DENTAL MATERIALS 35 (2019) 825–846

Available online at www.sciencedirect.com

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Additive manufacturing of ceramics for dental applications: A review

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ARTICLE INFO

Article history:
Received 2 May 2018
Received in revised form
15 October 2018
Accepted 13 February 2019

Keywords:
Additive manufacturing
3D printing
Ceramics
Dentistry
Dental prosthesis

ABSTRACT

Objective. The main goal of this review is to provide a detailed and comprehensive description of the published work from the past decade regarding AM of ceramic materials with possible applications in dentistry. The main printable materials and most common technologies are also addressed, underlining their advantages and main drawbacks.

Methods. Online databases (Web of knowledge, Science Direct, PubMed) were consulted on this topic. Published work from 2008 to 2018 was collected, analyzed and the relevant papers were selected for inclusion on this review.

Results. Ceramic materials are broadly used in dentistry to restore/replace damaged or missing teeth, due to their biocompatibility, chemical stability and mechanical and aesthetic properties. However, there are several unmet challenges regarding their processing and performance. Due to their brittleness nature, a very tight control of the manufacturing process is needed to obtain dental pieces with adequate mechanical properties. Additive manufacturing (AM) is an emerging technology that constitutes an interesting and viable manufacturing alternative to the conventional subtractive methods. AM enables the production of customized complex 3D parts in a more sustainable and less expensive way. AM of ceramics can be achieved with an extensive variety of methods.

Significance. There is no perfect technology for all materials/applications, capable alone of fulfilling all the specificities and necessities of every patient. Although very promising, AM of ceramic dental materials remains understudied and further work is required to make it a widespread technology in dentistry.

Contents

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https://doi.org/10.1016/j.dental.2019.02.026

1. Introduction

In dentistry, as in many other fields, the production of dental pieces is increasingly becoming automated. Computer aided design (CAD) and/or computer aided manufacturing (CAM) have become progressively widespread within the medical and dental fields [1–4]. These tools are generally used in the manufacture of dental pieces in machining centers, where extra material is removed from a block to obtain the piece with the desired shape. This technique is known as subtractive manufacturing (SM).

Nowadays, a new type of technology is emerging, additive manufacturing (AM), also referred to as 3D printing, that allow building up pieces by adding materials layer-by-layer, based on a computerized 3D model [5]. This type of technology has suffered great developments in a wide range of areas [6], allowing to produce pieces of all classes of materials (metals, polymers, ceramics and composites), including materials of biological origin [7]. AM focus has been moving from prototype fabrication to rapid manufacturing of small or medium quantities of end-use products. Among the main areas of AM application stands out:

- Aerospace: AM technology is particularly suitable to obtain a limited number of pieces that are usually required for aerospace applications, with complex geometries and made of advanced materials (e.g titanium alloys, nickel superalloys, special steels or ultrahigh-temperature ceramics) which are difficult, costly and time-consuming to manufacture [8,9].
- Automotive: AM technology is an important tool in this industry, since it can reduce the development cycle,manufacturing and product costs of automotive components. It allows producing small quantities of structural and functional parts and thus, is particularly interesting for racing vehicles, where light-weight alloys (e.g. titanium and aluminum) and composites are used to obtain highly complex structures [10,11].
- Energy: AM technology allows the fast development and fabrication of prototypes to reduce the cost and lead-time of research and development of new solutions that reduce the fossil energy dependency. It increases the design possibilities to improve energy efficiency and/or power density, in alternatives that use renewable and clean energies [12,13].
- Biomedical: Recent developments in the biomaterials field, biologic sciences and biomedicine have potentiated the use of AM techniques. Customization is a critical factor in this area and AM allows the production of a wide range of products with specific properties and shapes that meet the patient needs. For example, it is possible to produce diagnostic platforms, orthopedic and dental implants, drug delivery systems, medical devices, tissue scaffolds and artificial organs [14]. Biofabrication through AM emerged in the recent years as a new alternative to fabricate tissues. Here, living cells are deposited layer-by-layer in combination with different biomaterials to obtain complex living structures [15,16].

In the dentistry field, the use of AM to produce endurable dental structures is expected to bring advantages over conventional manufacturing methods, as reported on other fields [17,18]. In particular, it shall:

- Allow the production of customized near-net-shape dental pieces with intricate details (e.g. irregular grooves, crannies, valleys). Product complexity shall not add cost to produc-

tion beyond the design stage, because once the design is set, costs are independent of the shape (i.e. a crown and a cube are processed in the same way).
- Allow reduction of dental parts production time and consequently of time-to-market. Traditional subtractive technologies involve several time-consuming steps (prototype, tooling, setup), while AM allows a faster direct production starting simply from a 3D scan of the oral cavity.
- Limit human error relevance in the procedures. Minor human intervention is required in AM due to the lower number of manufacturing steps.
- Decrease the environmental impact, ensuring a higher manufacturing sustainability. Being an additive technique, it reduces material waste and energy consumption and eliminates the use of conventional manufacturing tools (e.g. drills and burrs).

Globally, AM allows moving from mass production to mass customization, with significant efficiency increase and production costs decrease. The expected dissemination of this technology applied to dental prosthesis shall result in equipment's cost decrease. Thus, the reduction of final product (dental structures) price is predictable, increasing the accessibility of dental care to the poorest sectors of the population.

Due to the recent expiration of the main 3D printing patents, the access to printers became easier and less expensive [19]. Thus, the healthcare market in this field is likely to increase [19]. Digital dentistry is reported to be one of the fastest growing sectors of the AM technologies [4]. There are several possible applications of AM techniques in dentistry, e.g. crowns, bridges, dentures, models, surgical guides, implants and orthodontics materials [19,20]. Several challenges emerge when this technique is considered to produce endurable dental devices. For example, the reliability of the process, surface finishing of the samples and materials density are among the major concerns.

Concerning dental materials that can be used in AM, polymers are the most studied and used ones [21], followed by metals. AM of ceramic dental materials is still underdeveloped, mainly due to the difficulties to produce pieces with suitable surface finishing, mechanical properties and dimensional accuracy. The available literature regarding AM of ceramic materials represents less than 5% of the total AM published related work. The studies are even fewer in what concerns ceramic materials for dental applications (>0.5%).

This paper presents a recent overview (last decade) of published work concerning AM of ceramic materials for dental applications. A summary of potentially printable dental biomaterials and brief descriptions of the most common digital manufacturing technologies are also provided, highlighting the main features, advantages and drawbacks, to better understand the potential and restrictions of each technology. Hints to overcome some of the problems are also given.

2. Methods

An extensive literature search of published articles was performed using the electronic databases PubMed, Web of Knowledge and Science Direct. The used keywords strings were: 3D printing AND Dental; Additive manufacturing AND Dental. The following filters were applied: (1) time interval: from 2008 to 2018, (2) Additional refined search within the results: "Ceramic"; (3) language: English.

Abstracts were analyzed and excluded if the reported work did not have any possible application in dentistry or was opinion-based. Literature reviews were excluded from the description of works presented in "section 5. Additive manufacturing of bioceramics for dental applications", but included in the remaining sections to complement this review and provide any additional remarks.

3. Ceramic dental materials

Bioceramics are broadly used in the dental field (e.g. crowns, implants, bridges, inlays/onlays). These materials have some attractive features/attributes which are similar to natural dentition properties, e.g. compressive strength, thermal conductivity, radiopacity, colour stability, aesthetics [22]. However, these materials are brittle, hard and sometimes difficult to process [23,24].

Bioceramics can be divided in 4 categories, depending on their main system composition [23]:

(1) glass-based systems (mainly silica);
(2) glass-based systems (mainly silica) with fillers, usually crystalline (e.g leucite or lithium dissilicate);
(3) crystalline-based systems with glass fillers (mainly alumina);
(4) polycrystalline solids (alumina and zirconia).

Glass-based systems consist of materials that are made mostly of silicon dioxide (i.e. silica or quartz) and can comprise different amounts of alumina. Feldspars are composed of aluminosilicates, found in nature, containing different quantities of potassium and sodium [23,25]. Feldspars can be modified in several ways in order to produce the glass used in the dental area [23]. Additionally, synthetic forms of alumina silicate glasses may as well be manufactured for dental ceramics.

Glass-based systems with fillers present a wide range of glass-crystalline ratios and crystal types. The glass composition is almost the same as the pure glass category, being that the difference resides in the amount of different types of crystals that can either be added or grown in the glassy matrix. Nowadays, the primary crystal types are leucite, lithium dissilicate or fluoroapatite [23].

Intended as an alternative to traditional metal ceramics, crystalline-based systems with glass fillers were developed. They are composed of glass-infiltrated, partially sintered alumina. This category was first introduced in 1988 under the name In-Ceram [23].

Polycrystaline solids are made by directly sintering crystals together, forming a dense, air-free, glass-free, polycrystalline structure [23].

In the next sections, a brief description is presented regarding the main properties of the most frequently used bioceramics in dental applications (Table 1).

Table 1 – Main properties of most common biomedical grade dental ceramic materials.

Material	Main features	Main applications	Ref.
Zirconia- based ceramics ZrO_2	- Modulus of elasticity: 100–250 GPa - Flexural strength: 177–1000 MPa - Fracture toughness: 1-8 MPa.m$^{1/2}$ - Hardness: 5–15 GPa - Tensile strength: 115–711 MPa	- Implants - Orthodontic brackets - Abutments - Copings - Crowns - Bridges	[26]
Alumina - based ceramics Al_2O_3	- Modulus of elasticity: 380 GPa - Flexural strength: 500 MPa - Fracture toughness: 3.5 - 4 MPa.m$^{1/2}$ - Hardness: 22 GPa - Tensile strength: 267 MPa	- Implants - Endodontic posts - Orthodontic brackets - Abutments - Crowns - Bridges - Filler for dental composites and bone cement materials	[27]
Leucite –based ceramics	- Modulus of elasticity: 65–67 GPa - Flexural strength: 55-134 MPa - Fracture toughness: 0.8–1.3 MPa.m$^{1/2}$ - Hardness: 5.3–7.9 GPa	- Metal-ceramic restorations	[28,29]
Lithium disilicate glass-ceramic $Li_2Si_2O_5$	- Modulus of elasticity: 90–100 GPa - Flexural strength: 250–365 MPa - Fracture toughness: 2-3.5 MPa.m$^{1/2}$	- Crowns - Bridges - Veneers - Inlay/onlay	[29,30]
Mica based ceramics	- Modulus of elasticity: 48–164 GPa - Flexural strength: 140–160 MPa - Fracture toughness: 0.6–2.2 MPa.m$^{1/2}$ - Microhardness: 3.2–4.5 GPa	- Ceramic restorations	[31,32]

3.1. *Zirconia*

Zirconia ceramics were introduced in dentistry in the early nineties, as endosseous implants in dental prosthetic surgery [33,34]. Nowadays, it has a wide application in this field (see Table 1). This material is known to have exceptional mechanical properties and ease of machining in the pre-sintering stage through CAD/CAM [22]. Zirconia is biocompatible with the tissues in the oral cavity and has been reported to be osteoconductive, which means that this ceramic facilitates bone formation when in contact with it [33,35,36]. Studies also report that zirconia does not produce allergic reactions or alterations of taste. Regarding mechanical properties, zirconia ceramics are considered to have high strength, hardness, wear resistance, resistance to corrosion, modulus of elasticity similar to steel, coefficient of thermal expansion similar to iron, and the highest fracture toughness among the most used ceramics [22,33].

Zirconia-based ceramics can be stabilized in tetragonal or cubic phases depending on the used dopant (Y_2O_3, MgO, CaO), its concentration and temperature during the thermal treatments [37]. For dental applications, zirconia is commonly stabilized with 3 mol% yttria. The excellent mechanical properties of stabilized tetragonal zirconia are related with the stress-induced from tetragonal to monoclinical transformation, which is accompanied by a 4.5% volume increase [22,37,38]. This behaviour leads to the development of compression zone, shielding the propagating crack tip which inhibits further crack propagation, successfully enhancing toughness.

Nevertheless, there are some disadvantageous aspects of zirconia ceramics. For instance, its opacity that may compromise aesthetics features; its aging which is promoted by moisture, facilitating the degradation and eventual increase of surface roughness and the presence of cracks that may compromise the performance at long term.

3.2. *Alumina*

Alumina, also called aluminum oxide (Al_2O_3), was first introduced in the 1970s. However, the initial applications presented a fracture rate of the order of 13% [39]. This observed failure was related to a higher porosity [27]. With further developments, a decade later, a second improved generation of alumina ceramics was presented, characterized by higher density and smaller grains. This led to a decrease of the fracture rate to less than 5% [40]. Nowadays, there is available a third generation of alumina ceramic components, with properties such as high purity, high density and finer microstructure [27].

Alumina is used in dental applications for fabrication of endodontic posts, orthodontic brackets, dental implants, crowns and bridges and in ceramic abutments (Table 1) [27]. High purity alumina has usually a purity of 99.99% and has been developed as an alternative to surgical metal alloys for dental applications [41]. According to US Food and Drug Administration (FDA), only the high-purity Al_2O_3 can be used for medical grade ceramics [42]. Impurities such as SiO_2, metal silicates and alkali metal oxides that form glassy grain boundary phases must be minimized to less than 0.1 wt% [42], since the in vivo degradation of such glassy phases leads to the appearance of stress concentration sites where cracks can be initiated, leading to the catastrophic failure of the component. It is possible to enhance alumina toughness and fracture strength by controlling the grain size and the porosity. This can be achieved using adequate sintering cycles (temperature, time, heating/cooling rates), and adding some additives (e.g. magnesium oxide (MgO), zirconium oxide (ZrO_2) and chromium oxide (Cr_2O_3)) [23,43].

3.3. *Leucite*

Leucite ($KAlSi_2O_6$) is a potassium alumina-silicate. This material displays a tetragonal structure at room temperature. At 625 °C, it suffers a displacive phase transformation from tetragonal to cubic, together with a volume expansion of 1.2% [44]. Leucite has been widely used as a constituent of dental ceramics to modify the coefficient of thermal expansion, which is very important when the ceramic is to be fused or baked onto metal [28].

Usually leucite-based materials are used for veneering ceramics in metal-ceramic restorations, also referred to as feldspathic porcelains. These systems have been available since the 1960s.

Leucite is attained by incongruent melting of feldspar (naturally occurring) at temperatures between 1150 and 1530 °C [44].

Despite the mechanical properties of feldspathic porcelains being the weakest within ceramic dental materials (Table 1), their global performance is perceived as quite successful [44].

3.4. *Lithium dissilicate*

Lithium silicate-based glass-ceramics were recently introduced as machinable materials to respond to the demanded increased strength, toughness and wear resistance, required for the fabrication of dental pieces [45,46]. This ceramic material is used in the fabrication of single and multiunit dental restorations, mainly dental crowns, bridges, and veneers (Table 1), due to its excellent mechanical and optical properties [30].

In general, lithium disilicate ($Li_2Si_2O_5$) presents a microstructure constituted by interlocking needle-like crystals embedded in a glass matrix. As a result of this morphology, cracks are forced to propagate around each individual lithium disilicate crystal [47]. This type of microstructure increases both strength and toughness relatively to other commonly used glass-ceramics: they have a strength twice as higher as that of the first generation of leucite-reinforced ceramics [44].

3.5. *Mica*

Mica minerals are a group of sheet silicate (phyllosilicate) minerals, or layer type silicates, that consist of varying complex formulae of Si, K, Na, Ca, F, O, Fe and Al [48]. The mechanical properties (Table 1) are dictated by the specific crystal structure formed by the cleavage planes situated along the layers [49]. Crack propagation is more likely to occur along the cleavage planes [50].

Mica-based glass-ceramics are relevant for dental materials due to their good machinability, high strength and resistivity to thermal expansion as well as biocompatibility [51].

3.6. *Others ceramic dental materials*

Besides the examples mentioned above, there are other ceramic materials used in the dentistry field.

The inorganic part of all the mineralized tissues of the human body is composed predominantly of calcium phosphate salts. For over 30 years, calcium phosphate-based formulations are recognized by their good osteoconductivity and biocompatibility in reconstructive surgeries [52]. Tricalcium phosphate (TCP) presents three polymorphs. These include: monoclinic (the less dense but more soluble), α and hexagonal α', and rhombohedral β form (with higher density) [53]. Hydroxyapatite (HA, $Ca_{10}(PO_4)6(OH)_2$) is the main component of enamel, and is responsible for the bright white appearance and elimination of the diffuse reflectivity of light by closing the small pores of the enamel surface [54]. HA can be used as filler in the repair of craniofacial defects or small holes and depressions on enamel surface, as grafting material and as coating in implant dentistry [54,55].

Bioactive glasses (BG) are silicate-based materials that can form a strong chemical bond with the tissues. They present great interest in regeneration and healing of bone tissue [53]. Their ability to support osteoblast cells, to bond to both soft and hard tissue and their capability of stimulating angiogenesis in the presence of vascular endothelial growth factor (VEGF) make them an attractive alternative relatively to other scaffold materials [53].

Finally, dental impression materials still play a significant role in dentistry. Gypsum products are among the most frequently used materials by dental professionals, since its properties are easily modified by physical and chemical means. Gypsum may be used as impression material, mold material for processing complete dentures, as binders for silica in gold alloy casting investment, soldering investment, and investment for low-melting-point nickel-chromium alloys [56].

3.7. *Composites*

A composite material is defined as a combination of two or more materials. The resulting combination renders unique properties with characteristics different from the individual components. In dentistry, ceramic composites may comprise combinations such as ceramic-metal, ceramic-polymer, or ceramic-ceramic [22,44,57,58]

Examples of current dental ceramic-ceramic composites include alumina–zirconia composites, commercially available as structural ceramics for dental devices. These materials, contain either alumina-toughened zirconia (ATZ) or zirconia-toughened alumina (ZTA), depending on the percentage of the main component. These composites combine the transformation toughening capabilities of zirconia along with the lower susceptibility to low temperature degradation in biological fluids [44].

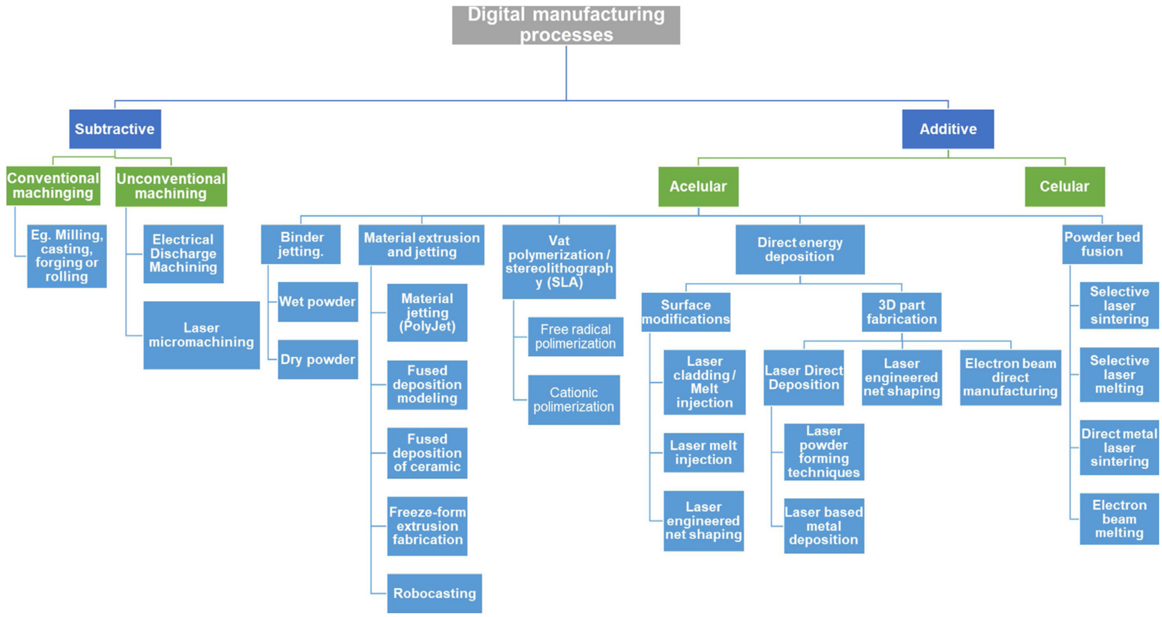

Fig. 1 – Main digital manufacturing technologies.

More recently, with the development of nanotechnology, the bionanocomposites have emerged [59]. These materials are expected to mimic native tissue structure, withstand high biting force and harsh *oral cavity* environment, e.g. sudden change of temperature or osmotic pressure and invasion of various pathogens [60]. Possible applications for bionanocomposites in the dental field include dental tissue regeneration (periodontal ligament or pulp-dentin complex) or its substitution (enamel) [60].

4. Digital manufacturing

CAD/CAM production of fixed prosthetic restorations such as inlays, onlays, veneers, crowns, and fixed partial dentures (FPDs) is a relatively well established technology used by dental health professionals for over 20 years [1].

All CAD/CAM systems involve three steps. The first one corresponds to the data acquisition, through various scanning technologies that allow to transform the site/product geometry into digital data to be processed by the computer [1,61]. This is followed by manipulation and processing of the data set using a CAD software. Finally, the processed data are used for manufacturing of structures in the desired material through CAM.

In dentistry, there are three different production concepts available, depending on the location of the steps of the CAD/CAM processes [61]:

- chairside production,
- laboratory production,
- centralized fabrication in a production center.

The production can be carried out through several different technologies, that can be divided into two manufacturing processes: subtractive and additive manufacturing [1]. These different technologies are summarized in Fig. 1 and explained in more detail in the following sections.

4.1. *Subtractive manufacturing*

There are several subtractive manufacturing (SM) techniques (Fig. 1). The most used in dental ceramics processing is based on milling of pre-sintered or fully sintered blocks, through a computer numeric controlled (CNC) machine. The CAM software automatically translates the CAD model into tool path for the CNC machine. This involves computation of the commands series that dictate the CNC milling, including sequencing, milling tools, and tool motion direction and magnitude. The accuracy of tool positioning has been reported to be within 10 μm [62].

The 3-axis milling systems are the most commonly used in dental milling systems. In such systems, the milling burs move in three axes (x,y,z) according to a defined path. [63]

SM is extensively used in dentistry for the production of dental pieces such as crowns and bridges [64,65]. SM technology allows the processing of materials, which would otherwise be difficult to manipulate. This way, the exhaustive artisanal production techniques are decreased or even eliminated, thus allowing the dental technician to enhance the creative component of his manual manufacturing process (e.g. aesthetic layering of porcelain) [66,67].

SM is a well-established technology which has the advantage of using intrinsically homogeneous materials which are unaffected by operating conditions. Furthermore, it requires low post-processing and the costs regarding the involved equipment are relatively reduced [66]. However, this is a wasteful process because the piece is milled from an intact block with a significant loss of material amount. Factors such as the objects' complexity, the dimension of the tooling equipment and the properties of the material can affect and limit

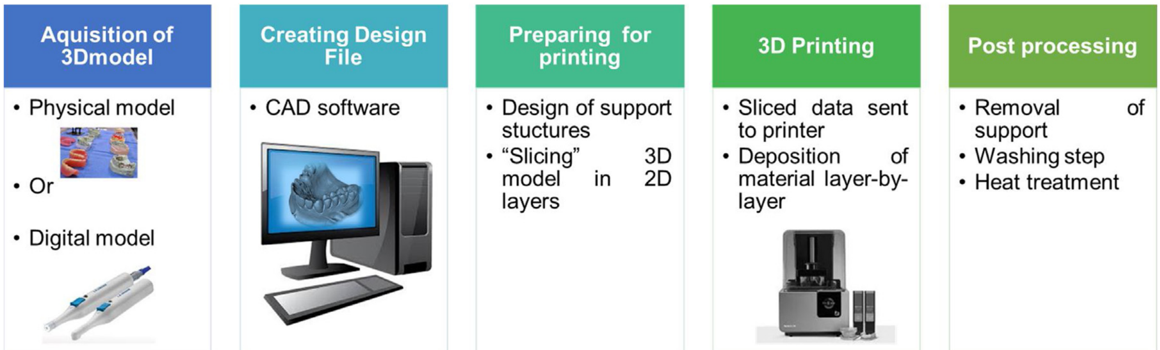

Fig. 2 – 3D printing process.

the accuracy of this process [66]. In addition, costs associated with tools are significant.

4.2. *Additive manufacturing*

Additive manufacturing (AM), also referred to as solid freeform fabrication, rapid prototyping or 3D printing (3DP), involves processing methodologies that are capable of producing structures by depositing materials layer-by-layer resorting to a computer generated design file (.STL) [68,69]. The workpiece is virtually sliced into several two-dimensional layers. Then, an AM machine generates the tool-path along the x and y directions [69]. Each material layer is deposited one on top of the other, consecutively, forming a three-dimensional part [69].

Ceramics present a higher melting point, higher susceptibility to thermal shook and lower sintrerability than the other group of materials. Thus, it is quite difficult to obtained fully consolidated parts, without defects, using AM methods that produced directly sintered bodies. In most of the cases, AM is used to obtain preliminary 3D structures in green that are built from mixture powders with organic or inorganic binder materials and need to be submitted to further steps of debinding (to eliminate the organic binder) and sintering (to increase the piece densification). Some authors refer to these methods as indirect, contrarily to direct methods where the ceramic powder is sintered during the manufacturing procedure [70].

The debinding step depends on the organic components and became diffusion limited by increasing the thickness of the part, leading to higher debinding times The debinding temperature need to be carefully chosen. If is to high the removal rate of the volatile products resulting from the binder decomposition is too high, the pressure may increase and lead to crack formation and/or delamination. A possible solution to overcome the internal stresses generated during debind-

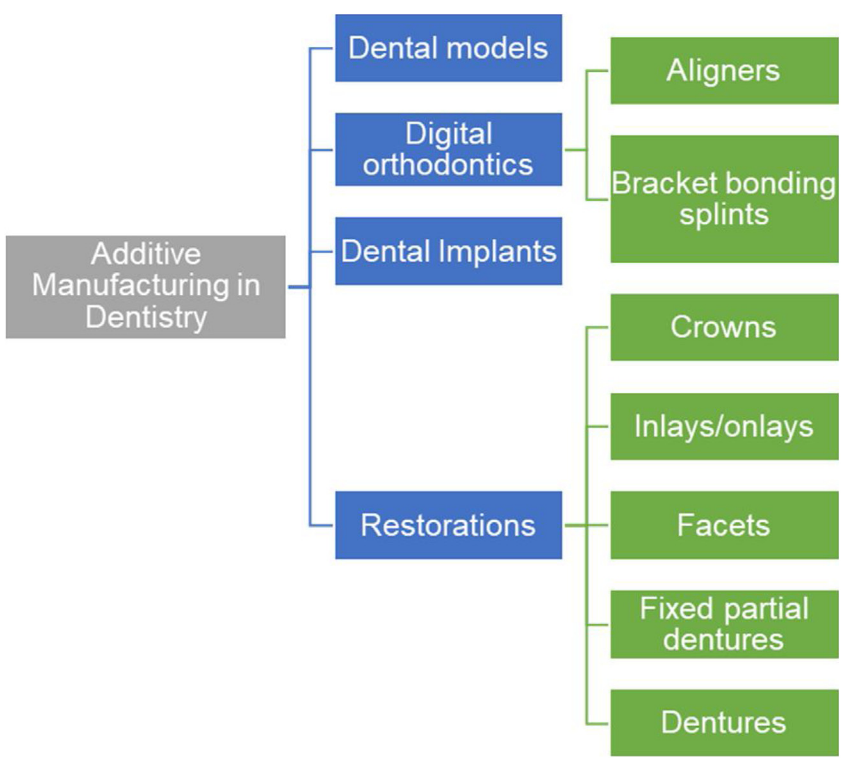

Fig. 3 – Applications of additive manufacturing in dentistry.

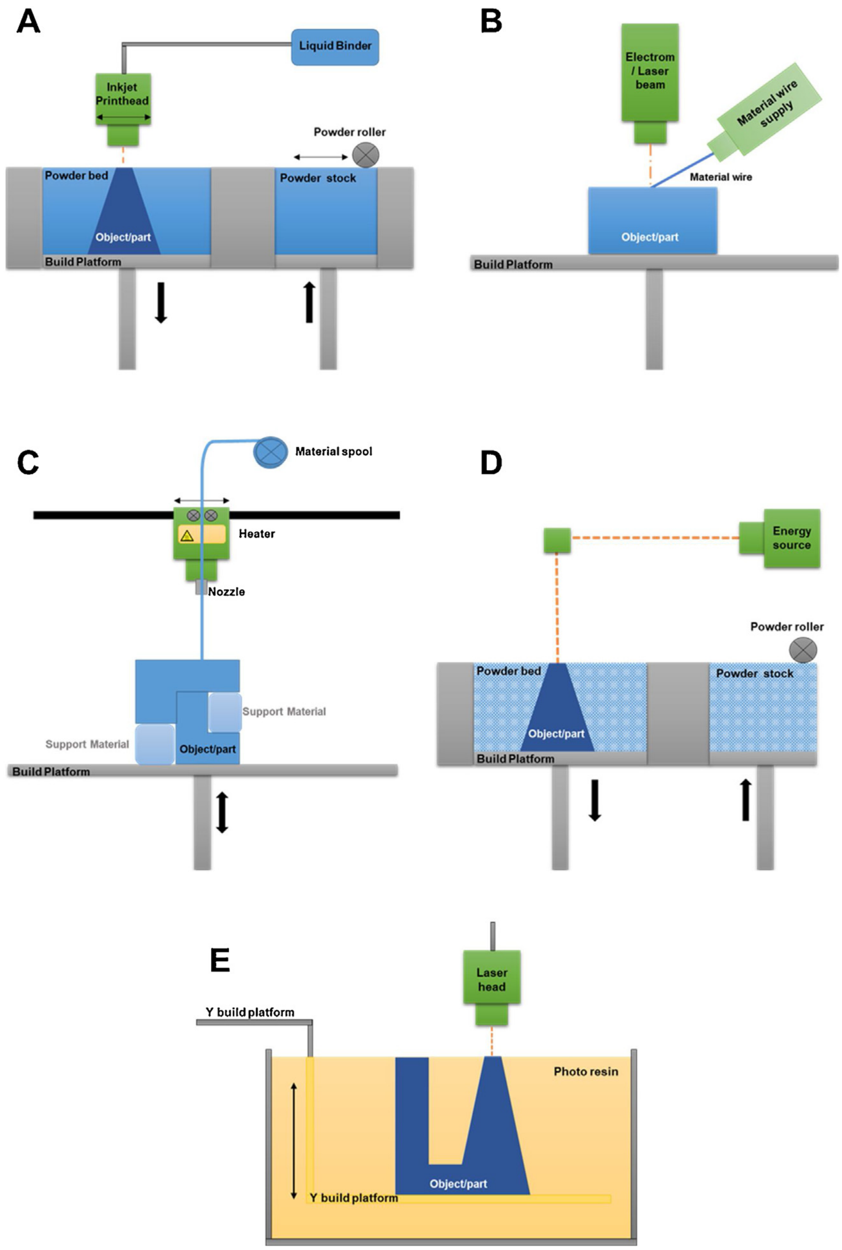

Fig. 4 – Schematic representation of: (A) binder jetting printing process, (B) material extrusion process (C) Vat polymerization process, (D) direct energy deposition printing process and (E) powder bed fusion printing process.

ing may be the use of plasticizing agents [71]. The defects can also be avoided through the introduction of open spaces in the structure. That can be achieved by adding compounds (e.g. solvents) able to evaporate/decompose at lower temperature than the debinding process temperature [71] Fig. 2.

There are several applications for AM in dentistry (Fig. 3). One of the earliest is medical modelling, for surgery guide, where anatomical 'study models' are created [72]. With these models, it is possible to carefully review complex or unusual anatomy and to plan/practice the surgical approach before surgery [73,74]. The models can also be used as supports for the fabrication of restorations, for example, to help in the addition of veneered materials. In digital orthodontics, there are systems available that digitally realign the patient's teeth to make a series of 3D printed models for the manufacture of aligners (e.g. Invisalign®) [75]. 3D printing technology can also be used to produce novel titanium dental implants with a porous or rough surface [76,77] and different types of restorations/components in metallic or polymeric materials (e.g. crowns, inlays, onlays, facets, dentures).

In the next sections, the main AM technologies available, referred in Fig. 1, are described, namely indirect methods, such as binder jetting, material extrusion and jetting and Vat polymerization/stereolitography, and direct methods, which include direct energy deposition and powder bed fusion.

4.2.1. *Binder jetting*

Binder jetting (BJ) uses two materials, a powder-based material and a binder. Usually in the liquid form, the organic binder acts as an adhesive between ceramic powder particles (the building material). A print head deposits alternated layers of the building material and the binding material, moving horizontally along the x and y axes of the machine (Fig. 4A). After each layer, the build platform is lowered and the process repeated over the previous layer.

BJ presents several advantages, such as the ability to use a range of materials (metal, polymer and ceramics) as well as a large number of combinations powder/binder, being generally a fast printing process.

The drawbacks of this technology are mainly related to the high porosity and consequent low mechanical properties of the printed pieces. This is due to factors such as the high friction within the powder particles, their random agglomeration and the absence of an external force to compress the powder and improve packaging [78]. The flowability and spreadability of powders are especially important for BJ. Using powders with large particle sizes can enhance the flowability, however it may jeopardize the sinterability and densification behaviour after printing. Contrarily, very fine particle size may lead to considerable agglomeration and reduced flowability [78]. Since after sintering, the pieces density rarely exceeds 50% of the theoretical value, this technology seems not to be suitable for structural parts. In order to overcome this issue, the printed piece may be infiltered under vacuum with a glass material that penetrates in the pores by capillary effect [79].

4.2.2. *Material extrusion and jetting*

Generally, in the material extrusion process the material is heated and extruded through a nozzle. Then, it is deposited one layer at a time (Fig. 4 B). The nozzle can move horizontally, and the build platform can move vertically to enable the addition of each subsequent layer.

This process, also known as fused deposition modeling (FDM), is the most widespread and inexpensive process within 3D printing technology. However, there are some drawbacks such as not being as fast as other AM processes and presenting an accuracy limited by the nozzle radius, which reduces the final product quality. In order to increase the final quality it is necessary to control factors such as extrusion speed and ensure constant pressure and flow [80].

Another form of AM using material extrusion is material jetting process, where the material is deposited in the form of droplets, instead of filament, to form a 2D pattern [69]. The printed layer is cured using ultraviolet radiation, immediately after the deposition. The process is repeated until the complete 3D part is formed. Fig. 5 shows an example of an occlusal surface of a dental crown produced by this technique from a ceramic suspension of yttria partially stabilized zirconia. It is possible to observe surface waviness associated with layer-by-layer deposition.

Material extrusion techniques also include robocasting. In this process, a filament of a paste (generally, a ceramic slurry called 'ink') is extruded through a nozzle while it moves over a platform, building the object layer-by-layer. The paste exits the nozzle with a given shape, without being necessary waiting for its solidification or drying to build the next layer.

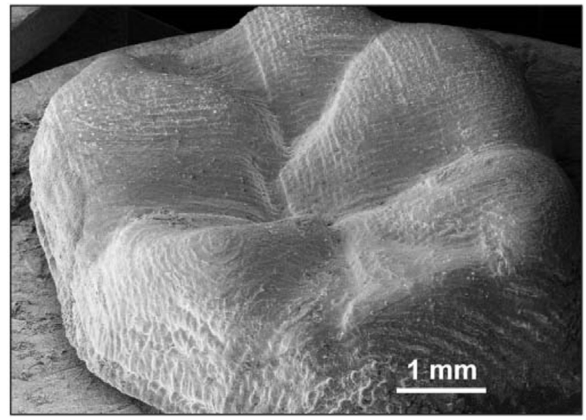

Fig. 5 – SEM image of a molar occlusal surface produced by material jetting process [with permission from Ref. [90]].

Freeze-form Extrusion Fabrication (FEF) is another example of extrusion-based AM technology. Contrarily to most of the other extrusion freeform fabrication methods, in FEF, the organic binder content is only 2–4 vol% and the solids loading of the paste can be higher than 50 vol% [81]. During FEF the piece is built by keeping the surrounding environment of the building platform below the freezing temperature of water. This solidifies the paste after the deposition on each layer during the fabrication process. FEF enables the production of relatively large parts, when compared with traditional robocasting.

In extrusion techniques, the mechanical properties can be improved by controlling the crystallographic texture of the materials. This may be achieved by mixing a small number of large particles of anisotropic shape with fine particles. During extrusion, the anisotropic particles align in the shear direction. In a later sintering step, the aligned particles grow absorbing the fine particles, leading to highly textured and dense ceramics [82].

4.2.3. *Vat polymerization/stereolitography (SLA)*

Vat polymerization/stereolitography (SLA) was created by Chuck Hull in 1986 and was the AM technology pioneer [19]. SLA was the first AM to be applied in medicine, which was used to produce surgical models for alloplastic implant surgery in 1994 [83].

In vat polymerization printing, a specific type of light (e.g. laser or LED light) is used to build parts one layer at a time, in a vat containing light-cured photopolymer resin mixed with ceramic powder (Fig. 4 -C) [84]. The light travels each layer through the surface of the liquid resin. Then, the building platform descends allowing that another layer of resin spreads over the surface, and thus repeating the process.

This technology enables a rapid fabrication and allows to create complex shapes with high level of accuracy and good finish. The curing depth is a critical parameter that determines the accuracy of the formability. Fig. 6 shows a zirconia implant printed trough this method.

When compared to conventional polymer-based SLA, using ceramics can affect the line width and the curing depth. Also, since conventional SLA equipment uses dispersions with vis-

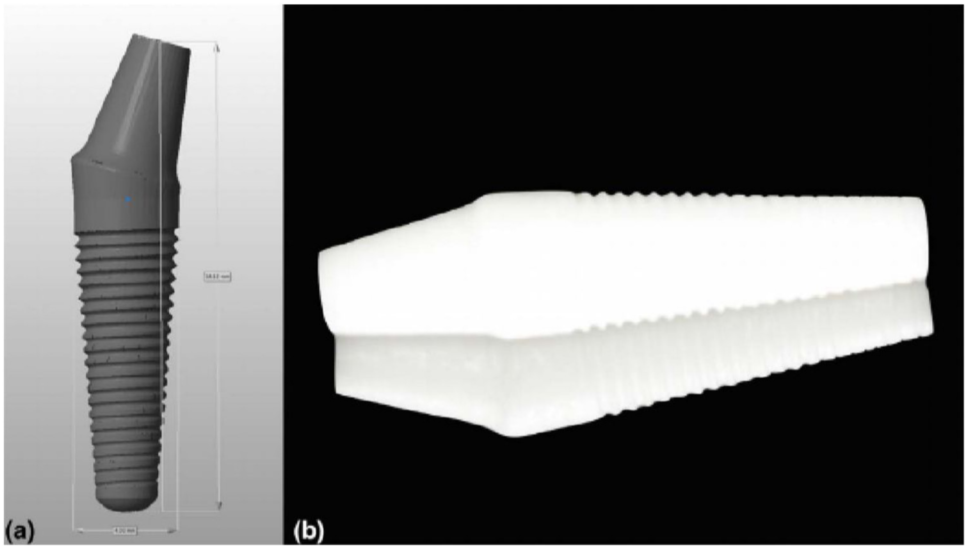

Fig. 6 – One-piece dental implant printed by SLA using digital light processing technique [with permission of Ref. [92]].

cosities lower than 5 Pa.s, the particle size and the solids volume fraction of the ceramics preparations must be adjusted to meet the requirements of both formability and sinterability [78]. To obtain ceramics with a high density, it is essential a fine particle size and a high solids volume fraction [78].

Overall, SLA presents excellent surface finishing, but is still considered to be relatively expensive and present a lengthily post-processing time for unprocessed resin removal and additional curing. For ceramics, a final thermal cycle allows to remove the organic resin and sintering the material, increasing its density.

4.2.4. *Direct energy deposition techniques*

Direct energy deposition (DED) is a more complex additive printing process, commonly used to repair or add additional material to existing components [80]. A typical DED machine consists of a nozzle mounted on a multi axis arm, which deposits melted material onto the specified surface, where it solidifies (Fig. 4 - D). The material is heated and melted using a laser, electron beam or plasma arc [80]. The piece is lowered by a distance equivalent to the layer thickness. These steps are repeated until all layers have been deposited.

Although this process typically uses metal, it can also use polymers and ceramics, either provided in wire or powder form. For ceramic materials, it allows achieving almost 100% density and avoids shrinkage or distortion, eliminating the need of debinding or sintering steps.

Wilkes and Wissenbach [85] were pioneer in studying the applicability of this method to manufacture ceramic components for medical applications.

4.2.5. *Powder bed fusion*

Powder-based printing technologies include selective laser sintering (SLS), direct metal laser sintering (DMLS), selective laser melting (SLM) and electron beam melting (EBM) [86]. All these technologies use heat to fuse the powdered materials. The differences rely on the energy source and powder materials [87]. For instance, SLS, DMLS, and SLM all use lasers, while EBM uses electron beam as energy source [88]

Fig. 7 – Dental bridge of 80 wt% zirconia/20 wt% alumina manufactured by selective laser melting [with permission of Ref. [85]].

In the sintering processes (SLS and DMLS), the powders are not completely melted. This leads to porous internal structures and rough surfaces. In the melting processes (SLM and EBM), the powders are well fused, creating parts with enhanced mechanical properties and higher densities [88].

The process begins with the spreading of a layer of material over the build platform, typically 0.1 mm thick (Fig. 4 - E). The energy source (laser/electron beam) fuses the first layer or first cross section of the model. The build platform is then lowered and a new layer of powder is spread across the previous using a roller. The process is repeated until the entire part/object is finished.

Fig. 7 shows a dental piece made of alumina-zirconia composite obtained by this process.

The manufacturing time for powder bed fusion based techniques is lower than for other AM techniques. In fact, as it happens with direct energy deposition (section 4.2.4), since these techniques do not involve the use of binders for the production of intermediate green pieces, it is not required any debinding process. Furthermore, sintering occurs during printing in a very short time. However, due to the high heating and cooling rates, thermal shock may occur, which may lead to cracking. This may be avoided by pre-heating the powder [89].

5. Additive manufacturing of bioceramics for dental applications

Ceramic materials where only recently considered in AM processing due to their intrinsic properties. The high melting points of ceramics make them difficult to melt under normal heating methods. Although it is possible to melt some ceramics, this process can cause new phase formation. During cooling, thermal shock can occur, giving origin to cracks. On the other hand, several factors associated to the processing of the ceramic materials and to the characteristics of the raw materials used (e.g. temperature and time of sintering, particle size and its distribution, binders nature and content) may affect the porosity (microporosity, mesoporosity, and/or macroporosity) of the final piece. An increase of porosity impairs the mechanical properties of the final product. However, it can be favourable for cellular growth or implant fixation, required for specific applications. Therefore, it is important to establish a coherent balance between the material properties and the biological needs for each application.

This section will report published work where different bioceramics, such as zirconia, alumina, calcium phosphates and ceramic composites, with possible applications in dentistry, are processed using various AM technologies.

5.1. *Additive manufacturing of zirconia*

The information concerning the AM of zirconia-based compositions, with possible applications in dentistry is present in Table 2.

Ebert et al. [90] demonstrated the possibility to build dense three-dimensional components of the size of a crown, with its characteristic occlusal surface topography, through material extrusion technology (direct inkjet printing), using zirconia ceramic suspensions. The printed and sintered samples were not completely free of process-related defects, mainly due to clogged nozzles during printing. However, it was possible to obtain specimens with relative density of 96.9%, with mechanical properties comparable to those of conventionally produced 3Y-TZP via cold isostatic pressing [90].

Moin et al. [91], established that it is feasible to use high-end digital light processing (SLA) technology to fabricate a root analogue implant (RAI) with a certain amount of precision. However, the results showed a printed RAI with a 6.67% larger surface area. In addition, 46.38% of the printed RAI presented a greater distance than 0.1 mm from the original tooth representing a volumetrically larger copy. A large number of factors are recognized to influence the precision of this printing technique, namely the resolution of the digital mirroring device and the composition of the ceramic/ photopolymer mixture. The authors claim that the precise control over spatially grade composition, microstructure design/distribution and shape are potential advantages over milling of unsintered ceramics.

Osman et al. [92] also used a SLA method to efficiently print customized zirconia dental implants with sufficient dimensional accuracy. The study evaluated among other aspects, the dimensional accuracy, surface topography and mechanical properties. The authors report that the dimensional accuracy of the printed implant was high and the achieved mechanical properties showed flexural strength (943 MPa) close to those of conventionally produced ceramics (milled zirconia 800–1000 MPa) [93].

SLA was again used by Xing et al. [94], to produce ZrO_2 complex shaped ceramic components with high dimensional accuracy and proper properties. The surface roughness (Ra) of the unpolished ZrO_2 showed an anisotropic behavior with values ranging from 0.41 μm to 1.07 μm on the measuring direction. This phenomenon could be eliminated through polishing, reducing Ra to a nanometer scale. The sintered ceramics had isotropic mechanical properties (fracture toughness and hardness) close to milled zirconia due to the homogeneity of the grain size.

In the work of Scheithauer et al. [95], the droplet formation behavior of zirconia suspensions for thermoplastic 3D printing (T3DP) was investigated. The precise deposition of small adjacent droplets of molten thermoplastic suspensions containing ceramic particles allowed to obtain filament-like structures by coalescence of adjacent droplets. The researchers introduced the droplet fusion factor (dff) in order to calculate the necessary distance between two droplets to produce those filaments. The results showed that filament-like structures with a smooth surface and a nearly homogeneous cross section could be produced for suspensions with a dff of 44% or higher. In a previous work, the same research group used the same process to print zirconia samples [96]. They were able to produce ceramic parts with high density (99% and higher) and homogeneous microstructures. Nevertheless, the authors pointed out some concerns relatively to this new technology. On one hand the heating rates required for thermal debinding are very low and it must be carried out in a powder bed, increasing the time and complexity of the process. On the other hand, very high abrasion of the equipment components occurs due to the use of highly loaded suspensions.

In another work of the same group [97], the authors combined AM and functionally graded materials (FGM) to create zirconia-based customizable smart materials ("4D components"). By using T3DP technology, it was possible to selectively deposit two different materials beside each other, offering the prospect of combining suspensions with different contents of a pore forming agents to obtained components with dense and porous areas inside. The presence of zones with different porosities reduces the elastic modulus, diminishing the stress shielding, which should be benefic for dental implants. More, the presence of open pores shall favor the osteointegration.

The work of Shao et al. [98], showed the possibility of successfully printing ZrO_2 ceramic parts by a new extrusion-based process, 3D Gel-Printing (3DGP). The authors were able to produce printed and sintered cuboid samples with a regular appearance. Parameters such as surface roughness, relative density, hardness and transverse rupture strength of printed and sintered samples were compared with those obtained in other 3D printing processes (e.g. gel casting and syringe extrusion). It was found that 3DGP led to samples with higher density, hardness and surface finishing than those obtained

Table 2 – Additive manufacturing of zirconia.

Composition	Application	3D Printing technology	Characterization of the slurries and/or printed components	Main findings	Year/Ref
Suspension (27 vol% of zirconia powder, 55% distilled water, boehmite sol, dispersants and 3 mol% yttria partially stabilized zirconia powder)	Dental Prostheses/Crown	Material extrusion/ jetting	- Density - Microstructure - Weibull parameters (characteristic strength and Weibull modulus) fracture toughness	- Homogeneous microstructure, with some submicron-sized pores. - Characteristic strength: 763 MPa, - Weibull modulus: 3.5. - Fracture toughness of 6.7 ± 1.6 MPa.m$^{1/2}$. - Single larger defects detected probably due to clogged nozzles during printing	2009 [90]
Commercial zirconia powder dispersed in a liquid solution of polyacrylate	Root analogue implant (RAI)	Vat Polymerization / SLA	- Dimensional accuracy	- 6.67% larger surface area - 46.38% of the printed RAI has a greater distance than 0.1 mm from the original tooth representing a volumetrically larger copy.	2017 [91]
Slurry composed of commercial yttria-stabilized zirconia dental material (TZ-3YS-E) mixed with photo-curable resin	Dental implant	Vat Polymerization / SLA	- Dimensional accuracy - Density - Biaxial flexural strength - Morphology - Surface roughness - Crystallographic phase	- Dimensional accuracy: high (average deviation: 0.089 and -0.129 mm ($\pm$ 0.068). - Presence of micro-cracks, porosities and interconnected pores. - Surface roughness Ra: 1.59 ± 0.41 μm - Flexural strength: 943 MPa	2017 [92]

Suspension composed of photosensitive acrylic resin containing 55 vol% ZrO_2 particles of ~200 nm	NA	Vat Polymerization / SLA	- Surface roughness - Morphology - Flexural strength - Vickers microhardness - Fracture toughness - Density	- Horizontal/vertical surfaces (XOY and XOZ) exhibited various surface roughness values - Flexural strength: 1154 ± 182 MPa - Vickers microhardness: 13.90±0.62 GPa - Fracture toughness: 6.37±0.25 MPa $m^{1/2}$ - Density: 99.3%	2016 [94]
Suspension composed of commercial zirconia powder TZ3Y-E mixed with paraffin and beeswax (binder)	NA	Material extrusion/ jetting (Thermoplastic 3D Printing)	- Droplet formation - Droplet Fusion	- Filament-like structures with a smooth surface and a nearly homogeneous cross section (droplet fusion factor of 44% or higher).	2018 [95]
Suspension composed of commercial zirconia powder TZ-3Y-SE (powder content 45 vol%), with d_{50} = 0.3 μm mixed with paraffin and beeswax (binder)	NA	Material extrusion/ jetting (Thermoplastic 3D Printing)	- Slurry rheological behavior - Density - Morphology - Porosity	- Pseudoplastic behavior of suspensions. - Samples sintered at 1350°C: - Density:99% - Porosity: 5.6 ± 1.1% - Mean grain size: 0.46 μm - Samples sintered at 1500°C: - Density:99% - Porosity: 0.03 ± 0.02% - Mean grain size: 0.96 μm	2015 [96]

Table 2 (*Continued*)

Composition	Application	3D Printing technology	Characterization of the slurries and/or printed components	Main findings	Year/Ref
Suspension composed of yttria-stabilized zirconia powders TZ-3Y-E, pore forming agent (polysaccharide, CERETAN MA 7008 or UFC100) and binder (paraffin and beeswax)	NA	Material extrusion/ jetting (Thermoplastic 3D Printing)	- Rheological behavior of suspensions - Density - Porosity	- Suspensions: shear thinning behavior - Sintered samples: defect-free - Porosity: 0.11 ± 0.04% - Outer density: 5.90 ± 0.04 g/cm^3 - Inner density: 5.93 ± 0.05 g/cm^3 - Production of a brick wall-like component consisting of dense (<1% porosity) and porous (approx. 5% porosity) zirconia areas to combine different properties in one component.	2017 [97]
Slurry composed of pre-mixture (Acrylamide monomer, N,N′-Methylenebisacrylamide, deionized water, ammonium citrate) and ZrO2 (3YTZP) powder with an average particle size of 0.5 μm	N/A	Material extrusion/ jetting (3D gel-printing)	- Surface and fracture morphology. - Surface roughness - Density - Vickers hardness - Transverse rupture strength	- Surface Roughness: ↓ upon sintering (Ra 8.90 μm to 8.25 μm) - Printed samples showed no defect or deformation upon sintering - Sintered Printed Samples relative density: 97.6% - Vickers hardness: ↓ upon sintering - Transverse rupture strength: ↓ upon sintering	2017 [98]
Commercial Yttria-stabilized zirconia (TZ-3YE) 50 nm particles with a D_{50} agglomerate size of 0.6 mm of high purity (>99.9%) and 2 commercially available UV-resins (XC11122 (DSM) and UV-A 2137 (Sadechaf).	NA	Material extrusion - based	- Rheological behavior and printability	- Viscosity: 28.6 Pa s (nozzle) and 400 Pa s (platform) - No formed agglomerates	2016 [99]

by syringe extrusion, and that presented higher transverse rupture strength than others produced by gel casting. More, no defects or deformation was observed from outside of the printed samples. The authors refer the importance of aspects such as printing conditions (e.g. nozzle diameter), rheological behavior of the slurry as well as the solid loading on the final properties of the printed/sintered samples. Faes et al. [99] combined the advantages of AM extrusion and UV curing (SLA) into a single 3D printing technique, to obtain pieces with an high shape stability and green strength. This novel syringe-based AM process, based on the use of a photopolymerizable dispersion, leads to economic benefits since it reduces the raw material consumption. High shrinkage was observed during sintering, leading to cracking. This must be due to a low load of ceramic particles in the dispersion (30% vol ZrO_2). It is suggested to increase the amount of ceramic particles, keeping the rheological behavior, which can be achieved through the introduction of steric repulsive forces in the dispersion, for example using other resins.

5.2. *Additive manufacturing of alumina*

Table 3 gathers the main findings of published work regarding the AM of alumina-based formulations with possible applications in the dental field.

Work carried out by Scheithauer et al. [96], showed the possibility of printing dense alumina pieces using 3D printing of high-filled suspensions with thermoplastic binder systems. The authors achieved samples with high densities (≥99%), homogeneous microstructures and very good bonding between the printed layers. This study also highlights the importance of the rheological properties of the slurries, i.e. low viscosity allows an easy flow through the needle to form small droplets, which can improve the printing resolution. It is concluded that thermoplastic 3D printing presents several advantages over other suspension-based technologies, namely the fact that the green layer solidifying occur by simple cooling, the versatility of ceramic materials that can be used and the applicability in limited areas. It is recognized the potential of the technique to print multimaterial and multifunctional components, as well as to obtain pieces with material and/or property gradients in different dimensions. However, the authors claim that heating rates for thermal debinding must be very low and that the process must be performed in a powder bed.

Dehurtevent et al. [100], presented a study which provides promising results for manufacturing dense 3D alumina crown frameworks by SLA. The authors established a comparison between the physical and mechanical properties of SLA-manufactured alumina ceramics of different compositions (dry matter content, particle size) and viscosity to those of subtractive-manufactured ceramics. Their results showed an acceptability window for viscosity of the slurries that allows producing SLA manufactured alumina pieces (137.7 ± 12.68 mPa s to 218.9 ± 12.78 mPa s). Additionally, the authors were able to achieve a composition that originated a reliablematerial with the anisotropic shrinkage, high density, flexural strength, and Weibull characteristics suitable for SLA manufacturing (high particle size $d_{50} = 1.58 \pm 0.03$ μm and dry matter content of 80% in weight). Nevertheless, it was observed that although an oversize of 35% allow manufacturing complex morphologies, differential shrinkage led to deformation of the final structure. In the work of Maleksaeedi et al. [78], a powder-bed inkjet 3D-printing and vacuum infiltration process was used for producing alumina parts with high density and improved mechanical properties. The authors utilized vacuum infiltration process to enhance the packing of the green parts after printing, by impregnating the 3D-printed parts with highly solid loaded slurries. Their results showed that the vacuum infiltration process was able to significantly increase the density, reduce the porosity and increase the strength of the 3D-printed alumina components. Moreover, the bending strength was improved up to 15 times of the original strength.

5.3. *Additive manufacturing of other ceramics*

The potential of AM has been explored in several dental applications with other ceramic materials. Table 4 summarizes information regarding various calcium phosphates compositions and other bioceramics, as well as gypsum, mainly for bone regeneration.

Lopez et al. [101], produced bioactive tricalcium phosphate (TCP) scaffolds using a material extrusion technology, robocasting. The printed scaffolds were able to restore critical mandibular segmental defects to levels similar to native bone after a 8 week period implant in an adult rabbit mandibular defect model. Histological and scanning electron microscopy (SEM) analysis showed directional bony ingrowth into the scaffold interstices, tracking healing pathway origins to defect walls and marrow spaces. More, it was observed new bone growth and scaffold resorption at bone/scaffold interfaces.

Another work using robocasting technology is the one carried out by Slots et al [102], in which porous TCP implants were developed using storable and reusable inks composed of fatty acid/TCP. The total fabrication time including ink preparation, printing and sintering was less than 5 h for 8 cm^2 of implant. The printed implants were able to retain their shape after sintering and were chemically unchanged by the printing and sintering process. Mesenchymal stem cells were able to grow on the implants, secrete collagen and alkaline phosphate and mineralize the implant. Additionally, they possessed clinically relevant mechanical strength and presented osteoconductive properties. The process demonstrated to be sufficiently simple and effective to enable rapid, on-demand, in-hospital production of patient-specific ceramic implants for treatment of bone trauma.

In the study conducted by Fahimipour et al. [52], a biomimetic porous TCP/alginate/gelatin scaffold containing PLGA (poly (lactic-co-glycolic acid)) microspheres for slow release of VEGF (vascular endothelial growth factor) was processed through extrusion technology. The printable ink was selected according to the gel point of different formulations of TCP/alginate/gelatin. The process faced some difficulties, for example in what concerns the needle blocking during extrusion if the gel point is above room temperature. Nevertheless, it was possible to achieve satisfactory mechanical and biological features supporting cell viability necessary for bone tissue regeneration.Tamimi et al. [103], prepared customized 3D-printed monetite onlays by binder jetting. The

Table 3 – Additive manufacturing of alumina.

Composition	Application	3D Printing technology	Characterization of the slurry and/or printed components	Main findings	Year/Ref
Suspension composed of 67 vol% alumina with d_{50} = 1–1.7 μm and a purity of 99.8 wt% mixed with paraffin and beeswax (binder).	NA	Material extrusion/ jetting (Thermoplastic 3D Printing)	- Slurry rheological behavior - Density - Morphology - Porosity	- Pseudoplastic behavior of suspensions. - Density:97.3% - Porosity: 0.8 ± 0.4% - Mean grain size: 6.5 μm	2015 [96]
Slurries prepared using small (S) and large (L) particle size alumina (Al_2O_3) powders d_{50} = 0.56 and 1.58 μm respectively	Crown frameworks	Vat Polimerization (Stereoliyhography)	- Particle size - Density - Viscosity - Flexural strength - Weibull modulus - Weibull characteristic strength - Shrinkage after the heat treatment	- Flexural strength:271.7-273.8 MPa - Weibull modulus: 5 to 15 - Overall shrinkage was higher for SLA-manufactured ceramics	2017 [100]
Slurries containing high purity alumina powder d_{50} = 0.32 μm. Poly vinyl alcohol (PVA, Mw: 17,000 g/mol) was used as a binder.	NA	Binder Jetting	- Morphology - Density (green and sintered) - Pore size distribution - Mechanical properties - Surface roughness	- Density: ↑ using vaccum infiltration process - Porosity: ↓ using vaccum infiltration process - Strength:↑ using vaccum infiltration process.	2014 [78]

onlays were design to facilitate the diffusion of cells and nutrients from high bone metabolic to low bone metabolic areas. The research showed that bone metabolic activity in onlays is anatomy-dependant and correlates with the ability of bone augmentation. The authors were able to achieve osseointegration of dental implants in bone augmented with the printed monetite onlays. Klammert et al. [104] also used binder jetting technology to produce several specific craniofacial implants of TCP. The printed parts were able to comply with geometric requirements and provide an adequate accuracy of fit, even though the authors did not use a commercial CAD solution. Fieldint and colleagues [105] face several challenges to adapt and optimize the processing parameters to produce scaffolds using a 3D binder jetting printer and commercially available binders. The authors report that the addition of dopants (SiO_2 and ZnO) to the ceramic powder decreased the β to α phase transformation of TCP sintered at 1250 °C. Additionally, the density increased leading to a 250% increase in compressive strength, when compared to pure TCP scaffolds.

Shao *et al.* [106] prepared by extrusion, four groups of bioceramic scaffolds for treatment of bone defects: (1) ~10% Mg-substituted wollastonite-based ($Ca_{90\%}Mg_{10\%}SiO_3$; CSi-Mg10); (2) β TCP-based (TCP); (3) wollastonite-based ($CaSiO_3$; CSi); and (4) bredigite-based (Bred). The study shows that robocasted CSi-Mg10 scaffolds presented higher osteogenic capability than those of the TCP, CSi, and Bred. Additionally, CSi-Mg10 printed parts revealed the largest pore dimension but the lowest porosity, mainly due to the considerable shrinkage of the scaffolds during sintering.

Asadi-Eydivand et al. [107], prepared gypsum-based scaffolds also for the treatment of bone defects. They investigated the effect of thermic treatment (between 300 °C and 1300 °C) on the structural, mechanical, and physical properties of samples produced by extrusion/jetting. For the lowest temperature, the samples showed adequate mechanical properties, but high cytotoxicity. In contrast, temperatures in the range of 500 °C–1000 °C led to lower cytotoxic scaffolds but insufficient mechanical strength. For temperatures higher than 1000 °C, higher compressive strength and greater viability were observed. However, above 1200 °C, decomposition of calcium sulfate occurs, leading to mass loss.

5.4. *Additive manufacturing of ceramic composites*

Table 5 gathers the information about AM of ceramic-based composites possible applications in dentistry.

In the work carried out by Goyos-Ball et al [108], porous robocasted structures made of 10 mol% ceria-stabilized zirconia and alumina composite were produced. The authors found that round lattice structures have compression strength similar to cortical bone, are not cytotoxic and induce osseous differentiation. More, the printed parts showed good aesthetics, chemical stability and negligible corrosion and wear. Due to the high structural integrity, the printed parts could be used as scaffolds for load bearing applications during the osteointegration process.

Rahim et al. [109] established a comparison between composites prepared by extrusion and by injection moulding. The samples were composed of polyamide 12, incorporated with bioceramic fillers (i.e. zirconia and hydroxyapatite), from 10 to 40% content. The results of their work showed that the addition of fillers improved or maintained the strength and stiffness of the parts, while reducing toughness and flexibility. Melting behaviour of polyamide 12 did not depend on the processing techniques, but was affected by the addition of fillers and by the cooling rate. Incorporation of fillers improved the thermal stability. It was found that fuse deposition modelling

Table 4 – Additive manufacturing of other ceramic-based dental materials.

Composition	Application	3D Printing Technology	Characterization of the slurry and/or printed components	Main findings	Year/Ref
β-tricalcium phosphate (TCP) colloidal gel composed of ammonium polyacrylate deionized water, hydroxypropyl methylcellulose and polyethylenimine.	Craniofacial tissue engineering	Material extrusion/jetting (Robocasting)	- Histology - Osseointegration	- Directional bony ingrowth into the scaffold interstices, tracking healing pathway origins to defect walls and marrow spaces. - New bone growth and scaffold resorption at bone/scaffold interfaces was observed.	2018 [101]
Tricalcium phosphate (TCP) combined at various ratios with lubricants such as decane, oleic acid, oleyl alcohol, oleyl ester, glycerol, triglycerides (sunflower oil) and heated paraffin.	Craniofacial implant	Material extrusion/jetting (Robocasting)	- Microstructure - Compressive strength - Chemical purity, - Mechanical testing - Osteoconductivity	- Compressive stress: 6.4–11.6 MPa - Young's modulus: 104–247 MPa - Osteoconductive properties	2017 [102]
Tricalcium phosphate (TCP) combined with gelatin/alginate (additives).	Craniofacial tissue engineering	Material extrusion/jetting	- Viscosity/printability - Morphology - Pore size and porosity - Compressive strength - Young's modulus - Cell proliferation	- Porosity: 73.42 ± 8.4%, - Young's modulus: 98.31 ± 10.21 MPa.	2017 [52]
Dicalcium phosphate anhydrous ($CaHPO_4$, monetite) and calcium carbonate ($CaCO_3$, calcite) heated at 1400 °C for 7 h to synthesize α/β-tricalcium phosphate (α/β-TCP).	Onlay	Binder jetting	- Osseointegration - Histology - Crystallographic composition	- Osseointegration of dental implants in bone augmented with synthetic monetite onlays. - Higher bone formation found in onlays with increased porosity facing the calvarial surface.	2014 [103]
Tricalcium phosphate powder (TCP, mixture of 45% α-TCP and 55% ß-TCP)	Craniofacial implant	Binder jetting	- Dimensional precision - Density - Porosity - Thermal conductivity at 37 °C - Bending strength	- Dimensional precision: satisfatory - Porosity: 28–35% - Thermal conductivity at 37 °C : 0.294–0.393 W/m K - Bending strength : 3.9–5.2 MPa	2010 [104]
β-tricalcium phosphate with an average particle size of 550 nm with dopants (SiO_2 and ZnO)	Scaffold/Tissue engineering	Binder jetting	- Microstructure - Phase analysis - Denisty - Mechanical properties - *In vitro* cell–material interactions	- Porosity: 32–51% - Denisty:89–95% - Compressive strength: 2–10 MPa - Addition of SiO_2 and ZnO dopants: ↑ mechanical strength ↑cellular proliferation	2012 [105]
- 10% Mg-substituted wollastonite (Ca90%Mg10%SiO3 ; CSi-Mg10) - β-tricalcium phosphate (TCP) - Wollastonite (CaSiO3; CSi) Bredigite (Bred)	Scaffold/tissue engineering	Material extrusion/Jetting (Robocasting)	- Physicochemical characterization - In vitro degradation - Mechanical properties	- CSi-Mg10 scaffolds: • Largest pore dimension but the lowest porosity. • Mild *in vitro* biodissolution. • Moderate weight loss of ∼7%. - Flexural strength: 31 MPa Higher osteogenic capability	2017 [106]

Table 4 (*Continued*)

Composition	Application	3D Printing Technology	Characterization of the slurry and/or printed components	Main findings	Year/Ref
Gypsum paste ($CaSO_4 \cdot 1/2H_2O+1$ $1/2H_2O = CaSO_4 \cdot 2H_2O$) $d_{90} = 68.83\,\mu m$	Scaffold/Tissue engineering	Binder jetting	- Chemical structure - Microstructure - Mechanical testing - Shrinkage - Density - Cytotoxicity	- Mechanical properties: inadequate - Cytotoxicity: Moderate to Severe.	2016 [107]

Table 5 – Additive manufacturing of ceramic-based composites.

Composition	Application	3D Printing Technology	Characterization of the slurry and/or printed components	Main findings	Year/Ref
Ink composed of 10 mol% ceria-stabilized zirconia and alumina powder composite (10CeTZP-Al_2O_3 (35 vol%)) mixed with aqueous solution of Pluronic® F-127 .	Scaffold/Tissue engineering	Material extrusion/Jetting (Robocasting)	- Ink rheology - Density - Mechanical testing - Microstructure - Biological characterization	- Density: 92-97% - Compression strength: similar to cortical bone. - Flexural strength: 575 MPa (maximal) - Non toxic	2017 [108]
Polyamide 12 powder (PA2200) with zirconia (230693) and/or hydroxyapatite (10–40%)	Implant materials	Material Extrusion/Jetting (Fused Deposition Modeling)	- Mechanical properties - Chemical composition - Morphology - Termal properties	- Tensile strength: 27-36 MPa - Young Modulus: 900-1050 MPa - Flexural strength: 43-54 MPa	2017 [109]
Mixtures containing 41.5 wt.% zirconia and 58.5 wt.% alumina	Dental restorations, /prototypes	Powder bed fusion (Selective laser melting)	- Density - Microstructure - Flexural strength - Biological characterization	- Density≈100% - Porosity: low - Flexural strength: 173.8 to 538.1 MPa. - Biological characterization	2013 [85]

allows producing medical implants with acceptable mechanical performances for non-load bearing applications.

Jan et al. manufactured ceramic objects by powder bed fusion, using selective laser melting technology [85]. The authors were able to produce parts with good mechanical properties, with approximately 100% density, without needing sintering processes or post-processing, which constitutes an advantage. The study reports some process challenges that need to be overcome, for instance, the thermally induced stresses, caused by the deposition of the new cold powder layers on top of the preheated ceramic, and the surface roughness values.

6. Challenges

Additive manufacturing is recognized as a promising technology with advantages not only in the production of customized healthcare products to improve population health and quality of life, but also by its possibility of decreasing environmental impact, enhancing the manufacturing sustainability.

However, the inherent challenges of 3D printing should not be overlooked. Aspects such as surface quality, dimensional accuracy and the mechanical properties need improvement to allow producing effective high-quality products.

Concerning surface quality, it depends on the AM used technique, processing conditions and raw material characteristics, which affect the thickness of each printed layer [110–112]. Powder bed AM leads to lower surface quality than the other AM techniques, due to the presence of large and partially melted powder particles in the printed pieces' surfaces. Relatively to the thickness of the printed layers, extrusion techniques typically lead to high layer thicknesses (≈ 0.2 mm) due to the large diameter of the deposition nozzle. Powder bed fusion and vat polymerization origin lower layer thicknesses (≈ 0.1 mm) due to the ability to precisely focus the energy beam radius. Material jetting techniques are the ones that produce the finest layer thickness (≈ 0.02 mm) due to the small jetted droplets.

Dimensional accuracy is critical in the production of dental pieces, because these must fit tightly the needs of each patient. A variety of issues affects dimensional accuracy. The work of Lee *at al.* summarizes the dimensional accuracy in different manufacturing processes [113]. According to the authors, it is generally accepted that the accuracy in the Z-direction is worse and harder to improve than in the other directions (X and Y) because it is influenced by a variety of process parameters which are difficult to control, e.g. spreading compaction/densification of the powder within the layers, evaporation of material by laser/heat and shrinkage during solidification.

Mechanical properties are influenced by the presence of defects: surface quality and porosity are critical factors. Different solutions have been proposed to reduce porosity [3]. For example, choosing ceramic powders with an adequate granulometric distribution, adding dopants or a viscous liquid-forming phase, infiltrating the sintered body with vitreous materials and applying cold/hot isostatic pressure to the green body [68,78].

Shrinkage is also a concern in AM processes since it affects significantly the pieces dimensions and may lead to cracking. The printing strategy needs to be optimized to prevent the impact of this phenomenon. Possible solutions to minimize this issue are:

- Increasing the amount of ceramic particles in the pastes, while keeping the rheological behavior unchanged, which may be achieved adding steric dispersants [99]
- Adding to the mixture particles that can expand due to phase transformation or reaction during sintering [114,115]
- Decreasing the sintering temperature, without compromising density [116,117]
- Considering it in the CAD design of the parts [112].

In most of the mentioned studies along this work, the ceramic materials are composed of mixtures of a sacrificial polymeric binder with ceramic particles for the production of the green product. This means that additional post-processing steps, such as sintering, are required to remove the binder and achieve a fully dense ceramic component. This is true for the majority of the AM technologies with few exceptions such as direct selective laser sintering and selective laser melting techniques, where the ceramic particles are directly sintered or melted, respectively.

Dental ceramic pieces made by direct ink deposition (material extrusion and/or jetting technologies) still present low mechanical properties, compared to other conventional means to produce molded parts. Limitations of this layering technique include poor bonding adhesion between layers and the occurrence of porosity. The formulation of the slurries or inks is a crucial step. The protocols should be as simple as possible, leading to slurries/inks with appropriate composition, flow consistency and behavior and specific viscoelastic properties. They should contain a high solid volume fraction not only to minimize shrinkage during drying and therefore resist the involved stresses, but also to increase the density of the final product.

Another important challenge is bacteriological safety of the final products intended to be in close contact with tissues/organs. These structures must be able to endure strict sterilization protocols without losing their intrinsic properties.

7. Final considerations

Ceramic materials play an important role as dental materials. Their high chemical and mechanical resistance, as well as their aesthetic properties, make them an excellent option to replace damaged dental tissues.

Conventional manufacturing methods to produce ceramic dental pieces are generally based on subtractive techniques. These lead to significant material and tool waste and present limitations in the production of parts with complex geometry.

The rising demand for custom-tailored and patient specific dental products renders dentistry to be one of the rapidly expanding segments of additive manufacturing (AM) technologies. These technologies have been successfully used in many production sectors and present many advantages for processing dental structures, compared with subtracting technologies. These include less production steps with consequent impact in the total manufacturing time, lower consumables and raw materials consumption, and adequacy to produce very small and complex dental parts. It thus opens possibility to mass production of customized dental products, with evident benefit to the patients and/or healthcare systems. However, there are still concerns about application of AM to ceramics due to their intrinsically poor mechanical properties, the accuracy of the obtained pieces, their density and surface finishing.

This comprehensive review shows that, dental bioceramics can be processed through AM by different techniques, e.g. material extrusion/jetting, vat polymerization, binder jetting, and powder bed fusion. The first technology is the most widely used. The studies confirmed that almost any shape could be produced, with different degrees of complexity. Additionally, it is possible to tailor production protocols in order to achieve structures with different characteristics and properties, e.g. specific mechanical properties, different degrees of porosity and/or density, biodegradability, osteointegration and cytotoxicity. Despite the great potential for dental industry, the application of AM to ceramic dental materials is still under study.

In resume, further developments of AM technology are expected to give a significant contribution to bring production costs down, improve manufactured materials properties and render the production processes more efficient and competitive. It is important to stress that no single technology alone is able to fulfil all the required specificities and necessities. An interesting approach, when printing 3D complex dental ceramic structures, could be to combine the best attributes of AM technologies with conventional surface finishing methods.

Acknowledgements

To Fundação para a Ciência e a Tecnologia for funding through the research project 3D-DentalPrint 02/SAICT/2016/023940 and the unit projects UID/QUI/00100/2013, UID/CTM/04540/2013 and UID/BIM/04585/2016 of CQE, CeFEMA and CiiEM, respectively.

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