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Recent Advances in Ceramic Materials for Dentistry

Mohsen Mhadhbi, Faïçal Khliissa and Chaker Bouzidi

Abstract

Dental ceramics constitute a heterogeneous group of materials with desirable optical and mechanical proprieties combined with chemical stability. They are inorganic non-metallic materials used in several applications. These materials are bio-compatible to tissue, highly esthetic, with satisfying resistance to tensile and shear stress. Over the past years, several developments in new ceramic materials in dental restoration were achieved, including processing techniques and high mechanical properties. Thus, concepts on the structure and strengthening mechanisms of dental ceramic materials are also discussed. The dental practitioner requires best knowledge concerning indications, limitations, and correct use of started materials. The purpose of this book chapter is to overview advances in new ceramic materials and processes, which are used in dentistry. The properties of these materials are also discussed.

Keywords: ceramics, dentistry, oxide ceramics, glass ceramics, zirconia, alumina, silicate, composites

1. Introduction

Nowadays, ceramics are applied in a wide range of industrial applications such as cutting tools, nuclear reactors, automotive, biomedical, etc. Therefore, ceramics have been the subject of considerable researches because their chemical stability and good mechanical properties compared to many other materials. Physical and mechanical tests, combined with fundamentals of engineering science, were made to structure designs and restorative materials. However, although these materials are esthetically attractive and resistant to wear, they are prone to brittle fracture at stress concentrations.

Dental ceramics are mainly consisting of glass ceramics enriched with lithium disilicate, leucite, polycrystals of zirconia and alumina, etc. [1–4].

Additionally, dental ceramics, available for dental castings, were first developed in early 1960s, increasing demands for ceramic restorations materials with respect to both esthetic and mechanical properties.

In 1800s, the long process of moving ceramics from a craft to a science based technology was underway under the direction of engineers [5].

In 1830s, a new composition made from 78% feldspar, 15% kaolin, dehydrtared borax, and potash silicate was developed [6]. Thus, the surface of this ceramic was glazed using a glossary glass forming materials.

In 1889s, the utilization of ceramics to build crowns was patented as the all ceramic “jacket crown” [7]. These crowns were often failed because of internal

micro-cracking, but, in 1950s, they are utilized considerably until the invention of porcelain fused to metal (PFM) crowns.

In the early of 1980s, the first major breakthrough in full ceramic restoration with the application of computer-aided technologies [8].

Therefore, several works have been made in the field of dentistry by using of computer-aided digitizing (CAD), computer-aided design (CAD), and computer-aided manufacturing (CAM) [9, 10].

The purpose of this chapter is to provide an overview of the recent progress of new materials and processing methods for dentistry.

2. Classification of ceramic materials

Ceramic materials are utilized for several dental applications and are distinguished by their good mechanical properties, high electrical resistance, high thermal conductivity, and excellent biocompatibility. Thus, the oxides, particularly alumina, zirconia, and silica are the most commonly used ceramic materials in the area of dentistry. These materials are classified based on their chemical compositions or based on processing methods.

2.1 Based on chemical compositions

In the past decades, the ceramic materials have attired much attention due to their excellent properties depend to their chemical composition. However, several researches have been studied to develop nanoceramic materials, will be further expanded in future.

2.1.1 Silicon oxide ceramics

Silicon oxides ceramics have been widely employed in biomedical applications because its mechanical stability, biocompatibility, and high specific surface, which can be modified [11–15]. The silanol group on the support of the silicon atom can be activated to make a chemical bond with organosilane, which can also lead to providing various functional groups that can mediate a vast selection of particular bioconjugation strategies [16]. When stable silanes layers are formed on the silicon surface conventional bioconjugation process are used to physisorb or chemisorb a broad bioactive nanoparticles and molecules on the silicon surface.

Zhang et al. [15] observed a reduction of 90% in albumin adsorption on silicon surfaces by 0.05% Tween 20 over 4 h. The self-assembly of polyethylene glycol (PEG) with monomethoxypoly(ethylene glycol) (MPEG) have been used with great success for functionalization of silicon surfaces and for suppressing the adsorption of platelets, fibroblasts, and Hela cells. The water contact angles of the different silicon surfaces are showed in **Table 1**. The maximum value was found for the case of the methylated silicon surface with 2% of dichlorodimethylsilane (in the range of 99–102 °).

Porous silicon (pSi) is a biocompatible and biodegradable material due to its high surface area, which induces a fast oxidation of silicon in aqueous solution [17–19]. Hence, it is shown that particles synthesized out of pSi are biodegradable in plasma, blood, and tissue and then stable [20].

Additionally, the internalization of pSi particles by endothelial cells and macrophages in vivo and in vitro with no adverse effects associated to particles partitioning and cell proliferation [21]. The controlled release of cytokine is near to that of controls, showing that pSi particles are also non-immunogenic. Hence, no toxicity has been revealed in healthy receiving several injections of these pSi particles [22].

Surface	Dominating surface groups	Wetability (°)
Hydrophilic silicon	O ⁻ and Si-OH	<10
Intermediate silicon (with HF)	Si-H and Si-OH	55–60
Intermediate methylated silicon (with 0.008% DDS)	Si-CH ₃ and Si-OH	55–60
Methylated silicon (with 2% DDS)	Si-CH ₃	99–102

Table 1.
The water contact angles of different surfaces [15].

Indeed, polymers coatings have been employed to coat pSi particles to protect them from cellular degradation although the conjugation of antibodies has promoted the efficient delivery of payloads [23].

2.1.2 Aluminum oxide ceramics

Bioceramics (like alumina, zirconia, etc.) are mainly employed in orthopedic and dental reparation. Alumina (aluminum oxide) is the only solid oxide form of aluminum (Al₂O₃). Thus, corundum is the crystalline form of alumina. Alumina was first used since the 1970s and its clinical results revealed a fracture rate greater than 13% [24]. However, the disadvantage of these materials was related to the fact that they could not be processed to full final density. In the late of 1980s, a second generation ceramic materials, with a smaller grain sizes and a higher density, was developed. The fracture rate of these materials was less than 5% [25]. Today, a third generation ceramic materials, characterized by high purity, full density, and finer microstructure was appeared. The properties of biomedical grade alumina are illustrated in **Table 2**.

Additionally, it is shown that the degree of tensile bending strength of ultrafine Al₂O₃ particles is remarkably over that of all other ceramics [27]. The ceramics for substructures of “jacket crowns” enriched by alumina (up to 60% of weight) of different grain size (10–30 μm) have been used to increase the stability. Hence, intense refraction of light takes place at the alumina (in the feldspar) due to the difference in the refraction index between feldspar and corundum.

2.1.3 Aluminum oxide ceramics reinforced with zirconium oxides

Mechanical properties of alumina were improved by addition of ceramic composites, as reinforcing agents, like zirconia. Generally, these ceramic–ceramic composites present a great hardness as compared to the all composites. Although most ceramic second phases improve strength and hardness they modestly improve fracture toughness [28, 29]. Al₂O₃–SiC nanocomposite has been reported to have the

Property	Value
Density (g/cm ³)	3.96–3.98
Fracture toughness (MPa.m ^{1/2})	3.4–4
Bending strength (MPa)	550–630
Hardness (GPa)	19–20
Young’s modulus (GPa)	380

Table 2.
Mechanical properties of alumina [26].

most improved properties [30]. Thus, it has been shown that SiC increases significantly the wear resistance of aluminum oxide.

Doğan and Hawk [31] revealed that the toughness of alumina with 34 vol%SiC increased from 3.4 to 4.6 MPa.m^{1/2}. Similarly, Belmonte et al. [32] showed that the fracture toughness of the sample of alumina with 20 vol%SiC reached a value of 5.9 MPa.m^{1/2}.

However, the zirconia system uses a mixture of zirconium oxide and aluminum oxide as a framework to achieve a marked increase in the flexural strength. Alumina constitute approximately two third of the structure and the remaining structure was composed of tetragonal zirconia. In addition, the proportion of glass phase covers 20–25% of the total structure. The increase over alumina is due to the zirconia particles that protect the structure against crack propagation. It has a very high strength of around 700 MPa and very poor translucency.

Tuan et al. [33] incorporated zirconia particles into alumina and reported that the fracture toughness was improved. For zirconia-toughened alumina including 10 vol% zirconia, they recorded that fracture strength and fracture toughness were 943 MPa and 11.8 MPa.m^{1/2}, respectively. Toughness values of 10 MPa.m^{1/2} for 10 vol% zirconia [34] and 7.02 MPa.m^{1/2} for 50 vol% zirconia content have also been reported [35]. Zirconia is a bioinert ceramic and can suffer from low cellular attachment, which could be compensated when mixed with biopolymers [36]. Alumina-zirconia composites have received great attention in dentistry as promoted bioceramics due to their excellent biocompatibility [37].

In the last years, many recent studies were focused on the investigation of the tribological-mechanical behaviors and biosafety of alumina toughened zirconia (ATZ) composites [38–41]. Thus, the benefits of these composites are the combination of the properties of alumina and zirconia.

Daskalova et al. [42] studied the effect of surface modification by femtosecond laser on zirconia based ceramics for screening of cell-surface interaction. The X-ray diffraction analysis demonstrated preservation of the tetragonal phase of Zr ceramic materials for a particular fs-laser treatment conditions (see **Figure 1**).

Moreover, scaffolds design and fabrication are major areas in dentistry for tissue engineering applications that need controlled positioning of cells on solid substrates with predefined orientation. Hence, surface functionalization generated by defined surface structure was strongly depending on the quality and surface texture.

2.1.4 Zirconium oxides ceramics

Zirconia (ZrO₂) is a ceramic material which has been applied in the health field and distinguished by its high mechanical properties, biocompatibility, and chemical stability [43]. The polycrystal tetragonal zirconia, stabilized with yttria (3Y-TPZ) contains 3 mol% yttria oxide (Y₂O₃), was first applied in the field of medical. The 3Y-TPZ has been the most studied and utilized in dentistry [44]. Thus, the 3Y-TPZ was fabricated in small grains (0.2–0.5 mm in diameter), which minimizes the phenomenon of structural deterioration or destabilization in the presence of saliva, decreasing the subcritical crack growth [45]. **Figure 2** shows the SEM micrograph of the powder after sintering. However, for the formation of a great amount of monoclinic zirconia a powerful machining should be used because of the high compression applied by machining, leading to the formation of micro-cracks on the surface of material [3].

Similar to that of stainless steel, zirconia is characterized by good chemical stability, good biocompatibility, mechanical strength, toughness, and Young's modulus [46]. No adverse reactions have been found, when osteoblasts were seeded on zirconia and were able to proliferate and differentiate on it [47]. Zirconia ceramics are becoming a prevalent biomaterial in dentistry and dental implantology [48].

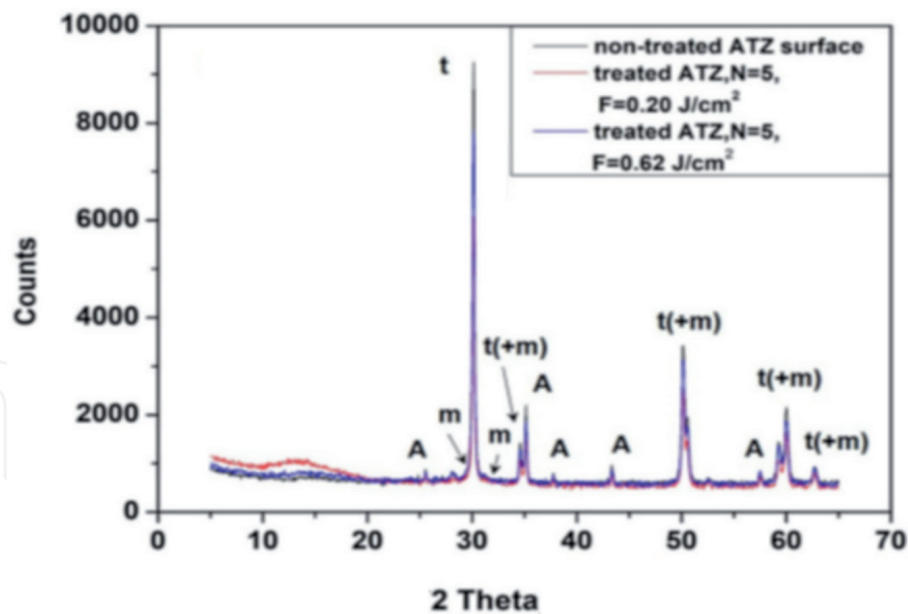


Figure 1.
XRD patterns of the surface of sample [42].

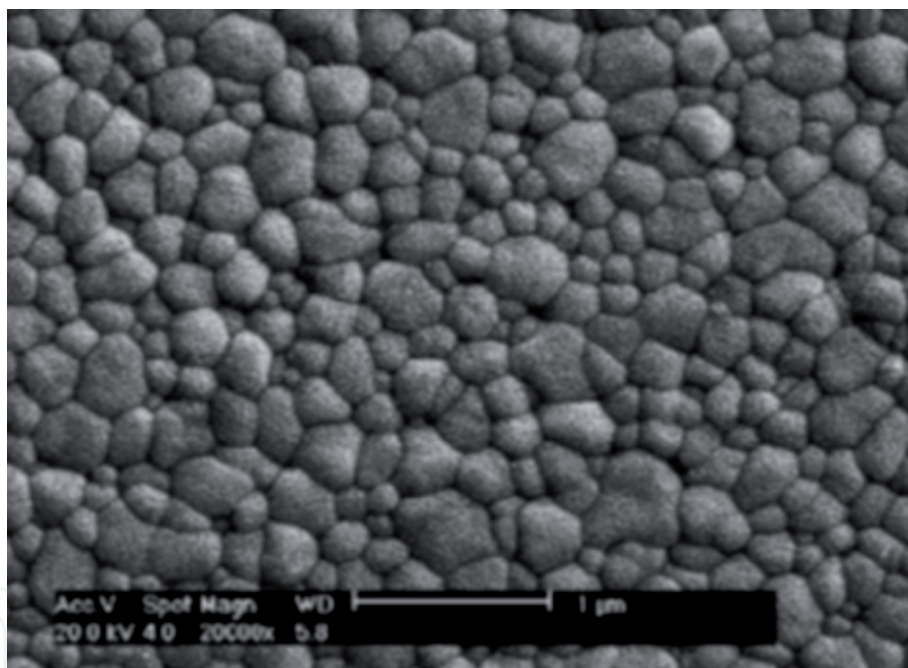


Figure 2.
SEM micrograph of the sample obtained after sintering [45].

2.1.5 Hybrid ceramics

In recent years, all ceramic and composite restorations have been widely used because of their biocompatibility and esthetic features compared with metal-ceramic restorations (MCR) [49, 50]. A range of ceramic systems are commercially available like leucite, alumina, zirconia, and feldspar based ceramics [51]. Thus, many indirect composites categories, with various size of filler particles, are also used [52].

Recently, new ceramic/polymer materials, used in CAD/CAM technology, have been developed [53]. In fact, the use of mixed materials enhances crack propagation and reduces fracture stress. The protocol for glass–ceramic materials requires acid etching followed by silanization and the application of resin cement [54–56]. Silane

coupling agent is a molecule having two functional groups, which has the ability to form a durable bond between organic and inorganics materials [56, 57].

The adhesive cementation technique improves the clinical performance of all-ceramic dental restorations due to the ability of resin to penetrate the microporosities that are created by etching process [58, 59]. However, the indirect restorations with composite, such as resins, can be produced by the application of physical conditioning technique using air-particle abrasion and silanization to achieve optimum adhesive bond between different materials [60].

Recent studies [61] showed that hardness of hybrid ceramic materials was given from the ceramic content because the indenter was highly sensitive to making this portion. Moreover, there was a significant interaction in the interface between resin cements and hybrid ceramic materials. The longevity of restorations can be affected by storage because of the high concentration of the water and smaller molecules, which cause a reduction in free spaces between functional groups and polymer chains [62].

New hybrid ceramics filled and un-filled polyamide 12 (PA 12) were developed by a fused deposition modeling framework [63]. The proprieties of hybrid ceramics filled and un-filled polyamide 12 are summarized in **Table 3**. The highest tensile strength was recorded at 40% filled PA 12 as compared to un-filled PA 12. The highest tensile modulus was recorded at 35% filled PA 12 as compared to un-filled PA 12. Indeed, the highest impact strength was recorded at 35% filled PA 12 as compared to un-filled PA 12.

2.2 Based on processing methods

In the last few decades, there have been remarkable advances in the mechanical properties and methods of fabrication of ceramic materials.

2.2.1 Casting

Casting is based on the solidification of a fluid that has been poured or injected into a mold. The final product is also known as a casting. Thus, casting process consists of three steps: melting, casting, and recovery.

The biocompatibility effects of indirect exposure of base-metal dental casting alloys were analyzed [64].

The effects of the rare earth element lanthanum on the metal-ceramic bond strength of Co-Cr alloys prepared by casting were studied [65]. XRD and SEM analysis of the samples revealed the presence of dendritic microstructures with some defects and an island shaped intermetallic compounds rich in Cr and Mo. The increasing of the number of “La” leads to the increasing of the diffusion layer at the interface, the increasing of thickness of the native oxide layer, and to improving the wettability. In addition, the results showed that the debonded surfaces of the specimens exhibit mixed fracture modes (adhesive and cohesive failure).

Samples	Tensile strength (MPa)	Tensile modulus (MPa)	Impact strength (kJ/m ²)
Un-filled PA 12	41.38 ± 2.93	1006.28 ± 101.66	6.02 ± 2.51
30% filled PA 12	36.82 ± 1.61	1087.08 ± 126.89	11.92 ± 1.49
35% filled PA 12	36.71 ± 1.81	1382.34 ± 89.21	16.96 ± 7.01
40% filled PA 12	36.99 ± 1.41	1327.06 ± 157.62	12.42 ± 2.96

Table 3.
Proprieties of hybrid ceramics filled and un-filled polyamide 12 [63].

Similarly, Atwood et al. [66] modeled the surface contamination of dental titanium produced by casting. They showed that the contamination of the wedge sample was established to extended range from 30 to 120 mm. Hence, they concluded that the addition of micro- and nano-models revealed the predictions are shown to be in good agreement for the pattern of contamination. **Figure 3** shows the image of the mold metal interface, which was characterized by three layers: (i) irregular contact surface and with topography in the scale of 20 μm , (ii) globular structure, and (iii) dendritic structure.

2.2.2 Sintering

Sintering is a heat treatment under pressure applied to a powders compact without melting. The final product is a solid or porous mass with excellent properties.

Fan et al. [67] studied the mechanical properties of sintering temperature on the microstructure of dental zirconia-toughened alumina (ZTA). By increasing temperature, they concluded that the mechanical properties of the samples were improved, the crystal structure of ZrO_2 was changed (from tetragonal into monoclinic), and the porosity was decreased. However, the ceramics sintered at 1450 $^{\circ}\text{C}$ showed greatest fracture toughness ($5.23 \text{ MPa}\cdot\text{m}^{1/2}$) and greatest flexural strength (348 MPa). The authors concluded that the properties of ZTA ceramic depend on sintering temperature, and the optimal temperature was about 1200–1250 $^{\circ}\text{C}$. Ghayebloo et al. [68] revealed that it is possible to fabricate ZLS glass–ceramics by sintering (**Figure 4**). The results showed a highest flexural strength of $255.10 \pm 15.44 \text{ MPa}$, a fracture toughness of $3.15 \pm 0.62 \text{ MPa}\cdot\text{m}^{1/2}$, a Vickers micro-hardness of $7.96 \pm 0.13 \text{ GPa}$, and a bulk density of $2.63 \pm 0.02 \text{ g/cm}^3$. Thus, the lowest water absorption was of 0.11 ± 0.12 and the apparent porosity was of 0.25 ± 0.32 .

2.2.3 Partial sintering

Partial sintering is considered as the most straightforward processing route for macro-porous scaffolds and involves the partial sintering of initially porous powder compacts.

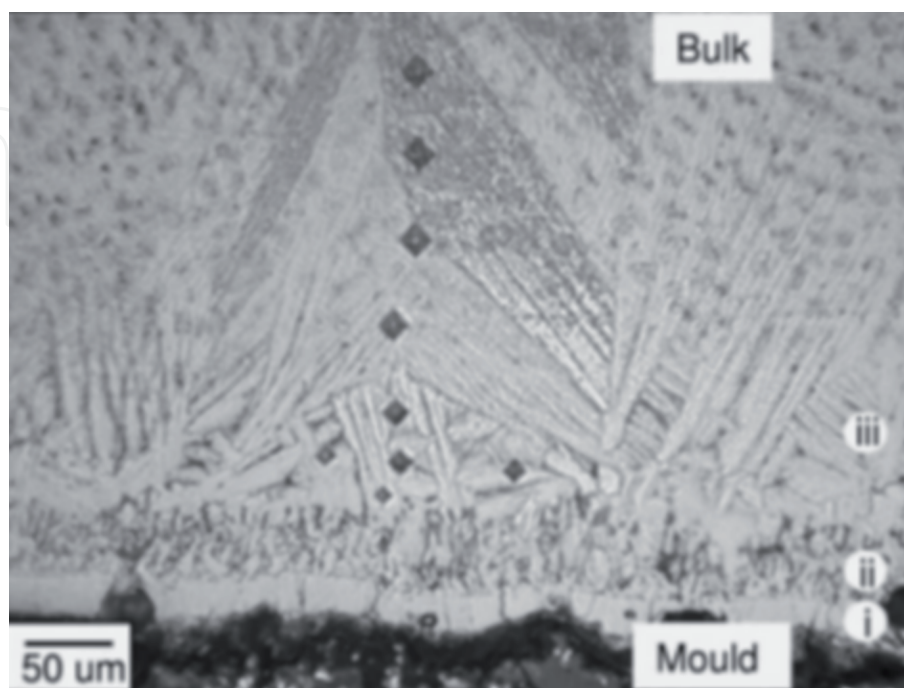


Figure 3.
 Light micrograph of the bulk sample [66].

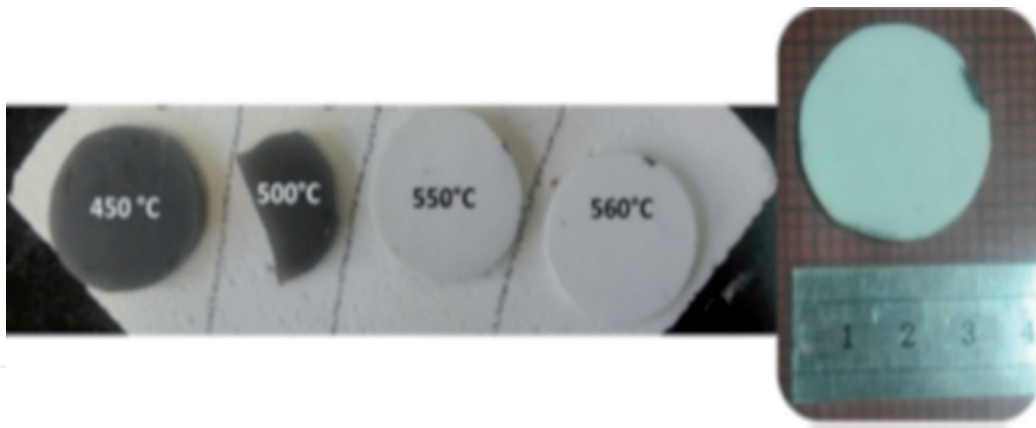


Figure 4.
The final samples obtained by spark plasma sintering [68].

A homogenous although closed pore structure can be produced when sintering is terminated before full densification [69]. The pore size and porosity are controlled by the size of the powder particles and the degree of partial sintering, and the size of the raw powder should generally be 2–5 times larger than the desired pore size. Chen et al. [70] studied the properties of YB_2C_2 ceramics prepared by partial sintering. Thus, a porous YB_2C_2 ceramics were prepared by partial sintering. The results showed a good mechanical behavior: high porosity (57.17–75.26%) and a high compressive strength (9.32–34.78 MPa). In another work [71], alumina powder agglomerates were prepared by partial sintering. The SEM micrographs of the porous ceramic obtained after sintering are given in **Figure 5**. The final ceramic material is characterized by a hierarchical porous network that can contain three levels of interconnected pores: the voids existing between the agglomerates ($\geq 10 \mu\text{m}$ in size), the porosity remaining inside the agglomerates after partial sintering (≈ 100 – 1000 nm in size), and the pores that may exist within the initial ceramic particles ($< 100 \text{ nm}$ in size). Such porous ceramic structures are developed to be applied in the field of dentistry.

2.2.4 Glass infiltration

The glass infiltration processing is a powerful technique for the fabrication of ceramic/glass composite with exceptional mechanical properties and low shrinkage.

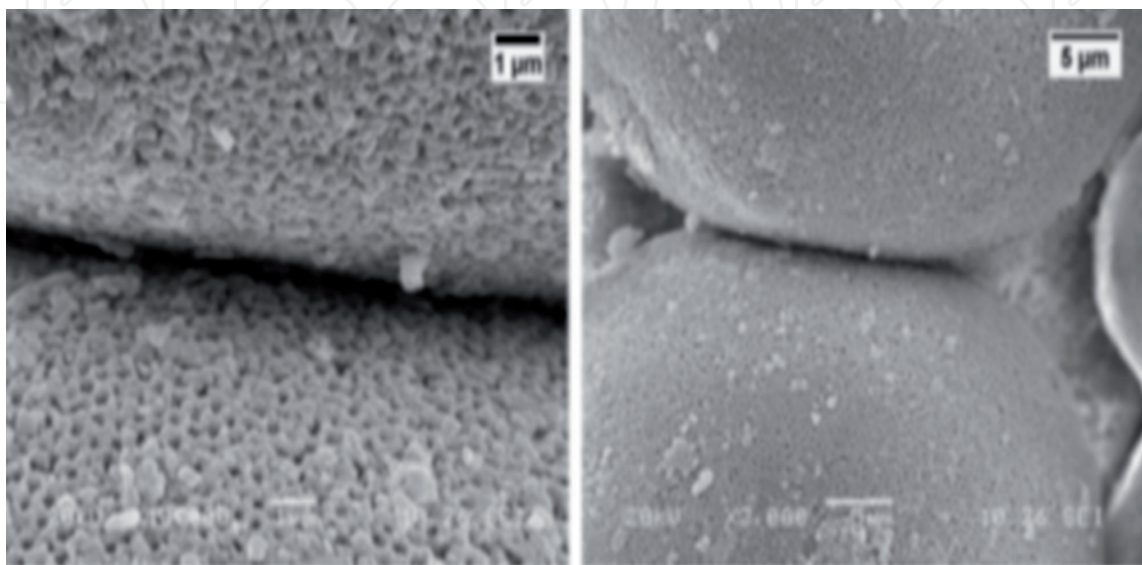


Figure 5.
SEM micrographs of the porous ceramic after sintering [71].

Porous Y-TZP nano-ceramics, with hierarchical heterogeneities, were prepared by partial sintering method from meso-porous powder [72]. The results showed that the products have a crystallite sizes between 34 and 71 nm for relative densities between 54 and 81.7%. They also revealed a surface area of $18 \text{ m}^2/\text{g}$, a thermal conductivity of $0.63\text{--}1.88 \text{ W.m}^{-1}.\text{K}^{-1}$, an elastic modulus of 32–156 GPa, and a strength in the range of 70 and 540 MPa.

Yang et al. [73] investigated the effects of process parameters and material characteristics in glass infiltration of gel cast zirconia-toughened alumina (ZTA) ceramic for dental applications. They showed that the strength of the obtained ceramic was 291 MPa and the shrinkage was 1.8548%.

In another work [74], biocomposites were obtained by infiltrating porous alumina-titania ($\text{Al}_2\text{O}_3\text{-TiO}_2$) substrates with a lanthania-rich (La_2O_3) glass. $\text{Al}_2\text{O}_3\text{-TiO}_2$ substrates were fabricated using high energy milled powder mixtures of two different compositions. The sintered substrates presented $\alpha\text{-Al}_2\text{O}_3$ and $\beta\text{-Al}_2\text{TiO}_5$ as crystal phases and relative densities ranging between 65.5 ± 2 and $69.4 \pm 1.2\%$. These products were then infiltrated by lanthania containing glass at a higher temperature (1140°C) for 2 hours. These ceramics showed a fracture toughness up to $2.6 \text{ MPa.m}^{1/2}$, a fracture strength in the order of 218–254 MPa, a high density of 94–99% (**Figure 6**), and a Vickers hardness in the order of 895–1036 HV. However, phase identification of the samples by XRD indicated the decomposition of aluminum titanate into alumina and titania besides the formation of lanthanum borosilicate (LaBSiO_5). In addition, all studied compositions presented non-cytotoxic behavior and low chemical solubility (inferior to $75 \mu\text{g}/\text{cm}^2$).

2.2.5 Slip casting and sintering

In-Ceram zirconia bulk composites were synthesized via slip casting of alumina or zirconia. Slip was a dispersion of particles of ceramic powders in a liquid (such as water). Thus, the pH of water was then regulated to the desired value to charged particles.

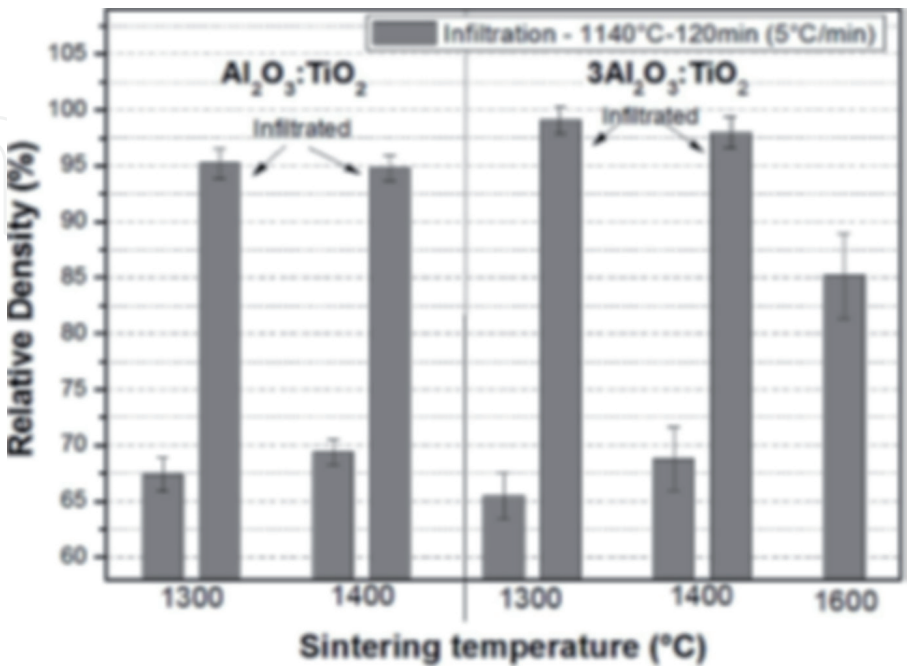


Figure 6.
Variation of relative density with sintering temperature of the $\text{Al}_2\text{O}_3\text{-TiO}_2$ and $3\text{Al}_2\text{O}_3\text{-TiO}_2$ composites after glass infiltration [74].

Kim et al. [75] fabricated dense zirconia compacts by slip casting and sintering from zirconia nanopowders. Thus, the green compacts obtained from slip casting were cold isostatic pressed to enhance the close packing and densified by sintering at 1450 °C for 2 h. Highly dense zirconia compacts with a relative density of 99.5% and grain size of 350 nm were obtained based on the powder type and solid loading in the slurry. The microstructure and mechanical hardness of the sintered specimen after slip casting were dependent on the yttria content in the 3 mol% yttria-stabilized tetragonal zirconia polycrystal powder and the solid loading within the slurry.

Additionally, Kim et al. [76] prepared dental zirconia implants by sintering. They showed that the zirconia blocks have many surface cracks that lead to the deterioration of mechanical strength and the failure of the implant in the body. Thus, highly dense 3Y-TZP samples with a relative density of 99% and grain size of 200–400 nm were obtained at a solid loading of 50–65 wt%. Recently, removable partial dentures (RPD) cobalt-chromium (Co-Cr) alloys are fabricated using a casting technique [77]. New additive manufacturing processes based on laser-sintering has been developed for quick fabrication of RPD metal frameworks at low cost. **Figure 7** illustrates the SEM micrograph of the fractured surface of Co-Cr alloy after casting. As can be seen, the Co-Cr alloy exhibited smaller grain size, higher microstructural homogeneity, and low porosity (2.1–3.3%). It has been shown that laser sintered alloys are more precise and present better mechanical and fatigue properties than cast alloys for RPD.

2.2.6 Hot isostatic pressing

For a decade, hot isostatic pressing (HIP) has been used successfully by manufacturers around the world to increase productivity. HIP was used to eliminate pores and remove casting defects (such as oxides and carbides) to dramatically increase the material properties.

Giunea et al. [78] synthesized zirconia powders by HIP at 500 °C for 2 h. The results showed that a pure cubic phase, with average particle dimension

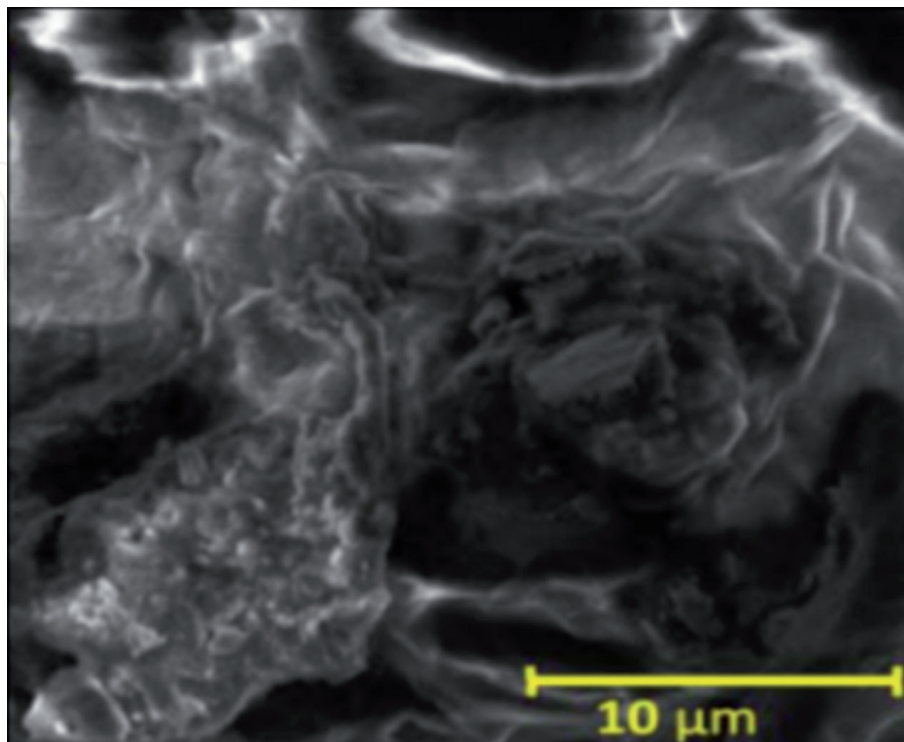


Figure 7.
SEM image of the fractured surface of Co-Cr alloy after casting [77].

about 70 nm, was obtained. Thus, the obtained samples presented a mixture of monoclinic-tetragonal or monoclinic-cubic phases. Final dense ceramic materials (relative density of 94%) were achieved. However, ZrO_2 -CaO ceramics have high biocompatibility and excellent mechanical properties characterized by strength of 500–708 MPa and Young's modulus of 1739–4372 MPa. Hu et al. [79] synthesized tetragonal zirconia polycrystalline (3Y-TZP) ceramics by HIP. The grain size of the final products reached about 138 nm. This fine grain size leads to an increase in Vickers hardness to achieve 13.79 MPa. These materials also revealed an elevated transmittance (in the range of 76–78%). The result showed that HIP was an effective process to prepare infrared-transparent 3Y-TZP ceramics with small grain size and with good optical and mechanical properties. Similarly, Klimke et al. [80] fabricated ZrO_2 ceramics by HIP. They demonstrated that the particle size, determined by TEM, was less than 50 nm (**Figure 8**) and the maximum in-line transmission was about 77%, which observed at IR wavelengths in the range of 3–5 μm .

2.2.7 CAD/CAM milling and copy milling

CAD/CAM milling and copy milling is an important field of dentistry and prosthodontics using CAD/CAM (computer-aided design and computer-aided manufacturing) to improve the design and creation of dental restorations [81, 82]. Thus, leucite-reinforced glass-ceramics involve Authentic and Empress CAD. Both have the identical microstructure and containing feldspathic glass with about 45 wt%. These blocks may characterize utilizing external strains and containing finer leucite crystals (about 5–10 μm in size). Additionally, the strength behavior of Empress CAD was comparable with Vitablocs. During the last two decades, dental CAD/CAM technology has been used to replace the laborious and time consuming, conventional lost wax technique for efficient fabrication of restorations [83]. Hence, this technology enables dentists to produce complex shapes of ceramics.

Typically, CAD/CAM dental restorations are milled from solid blocks of ceramic or composite resin that closely match the basic shade of the restored tooth. Metal alloys including zirconia can also be milled. The software sends this data to a milling machine where the prosthesis was milled [84]. CAD/CAM allows easy production of precise, esthetic, and durable prostheses [85]. CAD/CAM complements earlier technologies employed for these goals by enhancing

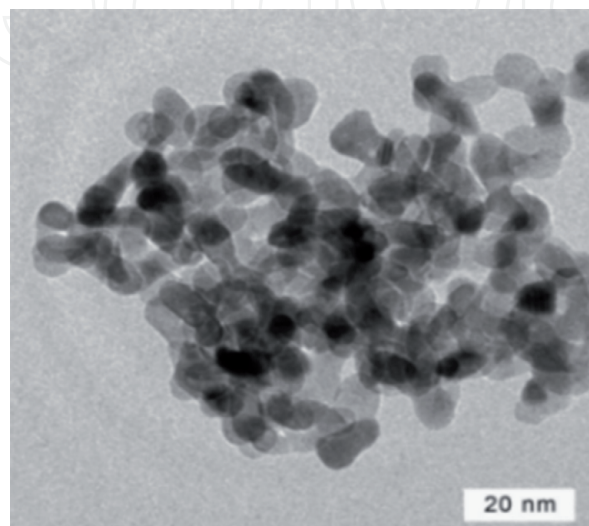


Figure 8.
TEM image of the ZrO_2 ceramic powder [80].

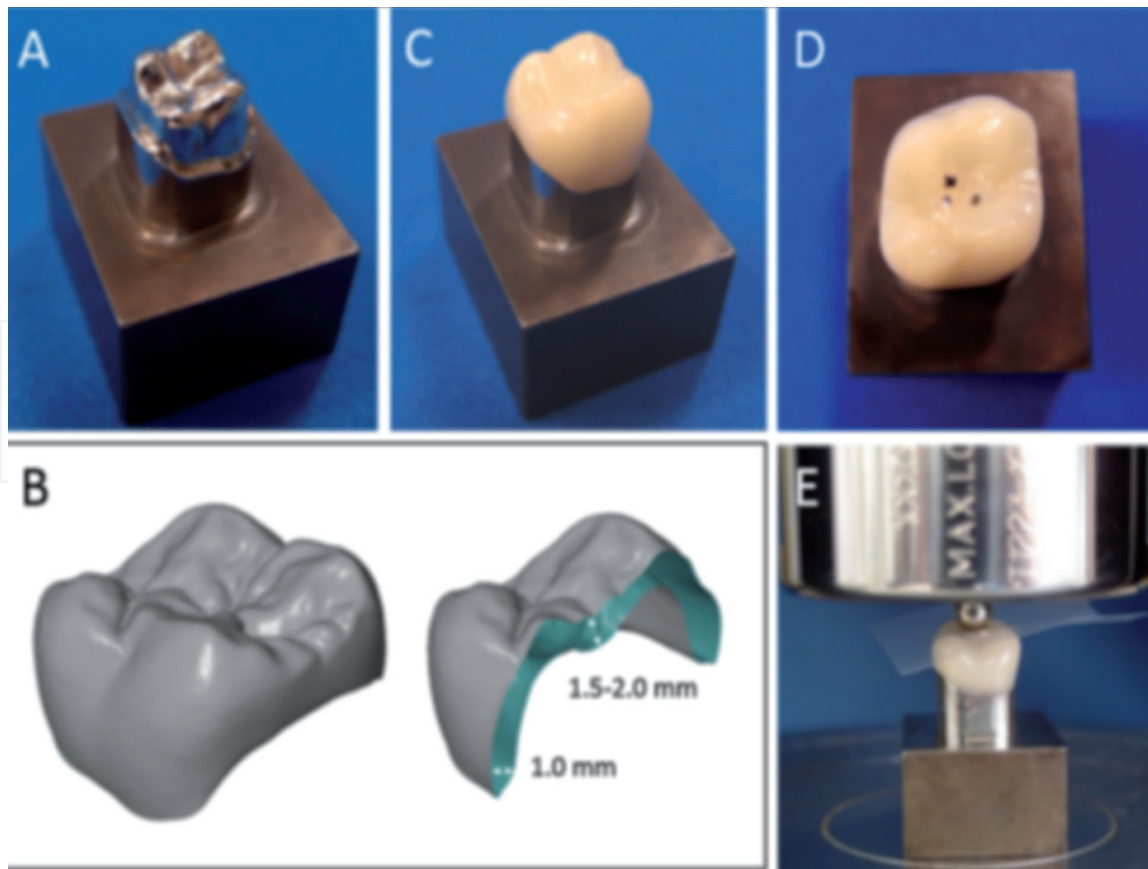


Figure 9.

Photographs of (A) stainless steel abutment, (B) CAD design for a crown specimen, (C) CAD/CAM composite resin crown bonded to the abutment, (D) loading points on the occlusal surface, and (E) the used machine [87].

the speed of design and creation, making affordable restorations, reducing unit cost, etc. Nevertheless, chair-side CAD/CAM equipment requires more time on the part of the dentists, and the fee was much higher than conventional restorative treatments. During the years 2015–2018, the data of 21 patients undergoing fibula free flap reconstructive surgery with CAD/CAM patient-specific reconstruction plates were analyzed, including the applicability of the virtual plan, flap survival, duration of surgery, ischemia time, simultaneous dental implantation, implant exposure, and postoperative complications [86]. At the time of primary reconstruction, a number of 76 dental implants were inserted in the 21 patients. The results showed that, in the secondary surgery, the implant can be uncovered 38.1% of the total patients in 7.6 months. Thus, the overall success rate for implants was 97.4%. Virtual surgical planning with CAD/CAM plates allows early and functional dental rehabilitation. Okada et al. [87] fabricated composite crowns using four computer aided design/computer aided manufacturing (CAD/CAM) blanks composed of a resins (sample 1) and a lithium disilicate (sample 2), which exhibited distinct tendencies (see **Figure 9**). The results revealed that the flexural strength was in the range of 175 to 247 MPa for sample 1 and 360 MPa for sample 2 while the fracture strength was in the range of 3.3 to 3.9 kN for the sample 1 and 3.3 kN for the sample 2.

3. Dental implants

Ceramic materials are good biomaterials widely used in dental implant because of their excellent biocompatibility and mechanical properties.

3.1 Bioglass implants

For the first time, the bioglass implants were introduced by Hench’s team at the late 1960s [88]. Because of the great bioactivity of bioglasses, they are one of the best biomaterials for renovation and bone repair. Moreover, to combine great mechanical strength and excellent bioactivity of bioglasses, they can be successfully used as coatings on inert substrates [89]. A bioactive surface can be considered as important agent to avoid many simultaneous reactions, which take place between the implant and the targeted tissue at the implant surface. **Figure 10** shows the interfacial reactions involved in forming a bond between bioactive glass and bone. As can be seen, the first five stages take place at the periphery of bioactive glass and involve release of alkali ions (bacterial growth is inhibited as a result of pH increase) along with the formation of crystallized hydroxycarbonate apatite (HCA). Hence, the implanted material fastens down with the tissue from step 6 to 11 in consequence of osteostimulation and bone growth.

The bioactive glass with its composite coatings can be classified as following categorization according to the coating structure:

3.1.1 45S5 Bioglass

Ceramic 45S5 bioglass with 24.5% sodium oxide, 45% silicon dioxides, 24.5% calcium dioxide and 6% phosphorus pentoxide, shown on **Figure 11**, have attracted the attentions of researchers as a biomaterial substance because of its osseointegration capability, bioactive surface and the ability of healing bone damages [90–92]. It can be prepared by melt-cast method with various crystallinity including amorphous and crystalline [93]. But, to guarantee the perfect amorphous sample crystallization, the heat-treatment should be continued for 1 hour at 1000 °C.

3.1.2 58S bioglass

Ceramic 58S bioactive glass is a great bioactive, biodegradable glass with the capability of bone bonding. This bioactive glass, having 33% calcium oxide, 58% silicon dioxide 9% phosphorus pentoxide, is able to receive specific attention as scaffold substance [94–96]. The reaction of 58S bioactive glass with physiological fluids occurs after implantation quickly and makes bond to the tissue of bone. This

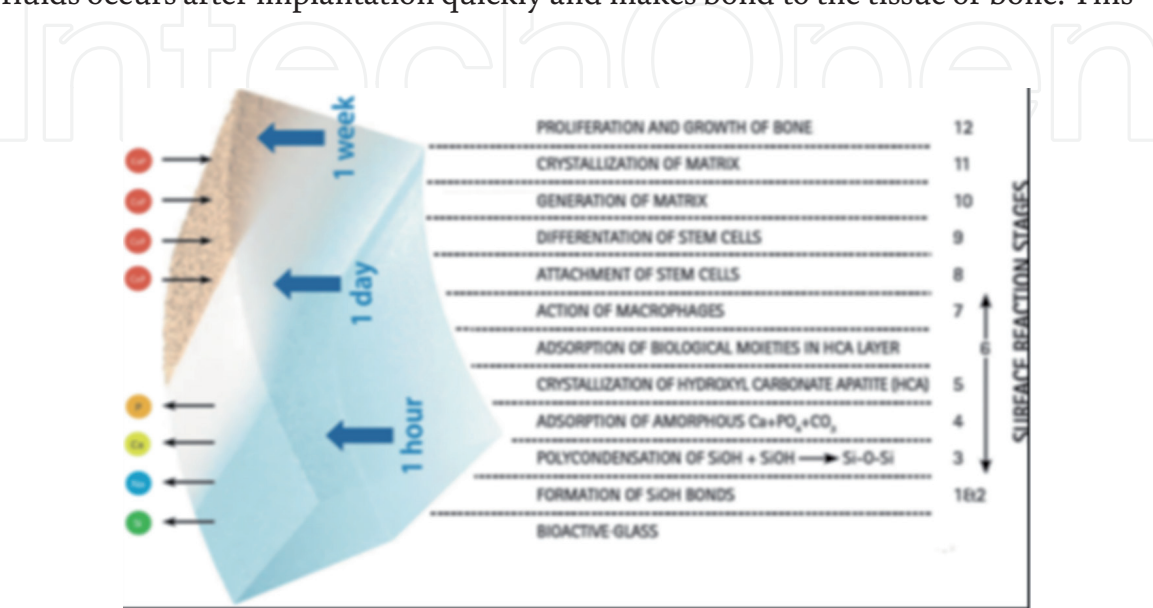


Figure 10. Sequence of interfacial reactions involved in forming a bond between bioactive glass and bone [89].

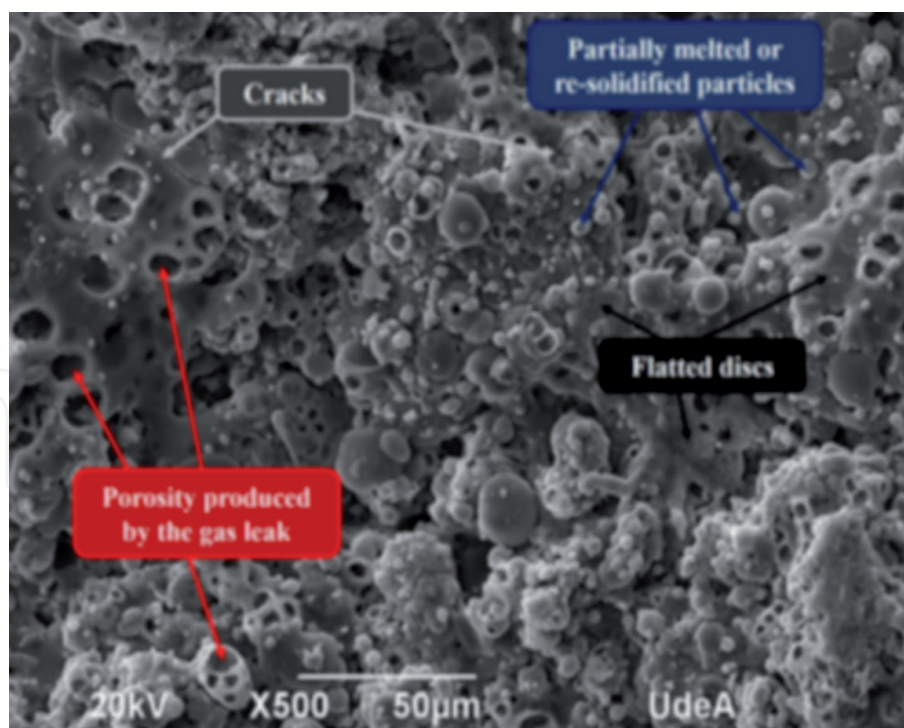


Figure 11.
The typical surface structure of 45S5 bioglass coatings sprayed [90].

happens without inflammatory, toxicity and foreign-body reaction. The fast ionic dissolution as well as the hydroxyl-carbonated apatite layer formation was seen after the rapid in-vivo surface reactions. With the release of calcium, silicon and phosphorous ions, the gene expression and the proliferation of osteoblast happens to form the bone quickly. This produced hydroxyapatite layer was as the bioactivity evidence of prepared bioglass, which both X-ray diffraction and scanning electron microscope images can confirm.

3.2 β -Tricalcium phosphate implants

β -tricalcium phosphate (β - $\text{Ca}_3(\text{PO}_4)_2$) and hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) belong to the family of calcium ceramics, which are widely and successfully used bioceramics for bone regeneration, drug delivery, biological cement, and tissue engineering scaffolds [97]. They exhibit pronounced resemblance to bone tissue minerals, excellent biocompatibility, good cell attachment properties for ensuring natural biodegradability, and bioresorption [98–100]. However, β -tricalcium phosphate is a bone substitute that has high biocompatibility, favorable resorption properties, and osteoconductivity [101–103]. In comparison with other bone substitutes, tricalcium phosphate, α -tricalcium phosphate (α - $\text{Ca}_3(\text{PO}_4)_2$) and β -tricalcium phosphate (β - $\text{Ca}_3(\text{PO}_4)_2$), are two polymorphs of tricalcium phosphate (TCP). The study of the phase equilibrium diagram of the $\text{CaO-P}_2\text{O}_5$ system shows that β -TCP, which crystallizes in the rhombohedral system and belongs to the space group $R3C$, transforms into α -TCP (monoclinic, $P21/a$), after heating at 1125 °C. The α -TCP has a less densely packed structure but it is more soluble than β -TCP. Its rapid hydrolyses produces calcium deficient hydroxyapatite [104].

3.3 Alumina implants

Alumina is very inert and resistant to corrosion in an in vivo environment [105]. It elicits minimal response from the tissues, and remains stable for many years of

service. Few minutes after the implantation of alumina device, proteins and other biomolecules adsorb on its surface, to form a fibrous capsule around the implant that protects it from immune system. The fact that alumina is biocompatible does not mean that tiny particles formed by the implant wear cannot generate a significant foreign body reaction [106]. Hence, α -alumina is dense (with a specific gravity of 3.97), nonporous, and nearly inert material. It is extremely hard and scratch-resistant (9 on the Mohs scale, next only to diamond). It has excellent corrosion resistance in vivo environments (**Figure 12**). Dense alumina implants were used as dental implants, since the 70's, because of their excellent wettability, allowing them to easily adsorb water and biomolecules, resulting in a low coefficient of friction. However, the most disabling property of alumina is its brittleness (high elastic modulus), hence the need to optimize the composition, the porosity and the grain size to improve the mechanical properties of alumina, such as strength, fatigue resistance and fracture resistance. Because of the better resistance to fracture and the higher bending strength (13.000 kg/cm^2) of single crystal alumina, compared to that of polycrystalline alumina (3500 kg/cm^2), single crystal alumina is used for dental implants. Thus, a typical alumina implant is made of single crystal alumina cylindrical core around which polycrystalline alumina is fused. Currently, alumina dental implants are declining in popularity and being replaced by other material having better properties [107].

3.4 Zirconia implants

The demand for zirconia dental implants are increasing recently. In comparison with the Ti dental implants, their increased esthetic, due to similarity to the human tooth color, is the main benefit of these implants [88, 108].

Zirconia with better optical, esthetic, mechanical and biological qualifications, is a hopeful substitute to traditional Ti implant system for oral recovery [109], and is produced by the oxidation of zirconium [110]. Zirconium, which is a transition metal [111], with gray white color [112], can be used to make zirconia implant. Segments of the metal implant can be uncovered by recession of gingiva and the loss of apical bone, which this can disclose a discolored overlying gingiva [113]. These concerns make an opportunity to use the zirconia ceramics because they enjoy great esthetic, biological and mechanical characteristics and they also lack electrically corrosion. Polyethylene and Ti show more inflammatory reactions than zirconia. Less inflammatory response along with the lack of mutagenicity and toxicity in zirconia, can be considered as the most attractive zirconia properties [114]. Zirconia-based ceramics are attractive materials because they exhibit satisfying strength (more than 1000 MPa) and toughness (about $6\text{--}10 \text{ MPa m}^{1/2}$), allowing them to contribute

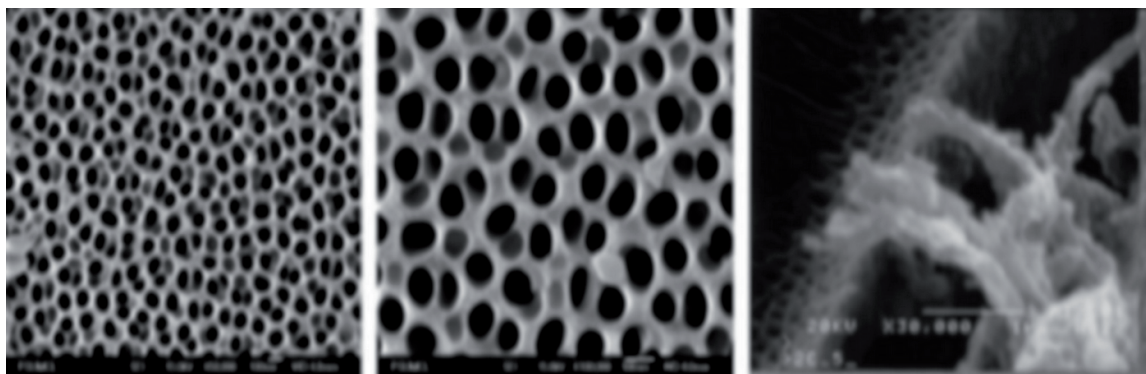


Figure 12. Nanoporous alumina fabricated using the anodization process (left and center). Osteoblast interaction with the nanoporous architecture (right) [106].

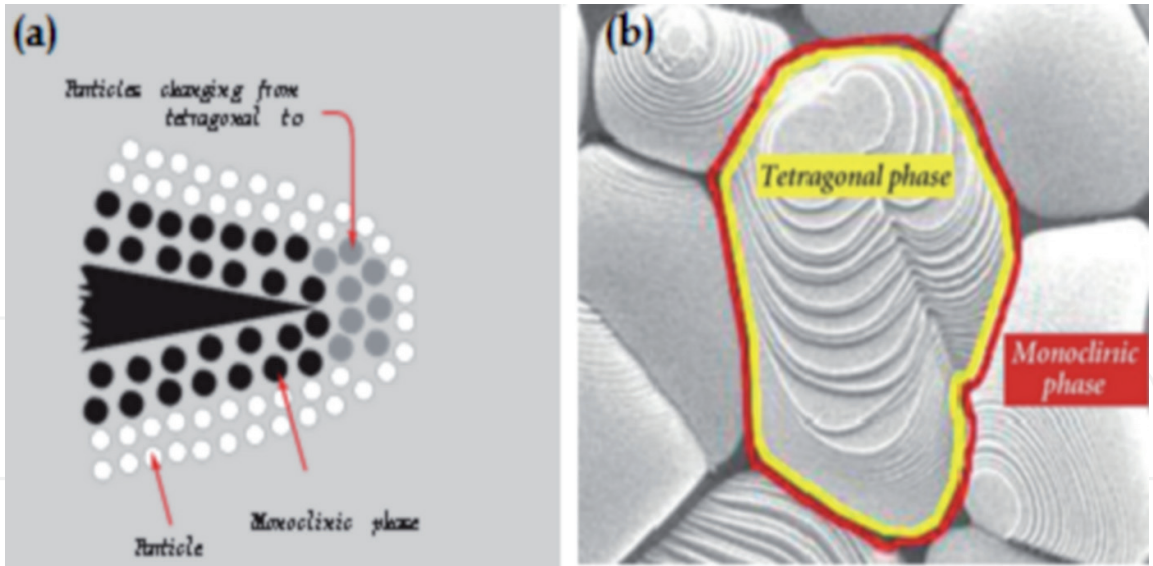


Figure 13. (a) Zirconia has the ability to phase change from a tetragonal phase to a monoclinic phase to stop ensuing cracks, which is referred to as “transformation toughening” and (b) during phase change, there is approximately 3 to 5% volume increase from tetragonal to monoclinic phase [7].

to solve the problem of the fragility encountered when using alumina, as implant. Indeed, zirconia owes its importance to the stress-induced transformation of the metastable tetragonal crystallites phase into monoclinic phase, when it is localized around a propagating crack. As shown on **Figure 13**, this transformation contributes to increase the fracture toughness and the resistance to crack propagation by expanding the volume (3–6%) and absorbing a part of the energy required for crack propagation, which leads to crack shielding. The negative aspect of this transformation is “aging”, which happens when it is localized on the surface of the implant, in presence of acidic liquids. Hence, the surface of the implant presents some signs of “aging”, such as the roughness and the appearance of micro-cracks [115].

3.5 Hydroxyapatites implants

Hydroxyapatite is a bioceramic of great clinical interest due to its nontoxicity, bioactivity, good biocompatibility, osteoconductivity, and its non-inflammatory nature. However, since it has a high elasticity modulus (brittle), hydroxyapatite is usually associated to other materials to form an implant in load-bearing applications. In fact, implants for load bearing, such as titanium screw, can be coated with

Property	Value
Thickness	—
Crystallinity (%)	62
Phase purity (%)	95
Density (g/cm ³)	24
Tensile strength (MPa)	>50.8
Shear strength (MPa)	>22
Ca/P ratio	1.67–1.76
Heavy metals (ppm)	<50

Table 4. Properties of hydroxyapatites coat [117].

hydroxyapatite. The application of hydroxyapatite coatings is an interesting surface amendment on dental implants [116]. As its coatings apply on implanted material, it provides enough calcium and phosphate ions at initial implantation stage and makes the implant material biocompatible [117]. The properties of hydroxyapatites are given in **Table 4**.

However, hydroxyapatite has osteogenic nature and is able to form strong bond with host tissues, so it is widely used in biomedical field for osteointegration, bone replacement and regeneration, coating metallic implants, and to fill the defects generated in bones [118].

4. Challenges

Despite their benefits, all ceramic dental materials and their applications show challenges which still need to be tackled.

The challenges in dentistry remain in understanding and improving the clinical performance of the biocompatible restorative materials by improving definition of failures, laboratory testing, and clinical studies. In fact, material factors, including differences in thermal conductivity and coefficient of thermal expansion between core and veneer, likely create residual stresses that predispose a restoration to chipping. Only requirements of patients further complicate the challenge of understanding factors that contribute to long term success of restoration. In this context, some works include report patient or provider factors or patient control groups.

Few recent works [119, 120] have been reported on clinical trials. Several improvements have been recently made in structural reliability via damage tolerance and flaw control [121, 122]. Predictive laboratory tests can reduce the need for expensive and time-consuming clinical tests, which sometimes exceed the commercial lifetime of the materials being evaluated. In addition, laboratory tests, likely over estimate clinical lifetimes, can replicate clinical failure modes.

Several parameters like dimensional accuracy, surface, and mechanical properties of ceramic dental materials should be improved to obtain high quality final products [123]. Another challenge is bacteriological safety of the final products which are in contact with human organs and tissues. However, it is necessary to make sterilized protocols while keeping intrinsic properties [123]. In addition, Lee et al. [124] showed that the accuracy in Z-direction is harder to enhance than in the directions X and Y because the presence of uncontrolled parameters like evaporation of material during machining, shrinkage, and spreading densification of the powder. Hence, the porosity of the ceramics is another challenge in dentistry. It has been showed that the porosity was reduced by adding dopants or viscous liquid forming phase, choosing the corresponding powder granulometry, and applying HIP to the green body [125]. Several studies revealed that the surface quality of ceramic materials depends strongly on the technique, raw material characteristics, and processing conditions [126, 127].

Moreover, there maining challenges for future advances are present abundant arenas for future innovations. Moreover, it will be important to determine where and how informed simplifications in testing conditions can be made.

Machining techniques and design methods should to be improved and innovated to achieve good ceramic restorations with subsurface damage and little surface.

CAD and CAM and fabrication processes creating veneers and cores separately will further evolve [128]. Thus, these approaches will be complemented by additive approaches, laying down materials only in places where it is needed to create a restoration [129]. However, these approaches have shown significant substantial hurdles.

5. Conclusion

For over 200 years, ceramic materials have been utilized in dentistry. This chapter shows that dental ceramics can be fabricated by different techniques. The CAD/CAM technology is the most widely used in dentistry.

Dentistry as an art of oral health is one of the major affiliates of dental science. Operative dentistry continues to evolve toward bright future with the innovations and development of new materials, techniques, and equipments. Several numbers of dental ceramic materials have been developed with respect to strength, survival, applications, and esthetics. The success of dental ceramic materials depends on various factors like design, type of material, cementation media, clinical data, etc. These factors help the dentist to enhance the relation between laboratory studies and clinical data and to choose the appropriate ceramic material.

Although the remarkable evolution of ceramics in dentistry not all the challenges have been solved.

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Conflict of interest

The authors declare no conflict of interest.

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