

In clinical situations that require highly demanding esthetic restorations, all-ceramic restorations have the potential to be a more effective selection when compared to metal ceramic restorations. The alloy structure in metal restorations may create an opaque appearance, while ceramic materials seem to generally produce a more translucent look that replicates the appearance of the natural tooth ⁽¹⁾. All-ceramic fixed partial dentures (FPDs) have been routinely used in clinical dentistry because various all-ceramic materials have been introduced and available for a clinical use. Favourable clinical performance for all-ceramic systems has been reported especially when they are used in the anterior region ⁽²⁾. However, fractures of posterior all-ceramic FPDs were reported to be the main cause of failure for these restorations ⁽³⁾. To overcome this problem, ceramics with different compositions and reinforcing crystalline phases have been developed, such as a glass-infiltrated zirconia, toughened alumina, a lithium-disilicate-based glass-ceramic and zirconia-based materials. Most of the zirconia-based ceramic systems that are currently used in dentistry are yttrium-stabilized zirconia polycrystals (3Y-TZP) ⁽⁴⁾. This zirconia contains 3 mol% of yttria (Y₂O₃) as a stabilizer. The major advantage of this material is its high fracture resistance which is represented by their superior flexural strength (900-1000 MPa) and fracture toughness (5.5 - 7.4 MPa·m^{1/2}) compared with other all-ceramic core materials ⁽⁵⁾. The processing procedures of 3Y-TZP usually use a CAD/CAM technology for machining a presintered zirconia blank to a desired size and shape of a prosthesis and subsequent firing at 1350 - 1550°C which is carried out to produce a densely sintered product. Compensation for 20 - 30% firing shrinkage is made during a CAD

procedure. There is a growing interest in the use of Zirconia oxide ceramics as substitutes for metal core structures⁽⁶⁾.

As Zirconia is relatively opaque and monochromatic in color, a layer of veneering ceramic is built on to provide the restoration with the required esthetics. While manual layering of the veneer ceramic gives the dental ceramist full control over the expected color and shape, it is still in principle a lengthy and a time-consuming process. Even with maximum care and attention, structural defects, such as air bubbles, voids, and micro-gaps at the core-veneer interface remain unavoidable. These structural defects act as stress concentration sites where crack initiation and propagation are highly expected, leaving the veneered restoration susceptible to delaminating or chipping⁽⁷⁾.

Establishing a strong and stable bond with Zirconia has proven to be difficult, as the material is acid resistant and does not respond to common etching and silanation procedures used with other glass containing ceramic materials which react to silane coupling agents⁽⁸⁾. Several surface roughening and coating methods have been used to optimize the surface of Zirconia and to improve its bond strength.

Several techniques based on increasing the surface roughness, such as airborne-particle abrasion and roughening with diamond points, also failed to establish adequate mechanical retention to Zirconia substrates. Also selective infiltration etching (SIE), was developed for dental and biomedical applications.⁽⁹⁾

In spite of being the golden standard in terms of strength and toughness, 3Y-TZP may lack long-term stability, which has been a major issue for medical use and has led to the replacement of several zirconia

femoral heads in orthopedic patients. Low-temperature degradation (LTD) has been associated with several 3Y-TZP-based biomaterials, but is difficult to simulate in the laboratory. Aging occurs experimentally in zirconia, mostly in humid atmosphere or in water. An accelerated ageing test using steam and pressure has been developed to simulate LTD, s-LTD (simulated LTD)⁽¹⁰⁾.

The bond strength between zirconia and its veneering ceramic depends on so many interrelated factors and the effects of these factors together on the bond between veneering ceramic and Zirconia framework is currently the subject of comprehensive investigations.

Thus the purpose of this study is to investigate the effect of a new method of surface treatment of Zirconia on its bond strength with the ceramic veneering ceramics with different veneering techniques and before and after artificial aging.

Dental crown and bridge restorative materials are changing from porcelain fused to metal (PFM) to all-ceramic systems. Techniques, which have been developed over decades in the case of PFM systems, must now be redeveloped for all-ceramic systems⁽¹¹⁾.

All-ceramic systems can provide a better esthetic result for a wider range of patients than can metal-ceramic systems, because a wider range of translucency and opacity (value) can be achieved.⁽¹²⁾

Ceramics as dental materials have desirable characteristics such as chemical stability, biocompatibility, high compressive strength, and a coefficient of thermal expansion similar to that of tooth structure. In addition, dental ceramics have esthetic properties that simulate the appearance of natural dentition; however, they are susceptible to fracture, which is a result of material characteristics and surface and bulk defects⁽¹³⁾.

Ceramics fall into three main composition categories: predominantly glass; particle-filled glass; and polycrystalline. Zirconia is a polycrystalline ceramic without a glassy phase and exists in several forms.

History of zirconia:

Zircon has been known as a gem from ancient times. The name of the metal, zirconium comes from the Arabic *Zargon* (golden in colour) which in turn comes from the two Persian words *Zar* (Gold) and *Gun* (Colour). Zirconia, the metal dioxide (ZrO_2), was identified as such in 1789 by the German chemist Martin Heinrich Klaproth in the reaction product obtained after heating some gems, and was used for a long time blended with rare earth oxides as pigments for ceramics.⁽¹⁴⁾ Good chemical and dimensional stability, mechanical strength and toughness,

coupled with a Young's modulus in the same order of magnitude of stainless steel alloys was the origin of the interest in using zirconia as a ceramic biomaterial. In the early stages of the development, several solid solutions ($\text{ZrO}_2\text{-MgO}$, $\text{ZrO}_2\text{-CaO}$, $\text{ZrO}_2\text{-Y}_2\text{O}_3$) were tested for biomedical applications. But in the following years the research efforts appeared to be more focused on zirconia-yttria ceramics, characterised by fine grained microstructures known as Tetragonal Zirconia Polycrystals (TZP).

Zirconia is a well-known polymorph that occurs in three forms: monoclinic (M), cubic (C) and tetragonal (T). Pure zirconia is monoclinic at room temperature. This phase is stable up to 1170°C . Above this temperature it transforms into tetragonal and then into cubic phase at 2370°C . During cooling, a T-M transformation takes place in a temperature range of about 100°C below 1070°C . The phase transformation taking place while cooling is associated with a volume expansion of approximately 3-4%. Stresses generated by the expansion originate cracks in pure zirconia ceramics that, after sintering in the range $1500\text{-}1700^\circ\text{C}$, break into pieces at room temperature. It was **Ruff and co-workers 1929**⁽¹⁵⁾ that showed the feasibility of the stabilisation of C-phase to room temperature by adding to zirconia small amounts of CaO. The addition of stabilizing oxides, like CaO, MgO, CeO_2 , Y_2O_3 , to pure zirconia allows to generate multiphase materials known as Partially Stabilized Zirconia (PSZ) whose microstructure at room temperature generally consists⁽¹⁶⁾ of cubic zirconia as the major phase, with monoclinic and tetragonal zirconia precipitates as the minor phase. These precipitates may exist at grain boundaries or within the cubic matrix grains.

In *Garvie and Nicholson 1972*⁽¹⁷⁾ showed that the mechanical strength of PSZ was improved by a homogeneous and fine distribution of the monoclinic phase within the cubic matrix. The development of zirconia as an engineering material was marked by *Garvie et al. 1975*⁽¹⁸⁾, who in their article ‘Ceramic Steel?’ showed how to make the best of T-M phase transformation in PSZ improving mechanical strength and toughness of zirconia ceramics. The tetragonal metastable precipitates was observed to be finely dispersed within the cubic matrix were able to be transformed into the monoclinic phase when the constraint exerted on them by the matrix was relieved, i.e. by a crack advancing in the material. In that case, the stress field associated with expansion due to the phase transformation acts in opposition to the stress field that promotes the propagation of the crack. An enhancement in toughness is obtained, because the energy associated with crack propagation is dissipated both in the T-M transformation. This remarkably increases the fracture toughness of the material by hindering, but not preventing, the propagation of a crack; tensile stress concentration converts the transformation from (t) phase to the (m) phase⁽¹⁹⁾. Increasing the crystal volume, constrained by the surrounding ones, leads to a favourable compressive stress. This limits growth of cracks. Transformation toughening or “phase transformation toughening” (PTT) is the reported mechanism for exceptional flexural strength and fracture toughness of zirconia among all the other ceramics⁽²⁰⁾. At room temperature, the transformation from tetragonal to monoclinic is a one-way process. This means that, once it takes place, the crack-hindering effect cannot be exploited for limiting further fractures, “like a used match cannot be lit again”⁽²¹⁾. Heating the material at a temperature between 900 °C and 1000 °C for a short time, can reverse the process⁽²²⁾;

in this case, the phase transition from monoclinic back to tetragonal form, rather than making crystals available again for further transformation and crack repair, generates a relaxation of the advantageous compressive stress at the surface, reducing the material toughness. From this point of view, the high temperature thermal process of veneering zirconia with feldspathic ceramic should be taken into account as a possible risk of such a detrimental reverse transformation⁽⁴⁾.

The grain size dramatically influence the mechanical behaviour of zirconia, in that higher temperatures and longer sintering times produce larger grain sizes⁽²³⁾. The critical crystal size is approximately 1µm: above such dimension, zirconia is more prone to spontaneous PTT due to lower stability, whereas a smaller grain size makes zirconia less susceptible to this phenomenon, although below 0.2µm PTT does not happen and zirconia fracture toughness decreases. Consequently, the sintering conditions are paramount since they influence the crystal size, strongly affecting the mechanical properties and the stability of zirconia and have to be strictly controlled in the whole production process⁽²⁴⁾.

Characteristics of Zirconia:

Biological characteristics of zirconia:

- ***Biocompatibility and bioinertia:***

In vitro and in vivo studies have confirmed a high biocompatibility of zirconia, especially when it is completely purified of its radioactive contents⁽²⁵⁾. Zirconia based ceramics are chemically inert materials, allowing good cell adhesion, and while no adverse systemic reactions have been associated with it.⁽²⁶⁾ However, particles from the degradation

of zirconia at low temperature (LTD) or from the manufacturing process can be released, promoting an immune localized inflammatory reaction.⁽²⁷⁾

- ***Degree of toxicity***

In vitro tests have shown that zirconia has a lower toxicity than titanium oxide and similar to alumina. Cytotoxicity, carcinogenicity, mutagenic or chromosomal alterations in fibroblasts or blood cells has not been observed⁽²⁸⁾.

Optical characteristics

- ***Degree of opacity and translucency***

The ceramic systems used in dentistry must have adequate translucency to achieve good dental esthetics while at the same time provide adequate strength during chewing. Considering the currently available ceramic materials, these two properties cannot be obtained by a single material, especially in the manufacturing of fixed prostheses. Thus, an oxide ceramic material should be used as an infrastructure, while a glass or feldspathic ceramic must be used as an esthetic coating material. The infrastructures of zirconia provide good masking of darkened substrates due to an adequate level of opacity, and they also allow a controlled translucency after lamination, due to their homogeneity and high density (residual porosity <0.05%), even limited in thickness (0.5mm). Its opaque optical behavior can be attributed to the fact that the grain size is greater than the length of light, and also that zirconia has a high refractive index, low absorption coefficient and high opacity in the visible and infrared spectrum.⁽²⁹⁾ Therefore, zirconia cannot be used as a restorative material alone. Because of its opacity and the current

processing technologies, zirconia must be covered with translucent ceramics which exhibit characteristics that may look like natural teeth⁽³⁰⁾.

Mechanical characteristics

The mechanical performance of zirconia were extensively investigated on both single crowns and 3- and 4-unit FPDs, with variable reported data, due to a noticeable difference of experimental conditions and measurements. Mechanical properties of zirconia were proved to be higher than those of all other ceramics for dental use, with a fracture toughness of $6\text{--}10\text{MPa/m}^{1/2}$, a flexural strength of $900\text{--}1200\text{MPa}$ and a compression resistance of 2000MPa ^(4,14). An average load-bearing capacity of 755N was reported for zirconia restorations ⁽³¹⁾. Fracture loads ranging between 706N ⁽³¹⁾, 2000N ⁽³²⁾ and 4100N ⁽³³⁾ were reported; all of the studies demonstrated that in dental restorations zirconia yields higher fracture loads than alumina or lithium disilicate. A recent in vitro investigation on zirconia FPDs evidenced failure loads ranging between 379 and 501MPa , thus higher than average human biting force, confirming a satisfactory serviceability of such frameworks ⁽³⁴⁾.

- ***Flexural strength***

Flexural strength is an important mechanical property that aids in predicting the performance of fragile materials. It can be defined as the final force required to cause fracture and is strongly affected by the size of flaws and defects on the surface of the material tested⁽³⁵⁾. Micro cracks and defects that inherently grow during the thermal and mechanical processes can significantly influence the measurement of resistance. However, data alone cannot be extrapolated to predict the clinical performance of a material. Resistance values are significant when

incorporated into context, through knowledge of the material microstructure, processing history, methodology, test environment and failure mechanisms. Structural failure probabilities are determined by additional failure, variables that describe the stress distribution and sizes of defects, which may be considered as single or multiple failure modes. An understanding of the current clinical failure modes is absolutely necessary before the results of in vitro resistance testing can be considered with clinical validity⁽³⁶⁾. Values of mechanical strength of fragile materials usually exhibit a large dispersion of values (above 50%), even for high performance ceramics⁽³⁷⁾. This known phenomenon is based on the distribution of defects or failures. The hypothesis that surface defects and micro-cracks in ceramic Y-TZP zirconia are made internally on the surface machined by CAD-CAM technique was confirmed by **Luthardt et al. 2004**⁽³⁸⁾. Milling may introduce residual surface compressive stresses that can significantly increase the resistance of zirconia ceramics. On the other hand, severe wear can make profound defects, which act as stress concentrating areas. Alternative methods, such as the partially sintered method of ceramics manufacturing, as well as wear-free procedures, should be developed to obtain crowns and bridges of the Y-TPZ system that increases strength and reliability. Another important fact is that the accumulation of microcracks resulting from loading in an aqueous environment (such as that found in the oral cavity), can cause surface defects that act as enhancers of tension in areas of local concentration, facilitating the initiation of fracture under low level applied stresses⁽³⁹⁾.

- ***Fracture toughness***

Fracture toughness is defined as the level of critical stress at which a particular defect starts to grow. This property indicates the material's ability to resist rapid crack propagation and catastrophic fracture⁽⁴⁰⁾. It also measures the ease of crack growth from an initial failure. Steel and ductile metals show values above 50MPa m^{1/2}. Ceramics cover a range of fracture toughnesses which rarely exceeds 5MPa m^{1/2}. Not surprisingly, these low values affect their clinical performance⁽⁴¹⁾. In zirconia, the process of phase transformation induces compressive stress at the crack tip and shear stresses that act against the stress field generated in this region. The addition of an oxide stabilizes the system transformation of zirconia in the tetragonal phase and retains a layer of compressive stresses, resulting in the formation of a tougher stabilized tetragonal zirconia polycrystal⁽⁴²⁾.

- ***Subcritical crack growth***

The subcritical crack growth (SCG), which consists of a slow propagation of failures, is one of the major causes of damage to ceramics and usually occurs as a function of time. SCG under constant load is due to the corrosive action in the region under stress at the crack tip.⁽⁴³⁾ The amount of SCG is affected by different factors that add to the strain rates. The format, depth and width of the defects within the material affect the tension intensity factor. In ceramics, the cyclic loading also accelerates the crack propagation and decreases its threshold due to degradation of toughening mechanisms⁽⁴⁴⁾. A faster spread of the crack is observed in the presence of water, which can be attributed to a high concentration of water molecules around the crack. This environment increases the rate of crack

growth because it facilitates the Zr-O-Zr union cleavage at the end of the crack⁽²⁷⁾.

- *Aging*

Aging or zirconia low temperature degradation (LTD) is a progressive and spontaneous phenomenon that is exacerbated in the presence of water, steam or fluids. The consequences of the material aging process are many, including surface deterioration, micro cracks and decreased resistance in medium and long term periods. Aging occurs through a slow surface transformation to the monoclinic stable phase. This transformation begins in individual particles on the surface through a mechanism of stress corrosion. The initial transformation of specific particles can be related to a state of imbalance: greater particle size, lower yttria content, specific guidance from the surface, the presence of residual stress, or even the presence of a cubic phase. The transformation occurs through nucleation and growth processes. This phenomenon leads to a cascade of events occurring in neighbouring particles, leading to an increase in volume that stresses the particles and results in subcritical crack growth (SCG), offering a way for water to penetrate inside the material. The stage of growth again depends on various microstructure patterns, such as: porosity, residual stresses, and particle size, among others⁽⁴⁵⁾. The attempt to minimize the degradation at low temperature (LTD) of 3Y-TZP includes reducing the particle size, increasing the content of a stabilizing oxide, or even the formation of composites with aluminum oxide (Al₂O₃). The addition of alumina particles prevents the relaxation of the network of tetragonal zirconia under stress during the aging process, since relaxation is responsible for degradation⁽³⁹⁾. In the

literature, there is a major concern in evaluating the influence of superficial⁽⁴⁶⁾ and termic treatments⁽⁴³⁾ on the mechanical properties of partially stabilized zirconia. Fine polishing of the surface can reduce surface defects created in the finishing, improving the mechanical properties of the surface. However, prior to polishing, surface modifications such as adjustments and finishing, can introduce a compressive surface tension, initially increasing the flexural strength, but then changing the phase integrity of the material and increasing the susceptibility to aging⁽⁴⁷⁾.

Zirconia in dentistry:

In the biomedical field zirconia is used as hip prosthesis replacing femur heads. The introduction of zirconia (zirconium dioxide, ZrO_2) as a dental material has generated considerable interest in the dental community⁽⁴⁾. Zirconia is widely used to build single crowns, anterior and posterior fixed partial dentures, splinted crowns, zirconia implants and crowns on Implants, cantilever bridges, inlay and onlay bridges, and resin bonded bridges.

The most common type of zirconia used in dentistry is yttrium partially-stabilized tetragonal zirconia polycrystal (3Y-TZP). This type of zirconia is made of transformable, t-shaped grains stabilized by the addition of 3 mol% yttrium-oxides (Y_2O_3). It is placed in category 4-polycrystalline solids (alumina and zirconia) and has no glassy components. All the atoms are packed into a regular pattern making it dense and stronger⁽⁴⁸⁾. At the moment it is the most popular and frequently used form of zirconia commercially available for dental applications.

Manufacturing zirconia for dental application:

Computer aided design /Computer aided manufacture CAD/CAM zirconia dental frameworks can be produced according to two different techniques: “soft machining” of presintered blanks or “hard machining” of fully sintered blanks⁽⁴⁾.

The soft machining process is the most diffused manufacturing system for 3Y-TZP, based on milling of pre-sintered blanks that are fully sintered at a final stage. Such zirconia blanks, at the so-called “green state”, are produced by compacting zirconia powders (in presence of a binder that will be eliminated in the following pre-sinterization step) through a cold, isostatic pressing process; this results in a very narrow pore size (20–30 nm) and quite homogeneous distribution of the components inside the blank⁽⁴⁾. Processing at a proper pre-sintering temperature of zirconia is a crucial factor since this parameter affects hardness, machinability and roughness of the blanks. From the manufacturers’ point of view about the choice of the most convenient production technique, hardness and machinability act as opposite factors: an adequate hardness is necessary to manipulate the 3Y-TZP blanks safely, but, if excessive, it is detrimental to a proper machinability. Moreover, higher pre-sintering temperatures create rougher blank surfaces⁽⁴⁾.

After scanning a stone die of the supporting abutment(s) (or directly the wax pattern of the crown/FPD), a virtual, enlarged framework is designed by sophisticated CAD softwares⁽²³⁾. Then, through a CAM milling procedure, a framework with enlarged accurately controlled dimension is machined out of the blank. At the end, the sinterization is

completed at high temperature the zirconia framework acquires its final mechanical properties in that it undergoes a linear volume shrinkage of about 25%, so regaining its proper dimensions. Such processing is known to produce very stable cores containing a significant amount of tetragonal zirconia with surfaces virtually free from monoclinic phase⁽⁴⁾. Nevertheless, a certain amount of cubic zirconia may be present due to an uneven distribution of yttrium oxide. The cubic phase is richer in stabilizing oxides than the surrounding tetragonal crystals and this may negatively influence the stability of the material⁽²³⁾.

Frameworks can be colored either adding minimum amounts of metal oxides to the zirconia powder or, after machining, by soaking the core in solutions of metal salts (like cerium, bismuth or iron); the framework coloration seems neither to induce PTT nor to decrease the mechanical performance of the restorations⁽⁴⁾. Soft-machining is the preferred process by the majority of the manufacturers, like Procera Zirconia (Nobel Biocare AB, Goteborg, Sweden), Lava (3MESPE, Seefeld, Germany), Cercon (Dentsply Degudent, Hanau, Germany), and Crerec (Sirona dental system, Germany).

In the hard machining technique, on the other hand, the 3Y-TZP blocks are previously densely sintered through a process called “hot isostatic pressing”: at high temperatures (1400–1500 °C) and high pressure in inert gas environment, very hard, dense and homogeneous blocks of fully sintered zirconia are produced⁽⁴⁹⁾, out of which the frameworks are shaped to the proper, desired form and to the right, final dimension by using powerful and resistant milling machines with diamond abrasives. Hard-machining of Hipressed (“HiPed”) Zirconia is