Recent advances in the extrusion methods for ceramics

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Abstract: In recent years, extrusion 3D printing processes have undergone an important development. They allow obtaining complex shapes in an easy way and relatively low cost. Different plastic materials can be 3D printed with the fused filament fabrication (FFF) technology. Bioinert ceramics such as alumina or zirconia have excellent physical and mechanical properties (high melting point, high strength...) that make them appropriate in different fields: medicine, electronics, etc. However, 3D printing of ceramics is by far less developed than 3D printing of plastics or metals. A possible application for 3D printing of ceramics is the manufacture of prostheses, which usually have complex shapes with porous structures. Ceramic prostheses have several advantages over the use of other materials: they generate low debris, they are hard and they are inert and corrosion-resistant. In the present work the recent advances about extrusion 3D printing of ceramic materials are presented, with a special focus on the manufacture of prostheses.

Keywords: 3D printing, Technical ceramics, Direct ink writing, Fused deposition modelling, Ceramic filled polymers.

1. Introduction

In recent years, 3D printing processes have undergone an important development. They allow obtaining complex shapes, for example with porous structures, in an easy way and with relatively low cost. Different plastic materials can be printed with the FFF technology. Metals such as titanium alloys are also printed with success for the manufacture of prostheses [1]. However, 3D printing of ceramics is by far less developed than 3D printing of plastics or metals. Additionally, the 3D printing ceramic pastes is difficult. Ceramics are versatile materials thanks to their excellent properties including high mechanical strength and hardness, good thermal and chemical stability, and viable thermal, optical, electrical, and magnetic performance as well as great biocompatibility. However, the machining (injection moulding, die pressing, tape casting, gel casting, etc.) of ceramics is difficult because the material is fragile and the thermal stresses due to the cutting operation may lead to breakage of the pieces. That is why, Additive Manufacturing (AM) technologies appear as a possible solution to deal with the manufacture of ceramics. However, AM processes applied to ceramics are still under development. A possible
application for 3D printing of ceramics is the manufacture of prostheses, which usually have complex shapes and porous structures. Ceramic prostheses have several advantages in front of the use of other materials: they generate low debris, they are hard and they are inert and oxidation-resistant [2].

ISO/ASTM 52900 standard [3] divides the additive manufacturing (AM) processes into seven different categories: 1-VAT polymerisation, 2-material jetting, 3-binder jetting, 4-material extrusion, 5-powder bed fusion (PBF), 6-sheet lamination and 7-direct energy deposition (DED). Specifically, different printing techniques have been applied for manufacturing ceramic parts, which are summarized in table 1 with some examples.

Table 1. Summary of the 3D printed ceramic examples.

| Group | Name of the group | Name of the technology | Material | Reference |
|-------|-------------------|------------------------|----------|-----------|
| 1     | VAT polymerisation| Ceramic stereolithography (CerSLA) | Alumina | [4]       |
| 1     | VAT polymerisation| Lithography-based ceramic manufacturing | Alumina | [5, 6]    |
| 1     | VAT polymerisation| Two-photon polymerisation (TPP) | Alumina toughened zirconia (ATZ) | [7]       |
| 2     | Material jetting  | Inkjet printing (IJP) | Zirconia/alumina, lead zirconate titanate (PZT), Si₃N₄, 3Y-TZP | [8, 9, 10, 11, 12] |
| 3     | Binder jetting    | Binder jetting (BJ) | Alumina | [13, 14]  |
| 4     | Material extrusion| Free-form extrusion (FFE) | Alumina | [15]      |
| 4     | Material extrusion| Fused deposition of ceramics (FDC) | Silicon nitride, fused silica, PZT | [16]      |
| 4     | Material extrusion| Direct ink writing (DIW) Selective laser sintering (SLS) | Zirconia | [17]      |
| 5     | Powder bed fusion| Selective laser melting (SLM) Laminated object manufacturing (LOM) | TiC/AlSi10Mg | [20, 21] |
| 6     | Sheet lamination  | Direct laser deposition (DLD) | Alumina / zirconia | [22]      |

Among AM technologies, extrusion processes stand out due to different advantages, such as the possibility to obtain complex shapes including porous structures, the easiness of use, the option to employ low-cost machines, the wide range of possible materials, etc. Some drawbacks of the technology are the poor dimensional accuracy and surface finish of the parts [24]. Two main extrusion technologies are used for ceramics, namely direct ink writing (DIW) [17] and fused deposition of ceramics (FDC) [18], which is similar to FFF but with ceramic filled filaments.

On the other hand, the 3D printed parts are classified into different categories depending on their structures, according to Lewis et al. [25] and Feilden [26]: (1) filling; (2) spanning; (3) overhanging; (4) floating; and (5) closed cavity. Among the 3D printing techniques that have been summarized in table 1, some have better capability for achieving better results in some of the features mentioned. Table 2
compares the abilities of each 3D printing technique: (1) ‘easy’ to manufacture the ceramic part (green); (2) ‘difficult’ in the 3D printing of this type of ceramic shape (yellow); and (3) ‘impossible’ to obtain that shape (red).

Table 2. Achievement of different features by the different AM groups of technologies (adapted from [26]).

| Features         | Group              |
|------------------|--------------------|
|                  | Filling | Spanning | Overhanging | Floating | Closed Cavity |
| VAT polymerisation|         |          |             |          |              |
| Material Jetting  |         |          |             |          |              |
| Binder Jetting    |         |          |             |          |              |
| Material Extrusion|         |          |             |          |              |
| Powder Bed Fusion |         |          |             |          |              |
| Sheet Lamination  |         |          |             |          |              |
| Direct Energy     |         |          |             |          |              |
| Deposition        |         |          |             |          |              |

According to table 2, the extrusion processes are able to print closed cavities, while spanning and overhanging are restricted.

The main aim of the present work is to summarize the existing AM extrusion technologies for ceramics, including their main advantages and drawbacks, as well as the possibilities to apply them to the medical sector, for example to manufacture prostheses. The research methodology consisted of summarizing the most recent innovations about ceramic extrusion printing processes, mainly focusing on direct ink writing (DIW) and fused deposition of ceramics (FDC). Future trends are also considered.

2. Direct ink writing

Direct Ink Writing (DIW), also known as Robocasting (RC) is nowadays one of the most employed printing technologies for ceramics nowadays (figure 1).

![Figure 1. Direct ink writing (DIW) of yttria-stabilized zirconia (YSZ) parts.](image)

It consists of extruding an ink through a nozzle by means of pressure, which can be provided by either a plunger, a screw or a pump [27]. The material does not have to be heated during printing. For this reason, it is suitable for biomedical applications [28]. Many different ceramic materials can be printed with this technology, for example zirconia in porous structures [17], alumina in tailored architectures [29], alumina-based ceramic cores modified with nanosized MgO [30] or porous SiOC ceramic scaffolds [31]. Shao et al. used 3D gelation to print yttria-stabilized zirconia (YSZ) with a 2-
hydroxyethyl methacrylate (HEMA) gelation system [32]. Yu et al. employed ammonium polymethacrylate as dispersant to print YSZ ceramic [33]. Other ceramics such as calcium phosphates were printed, with release of antibacterial functions for bone repair [34]. Printed kaolinite clay is used in buildings [35]. In graphene-based ceramic nanocomposites graphene is known to increase the flexural strength and fracture toughness of ceramic materials [36, 37]. Main disadvantages of DIW are that the extrusion of liquid materials is complicated [38] and that the surface finish in lateral walls is poor and it requires subsequent finishing operations [17]. An example of a surface topography obtained in the lateral walls of DIW printed zirconia parts is presented in figure 2. The topography corresponds to parallel printed layers, with smooth crests and sharp valleys.

![Figure 2. Example of a surface topography of zirconia printed by means of the DIW process.](image)

Some medical applications of the DIW process include the manufacture of dental prostheses, with potential application in tissue engineering, drug delivery, bone regeneration and implant medicine [39]. For example, Ebert et al. [40] obtained 3% mol yttria stabilized tetragonal zirconia polycristal (3Y-TZP) specimens with 96.9 % of the theoretical density, with mechanical properties that are similar to those obtained by means of cold isostatic pressing of the same material.

![Figure 3. Schematic of the fused deposition of ceramic (FDC) process.](image)

3. **Fused deposition of ceramics**

Ceramic parts can be obtained from fused deposition of ceramics (FDC), using a ceramic filled plastic filament, which is heated, melted and deposited on a printing bed (figure3). It is an analogous process
to fused filament fabrication (FFF) for plastics.

Different ceramic materials have been printed with the FFF technique, such as fused silica in order to manufacture tooling for investment casting [16], silicon nitride, which is used as a high-temperature resistant component for combustion engines [41], or lead zirconate titanate ceramic (PZT) for the fabrication of piezoelectric transducers [42]. Nowadays, hydroxyapatite (HA) filled polyvinyl alcohol (PVA) filaments can be employed to manufacture tissue scaffolds [43]. Main advantages of this technique are its easiness of use and the possibility to manufacture complex shapes, while some disadvantages are the poor surface finish in lateral walls, the limited dimensional accuracy and the possibility to obtain internal defects that will affect the mechanical strength of the parts [41].

4. Other extrusion technologies
An avant-garde 3D printing technique that has been specially used in tissue engineering is FRESH (Freeform Reversible Embedding of Suspended Hydrogels), first mentioned in 2011 [44]. It is an embedded 3D printing technique that uses a thermoreversible support bath, the reservoir, which enables the deposition of materials to manufacture complex structures, for example to mimic soft tissues. Additionally, it can face the problems of gravity and no supports are required. Different supporting gels have been developed and studied such as carbopol [45], Pluronic® F-127 [46, 47] and gelatin [48, 49].

Although this technology has been used mainly for silicone, Wang et al. [50] developed the Freeze-FRESH (FF) technique, which combines FRESH 3D printing and freeze-casting to produce 3D printed scaffolds with microscale pores. It can be used either with ceramics or polymer for medical applications.

5. Future trends
Future trends of the extrusion processes include the manufacture of multi-material machines, in which different FFF and DIW heads are used to obtain complex shapes such as surgical planning prototypes [51]. Such printed parts can combine, for example, the use of polylactic acid (PLA) from a filament and the use of silicones from a syringe. Within the use of multi-material 3D printer, a dual paste extruder could be developed in which two different ceramics can be deposited at the same time. This would lead to composite ceramics, for example made of alumina with zirconia. However, the success of a multi-material printer will depend highly on the interface between the different materials [52].

Another future prospect is the personalized medicine, in which medical devices are manufactured individually. For example, until nowadays, the hip and knee prostheses are produced in standard sizes, like a shoe. While it is true that most of them fit perfectly into the human body, both in height and width, it would be better to manufacture the devices in a customized size. For that, the use of medical imaging technologies such as CT (Computer Tomography) and MRI (Magnetic Resonance Imaging) might help, as a way to scan body parts and obtain a CAD part by means of image acquisition.

6. Conclusions
In the present paper, different AM extrusion technologies for ceramics are presented. Direct ink writing (DIW) is widely used to print different ceramic inks having components such as alumina, zirconia, calcium phosphates, etc. Fused deposition of ceramics (FDC) allows melting plastic filaments that are filled with ceramic powder. Some materials that have been printed with this technique are fused silica, silicon nitride or lead zirconium titanate (PZT) among others. Other extrusion processes include the combination of freeze-forming with freeform reversible embedding to produce 3D printed scaffolds with microscale pores. Future trends in extrusion 3D printing processes point towards the use of multi-material 3D printing machines having both DIW and FDC heads.

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