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CERAMICS FOR DENTAL RESTORATIONS – AN INTRODUCTION

UNA PERSPECTIVA DE LAS CERÁMICAS PARA RESTAURACIONES DENTALES

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ABSTRACT: Dental ceramics are the preferred materials for oral restoration due to some characteristics, such as adequate esthetics, high fracture strength and chemical stability. Currently, dental professionals have a large amount of ceramic systems to choose from, all of them having small differences regarding their chemistry, processing temperatures, mechanical strength and clinical applications. These differences lead to classification systems that are difficult to understand by professionals outside the dental field. The aim of this work is to review the current dental ceramic systems and present them from a compositional perspective to assure the comprehension of these materials by professionals who belong to the Biomedical Engineering field. A great effort was made to avoid classification methods imposed by manufacturers and to obtain a quick compilation of available information from the literature allowing the reader to have a general view of the state-of-the-art on dental ceramics.

KEYWORDS: Ceramic systems, feldspathic porcelain, leucite, zirconium oxide, glass-ceramics, mechanical and physical properties.

RESUMEN: Las cerámicas dentales son el material de elección para restauración oral debido a características como adecuada estética, elevada resistencia a la fractura y gran estabilidad química. En la actualidad, los profesionales de la Odontología tienen a su disposición una gran cantidad de sistemas cerámicos de restauración que presentan pequeñas o grandes diferencias en términos químicos, temperatura de procesamiento, resistencia mecánica y aplicación clínica, lo que lleva a sistemas de clasificación de las cerámicas que son poco útiles para profesionales ajenos a la odontología. El presente trabajo tuvo como objetivo hacer una revisión de los sistemas cerámicos de uso dental y presentarlos desde una perspectiva composicional para favorecer el entendimiento de profesionales ajenos a la Odontología. Se hizo un importante esfuerzo para evadir la clasificación que han impuesto las casas comerciales y tener así una rápida compilación de información disponible en la literatura que permita tener una visión general completa, pero no intensiva, del estado del arte de las cerámicas dentales.

PALABRAS CLAVE: Sistemas cerámicos, porcelana feldespática, leucita, alúmina, óxido de zirconio, vitrocerámica, propiedades físicas y mecánicas.

1. INTRODUCTION

Dental ceramics are materials that are part of systems designed with the purpose of producing dental prostheses that in turn, are used to replace missing or damaged dental structures. The literature on this topic defines ceramics as inorganic, non-metallic materials made by man through the heating of raw minerals at high temperatures [1].

Ceramics and glasses are brittle, which means that they display high compressive strength but low tensile strength and may be fractured under very low strain (0.1% - 0.2%). As restorative materials, dental ceramics have disadvantages, mostly due to their inability to withstand functional forces that are present in the oral cavity, hence initially they found limited application in premolar and molar areas, although further development in these materials has enabled their use as posterior long-span fixed partial prosthetic restorations and structures over dental implants.[2] All dental ceramics display low fracture toughness when compared to other dental materials, such as metals. [3].

The main objective of this work is to review ceramic dental materials, including their most relevant physical and mechanical properties. A brief historical review, including the evolution of these materials over time, a summary of different dental ceramic classifications, and the composition of dental ceramics will be presented.

2. HISTORICAL EVOLUTION OF DENTAL CERAMICS

Current dental ceramics are far from the early ceramics that started being used over 200 years ago. Early records of the first ceramics used as dental materials date back to 1774, when French apothecary Alexis Duchateau and Parisian dentist Nicholas Dubois de Chemant manufactured the first complete ceramic denture.

There are reports of complete dentures being manufactured earlier by French dentist Pierre Fauchard, although these dentures were fabricated in a different class of ceramic, namely enamel [4].

The initial use of ceramic materials in dentistry was in the obtention of complete dentures. Early in the 19th century, Italian dentist Giuseppe Fonzani was capable of manufacturing individual ceramic teeth attached to a metallic substructure which, in turn, was attached to complete dentures. The restoration of individual ceramic teeth in the oral cavity was delayed until the late 1800s, when Logan constructed ceramic teeth fused to metallic posts so that these posts could function as an intra-radicular retention for the restoration [4, 5].

The method to manufacture dental prostheses during the second half of the 20th century was through the fusion of ceramics and metallic structures that could function as a core. Metal-ceramic systems combine both the exceptional esthetic properties of ceramics and the extraordinary mechanical properties of metals [1]. Some metals used as restorative materials in dentistry may constitute a problem for some patients. These problems may reveal themselves as allergies [6], gum staining [7, 8], and release of metallic ions into the gingival tissue [9] and the gingival fluid [10]. These drawbacks, as well as the search for more esthetic materials by patients and dentists, have stimulated research and development of metal-free ceramic systems.

During the last 40 years, research has focused on improving metal-free systems and developing superior materials regarding esthetics and clinical performance to offer patients several alternatives to restore missing or damaged teeth.

3. CLASSIFICATION OF DENTAL CERAMICS

Dental ceramics may be classified according to several parameters, such as their use, manufacturing temperature, ceramic system, composition, microstructure, and translucency. The classification used in this article will be based on composition. Due to the fact that this review will discuss some mechanical properties exhibited by dental ceramic materials, table 1 summarizes the results of some mechanical tests published in the literature.

3.1 Feldspathic porcelains

Before discussing this division of ceramics, it is important to keep in mind that most ceramics have two different phases: the glassy phase and the crystalline phase. The glassy phase is often responsible for the esthetic behavior, while the crystalline phase is associated with mechanical strength. However, the crystalline phase (leucite in feldspathic porcelains) has a similar diffraction index as the glassy matrix; hence it also contributes towards the translucency of the whole structure. Therefore, both mechanical and esthetic properties are dependent on the ceramic composition [11].

Feldspathic porcelain is produced from the mixture of potassium feldspar, quartz, and kaolin. The latter improves plasticity and manipulation before the heating process. Other essential components are oxides of sodium, potassium, calcium, aluminum, and magnesium (employed to control ceramic's expansion coefficient and to try and match it with that of metals) [12], zinc, iron, copper, titanium, nickel, manganese, and cobalt (as pigments) and tin, zirconium, and titanium (as opacifiers) [13]. Feldspathic porcelain is highly brittle, hence it must be used as a veneering material in metal-ceramic and metal-free ceramic systems. [11].

This type of ceramic is made of extremely fine powders to which de-ionized water or a special modeling liquid is added. A paste is thus formed to be tooth-shaped by a technician. Then, this paste must be taken to an oven set at a pre-established temperature and time depending on

the ceramic being used. Currently, microprocessor-controlled ovens control all the thermal cycle steps and have optimized programs designed by manufacturers to process different types of ceramics[14]. The heating process may be carried out either under vacuum or in air, however the process under vacuum reduces ceramic's porosity. [15, 16].

The objective is to bring the raw paste's particles together to form a paste that will have solidified upon cooling.[17] During sintering, ceramics density will increase and this is associated to a volumetric contraction of 30 % to 40%, [17, 18] although other researchers claim that this contraction is between 20 % and 25% [19]. During the paste formation process, it is essential to avoid bubbles or pores formation, since their presence will reduce the ceramic's final mechanical strength, given that pores act as crack initiators [20]. The sintering process considerably reduces porosity since this procedure involves the melting/softening of the powder particle, causing reduction of surface energy, which renders pores to become spherical and volumetrically contracted, thus increasing densification [21].

Some methods to strengthen porcelain and avoid crack initiation and/or propagation have been reported by different authors. The most common methods are ionic exchange (chemical exchange of smaller sodium ions for larger potassium ions to create a compressive stress on the surface) [22-26], thermal tempering (forced cooling of ceramic in air) [23, 27, 28] or crack-propagation interruption by means of induction of residual compressive stresses on the surface (air-injection tempering) [29].

3.2 Leucite-reinforced feldspathic porcelain

Feldspar may form leucite, which is a potassium aluminum silicate mineral with a high thermal expansion coefficient [15]. Leucite may be present in feldspathic porcelain in two forms: Firstly, the formation of this mineral through the incongruent melting of potassic feldspar (incongruent melting is a process by which a material is melted to form a liquid and a different

crystalline material [15]). Secondly, the aggregate of leucite to ceramics as synthetic powder [30]. Leucite-reinforced ceramics may be used to manufacture metal-ceramic restorations. The large difference between thermal expansion coefficient of metals and that of ceramics is one of the problems encountered when manufacturing metal-ceramic restorations [31, 32] as well as the difference in thermal expansion coefficients between layers of ceramic [33] when cooling to room temperature. This imbalance creates residual stress between both materials that may trigger failure at the interface. [34] Hence, a layer to layer compatibility involving ceramics and underlying metal is required [32].

Also, leucite content in ceramics is associated to an increase in crack propagation strength [30]. A mechanism by which this increase is produced is the difference between leucite's thermal expansion coefficient ($22 \text{ to } 25 \times 10^{-6}/^{\circ}\text{C}$) and that of the glassy matrix ($8 \times 10^{-6}/^{\circ}\text{C}$), resulting in the formation of tangent compressive stresses in the glass around leucite crystals, that undergo a phase transformation from cubic to tetragonal upon cooling [17]. Sodium content has an effect on the tetragonal phase stability at high temperatures and lowers the thermal expansion coefficient, but it also decreases the ceramic's overall strength [35]. Another mechanism of strength increase is explained by microcrack formation within and around leucite crystals when cooling. Both mechanisms are essential to prevent crack formation and propagation in the ceramic [36]. Some researchers have suggested that ceramics reinforced with cubic leucite at room temperature display less flexural strength and less fracture strength than tetragonal-leucite ceramics [36].

Pinto *et al* assessed the effect that pH has on leucite-reinforced ceramics. These authors concluded that an acidic pH (3.5) produces a reduction in overall strength in leucite-reinforced ceramics [37].

3.3 Aluminous ceramics

Aluminous ceramics were first developed by MacLean and Hughes to manufacture prosthetic

dental crowns [38]. The principle of this type of ceramics is that a dispersion of high strength and high elastic modulus crystals exists within the glassy matrix to strengthen and harden the ceramic [38].

Alumina has the property of strengthening feldspathic porcelain, thus making it more fracture resistant. This fact may be observed when comparing aluminous ceramics strength to that of feldspathic porcelain [39] and when comparing hardness and strength values of aluminous ceramics with those of other ceramic systems [40]. Alumina particle size has been proposed as a factor that improves particles agglomeration and some mechanical properties, such as fracture strength, of the partially-sintered alumina matrix [41].

The presence of alumina decreases glasses' inherent brittleness and the risk of devitrification, which is a process whereby ceramics become opaque and brittle as a result of their crystallization, due to loss of the glassy structure [42].

3.4 Glass-infiltrated composites

Currently, there is a ceramic system marketed as In-Ceram (Vita-Zahnfabrik, H Rauter GMBH & Co.KG, Bad Säckingen, Germany) that includes glass-infiltrated porous sintered alumina. [43] This system, developed by Tyszblat, is comprised of an aluminous core that is further infiltrated with molten glass to fill-in the voids left by aluminous particles in order to obtain a restoration that exhibits better physical properties when compared to traditional ceramics (see table 1) and very similar to those of natural teeth [44].

3.5 Alumina Polycrystals

High-alumina ceramics contain a minimum of 95% pure alumina (aluminum oxide, Al_2O_3) [38]. Andersson and Oden [45] described the use of a high-purity (99.9%), densely-sintered alumina ceramic for the manufacturing of dental restorations [45]. Alumina displays a 15% to 20% contraction that must be compensated to manufacture such restorations. These

investigators compensated its high contraction by using enlarged models of teeth and restoration manufacturing using a technique known as copy-milling to obtain a properly-sized finished restoration. The amount of expansion necessary to be applied to the models may be calculated from the sintering of compacted powder [45]. Copy-milling is better described by Andersson elsewhere [46].

Table 1. Reported values for ceramic systems, enamel and dentin subjected to several mechanical tests

Material	3-point bending [MPa]	Hardness [GPa]	Fracture Toughness
Feldspathic porcelain	98 – 101 [47]	712.9 - 763.9 kg/mm ² 6.98 - 7.48 GPa [48]	1.0 - 1.49 MPa/m ^{0.5} [49]
Alumina-reinforced ceramic	116 - 117 [47]	3.7 – 5.2 [3]	1.95 MN/m ^{1/2} [40]
High-alumina content ceramic	155 [47]	5 - 10.8 [3]	4.58 MN/m ^{1/2} [40]
Glass-ceramic	239.2 [47]	3.4 – 4.1 [3]	1.28 MN/m ^{1/2} [40]
Leucite-reinforced glass-ceramic	78.37 - 133.56 [49]	6.53 [40]	1.26 MN/m ^{1/2} [40]
Lithium disilicate-reinforced glass-ceramic	na	5.6 - 6.2 [50]	na
Zirconium oxide ceramic	800 – 1590 [51]	1188-1274 kg/mm ² 11.64 GPa [52]	4.6 – 6.2 MPa.m ^{1/2} [52]
Dental enamel	na	343 kg/mm ² 3.36 GPa [53]	0.70 – 1.16 MN/m ^{3/2} [54]
Dentin	137.9 – 220.63 [55]	64.75 - 73.75 kg/mm ² 0.63 – 0.72 Gpa [56]	3.08 MN.(m) ^{-1.5} [57]

na. Data not available

3.6 Glass-ceramics

According to McLean [38], the first works on glass-ceramics were performed by MacCulloch, but his work did not receive much attention. Further investigations by Grossman and Adair [58, 59] concluded with the development of a tetrasilicic fluormica-containing ceramic system. According to both investigators, its composition is as follows: 45-70% SiO₂, 8-20% MgO, 8-15% MgF₂, 5-35% R₂O+RO, where R₂O has a range between 5-25% and is composed of at least one of the following oxides: 0-20% K₂O, 0-23% Rb₂O, and 0-25% Cs₂O to improve translucency and RO, which has a range between 0-20%, and is composed of at least one of the following oxides: SrO, BaO, and CdO. Additional components may account for up to 10% of Sb₂O₅ and/or up to 5% of traditional glassy colorants [58, 59].

The thermal treatment known as ceramming [15] is composed of two processes: glass is heated up to a temperature where nuclei form (750° - 850°C) and this temperature is kept for a period of time ranging from one to six hours so that crystalline nuclei form in the glass (process known as nucleation). Then, the temperature is risen to the crystallization point (1000°-1150°C) and this temperature is maintained for a period ranging from one to six hours until the desired level of glazing is obtained (process known as crystallization) [58-60]. Developers of this type of ceramic system claim that fracture strength and hardness are better than those of traditional ceramic systems [58, 59], although other authors have shown that after the ceramming process a surface layer that decreases its strength and esthetic characteristics forms on this ceramic [61]. However, some researchers claim that fractures in this type of ceramic have an internal origin, but no explanations are provided as to what particular factor causes fractures to appear in restorations manufactured with this material [62]. However, there is an investigation that suggests that this ceramic's strength and hardness may be improved by performing a chemical shift on the surface layer (addition of lithium fluoride) [61].

3.7 Leucite-reinforced glass-ceramics

Pressed glass-ceramics are materials containing high amounts of leucite crystals (35% by volume) [15]. The basic component of this ceramic is feldspathic porcelain consisting of 63% SiO_2 , 19% Al_2O_3 , 11% K_2O , 4% Na_2O , and traces of other oxides. Leucite crystals are added to the aluminum oxide [63, 64]. This material is manufactured using a process known as heat-pressing, which is performed in an investment mold. This mold is filled with the plasticized ceramic, thus avoiding the sintering process and the subsequent pore formation [65]. This ceramic undergoes dispersion strengthening through the guided crystallization of leucite. Dispersion strengthening is a process by which the dispersed phase of a different material (such as alumina, leucite, zirconia, etc.) is used to stop crack propagation, since these crystalline phases are more difficult to penetrate by cracks [15, 66]. Leucite crystals are incorporated during ceramming, hence performing this process again is unnecessary when inducing crystal growth [64].

The method of dual ionic exchange has been proposed in the literature to increase the resistance of this ceramic to separation, as long as potassium and sodium ions are available in the ceramic for the exchange. Long-term chemical effects on the ceramic should be further studied [67].

3.8 Lithium disilicate-reinforced glass-ceramics

This material is also a heat-pressed glass-ceramic with a 60% content of lithium disilicate crystals, which form an intertwined structure after being pressed, hence fracture strength is increased [65, 68]. Li_2O and SiO_2 aid in the crystallization of the required phase of lithium disilicate, BaO and Cs_2O stabilize residual glass and Al_2O_3 and B_2O_3 render this ceramic chemically durable [69]. The crystallization process is comprised of two steps: nucleation (one hour at 645°C) and crystal growth (four hours at 850°C) [69].

3.9 Zirconium oxide ceramics

Since Garvin *et al* [70] published their work titled "Ceramic steel?", zirconia has been considered a tough ceramic. Zirconia occurs as a natural mineral called baddeleyite. This mineral contains 80% to 90% zirconium oxide. The major impurities are usually TiO_2 , SiO_2 , and Fe_2O_3 . This oxide exists in three different crystal structures: monoclinic at room temperature, tetragonal at $\sim 1200^\circ\text{C}$, and cubic at 2370°C . A phase transformation from tetragonal to monoclinic occurs during cooling. This change produces a volumetric expansion ranging from 3% to 4%, which in turn causes crack formation within the material. Oxides such as CaO , MgO , Y_2O_3 , and CeO_2 are added to pure zirconia to stabilize it in multiphase materials known as Partially-Stabilized Zirconia (PSZ). These materials basically consist of cubic zirconia as the major phase and precipitates of monoclinic and tetragonal as the minor phase at room temperature [71]. At room temperature, the tetragonal phase is in metastable state, since transformation from tetragonal to monoclinic may be induced by external factors, such as pressure or temperature [72, 73]. The resulting compressive stress from the volumetric expansion developed at the vicinity of a crack and the energy needed to carry out such phase transformation, provide this ceramic with high fracture strength [72, 74]. This process is known as transformation toughening [71-73, 75]. It may generate a process known as ceramic aging, which is the spontaneous transformation from metastable tetragonal zirconia to monoclinic zirconia [71], therefore a decrease in mechanical properties may occur in the ceramic over time [74]. An investigation carried out by Ardlin demonstrated that strength was not affected by aging, although the ceramic's crystalline structure and surface were, indeed, affected [51].

As mentioned above, pure zirconia may be stabilized with Y_2O_3 . Yttrium oxide is used to retain the tetragonal phase at room temperature as much as possible after sintering and avoid the monoclinic phase, since the accumulation of the latter is associated with a decrease in strength, toughness and density [76].

The resulting stabilized ceramic is known as Tetragonal Zirconia Polycrystals (TZP) and when it is doped with 2-3% mol of yttrium oxide, this material is known as Yttrium Tetragonal Zirconia Polycrystals (3Y-TZP) [71]. The amount of yttrium oxide in the ceramic has an essential role in the capacity of transformation of the tetragonal phase and, therefore, in the ceramic's toughness [52]. This material consists of tetragonal grains, whose size is in the submicron scale, without a glassy phase at the edge of the crystals. The amount of tetragonal phase that remains at room temperature depends on many factors, such as grain size, yttrium oxide content, and the degree of constriction exerted upon them by the matrix [71]. Most commercial Y-TZP powders are manufactured using a process known as co-precipitation [77]. The objective of this procedure is to manufacture multicomponent ceramic oxides through the formation of intermediate precipitates with the final goal of achieving an intimate mixture of the components during precipitation and keeping chemical homogeneity during calcination [77].

4. CONCLUSIONS

Today's ceramic materials used in the dental field comprise a large and diverse group of materials that offers patients a number of alternatives when dealing with prosthetic treatments.

These ceramic systems have been developed over time seeking highly-esthetic but also functional materials. Current dental ceramic systems (leucite or lithium disilicate-reinforced glass-ceramics, high-alumina or zirconia ceramics) offer better physical and mechanical properties than those of older, more traditional systems.

Mechanical values summarized in table 1 show that zirconium oxide ceramics display the highest values of flexural strength under 3-point bending tests. When it comes to hardness, enamel and dentin display the lowest results when compared to all ceramic systems, and zirconium oxide ceramics exhibit the highest hardness value. The highest value for fracture

toughness is showed by zirconium oxide ceramics, although dentin shows higher values than most ceramic systems and enamel displays lower values than dentin and ceramics. Dental ceramics is an interesting area of research, since countless possibilities are open for research, such as esthetics, processing of new ceramics with biological properties (increasing its interaction with cells or reducing bacterial adherence) and surface modification processing.

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