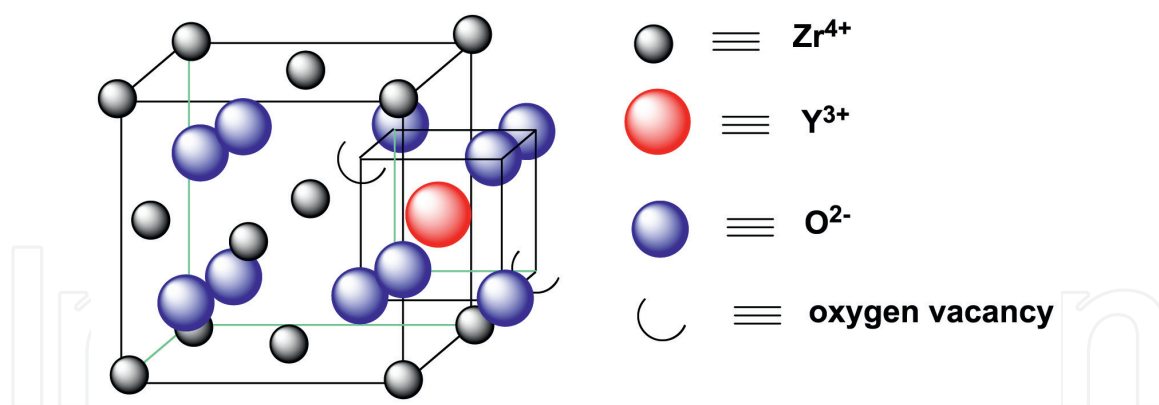


Figure 1.
Yttria-stabilized zirconia.

temperatures that upon immediate cooling, a natural crack forms, weakening the material. Fracture toughness characterizes the potential stress directed through the developed crack or flaw. When stress occurs on a zirconia surface, there is a $t \rightarrow m$ transition associated with cracking, followed by a volumetric expansion [9]. By inducing external stress or a higher tensile stress, there is an increase in volumetric expansion resulting in compressive stress around the crack tips [2] and there is an increased resistance to crack propagation. Hence, these cracks are shielded by controlled transformation from $t \rightarrow m$ and result in a gradual stabilization. The strength and fracture toughness is dependent on grain size and also the dopant concentration (yttria) [10]. This concept is called “transformation toughening”, first reported by Garvie, Hannink, and Pascoe in a paper titled “Ceramic Steel?” [11]. Zirconia-based ceramics used in dentistry mostly consist of tetragonal zirconia polycrystals, partially stabilized with 3 mole % yttrium (3Y-TZP) [1].

Initially zirconia was used in root posts, orthodontic brackets dental implants. With the development of CAD/CAM, traditional metal-based crowns, prosthesis and FPD’s have been replaced by improvised esthetics and enhanced tissue compatibility obtained using tooth-colored metal-free systems [3].

2. Types of zirconia in dentistry

2.1 Yttrium tetragonal zirconia polycrystals (Y-TZP)

As mentioned previously, zirconia used in dentistry usually contains 3 mol% yttria (Y₂O₃) as a stabilizer (3Y-TZP) is indicated for the fabrication of crowns and fixed partial dentures. 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. Yttria stabilized zirconia was first introduced in the dental market in the year 2002 via soft machining [12].

The mechanical properties of 3Y-TZP are strongly influenced by its grain size. Optimum $t \rightarrow m$ transformation occurs only in a limited range of grain size of 0.2 μm to 0.8 μm [13]. Above a critical grain size of $>1 \mu\text{m}$, 3Y-TZP is less stable and more susceptible to spontaneous $t \rightarrow m$ transformation whereas, grain sizes of $<1 \mu\text{m}$ have a lower transformation rate. Below a grain size about 0.2 μm transformation is not possible, leading to reduced fracture toughness. Grain size is controlled through sintering

and the sintering conditions have a strong impact on both the stability and mechanical properties of the final product. Higher sintering temperatures and longer sintering times lead to larger grain sizes [12].

Currently, available 3Y-TZP for soft machining of dental restorations employs final sintering temperatures between 1350°C and 1550°C, depending on the manufacturer. Restorations produced by soft machining are sintered after milling the restoration. This process prevents the stress-induced transformation from tetragonal to monoclinic and leads to a dense restoration and a surface virtually free of the monoclinic phase unless grinding adjustments are needed or sandblasting is performed [14].

Most manufacturers of 3Y-TZP blanks do not recommend grinding or sandblasting to avoid both the $t \rightarrow m$ transformation and the formation of surface flaws that could be detrimental to long-term performance. In contrast, restorations produced by hard machining contain a significant amount of monoclinic zirconia, usually associated with surface microcracks, higher susceptibility to LTD and lower long-term reliability [7, 12].

Other less commonly used TZPs contain 4% or 5% mol concentrations of yttria. Increasing yttria content increases the cubic phase which does not undergo transformation to the monoclinic phase. This results in a ceramic that is highly translucent but with weaker mechanical properties as transformation toughening does not occur [15, 16].

2.2 Glass-infiltrated zirconia: Toughened alumina (ZTA)

Alumina matrix is added to zirconia in order to utilize the stress-induced transformation capability of zirconia. In-Ceram Zirconia (Vident™, Brea, CA) was introduced as a core ceramic by the addition of 33 vol% of 12 mol% ceria stabilized zirconia (12Ce-TZP) to In-Ceram Alumina [12]. It is processed by either slip casting or soft machining. In slip-casting, initial sintering takes place at 1100°C for 2 h, followed by lanthanum glass infiltration of this porous ceramic. The glass phase represents approximately 23% of the final product. The amount of porosity is greater than that of sintered 3Y-TZP and comprises between 8 and 11%, explaining the lower mechanical properties of In-Ceram® Zirconia® when compared to 3Y-TZP dental ceramics [12]. In-Ceram Zirconia is stronger and more opaque than In-Ceram Alumina and In-Ceram Spinell, therefore its use is limited to posterior crowns and fixed partial dentures [17].

2.3 Partially stabilized zirconia (PSZ)

There was a considerable amount of research on magnesia-stabilized zirconia (Mg-PSZ) for biomedical use but it was stopped in the 1990s to many causes. Mg-PSZ had higher residual porosity, which resulted in a less dense and weak final structure. The large grain sizes (30–60 μm) led to wear of the opposing structure. It also requires a higher sintering temperature of 1800°C as opposed to 1400°C of TZP, and a strictly controlled cooling cycle, especially in the aging stage. Partially stabilized zirconia usually contains a cubic matrix as the major phase and monoclinic and tetragonal zirconia as the minor phases [6]. The amount of MgO in the composition of commercial materials usually ranges between 8 and 10 mol% [18]. Precipitation of the transformable t-phase occurs during this stage, in which volume fraction is a critical factor in controlling the fracture toughness of the material [7]. Denzir-M® (Dentronic AB) is the sole Mg-PSZ ceramic available for dental restorations fabricated via hard machining [19].

Another oxide that is used to stabilize zirconia is ceria (CeO_2). Ceria provides better thermal stability and resistance to LTD than yttria-stabilized zirconia although the amount of ceria required to maintain the same stability is greater [20]. Ce^{4+} itself is unstable as such and reduces to Ce^{3+} which does not have a very good stabilizing effect on zirconia [19]. It also has a lower flexural strength but this could be improved by adding nanosized alumina in the matrix, called ceria-stabilized zirconia/alumina nanocomposite available commercially as Nanozir (Hint-Els, Griesheim, Germany) [20].

2.4 Zirconia containing lithium disilicate (ZLS)

Lithium disilicate has gained popularity as a monolith ceramic for single crowns and partial coverage restorations due to its excellent optical properties and strength and is available as machinable blanks [21]. To this technology, tetragonal zirconium oxide with a mean grit size of approximately 0.5 to 0.7 μm is added as fillers. Zirconia crystals act as a nucleating agent but remain in solution in the glassy matrix. The flexural and fracture strengths are higher than lithium disilicate glass ceramics. The mechanical properties are approximately three times higher than those determined for leucite-reinforced glass ceramics. ZLS ceramics offer an excellent combination of high strength and outstanding optical properties. Thus, these materials are interesting for the fabrication of monolithic restorations. ZLS ceramics are marketed as Vita Suprinity and Celtra Duo developed by Vita (Vita Zahnfabrik, H. Rauter GmbH & Co., Bad Säckingen, Germany) and Dentsply (Dentsply Sirona, DeguDent, GmbH, Hanau-Wolfgang, Germany), respectively [22, 23]. These materials are available as industrially prefabricated blanks for various CAD/CAM systems [7].

2.5 Resin nanoceramics

Resin-matrix ceramics also called hybrid ceramics, were specially formulated for CAD/CAM and mostly contain zirconia as fillers (5). Lava Ultimate (3 M ESPE) is a highly cross-linked polymeric matrix that contains a proprietary blend of three types of fillers: silica nanoparticles, zirconia nanoparticles and zirconia-silica nanoclusters in 80% wt. (65% vol.) [24]. This material may offer higher flexural strength and fracture toughness, which results in better long-term durability and polish over time. It is available in eight shades, in both high and low translucencies. The material is indicated for single-tooth restorations, including implant abutments [7].

Novel zirconia materials have also been chronologically divided into the following three generations:

- i. The first generation, tetragonal zirconia polycrystals (3Y-TZP), consisted of 5.2 wt% or 3 mol% yttria and 0.25 wt% alumina and has a small grain size (0.3–0.5 μm), high fracture toughness (9–10 MPa/m²), high flexural strength (900–1200 MPa), and Young's modulus of 210 GPa at room temperature. It was sintered at a relatively low temperature. They exhibited high opacity due to the birefringent nature of the non-cubic phases of zirconia. However, clinical studies revealed high failure rates of fixed partial dentures, anterior and posterior crowns and zirconia implants, thus lacking mechanical integrity [14, 16].
- ii. The second generation was refined drastically by eliminating the sintering aid (alumina), and increasing the sintering temperature and/or duration. The

grain size of 3Y-PSZ is increased to 0.5 to 0.7 μm , and the cubic phase content is increased from 6 to 12% to 20–30%. As a consequence, the translucency is increased marginally, and the biaxial strength is decreased to 900 to 1150 MPa. Although translucency is improved, it was still insufficient for use in the anterior esthetic zone, especially single tooth restorations [16].

- iii. The third generation aimed at reducing the opacity, incorporates more optically isotropic cubic zirconia (50–80%), has a grain size of 1.5 μm and is produced by increasing the yttria dopants to 4–5 mol% and increasing the sintering temperature and/or duration more than that of the second generation. This is known as 5Y-PSZ. However, cubic zirconia is weaker and more brittle than its tetragonal counterpart, which jeopardizes the strength and toughness of the zirconia. The translucency is increased significantly, but the biaxial strength is decreased to 450 to 740 MPa.

Additional experimental novel zirconia types with improved translucency have been developed, including graded zirconia and nanostructured zirconia [14, 16]. Zhang and Kim developed graded zirconia in which feldspathic glass was infiltrated into Y-TZP with improved hardness and esthetics. The graded zirconia cross-sectional structure consists of an outermost glass layer, a glass-Y-TZP layer, and a Y-TZP interior. This type of gradation occurs to have eliminated delamination of the glass [25, 26].

3. Applications of zirconia in dentistry

3.1 Dowels or posts

Generally, endodontically treated teeth have undergone significant tooth destruction, both coronal and radicular, which compromises the mechanical integrity of the tooth [27]. All endodontically treated teeth also require a build-up to replace the tooth structure that had been lost due to caries or other pathologies, and access cavity preparations [28]. An assessment is made after the treatment to determine if the prospective build-up requires additional support to be retained on the tooth in the long term. This support comes in the form of a post that is inserted from $\frac{1}{2}$ to $\frac{2}{3}$ rds the length of the root [29]. Posts are available in different materials such as stainless steel, nickel chromium alloys, carbon fiber and glass fiber [30]. Zirconia esthetic posts are used in the anterior teeth to overcome the black color and shadow of metal posts under translucent crowns. They have high strength and fracture toughness and are extremely hard and stiff materials which makes their removal difficult in an event that necessitates retreatment [3]. Although zirconia posts are esthetically acceptable, their clinical use is limited due to a lack of retreatability and higher stiffness than dentin which may cause functional stresses to be transferred to the dentin [31].

3.2 Crown and bridge

Missing teeth cause not only functional and structural disturbance but also influence a person's psychology and social interactions. All-ceramic restorations were limited to anterior or single-tooth restorations due to their weak mechanical strength. Porcelain-fused-to-metal has been considered as the gold standard for load-bearing

restorations and multiple units till recent research focused on reinforcing ceramics which resulted in the development of lithium disilicate and oxide ceramics (alumina and zirconia) [32]. In fixed partial dentures, zirconia is used as the framework (or matrix) over which the veneering ceramic is fired. It has been found that fabricating the framework in the anatomic design rather than an arbitrary form contributes to increased strength and bonding to the veneering ceramic [33]. The cumulative survival rate for zirconia single tooth crowns was 92.7% after 3 years and for fixed partial dentures is 73.9–100% after 2–5 years [34].

3.3 Implant abutments

Dental implants have shown a high success rate for single tooth rehabilitation. Titanium, stainless steel, gold alloy, zirconia and polyether ether ketone (PEEK) are the most commonly used abutment materials in implant dentistry [35]. Titanium abutments have excellent biocompatibility and mechanical strength and are considered the gold standard for posterior regions; nonetheless, they cause a grayish discolouration of the soft tissues around the abutment [36]. In its stabilized form, zirconia ceramics show better tissue adaptation and lower plaque retention as compared to alumina and titanium when used as implant abutments. Four-year survival rate is 100%, although long-term studies show that zirconia is prone to delamination and degradation in the oral environment [3].

4. Fabrication of restorations

Zirconia restorations are fabricated using CAD/CAM by either soft machining of pre-sintered blanks or hard machining of fully sintered blanks. The conventional CAD/CAM procedure involved purely laboratory works followed by first generation developed by Duret and colleagues combining intraoral scanning and final crown produced by controlled machining and milling. As it was not widely used due to the lack of accuracy, another approach called networked CAD/CAM processing was introduced into dental technology. While computer-aided designing (or CAD) allows one to determine the 2-D geometry, computer-aided machining (or CAM) allows the processing of the proposed design to calculate the path of cutting using various tools. CAM is nothing but a machine language used by copy-milling to fabricate a ceramic prosthesis. In spite of CAD/CAM having a high success rate in terms of design and fitting, final crown fabrication and veneering are done in a dental lab [37].

Normally, there are three different approaches by which ceramic restorations are processed in dentistry: green stage processing, white stage processing and processing through hot isostatic pressing (HIP). The difference between these approaches lies in the heat treatment of the raw material used for processing. The green stage of ceramic is only ceramic powder and binder pressed into a blank. It is very soft as it is extremely porous and is not used for processing zirconia. The heat-treated (or pre-sintered) green stage gives the white stage of ceramic which is processed via soft machining. Further heat treatment of this white body results in an extremely dense (~99% theoretical density), fully sintered blank which requires custom coloring [7, 38, 39]. Sintering is a thermal treatment for bonding particles into a coherent, predominantly solid structure via mass transport events that often occur on the atomic

scale. Bonding leads to improved strength and lower system energy. Sintered blanks are characterized by enhanced density and improved properties [40].

4.1 Soft machining

Soft machining of pre-sintered blanks is the most common method of processing zirconia restorations. Pre-sintered zirconia blanks are manufactured by cold-isostatic pressing (CIP) of a mixture of zirconia powder, stabilizing oxides and binding agents (the latter removed during the pre-sintering process) [21]. The prosthesis is milled from this pre-sintered block but with bigger dimensions so as to compensate for the sintering shrinkage [39]. The most common sintering method for zirconia uses conventional furnaces at temperatures between 1350°C and 1400°C and holding times ranging from 2 to 4 hours. An alternative protocol that is recommended by manufacturers using conventional ovens is a short “speed” sintering protocol which uses temperatures of 1500–1600°C and a holding time of 30 minutes that is supposed to save time and be more economical [14]. The zirconia framework attains its final mechanical properties at the end of the sintering process when it undergoes a contraction at about 25%, and reaches its correct dimensions. In order to optimize the fitting of the restoration it's imperative to know the exact volume shrinkage for every zirconia blank. The vast majority of blocks have barcodes that give information fed into the computer regarding the density of the milling block so that the framework is milled adequately oversized [39].

4.2 Hard machining

Fully sintered blocks are processed through hot isostatic pressing (HIP) at temperatures between 1400 and 1500°C. Unlike cold isostatic pressing which uses room temperature fluid under pressure to process zirconia blanks, HIP uses heat and high pressure in an argon atmosphere. This is done using special furnaces, which in addition to heavy milling procedures makes the prosthesis fabrication an expensive task [41]. Although fully dense blanks have better mechanical properties, they lack the popularity of partially sintered blanks owing to their long milling times and the hardness of the dense blanks, especially in the fabrication of fixed partial denture frameworks [38].

5. Clinical aspects

5.1 Mechanical and physical properties

Mechanical properties of the final restoration are influenced by the very first step of synthesis of the Y-TZP nanopowder. Starting powders must be crystalline, homogeneous, with high purity and narrow particle size ranges [42]. The powder is then compacted most commonly by cold isostatic pressing, to achieve a certain level of densification, followed by sintering. Many studies have been done to assess the effect of sintering temperature on the mechanical properties of zirconia and it was found that monolithic zirconia retained its biaxial flexural strength at a sintering temperature of 1550°C whereas, the biaxial flexural strength of core zirconia decreased significantly. It is established that monolithic zirconia has higher flexural strength and fracture resistance than not only conventional glass ceramics but also lithium disilicate [15]. Zirconia shows similar mechanical properties to stainless steel [6] and

Property	Flexural strength (MPa)	Fracture toughness (MPa m ^{1/2})	Modulus of elasticity (GPa)
3Y-TZP	900–1200	9–10	200–210
ZTA	426–688	3.1–4.61	210
Mg-PSZ	898–1118	5–10	200
ZLS	123–553	1.30–2.98	61–108.2
Resin nanoceramics	200	1.09	16.4–28.1

Table 1.
 Mechanical properties of types of zirconia in dentistry.

is the highest one among ceramics used in dentistry. As the strongest and toughest of all dental ceramics, zirconia has 900–1200 MPa flexural strength, and 9–10 MPa.m^{1/2} fracture toughness [43]. Some mechanical properties comparing the different types of zirconia ceramics are summarized in **Table 1**.

5.2 Optical properties of zirconia

In an all-ceramic restoration, the ceramic material may be monolithic consisting of a single ceramic material, or a ceramic core material that is covered with a ceramic veneer and is known as a bi-layered all-ceramic restoration. In the bi-layered all-ceramic restoration, the core supports the restoration and gives it strength, and the veneer provides the restoration with its final shape, shade and esthetic. However, the core may also play a part in the development of the final restoration's shade [44]. An inherent drawback of the multi-layered restoration is the chipping or delamination of the veneering ceramic, which was overcome by introducing the monolith zirconia restoration. The color of monolithic zirconia restorations is initially affected by the original shade and optical properties of zirconia ceramics determined by the manufacturing processes. Various laboratory procedures conducted to fabricate monolithic zirconia restorations may influence the color. Clinical factors such as dental background, cement and zirconia restoration features can impact the resulting color. Shade reproduction of monolithic zirconia restorations may be affected during the long process from the production of zirconia ceramic to restoration delivery. The final color of restoration is the result of manufacturing processes, laboratory procedures and clinical factors [45].

The most significant disadvantage of zirconia crowns is their relatively opaque appearance. The least translucent zirconia has 42.1% translucency of a typical glass ceramic and 72% translucency of a lithium disilicate ceramic. Two factors determine the appearance of a restoration: first, the intrinsic character and color of the material and the second is extrinsic parameters like cement layer, restoration thickness and low thermal degradation. The gloss and translucency of zirconia are brand dependent and are greatly affected by grain size and content, yttria content and the amount of impurities. Light scattering and thickness are two important factors determining the translucency of ceramic [46].

As natural zirconia is white, an immediate advantage over PFM restorations is the absence of the metallic collar usually placed on the margin, and identified by patients as a “black line” as seen with gingival recession. The high opacity of zirconia can be used as an advantage to a certain degree. The presence of discolored tooth stumps, amalgam or other heavily colored restorative materials, metallic posts and cores or

carbon fiber posts may be masked up to an extent to achieve a natural appearing restoration [47]. Manufacturers have presented zirconia ceramics with different visible light transmission percentages (VLTPs) ranging from 20–50%. Five types of translucency are available for zirconia including low, medium, high, super and ultra-translucency. Low and medium translucency zirconia are commonly indicated for zirconia frameworks, whereas high, super and ultra-translucency zirconia are mostly designated for monolithic restorations [45].

Much research and development has been done to improve the optical properties of zirconia. The opacity is said to be a result of the interaction of grain sizes with the wavelength of light, refractive index mismatch between zirconia grains and the matrix, and refractive indices of the monoclinic, cubic and tetragonal phases. These factors cause light to be scattered instead of being transmitted through zirconia, leading to an opaque appearance [46]. Therefore, light scattering must be reduced to increase translucency.

5.2.1 Factors that affect zirconia translucency

- i. **Composition:** The addition of alumina as a sintering aid to Y-TZP enhances densification creating fine-grained and homogeneous microstructures while decreasing the sintering temperature and time required [13]. Alumina also contributes to the stabilization of the tetragonal zirconia phase. However, due to the difference in the refractive index of alumina and zirconia, which at 600 nm wavelength are $n = 1.76$ and $n = 2.21$, respectively, alumina inclusions are considered significant scattering centres. Lowering the amount of alumina from 0.25 to 0.1 or 0.05 wt. % can significantly improve translucency but requires higher sintering temperatures ($>1500^{\circ}\text{C}$) in conjunction with a longer holding time (6 h) which in turn increases the grain size, thereby leading to reduced translucency. The introduction of 0.2 mol% lanthanum oxide (La_2O_3) in conventional 0.1–0.25 wt.% Al_2O_3 -doped 3Y-TZP resulted in an excellent combination of high translucency and superior hydrothermal stability while retaining excellent mechanical properties [13].
- ii. **Increasing the yttria dopant content to 4–5 mol% increases the cubic phase which results in an increase in the translucency, referred to as high-translucency (HT) zirconia.** In 2014, 3 M ESPE presented a translucent experimental zirconia containing 7.10 wt% yttria and a reduced grain size of 150 nm (1.5 μm). This combination resulted in a highly translucent ceramic albeit the decreased transformation toughening, flexural strength and fracture toughness, all due the result of a reduced tetragonal phase (46). An even higher content of 8 mol% of yttria has been marketed as ultatranslucent zirconia [Prettau Anterior (Zirkonzahn), DD cube X2 (Dental Direkt), Katana Zirconia St and Katana Zirconia Ut Noritake (Kuraray Noritake Dental)] [46, 48].
- iii. **Sintering temperatures:** Higher sintering temperatures report an increase in translucency, generally correlated to an associated increase in grain size, pore elimination through solid-state diffusion and consequently an increase in density. Most monolithic zirconia ceramics should be sintered in a sintering temperature between 1400 and 1550 $^{\circ}\text{C}$ and no higher than that, as at temperatures of 1600 or 1700 $^{\circ}\text{C}$ or after prolonged sintering, grain boundary cracks can be generated, increasing light scattering [13]. Improving color and

translucency can be done by increasing the sintering temperature and time, though speed-sintered Y-TZP can acquire less desirable wear properties than normal sintered zirconia [48].

- iv. Porosities: Pores of a similar size to that of visible light wavelength (400 nm to 700 nm) is the main cause of light scattering. Pores larger than 50 nm can cause significant scattering negatively affecting light transmittance. In order to minimize pore size, the starting zirconia powder needs to be on nanometric scale to give a dense zirconia blank [13]. For high-density zirconia, employing 40 nm-sized particles instead of 90 nm amplifies the sintering density, and reduces pores and scattering [13, 48].
- v. Defects such as oxygen spaces: Sintering conditions have a significant effect on oxygen vacancies. When the Y-TZP is under controlled firing or sintering is done in a reduced environment, oxygen vacancies occur. This means that some of the oxygen atoms leave their respective positions in the crystal lattice creating a defect. The amount of these oxygen vacancies affect light scattering as they serve as scattering centres. On the other hand, post-sintering in an oxidizing environment could put some oxygen back into Y-TZP crystals. However, this process also creates porosity due to the combination of vacancies to produce larger ones at high temperatures. Therefore, the main consideration is to control the heat treatment to decrease the number of oxygen vacancies in the material [48, 49].

Grain size: The large grain size of tetragonal zirconia polycrystals has been correlated to reduced translucency and increased light scattering. According to classical physics, materials containing grain sizes of less than 1 μm appear less opaque due to the reflection and absorption of visible light. On the other hand, particles larger than 10 μm scatter more light and appear more opaque. Due to the birefringence (double refraction) and polycrystalline nature of zirconia, there is more scattering than transmission. Reducing the grain size of TZP zirconia improves translucency. The higher sintering temperature is associated with increased grain size but reduced strength of the ceramic. A grain size of less than 100 nm is necessary for acceptable translucency. Currently, the mean grain size of contemporary zirconia ceramics lies between 0.2 and 0.8 μm [13, 48]. To achieve a translucency comparable to dental porcelains, the mean grain size of 3Y-TZP should be about 82 nm for 1.3 mm restorative thickness, 77 nm for 1.5 mm and 70 nm for 2 mm [25].

Restoration thickness: Translucency decreases with increased restoration thickness and seems to be brand-dependent [45]. A restoration as thick as 0.5 mm has better tooth-like translucency. A minor increase or decrease in the restoration thickness can alter the translucency significantly. A minimum thickness of 0.9 mm is required for acceptable shade matching of HT zirconia. For color masking, a minimum thickness of 1 mm is required or 1.6 mm thickness for ideal masking [45, 46].

5.3 Low temperature degradation (LTD)

LTD is also called aging and is defined as a spontaneous $t \rightarrow m$ transformation occurring over time at low temperatures, and the transformation is not triggered by local stresses or an advancing crack [50]. This occurs in the presence of water and starts in isolated grains on the zirconia surface leading to an increase in volume [51]. Due to this, there are stresses created in the neighboring grains and resulting in microcrack

formation which allows the water to penetrate and ultimately there is a significant decrease in the strength [20]. This transformation may be accelerated by water humidity [52], and slowed using smaller grains and higher amounts of stabilizing oxides [39]. CeO₂ in 12 and 14 mol% is more resistant to LTD than Y-TZP, however, it appears more yellow. When Ce⁴⁺ is reduced to Ce³⁺, the Ce-TZP becomes dark gray due to the high concentration of oxygen vacancies. LTD in Ce-TZP may be accelerated on intake of reducing foods like glucose and lactose [50]. Other factors that influence LTD are tensile stresses, grain size and residual stressed post sintering [20]. Tensile stresses as low as 400 MPa can induce LTD over a course of 5 years. A crack tip forms on the surface of zirconia which are exposed to water (or any other fluids) and the grain transforms to monoclinic. As $t \rightarrow m$ is associated with a volume expansion, there is an uplift of the surface at the site of transformation. Under this grain, there is a large compression that subjects the underlying grains to small tensile stresses. These grains transform to monoclinic and as a cycle, continue to crack through the depth of the zirconia, thus weakening the entire structure. Reducing the grain size is said to have a restraining effect on LTD. Critical grain size for pure zirconia at room temperature falls in the range of 5–10 nm, although this number was calculated at above 100°C in various experiments [50].

5.4 Other considerations

Technical problems associated with the clinical performance of zirconia crowns and fixed dental prostheses have been reported, in particular, chipping of the veneering porcelain when applied to zirconia framework structures and loss of retention. Attempts to minimize the chipping of veneering porcelain by milling the veneers and frameworks separately and subsequently luting them with either a luting agent or using fusing firing (CAD on) have not been quite sufficient to address the chipping concerns. Another attempt to overcome the veneer chipping problem was the introduction of zirconia in the form of fully anatomical contoured monolithic prostheses intended to be used without veneering porcelain [14]. The problems of layering in zirconia-based restorations, such as veneering ceramic delamination/chipping and veneering ceramic zirconia ceramic incompatibility, do not exist in monolithic zirconia restorations [45]. Although monolithic zirconia ceramics have lower flexural strength than the framework zirconia of zirconia-based restorations of equal thicknesses, monolithic zirconia crowns have a higher fracture resistance than zirconia-based crowns due to increased zirconia thicknesses and lack of veneering ceramics [45].

Ideally, chair-side grinding and adjustment of anatomically contoured zirconia restorations should be avoided as they can produce rough surfaces. However, for many restorations, it is necessary to optimize occlusion, proximal contacts and axial contour. Grinding has two counteracting effects on zirconia: either it produces surface compressive stress that can positively enhance crack healing (by transformation toughening) and increase the material strength by transformation toughening or it can induce surface flaws that may exceed the depth of the compressive layer and negatively influence the strength of the material. Microcracks can be triggered by a number of stimuli such as thermal changes, humidity, airborne-particle abrasion and grinding, as mentioned previously [53]. There are a number of finishing and polishing systems available for zirconia restorations in different grades of diamond grits.

Aging of anatomically contoured Y-TZP restorations could be more crucial because restorations are in direct contact with oral fluid. Hydrothermal aging of zirconia, known as low-temperature degradation, can occur over time within the temperature range of 65–500°C in the presence of water and other solvents. Although this

mechanism is very slow in oral temperatures, zirconia restorations are exposed to other factors such as constant humidity, thermal changes, pH fluctuation, and repeated high occlusal loads due to mastication and parafunctional habits that can accelerate the aging process and reduce the material's fracture resistance. Also, the chemical composition, the microstructure of various brands of high-translucency zirconia, the thickness of the restoration, and the processing can influence resistance to aging [53].

There are few long-term clinical trials to assess the longevity of zirconia restorations. Most studies concluded that the most common cause of failure was the chipping of the veneering ceramic. Moreover, secondary caries and marginal gaps were found in 56 to 59% of fixed partial denture abutments, although periodontal health was maintained as zirconia is shown to be highly biocompatible with gingival tissues. Zirconia implants were well-tolerated with healthy peri-implant bone and no bleeding on probing in a 2-year clinical study [54].

6. Conclusion

The innovation of newer materials in the field of dentistry has been expanding over the past decade. Most research is focused on eliminating the inherent opaque nature and susceptibility to LTD. With single-day, chairside fabrication of prosthesis through CAD/CAM, zirconia is still in its early stages and has a long way ahead to meet various criteria that make it perfectly fit for use as long-term restorations.

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