UNIVERSITAT DE BARCELONA

Development and optimization of a Low Temperature Co-fired Ceramic suspension for Mask-Image-Projection-based Stereolithography

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INTRODUCTION

CHAPTER I

Nowadays, the AM is one of the most promising area of research in terms of manufacturing of three-dimensional objects.

The main objective of this chapter is to introduce the reader to the basic concepts of additive manufacturing (AM) and the state-of-art of ceramic materials.

1.1. Additive manufacturing

From a historical point of view, the first signs of Additive Manufacturing (AM) go back nearly 150 years, with photo-sculpture, topography, and lithography. However, the first development about modern AM techniques was proposed by Wyn K. Swainson in 1971. Swainson patented a mechanism where 3D objects could be fabricated using photopolymers. The polymerization process is based on the intersection of two beams of light which control the curing state of the photopolymer at any point. [1]

During the same year, Pierre A. L. Ciraud proposed a process similar to Selective Laser Melting (SLM). In the presented method the powder is deposited in a specific configuration and then thermal energy is applied to melt the powder. Following the idea of the photopolymerization process, in 1986, Charles W. Hull, the co-founder of 3D Systems, patented the first Stereolithography (SLA) machine. Nowadays, the most popular and well-known process of AM is Fused Deposition Modeling (FDM) due to its simplicity and user-friendly and low-cost machine. [2]

The American Society of the International Association for Testing and Materials (ASTM) founded a committee (F42) in 2009 where the main goal was the standardization of Additive Manufacturing Technologies (AMT). In this sense, AM is formally defined as "a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies" (ISO/ASTM 17296). Subtractive manufacturing is a process where the final parts are machining, stamped, or molded, starting form a larger piece of materials. Many other terminologies are also used for AM such as additive fabrication, freeform fabrication, additive processes, layer manufacturing, direct digital manufacturing, and is most commonly known as 3D printing. The terminology of rapid prototyping is not a synonym for AM, in the sense that it refers to the fabrication of a part that is not used for a final application, but as a prototype. Thus, the AM technologies can be used for rapid prototyping.

The AMT are based on the same basic principles, firstly the three-dimensional (3D) *Computer-Aided Design* (CAD) model in a STL -file format is sliced into a two-dimensional (2D) image, and then, each slice is used to build the 3D object layer upon layer, Figure 1.1

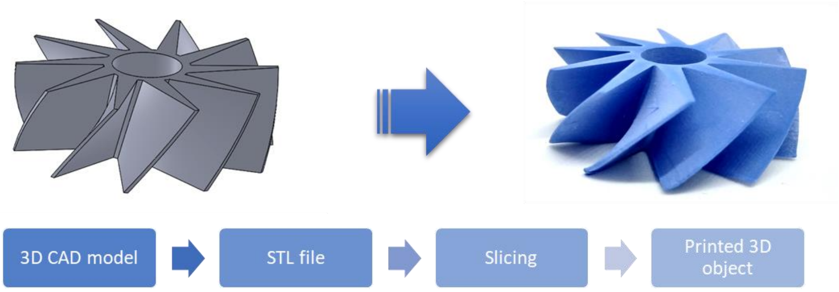

Figure 1.1 - Workflow of AM processes from the CAD model to the printed object

In 2013, the Royal Academy of Engineering stated that “AM’s unique processes, techniques and technologies open up new ground for innovation and offer a range of logistical, economic and technical advantages”. The main advantages of AMT are the following [1]:

1) Small production batches are feasible and economical.
2) Possibility to quickly change design, allows to shorten the time of the new product development reducing the lag time between design and production.
3) Economic custom products can be fabricated for low volumes.
4) Possibility to reduce waste, as the leftover material can be reused (according to the technology).
5) Design customization: Design freedom gives the ability to easily change the design, thus eliminating penalty for redesign. At the same time new design solutions can be offered.
6) Following the lean manufacturing concept, AM has the potential for simplification of supply chains: shorter lead times, lower inventories.

The ASTM F42 committee classified the AM process in seven different categories, considering two factors: on one hand, the technique used for the deposition of each layer and on the other hand, the method used to bond together the deposited layers. Table 1.1 presents a short description of the existing technologies for the seven AM processes: For each process the ASTM F42 definition is presented and a more detailed description of each process will be presented in this chapter. [3]

Table 1.1 - AM processes and technologies and its description (1) ISO/ASTM, 17296 Standard on Additive Manufacturing (AM) Technologies.

AM process	Technology	ASTM F42 definition (1)
Vat photopolymerization	Stereolithography (SLA)	additive manufacturing processes in which liquid photopolymer in a vat is selectively cured by light-activated polymerization
	Digital Light Processing (DLP) Mask Image Projection-based SLA (MIP-SLA) Lithography-based Ceramic Manufacturing (LCM)	
Material Jetting	Inkjet Printing (IJP)	additive manufacturing processes in which droplets of build material are selectively deposited
	Aerosol Jet Printing (AJP)	
	Photopolymer Jetting (PJ)	
Binder Jetting	Three-Dimensional Printer of Dry Powder Agglomerates (P-3DP)	additive manufacturing processes in which a liquid bonding agent is selectively deposited to join powder materials
	Slurry-Based Three-Dimensional Printing (S-3DP)	
Material Extrusion	Fused Deposition Modeling (FDM)	additive manufacturing process in which material is selectively dispensed through a nozzle or orifice
	Robocasting Direct Ink Writing (DIW)	
Powder Bed Fusion	Selective Laser Sintering (SLS)	additive manufacturing process in which thermal energy selectively fuses regions of a powder bed
	Selective Laser Melting (SLM)	
	Electron Beam Melting (EBM)	
Direct Energy Deposition	Laser Metal Deposition (LMD) Laser Engineered Net Shaping (LENS)	additive manufacturing processes in which focused thermal energy is used to fuse materials by melting as they are being deposited
Sheet Lamination	Laminated Object manufacturing (LOM)	additive manufacturing process in which sheets of material are bonded to form an object

The number of AM manufacturers are increasing day by day; nevertheless, the most known companies are 3D System, EOS, Arcam, Formlabs, MakerBot, Stratasys, Renishaw, and Envisiontec. [4]

The idea that AM processes are just applied to rapid prototyping is changing, following the improvement of materials and machines (hardware and software). The following examples show different approaches where AM processes can be successfully applied for both prototyping and final parts.

The design freedoms given by AM technologies allow the creation of new material structures such as porous mesh arrays and open cellular foams, enhancing the attributes of the fabricated component. The possibility of redesign to take advantage of AM's benefits allow for the improvements of the final performance, such as increased strength, stiffness, and energy efficiency (lighter pieces). [5]

One example is from the UK-funded SAVING (Sustainable product development via design optimization and AdditiVe manufacturING) project which includes the redesign of belt buckles on airplanes to reduce weight, thus saving material but at the same time maintaining strength and functionality.[5] The airline seat belt buckles have a weight between 155 g (steel) and 120 g (aluminum) constructed by traditional methods, however a significant weight reduction could be obtained by using titanium material printed by AM technology. This results in a weight saving of 87 g per seat belt, which means a total weight saving of 74 kg in an Airbus A380 with 853 seats. From an economic and environmental point of view, this redesign enhancement represents a fuel savings of 3,300,000 liters and 0.74 Mtonne CO2 emissions prevented over the lifetime of the plane. [6]

Figure 1.2 shows the seat belt buckles constructed by AM technology, in this cased based on powder bed deposition process, and the equivalent constructed by traditional processes.

Figure 1.2 - Lightweight seat belt buckles with Titanium Ti64 from EOS company (left) and traditional seat belt buckles (right) [6].

The aerospace industry has been exploring the adaptation of metal AMT, however the automotive industry has remained more restrained due to several factors, including productivity and cost-per-part.

The United Kingdom company, Betatype, demonstrated how to overcome these AM limitations for the automotive sector, redesigning a LED headlight with better performance than traditionally manufactured parts and, at the same time being economically viable. Typically, these new LED headlight components require comparatively large heatsinks which are often actively cooled. The specific geometry for these metal parts made them ideal for producing with powder bed fusion processes, which can consolidate multiple manufacturing processes into a single production method. Betatype shows that the redesigning of the LED heatsinks allows to maximize the number of parts per build volume, resulting in 384 printing parts in a single building process (Figure 1.3). In addition, through specific control of the printing parameters and minimizing the delays in between, the build time of each part could be reduced from 1 hour to under 5 minutes per part. This result is 10 times faster than using a standard building AM process. [7]

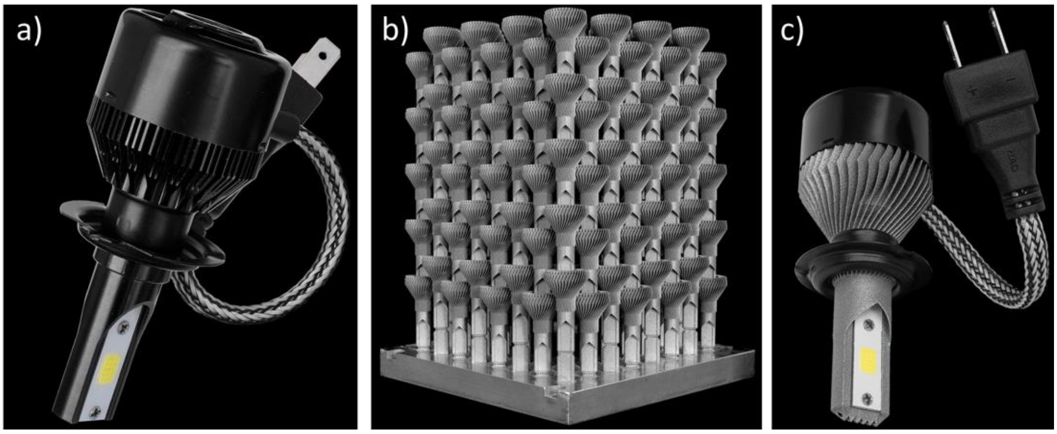

Figure 1.3 - Automotive LED Headlight (a) Example of a complete aftermarket product made by the traditional process b) Production Build of 382 Automotive LED Heatsinks 384 on an EOS M280. and c) Redesigned Heatsink, compatible with aftermarket design. [7]

Volkswagen Autoeuropa in Portugal, responsible for the manufacture of 100.000 cars per year, uses AMT to revolutionize its workflow. The AM facility manufacturing aids the assembly line with the tools printing daily. After having validated the concept in 2014, Volkswagen Autoeuropa currently has 7 Ultimakers (FDM-based 3D printing) producing 93 % of all externally manufactured tools in-house, saving 91 % in tool development costs and reducing the development time by 95 %. In 2016, Volkswagen Autoeuropa saved approximately 150.000 € by using 3D printing to manufacture their own custom tools and prototypes, with a target of 250.000 € for 2017. [8]

In the field of healthcare, AMT are currently used in the areas of dentistry, anatomical models, medical devices, tissue engineering and drug formulation. The printing of human organs using AMT is one of the latest advancements in the medical industry, such as liver, kidney, ear, cartilage, skin, cardiac tissue, and bone. Bioprinting is still in a very early stage of development and far from clinics; nevertheless, there is a growing interest, with promising outcomes for the future.[9] The healthcare market is expected to show significant growth as AM becomes widely used, mainly due to increasing demand for custom-tailored and patient-specific medical products. [10]

The pre-surgical planning and education with 3D-printed models may allow not just a better preoperative surgical planning, but also to avert unnecessary surgery in patients with potentially unsuitable anatomy, and thereby decrease the complications of liver transplant surgery.[11] An illustrative examples of an anatomical model of a human liver is presented in Figure 1.4.

Figure 1.4 -A 3D-printed replica of the human liver for pre-surgical planning procedures. [11]

1.3. Additive manufacturing of ceramic materials

SmarTech Publishing, the leading provider of market research and industry analysis in the 3D printing/additive manufacturing sector, published the Ceramics Additive Manufacturing 2018 report [12], showing that the ceramics AM market is expected to generate overall revenues of over $3.6 billion in 2028 as shown in Figure 1.5. This revenue does not come just from the final traditional (clay-like materials) or technical (advanced) printed parts but also from the raw materials, the machine itself (hardware), and from the services.

For the medium- to long-term future, the final part value for both technical and traditional ceramic parts is expected to represent the most significant opportunities. By comparing the final part and material revenues, the lower revenues generated by the raw materials indicated that the main value comes from the process in ceramics AM.

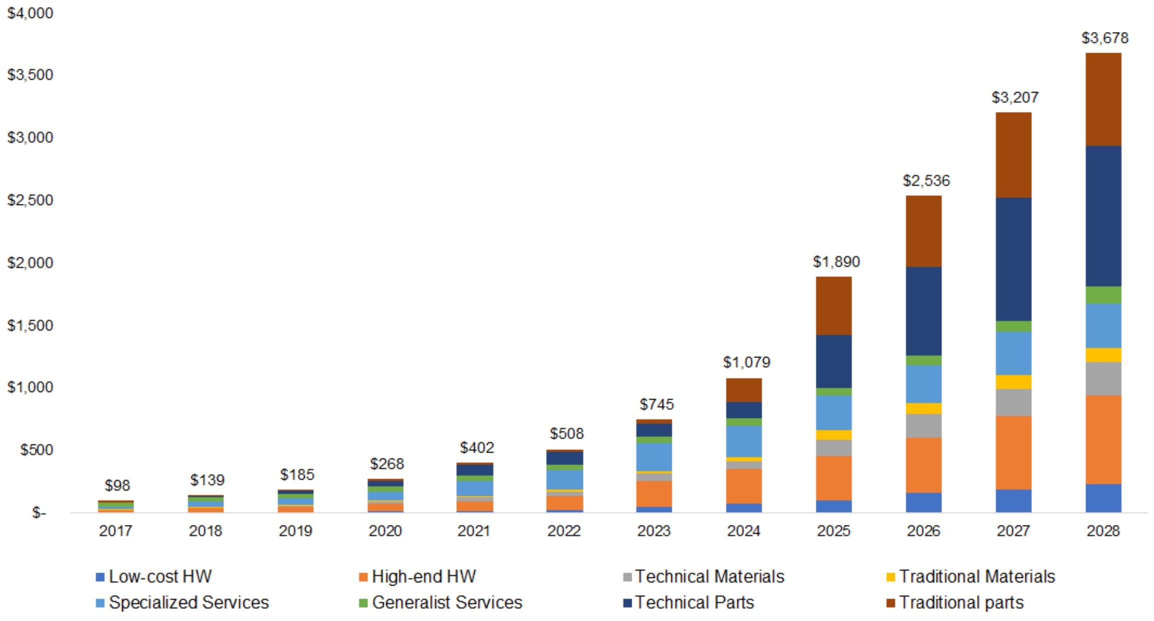

Figure 1.5 - Ceramics AM: Total market forecast by segment ($USM) 2017-2028. HW- Hardware. Source: SmarTech Publishing. [12]

SmarTech's forecasted timeline expects an inflection point after 2025 for the adoption of AM of ceramic materials, as a consequence of its technological maturity and its sufficient presence in the market to support serial part production. Particularly, the adoption of AM processes based on Ceramics Injection Molding (CIM) knowledge is expected to drive larger batch production in the same way as Metal Injection Molding (MIM) - based AM are now being predicted to significantly expand AM adoption and throughput capabilities, lowering costs. [12] Figure 1.6 shows the main points of the AM roadmap reported by SmarTech. The presented highlights show that SLA is the technology now adopted by aerospace and medical applications, following the material and technology validation for production. Before the inflection point, the expansion to new and high-potential manufacturing areas such as dental, energy, and electronic is expected, followed by its validation and/or adoption in 2025-2028.

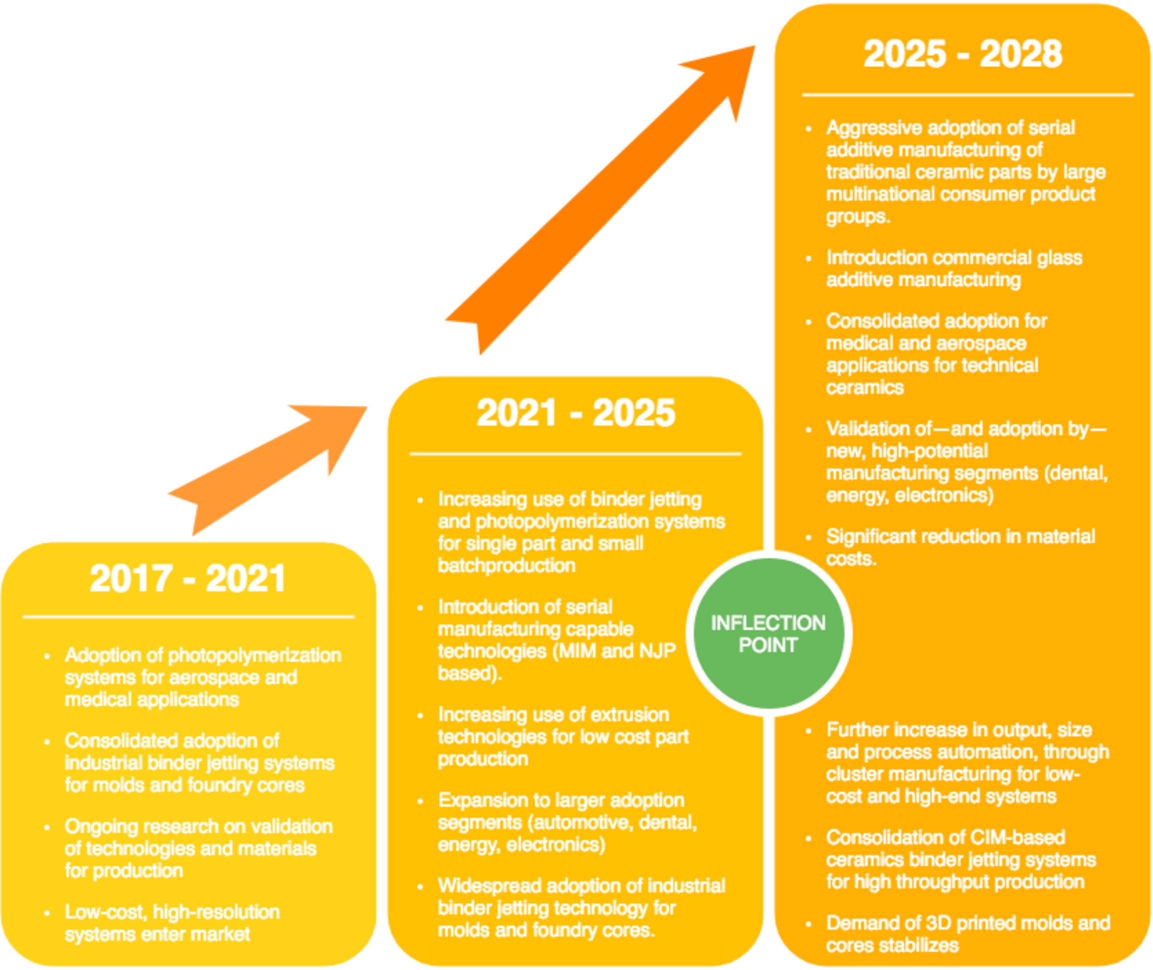

Figure 1.6 – Roadmap of AM of ceramic materials. NJP -NanoParticle Jetting. [12]

The following section is related to the state-of-art of ceramic material fabricated by AM processes and the seven processes are presented and exemplified. However, a more detailed state-of-art is presented for the vat photopolymerization process once is the main process used in this work.

1.3.1. Direct Energy Deposition

In this AM process, thermal energy, such as laser, electron beam, or plasma, is directly focused on the material deposition flow, meaning that the powder melts while it is deposited. There are two main technologies, regarding the deposition of the materials feed. The traditional Direct Energy Deposition is also known as laser cladding. This method consists of a nozzle that feeds material particles to the focal point of a laser beam. [13]The Laser Engineered Net Shaping (LENS^{tm}) is a commercial Direct Energy Deposition machine, that uses a Nd:YAG laser with a power of up to 2 kW. In 2008, Balla et al. demonstrated the possibility to build 3D α-alumina objects using this technology. The bulk density of the Al_2O_3 parts was 94% under the optimal printing condition, shown in Figure 1.7. Nevertheless, with thermal treatment, the density could increase up to 98%. In this work the difficulty to obtain crack-free parts was also mentioned, presumably due to high thermal stresses. [14]

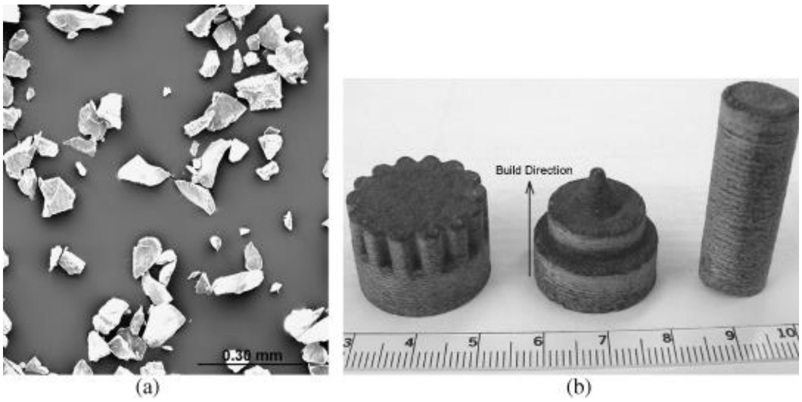

Figure 1.7 - Scanning electron microscope image of original alumina (Al2O3) powder (b) typical sound LENSt-processed Al2O3 structures processed at 175 W, 10 mm/s, 14 g/min.[14]

1.3.2. Powder Bed Fusion

In this process, the thermal energy that irradiates the powder particles comes from a laser beam or an electron beam. The technology that uses the electron beam is known as Electron Beam Melting (EBM), and is mainly used for metal or metal-matrix composites. The printing process is performed in a vacuum system to prevent metal oxidation. [13] There are two other technologies called Selective Laser Melting (SLM), where the powder is fully melted by the laser beam and Selective Laser Sintering (SLS), where the material is sintered by the laser. The building mechanism is similar in the tree technologies: first, the powder is deposited on a build platform by the roller from the feed platform; then, the laser/electron beam selectively sinters/melts the powder into the desired shape for each layer. The build platform moves down and, once again, the powder is spread on the building platform with a roller, for the next printing layer; this process is repeated along the printing until the 3D object is completed. Figure 1.8 represents the building mechanism of SLM/SLS technology.[15]

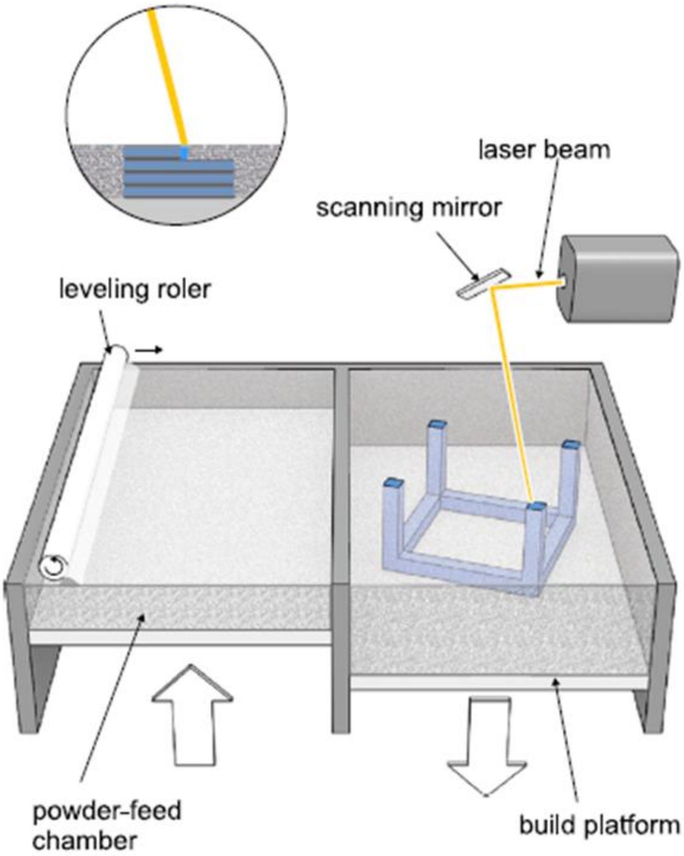

Figure 1.8 – Selective Laser Sintering technology. [15]

In this AM process, the powder that was not sintered/melted acts as a support for the printing object, meaning that, in principal, there are no supports. At the end of the printing process, the excess powder is simply removed and could be used in other printings, however, it must be mixed with new powder.

The Fraunhofer Institute of Laser Technology (ILT) in Aachen and the Netherlands Organization for applied scientific research (TNO) in Eindhoven investigated the SLM technology applied to ceramic powders. The first results were reported in 2006, where porous silica-tricalcium-phosphate and micro-crack-containing zirconia parts were fabricated using a CO_2 laser. The explanation of the generations of these micro-cracks can be explained by the thermal gradient during the printing process. In this sense, to reduce the thermal gradient, a high-temperature preheating system was developed. A CO_2 laser was used to preheat the powder layer and a Nd:YAG laser selectively melted the ceramic material. Although pure ZrO_2, Al_2O_3 and $MgAl_2O_4$ (spinel) ceramics could be processed with this approach, a huge number of micro-cracks were present in the parts. [16]

Another research group from France at Ecole Nationale d’ Ingénieurs de Saint-Etienne (ENISE), also tried to fabricate ceramic parts through SLM, by using a Phenix PM-100 machine (now from 3D Systems]. In 2007, Shishkovsky et al. [17] reported that zirconia and alumina-zirconium (Al_2O_3-Zr) printed parts are relatively dense, smooth, and uniform, but contain pores and cracks.

Another approach is to use indirect SLS, by using a sacrificial binder phase that permits the fabrication of crack-free ceramic parts, although the density of the final part is generally low, caused by voids between the particles and/or agglomerates of the powder on the deposited layer. Subsequently, if these free spaces do not disappear during the debinding and/or sintering processes, they will remain in the final part. [13]

Recently, in 2018, Sayed Mahmoud Nazemosadat et al [18]reported the use of indirect SLS to produce 3D objects from alumina particles coated by polystyrene (PS) with a Nd:YAG laser. The achieved densities of the green parts varied from 66.5 to 81.3 %, which is a higher accomplishment compared to the previous reported values, 52–67 %,Figure 1.9.

Figure 1.9 - Complex green parts created with indirect SLS by using one of the best laser parameters (Frequency: 10 kHz, Pulse width: 10 µs, laser power: 6 W, scan speed: 20 mm) [18]

Instead of a powder form, a suspension-based method could also be used in this AM process called layer-wise slurry deposition (LSD). T. Mühler et al, published the use of this approach to construct porcelain pieces, where silicate ceramics suspension were deposited on the building platform, dried by a heater and "sintered" by the laser, obtaining a so-called biscuit-fired porcelain body (65 % density). [19]

1.3.3. Sheet Lamination

Mostly, there are two sheet lamination technologies: traditional Laminated Object Manufacturing (LOM) and Computer-Aided Manufacturing of Laminated Engineering Materials (CAM-LEM). Focusing on the ceramic materials, the feed material used in the traditional LOM technology is a green ceramic body (binder, additives, and ceramic particles) previously obtained as a tape/sheet by tape casting technology. The tape thickness is the layer thickness of the printing process. The ceramic tapes are unrolled onto the printing bed where a CO_2 laser cuts the outline of the defined pattern of each layer. After this process, the binder of the ceramic tape is thermally activated and compressed by a heated roller, allowing for the lamination of the tape to the previous one. If there is not enough binder used in the ceramic suspension to promote the interconnection between tapes, some adhesives agents can be used. [20] After the debinding and sintering processes, the final ceramic pieces are obtained, e.g. alumina and silica pieces with 90-92 % and 70-80 % density, respectively [21], glass-ceramic with 95 % density [22], and Si_3N_4 parts with a density of 97 %. [23]

On the other hand, the CAM-LEM technology works similarly to the previous one, with the main difference being that each layer is pre-cut and robotically stacked onto the building platform for the lamination process. The advantage of this method is that internal voids within each layer can be easily shaped.[24] However, as the company Helisys Inc., USA (machine: Helisys 1015plus,), which previously commercialized the LOM technology for ceramic materials, is no longer in business, this process is not currently commercially exploited for ceramics.

1.3.4. Binder Jetting

This process is also known as Three-Dimensional Printers (3DP) and is based on the bonding of powder material by using an inkjet system that deposits a liquid binder, defining the pattern in each layer. The feed system is similar to the powder bed fusion: the powder is stored in the feed platform and the recoating system deposits a thin layer of new powder material on the building platform, shown in Figure 1.10. This process is continuously repeated until the part is completed: the first step is the recoating of the layer with a roller, followed by the printing the layer with a certain pattern by the binder deposition. Then the building platform goes down and the feed one goes up and the recoating of the layer is repeated. In the case of ceramic materials, the binder must be removed (debinding) and sintered to obtain the final ceramic part.

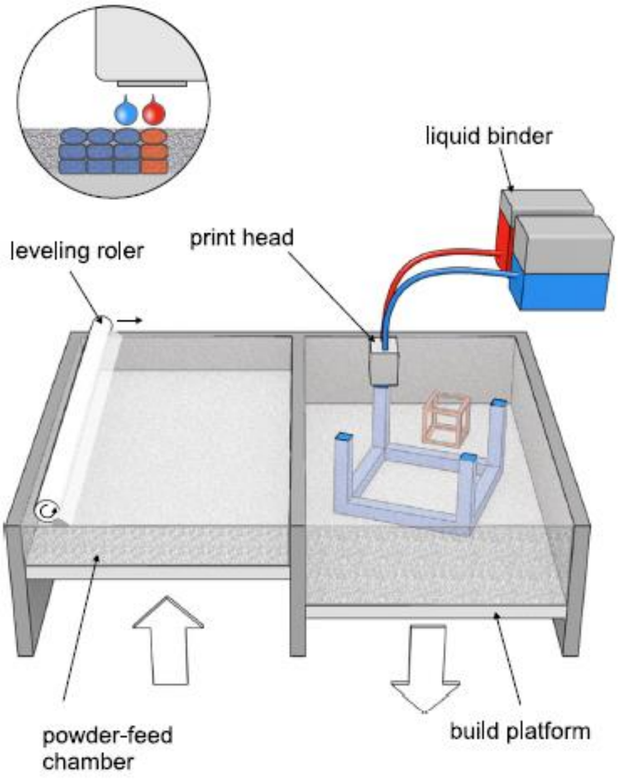

Figure 1.10 – Binder jetting process [15]

The co-inventors of the binder jetting process, M.J. Cima and E.M. Sachs from the Massachusetts Institute of Technology [25], demonstrated the viability of this process in 1991 by the printing of shells and cores for investment casting using alumina powder and colloidal silica binder.[26]

In 2014, Shu Cao et al. demonstrated the use of this technology for the fabrication of an alumina/borosilicate–glass composite part, using a urea-formaldehyde resin as a binder. The printed parts were sintered and then a glass melt infiltration with borosilicate–glass was performed to improve the mechanical properties. The obtained relative densities after sintering were around 86.7 %, shown in Figure 1.11. [27]

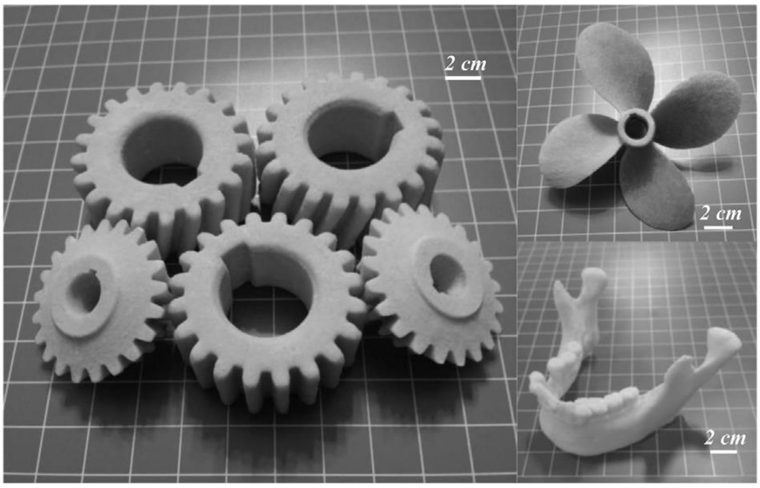

Figure 1.11 - Alumina/borosilicate–glass composite parts after the melt infiltration process. [27]

Guha Manogharan et al., demonstrated the possibility to print a solid oxide fuel cell (SOFC) using the binder jetting process in 2015. The used 3D printer was Ex One X1-lab, from ExOne Company, which has a layer thickness of 0.1 mm.[28] This work shows the feasibility of printing with different materials through 3DP technology: Ni-YSZ (nickel oxide–yttria stabilized zirconia) for the anode, LSM (lanthanum strontium manganite) for the cathode and, YSZ (yttria stabilized zirconia) for the oxygen ion-conducting electrolyte.

In general terms, in a SOFC system, the electrode layers must have a porous structure, required for the gas diffusion, and the electrolyte needs to be nonporous to form a physical barrier between the anode and the cathode. The densities that could be achieved by 3DP technology are not suitable for the electrolyte layer, thus the long-term challenge for AM of SOFCs is the densification of the electrolyte layer. [28]

Figure 1.12 shows the Ex One X1-lab setup, and the sintered SOFC, where the anode and cathode have a diameter of 15 mm and the electrolyte has a 20 mm diameter. All the layers have a thickness of 5 mm.

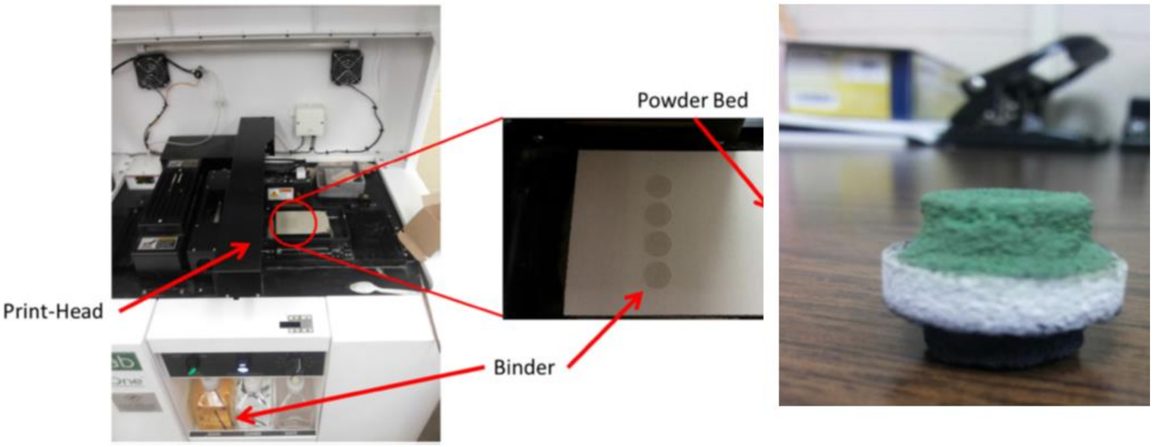

Figure 1.12 – ExOne X1-lab machine (on the left) and the printed SOFC (right). [28]

1.3.5. Material Jetting

There are two main different technologies of the material jetting process: Inkjet Printing (IJP) and Aerosol Jet Printing (AJP). In the IJP technology, the suspension is deposited directly from the nozzles, depositing individual droplets onto a substrate, as shown in Figure 1.13.

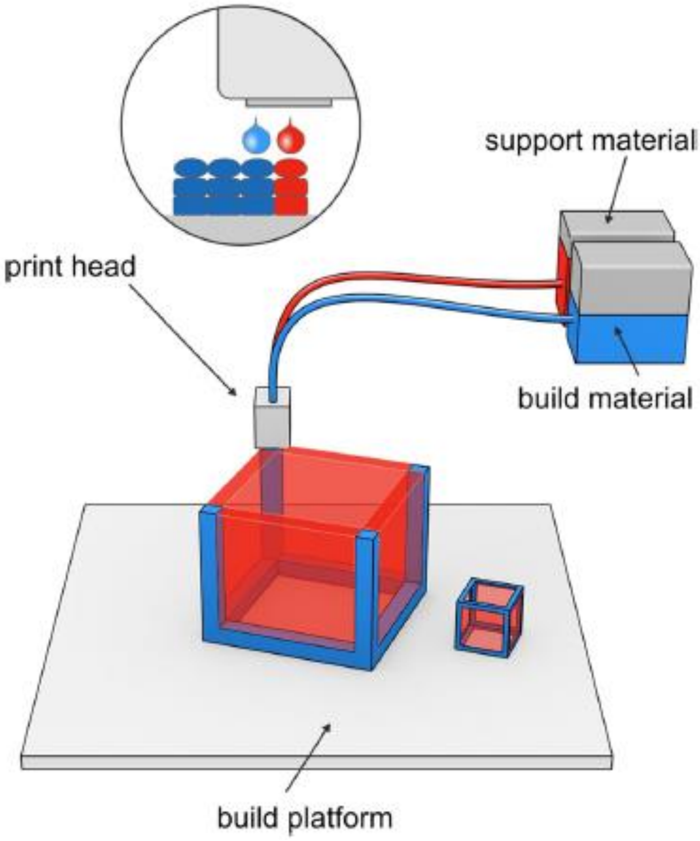

Figure 1.13 – Material jetting process: inkjet printing [15]

The suspensions that are possible to print are limited by the small range of viscosities and surface tension; in general, the suspensions must have a viscosity of less than 20 mPa·s and surface tension of 20-70 mN. In AJP, the suspension is atomized, creating a dense aerosol composed of droplets with diameters between approximately 1 and 5 µm, and then it is transported to the print head using an inert carrier gas. The Optomec company had developed an aerosol jet print head capable of printing with suspension loaded up to 70 %, particle size up to 500 nm, and viscosity between 1 mPa·s and 1 Pa·s. Another company that offers the possibility to print with suspensions with high viscosity is Ceradrop, that also use the print heads from Optomec. [29] The CeraPrinter F-Serie, is a hybrid materials deposition platform combining piezoelectric Inkjet (Dimatix printhead from Fujifilm, USA) and Aerosol Jet® (Optomec) technologies, reaching a wide range of application fields such as antennas, sensors, passive components, interconnection, flexible solar cells (OPV), OLED Displays, among others.[30] Ceradrop also offers the possibility to scale up the process with the Industrial platform.

In 2013, Mary Sukeshini A et al. reported the use of AJP M3D from Optomec, to print ink suspensions of NiO and Yttria-Stabilized Zirconia (YSZ) for SOFC applications. This printer machine also has an AJP dual atomizer system which allows for on-demand material mixing. In this sense, it was used to print porous composite anode layers with compositional gradation. For the fabrication of these composite anode interlayers (NiO/YSZ), two separate inks based on NiO and YSZ were used. The SOFC was completed by hand pasting cathode layers of LSM (strontium-doped lanthanum manganite) on the sintered anode support/anode and interlayer/electrolyte (NiO-NiO/YSZ-YSZ), that allows for better performance comparing with the cells with a non-graded anode interlayer. Nevertheless, the overall performance of all cells was not satisfactory, and requires further optimization of the anode interlayer by changing the ink characteristics. [31]

In 2018, N.M. Farandos and T. Li, G.H. Kelsall used the Ceradrop X-Serie which uses a piezoelectric inkjet print head for the fabrication of electrolyte (YSZ) and YSZ-LSM electrode for reversible solid oxide electrochemical reactors (SOERs) applications. The performances of inkjet-printed SOERs were demonstrated to exceed those fabricated by conventional powder mixing methods.[31]

1.3.6. Material Extrusion

In this process, there are two main technologies where the main difference is the material feed. Fused Deposition Modeling (FDM) works with a thermoplastic filament that is partially melted and deposited by the extruder head. In the field of ceramic materials, this technology is known as Fused Deposition of Ceramics (FDC), Multiphase Jet Solidification (MJS) or Extrusion Free Forming (EFF).[32] However, until now, the most investigated technology for the ceramic materials is Robocasting, also known as Direct Ink Writing (DIW).Figure 1.14 shows an scheme of both technologies.

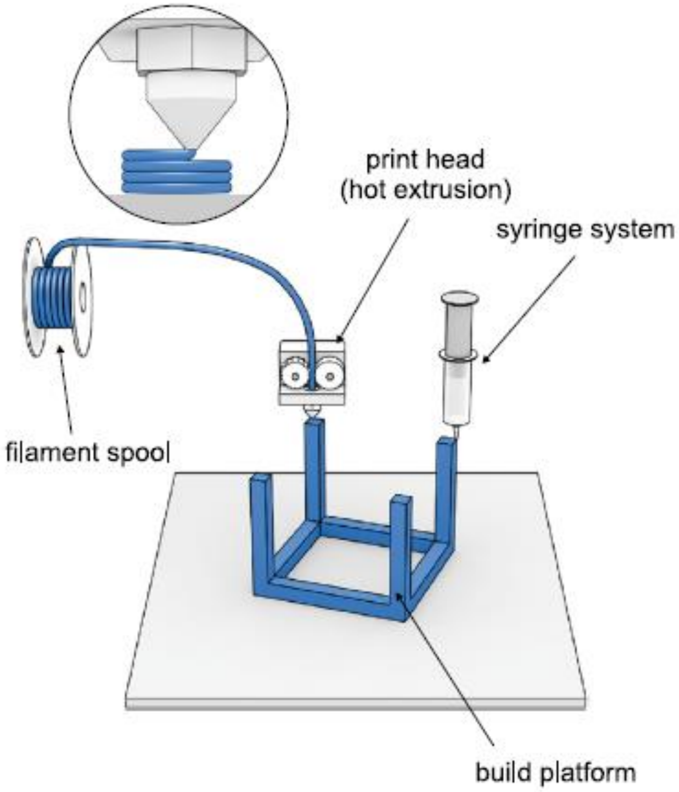

Figure 1.14 – Material extrusion: FDM and DIW technologies. [15]

In 2018, Dorit et. al., demonstrated the fabrication and the printability of alumina filaments with 50 vol.%, which can be printed through a nozzle with 150 micros, resulting in a density of 98.4 % for open structures and 97.3 % for dense parts. Using this technique, the fabrication of 100 % filled pieces without pores is a challenge due to the rounded profile of the extruded filament. [33]

In the DIW technology, a concentrated paste is extruded through a nozzle, forming a filament that is directly deposited onto the substrate, layer-by-layer. In contrast to FDC, a lower amount of polymer material is needed for the material paste formulation (less than 3 wt.%).[34]

In the field of electrochemistry for energy harvesting, 3D printing technologies allow for the creation of complex and customized shapes that can be used, taking advantage of the geometry design, to obtain better performances, reducing also the time of fabrication. One example is shown in Figure 1.15, reported by Ke Sun et al. in 2014, where a complex architecture of a lithium-ion microbattery was fabricated by robocasting. [35]

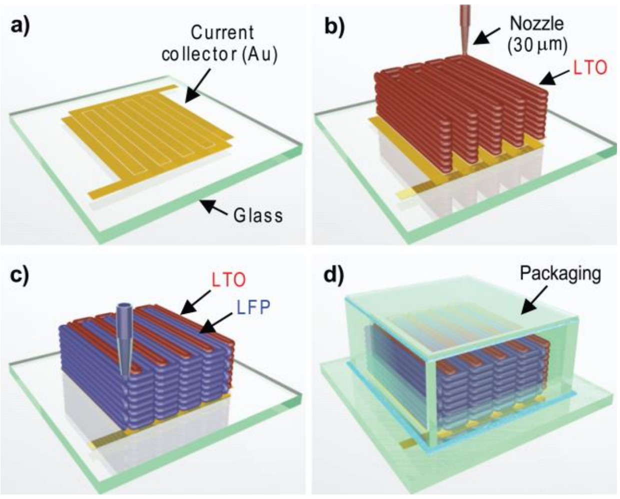

Figure 1.15 - Schematic illustration of 3D Interdigitated Microbattery Architectures (3D-IMA) fabricated on (a) a gold current collector by printing (b) $Li_4Ti_5O_{12}$ (LTO) and (c) $LiFePO_4$ (LFP) inks through 30 µm nozzles, followed by sintering and (d) packaging. [35]

In 2015, John Klein et al, from Massachusetts Institute of Technology, published the first molten glass material 3D extrusion system for the manufacture of optically transparent components. The results showed strong adhesion between layers and from the optical point of view, high transparency was observed, and complex caustic patterns were created with LED light sources, as seen in Figure 1.16. This technology opens the door for a new way to manufacture the glass material, not just for art and architecture applications, but also for the creation complex scaffolds or labware custom made for individual applications. [36]

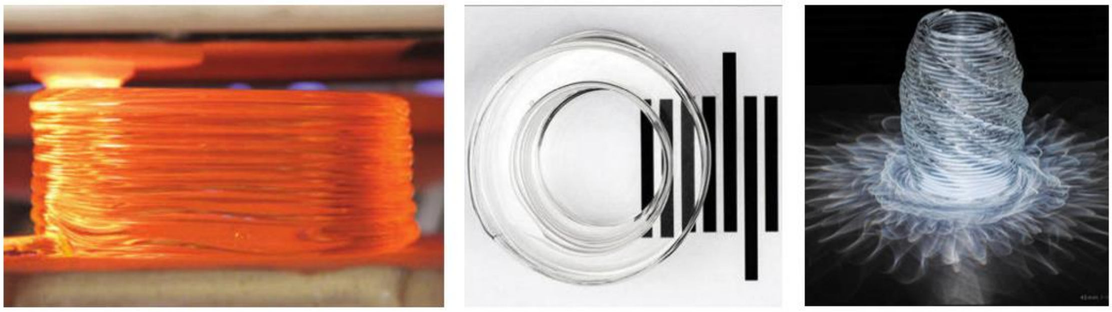

Figure 1.16 - Molten glass material 3D extrusion system (left), high object transparency (middle), and complex caustic patterns (right) [36]

In 2016, Ezra Feilden et al., presented the optimization of alumina and Silicon carbide inks DIW application with the purpose of achieving dense monolithic ceramic parts. The paste's rheological measurements show a thinning behavior with yield stress values higher than 1 kPa.[37]

The final densities of the part, printed with pastes with 40 vol% of solid contents, was up to 95 % for SiC and 97 % for Al_2O_3, and flexural strength values of 300 MPa and 230 MPa, respectively. While the strength and reliability of the printed parts are acceptable for many applications, the defects generated during the printing process must be limiting these properties. The four main reasons for the generation of these defects have been proposed as: (1) - residual pores after sintering, mainly for the lengthwise SiC samples, attributable to the difficulty to densify this material deprived of pressure. (2)—bubbles/agglomerates/contamination in the ink. (3)—Air trapped between deposited layers and filaments during printing, identified as the main critical defect in all widthwise and heightwise parts. (4)—Surface defects, mainly in the edges associated with the layer-by-layer manufacturing process. [37] Figure 1.17 shows the final sintered parts.

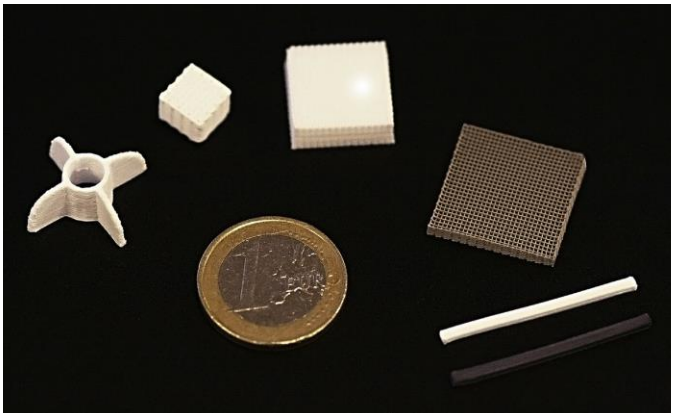

Figure 1.17 - Sintered SiC and Al_2O_3 scaffolds, parts, and test bars printed using the hydrogel inks [37]

In 2018, Amy Nommeots-Nomm used DIW technology to create bioactive glass scaffolds and high strength scaffolds for bone repair.[36] In the same year, Rong Wang et al., demonstrated that 3D TiO_2 bioceramic scaffolds manufactured by the DIW technique provide a biocompatible environment that favors cell growth and attachment. The scaffolds were printed with controllable and adjustable pore structures with a TiO_2 sol-gel ink, and after the sintering process, a 10 µm feature size was achieved. [38]

The new concept of 4D printing [39], 3D printing of smart materials which have the capability to transform their geometry under the influence of external stimuli such as water and heat, was recently applied to ceramic materials. In 2018, Guo Liu et al., demonstrated the viability of this concept in ceramic materials. [40]

1.3.7. Vat photopolymerization

Following the ASTM F42 standardization, the SLA is one of the technologies inside the classification of vat photopolymerization processes. As described previously, the stereolithography (SLA/SL) technology was patented in 1986 by Charles W. Hull, the co-founder of 3D Systems (U.S. Patent 4575330A “Apparatus for Production of Three-Dimensional Objects by Stereolithography”). The word “stereolithography” comes from the Greek words “stereo,” meaning solid, and “(photo)lithography,” which is the process of writing with light.[13]

The basic principle of these processes is the photopolymerization of a liquid resin (photocurable polymer) through the irradiation of a light source with a certain wavelength, supplying the energy needed to induce a chemical reaction (curing reaction). This curing reaction converts the liquid resin into a solid layer, resulting in a highly cross-linked polymer.[41]

In the top-down configuration, the printed object is immersed into the uncured liquid resin and the light source is on the top. In the SLA case, the light source is usually a UV laser, although other light sources could be used to photopolymerize the resins. After the polymerization of the whole pattern layer, the platform goes down a certain distance and the uncured liquid resin recoats the cured surface. Once again, the photopolymerization process takes place, stacking the new cured layer on the previous ones. This process is applied for each layer and in the end of the printing process the object is removed from the liquid resin, which was not used for printing. In this configuration, the resin must be leveled by a wiper blade before starting the photopolymerization of the following layer. Figure 1.18 shows the top-down SLA configuration.

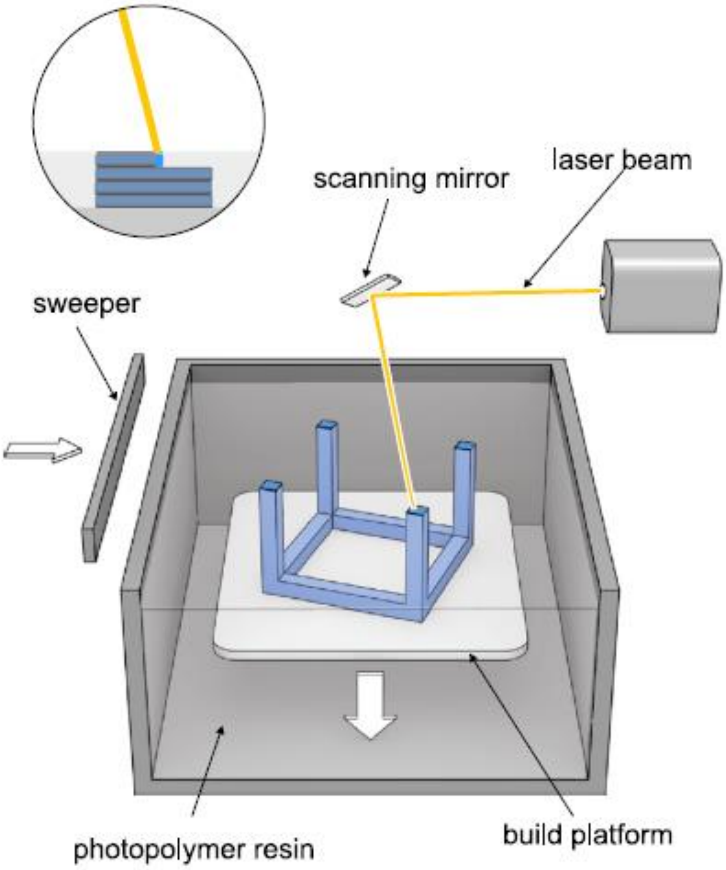

Figure 1.18 – SLA technology. [15]

John W. Halloran's research group, from the University of Michigan, published in 1996 one of the first results about the fabrication of ceramic components via SLA technology, using a commercial SLA from 3D Systems. In this case, the photocurable resin is loaded with ceramic particles and after the printing process, a thermal treatment must be applied to the green body, to remove the organic material and sinter the part. In this research, aqueous acrylamide-based suspensions of alumina and silica were successfully used on the fabrication of ceramic parts by SLA. The issues related to the high refractive index of silicon nitride were also reported, which drastically reduce the photopolymerization reaction, preventing the construction under SLA technology [42] One year later, Thierry Chartier's group published the formulation of a photocurable alumina suspension suitable for SLA, reporting the use of heat during the printing process to lower the viscosity of the suspension. This approach allows for the increase of the ceramic load with low viscosities. [43]

Over the years, several alternative processes have been presented with different light sources. For instance, the traditional UV laser can be replaced by LEDs or halogen lamps, and by using a pattern generator such as light crystal displays (LCDs) or digital micromirror devices (DMDs), the desired pattern could be projected on each layer.[44] In the AM ceramic field, there are different designations for this concept, sometimes associated to the company's marketing. Thus, other names could be called to describe this process, for example, the term Large Area Maskless Photopolymerization (LAMP^{TM})[45] from DDM Systems company, Lithography-based Ceramic Manufacturing (LCM))[46] is used by Lithoz company; furthermore, it could be also called as Digital Light Processing (DLP) [47], Mask Image Projection based Stereolithography (MIP-SLA) [48] or Ceramic Stereolithography (CSL).[49] There are slight differences depending on the machine manufacturer; nevertheless, the concept of polymerization by projecting an image is the same for all designations. The AM technology used in this work is based on this principle and from now on, the term MIP-SLA will be used.

1.3.7.1. Mask-Image-Projection-based Stereolithography

The MIP-SLA technology is also classified as a vat photopolymerization process, where the basic principles are mostly the same as SLA technology. As stated previously, the main difference is the light source, where instead of using a laser beam, which polymerizes the resin point by point, a light projection is applied to irradiate the whole layer. Since an entire layer is exposed with a single pattern, fast build speeds are achieved independent of layer complexity. The latest developments on digital devices such as LCDs and DMDs present relatively low-cost, powerful tools that can simultaneously and dynamically control energy inputs of a projection image. The DLP technology, developed by Texas Instruments, is an optical micro-electro-mechanical display device which uses a DMD device, usually used in commercial light projectors.[44] This sense, it could also be used as a light source for MIP-SLA, usually projecting the images as a bitmap of white and black areas. In the following chapters, a more detailed explication is presented about the machine design and printing resolution.

In both technologies, MIP-SLA and SLA, there are two main configurations regarding the position of the light source: top-down and bottom-up. As explained earlier, in the top-down approach the light source is placed on the top of the building platform and the object is moving downward during printing. In the bottom-up approach the light source is below the building platform and the object is pulled out of the resin during printing. Figure 1.19 shows both configurations, in this case for a MIP-SLA technology.

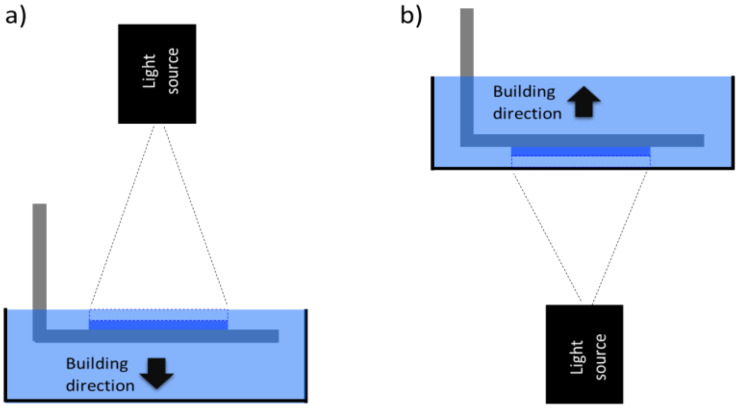

Figure 1.19 – schema of a) Top-down and b) bottom-up MIP-SLA configuration.

The following tables show the advantages and drawbacks of each MIP-SLA configuration.[50]

Table 2 – Advantages and drawbacks of the bottom-up MIP-SLA configuration.

Configuration	Bottom-up
Advantages	• The vat does not have to be full of resin. • The part height is not limited by the height of the vat • No oxygen inhibition in acrylic resins
Drawbacks	• The resin vat needs to be covered with an optic-transparent anti-stick layer • The vat needs to be made of a material which is also transparent to the wavelengths which the resin is sensible to. • Since the layer is cured directly to the bottom of the vat, a vacuum between the wall and the bottom of the product is formed. A force is needed to pull the product from the bottom of the vat. A tilt system must be added. • Stresses are induced into the printed part.

Table 3 - Advantages and drawbacks of the top-down MIP-SLA configuration.

Configuration	Top-down
Advantages	• Does not need a mechanism to break the vacuum between the resin vat and the object • No stresses are created in the printed part. • Easier integration with other printing techniques.
Drawbacks	• The depth of the vat limits the maximum height of the printable object since the object sinks deeper and deeper • The vat needs to be filled completely with resin • While the platform moves deeper into the fluid, it changes the fluid level of the resin. • Superficial tension creates rounded shapes. • Inhibition of the polymerization due to the oxygen in acrylic-based resins.

The MIP-SLA machine used in this work has a top-down configuration which allows the integration of an inkjet printing system. A better explanation of this AMT hybridization is detailed along the results discussion.

1.3.7.2. Ceramic applications

Hydroxyapatite (HA) has been widely studied for skeletal tissue engineering as its chemical composition is similar to the inorganic component of natural bone. In this regard, in 2012, the Neurosurgery and Maxillofacial Surgery Departments of Limoges University Hospital fabricated a custom HA ceramic implant for a large craniofacial bone defect using the 3DCeram stereolithography machine. By using AMT, the implants are printed directly with a surface porosity that favors the soft tissue adhesion. Beside the successfully customized HA implant, no major complications (infection or fracture of the implant) was observed and the cosmetic result was considered satisfactory. [51]

Bioactive silicate glass is another important material in the field of bone tissue engineering, due to its biocompatibility and biodegradability. However, the clinical applications as bone substitute or scaffold material are highly limited due to its poor mechanical properties. These scaffolds must exhibit high and interconnected porosity and should promote the regeneration of new vascularized bone tissue.[52], [53]

In 2015, Jürgen Stampfl's group used a Lithoz apparatus (LCM technology) to fabricate Bioglass material for the first time with excellent feature resolution. Additionally, dense parts with high biaxial bending strength (124 MPa) can be achieved when highly loaded and well-dispersed slurries are processed. These values are surprisingly high compared to previous reports in the literature with biaxial bending strength of 40-42 MPa.[52] shows the sintered scaffold structure made of bioactive glass.

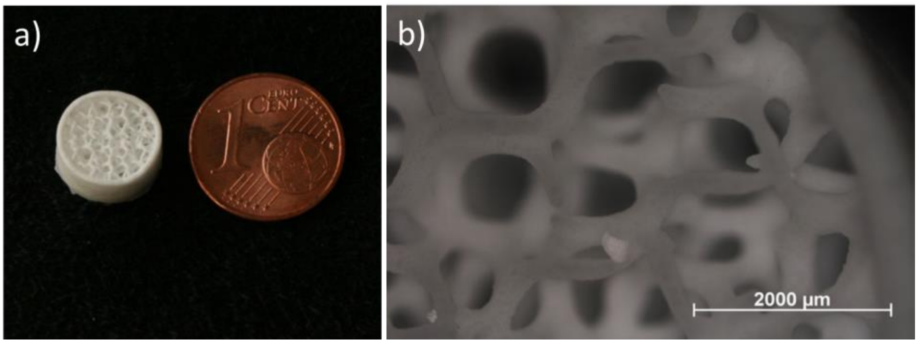

Figure 1.20 – a) Image of a sintered scaffold structure made of bioactive glass and (b) a microscopic view of the scaffold structures with dimensions of a few hundred micrometer. [52]

Also in 2015, Martin Schwentenwein and Johannes Homa, from Lithoz, published the viability of printing ceramic parts with over 99.3 % density and four-point bending strength of 427 MPa, showing complex printed parts, displayed in Figure 1.21. [54]

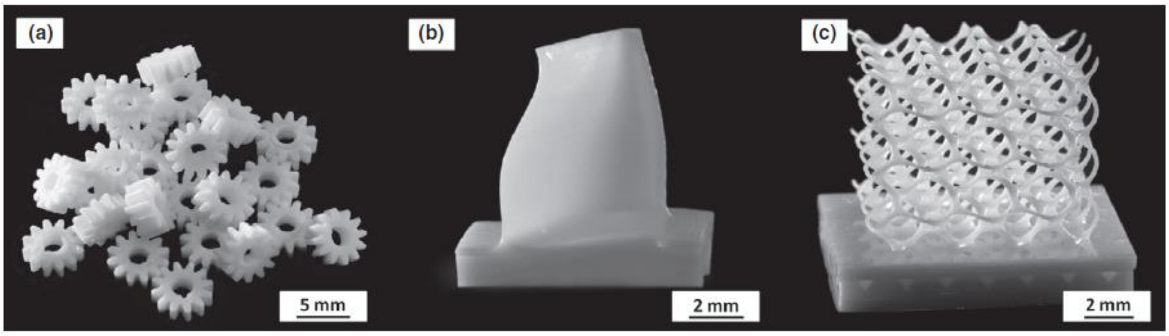

Figure 1.21 -Sintered alumina parts fabricated using the LCM technique: (a) gear wheels; (b) a turbine blade; and (c) a cellular cube. [54]

In 2016, Zak C. Eckel reported the use of preceramic monomers to print complex shapes and cellular architectures by SLA, shown in Figure 1.22. The advantage of this material is the possibility to pyrolyze it to a ceramic material with uniform shrinkage. The printed cellular silicon oxycarbide (SiOC) materials exhibit 10 times higher strength compared with commercial ceramic foams of similar density, resisting temperatures up to 1700°C in air. These cellular ceramic structures hold a high interest for applications where being lightweight and resistant to high temperature have an important role, for example, in hypersonic vehicles and jet engines. [55]

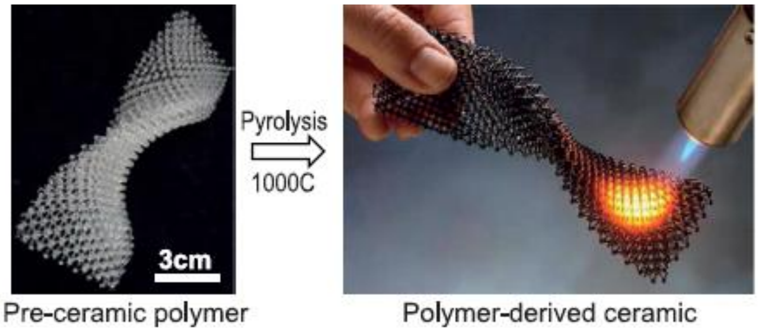

Figure 1.22 – Cellular SiOC ceramics structures; a) pre-ceramic polymer structure and b) pyrolyzed ceramic structure. [55]

Another interesting AMT application is on the development of auxetic metamaterials. In 2016, Lithoz and the Mechanical Engineering & Manufacturing Department of the Universidad Politécnica de Madrid presented a very promising approach for the development of an alumina auxetic metamaterial constructed using the LCM technology, shown in Figure 1.23. These materials are being progressively employed in the design of new products with interesting functionalities, such as active implantable medical devices, minimally invasive surgical actuators, or active scaffolds for dynamic cell culture. In the fields of telecommunications and optoelectronics, it could be applied for novel antennae designs, special photonic crystals, and stress–strain electromechanical micro-sensors. The possibility to print these structures with ceramic materials increases the range of applications, for example in energy-related applications, i.e. in the development of active filters for turbomachinery. [56]

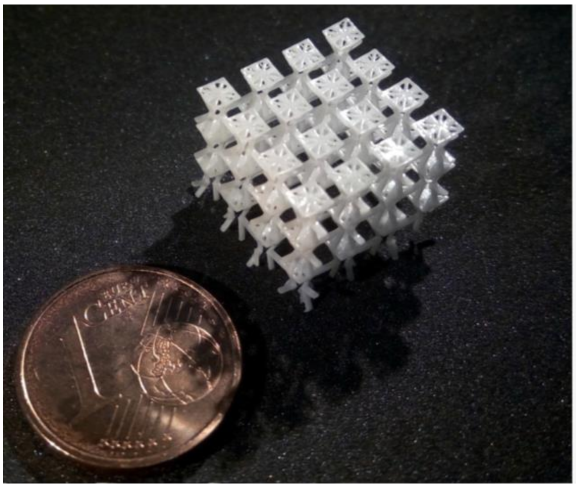

Figure 1.23 –Sintered auxetic alumina structure with micrometric details obtained by means of lithography-based ceramic manufacture (LCM). [56]

Taking advantage of the geometrical freedom, in 2017 Oscar Santoliquido et al, showed the possibility of printing catalyst support for automotive exhausts where a functional design which could not be produced by the traditional method, thus allowed an optimized flow of the exhaust gasses. [57]

In the same year, Albert Tarancón's research group, published the use of SLA (CERAMAKER from 3DCeram company) AMT for the construction of an electrolyte of yttria-stabilized zirconia (YSZ) for solid oxide fuel cell (SOFC) applications with a higher geometrical complexity. [58]

In this study, a commercial paste of lanthanum strontium manganite (cathode) and nickel composites (anode) was painted on the self-supported electrolyte for the cathode. Regarding the AM process, two different geometries were printed, one with a honeycomb-like structure, shown in Figure 1.24, and a flat one with a thickness of 340 µm. The honeycomb structure positively contributes to enhancing the performance of the cell compared to the flat counterpart due to 1) enabling a thinner membrane (260 µm) and 2) partly using the area increase associated to the beams.

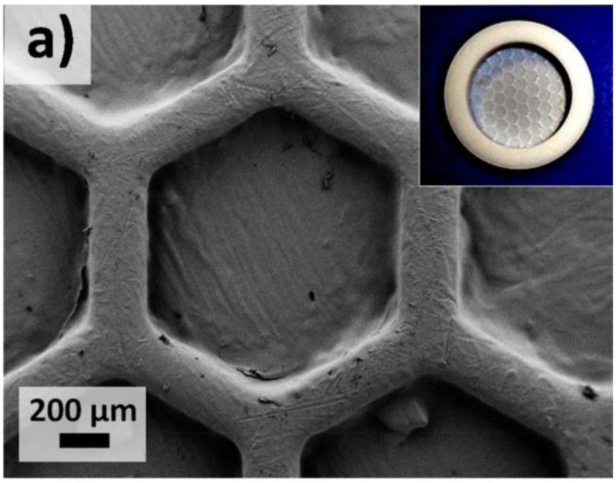

Figure 1.24 -SEM image of the surface of the 3D-printed membrane with honeycomb-like structure. A detail of one of the hexagonal cells and the reinforcing beams can be observed. The inset shows an optical image of the 3D-printed piece including the self-supported membrane and the bulky ring. [58]

These results show that the design freedom of ceramic materials will revolutionize the field of energy by opening a new avenue for the customization of systems, the fabrication of joint-less stacks, and the increase of the specific power. For further advancement, the development of more ceramic materials for AMT applications and the multi-material capabilities of the current 3D printing technologies is essential.

1.4. Comparison of AM technologies of ceramic materials

In AM of ceramic materials, two approaches could be considered to obtain a 3D-printed ceramic piece; on one hand by using the ceramic powder directly, called direct AM processes, such as the direct Powder Bed Fusion (without binder) and the Direct Energy Deposition, and on the other hand, by using a binder as a sacrificial material, called indirect AM processes.

Figure 1.25 shows the classification of the AM processes in the direct or indirect configurations. There are processes which could be used in both configurations, i.e., the powder bed fusion process could be used directly using the ceramic powder, or by mixing the ceramic powder with a polymeric phase, which in this case is classified as an indirect process.

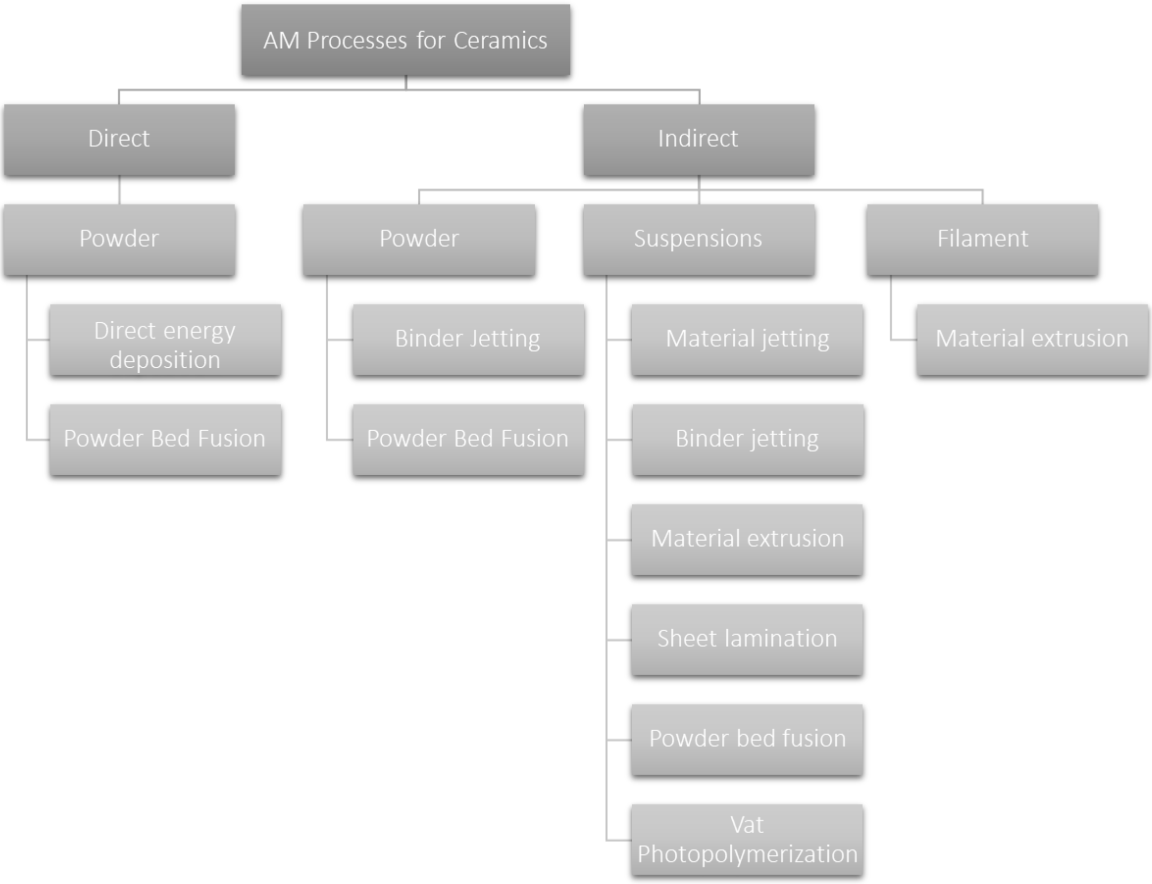

Figure 1.25 – AM process classification for ceramic materials.

The direct approach does not require the time-consuming process of debinding, but as shown previously, the results are not promising yet, due to the thermal gradient generated during the printing, even with preheating the powder before the laser sintering (which also increases the powder consumption). Following this line of reasoning, until now the indirect processes are the ones which have more promising results for ceramic materials.

Inside the indirect classification, the ceramic powder could be mixed with other polymeric powder, recoated with a binder or, in the case of the binder jetting, bonded by a binder agent (powder classification). The other approach is by using ceramic suspensions or by forming a filament.

Regarding the indirect processes, the cracks are not generated during the printing process as in the direct ones, but generally during the debinding process. Except for non-structural ceramic parts susch as scaffolds, where part strength is not a major issue, the piece porosity could be considered one of the principal defects. The porosity of the final parts could be correlated with the AMT itself, i.e., in the indirect process which directly use the powder/s, the particle packing on the powder bed is not ideal, generating voids between the particles and/or powder agglomerates. This fact results in low densification of the final pieces if no extra steps to densify the pieces are applied. As a result, the relative density of the ceramic parts do not exceed 81 % for the indirect powder bed fusion yet.[18] Regarding the binder jetting, even with a glass melt infiltration the final density was 86.7%. [27] Nevertheless, these technologies could be applied to applications where the porosity has an important role, such as for scaffold applications[59] or to produce molds for metals pieces.[60]

As detected during the state-of-art analysis, the strategy of using ceramic suspensions improves the packing and homogeneity of the ceramic particles, resulting in higher densities and quality of the final ceramic pieces. Note that in all AM processes, the adaptation of the powder based-technologies to suspension based-systems is presented in the state of art.

Sheet lamination processes use ceramic tapes, produced from a ceramic suspension by tape casting which is a well-established manufacturing process. The final densities of the produced part are 90-92 % for alumina, 70-80 % for silica[21], 95 % for glass ceramic[22], and 97 % density for Si_3N_4 parts.[23] Despite the relatively high densities, the Sheet

Lamination process itself does not represent a great advantage when compared with other AM processes because the complexity of the geometries are limited, an extra processing step to produce the sheet material is required, and also due to the large amount of waste material which is difficult to reuse or recycle. In addition, the company Helisys, which commercialized the LOM tehcnology for ceramics material no longer exists, so this AM process is not currently used for the AM of ceramic materials.

Material jetting has been used for multi-material printing with a small height (< 2-3 mm) and high resolution. XJET currently use this technology to produce 3D ceramic parts, however material jetting technologies are commonly used for electronic proposes (for multilateral and small height).

Regarding the material extrusion process, there are two main technologies for ceramic materials DWI and FDC. Regarding the DWI, the largest limitation is the level of detail, or resolution, and the complexity of the printed parts, usually corelated to the size of the nozzle. In this regard, a strategy to improve the resolution is to use smaller diameter nozzles, however the clog of the nozzle during the printing in one of the drawbacks of this technology For these reasons, it is not common to use nozzles with diameters smaller than 200 µm for ceramic pastes. [61]

Until now, the resolution obtained by robocasting has been inferior to that obtained by the vat photopolymerization processes, where the resolution of the apparatus could be 40 µm in the the x-y plane and 10 µm in the vertical build direction[62]. Using this process, nanoscale resolution could also be obtained using the two-photon photopolymerization with the Nanoscribe machine. With respect to the geometry freedom, these processes are able to print features of highly complex shapes, however these features are difficult in robocasting technology due to the rheological properties of the inks. For this reason, the geometrical complexity of the this DIW technology is limited to simple shapes such as grids, cubes, cylinders, and single-walled vases. Nevertheless, the mechanical properties are compared with conventionally-produced ceramics. [37]

Regarding the FDC technology, some drawbacks related to the complexity of the pieces printed by robocasting could be improved if, during the construction, the extruded material is directly solidified once deposited, presenting higher mechanical properties when compared with the robocasting pastes. The filament could be loaded up to 60 vol.% of ceramic particles, which is a relatively high value. This opens the door to construction of ceramic pieces by a low-cost AMT, once it could be printed with a commercial FDM machine. In addition, these filaments are commercially available by Nanoe-Zetamix with ceramic loads of alumina, YSZ, and Zirconia Toughened Alumina. Recently, Xerion-Fusion Factory offered an automated process chain from filament to ready-to-use component, with the printing, solvent debinding, and sintering stations (for ceramic and metallic filaments).

In fact, the huge advantage of the material extrusion processes is the possibility to print multi-materials at a relatively low cost and, is perhaps, the most versatile AM technolgy in terms of materials with low resolution (until now).

Nowdays, the SLA and MIP-SLA tehcnologies are the ones which allow the construction of highly complex ceramic parts with mechanical properties comparable to parts made by traditional manufacturing. For examples, Lithoz offers Al_2O_3 parts with densities of 3.96 g/cm^3 and 4-point bending strengths of 430 MPa[54].Nevertheless, by using a ceramic suspension the maximum part size is limited for monolithic pieces, mainly due to the crack formation during the debinding of large pieces.[63],[64] The most thermal treatments, mainly the debinding process, represent the biggest drawback of these technologies, with debinding rates are around 0.2 ^{o}C·min^{-1}.[65]

Apart from the long thermal treatment, using these AM processes results in both geometry freedom and good mechanical properties, which opens the door to the design innovation of ceramic parts to create and/or improve functionalities from a point of view of the piece geometry.

Table 1.4 presents the advantages and limitations of the indirect processes, considering the state of art presented in this chapter.

Table 1.4 – Advantage and limitations of the AM processes for ceramic materials.

AM indirect process	Advantages	Limitations
Material extrusion	Good mechanical properties Multi-materials process Fast and low-cost technology Scalable	Resolution limited by the filament diameter Support material is needed
Material jetting	High accuracy of droplet deposition Good surface finishing Multi-material process	Limited to thin layers Support material is needed
Binder jetting	Complex designs Free of support/substrate Large build volume High print speed Relatively low cost	High surface roughness Poor mechanical properties May require post processing
Sheet lamination	Free of supports High speed Low cost Ease of material handling	Difficulties to produce hollow parts Material waste
Vat photopolymerization	Complex designs Good surface finishing Good mechanical properties High accuracy No supports are needed for paste-based systems	Long thermal treatments
Powder bed fusion	Complex designs Relatively inexpensive Small footprint Powder bed acts as an integrated support structure	High roughness of the surface Relatively slow High power required Finish depends on precursor powder size

Figure 1.26 shows the companies which commercialize AM machines for ceramic materials for high tech application (not for ordinary objects).

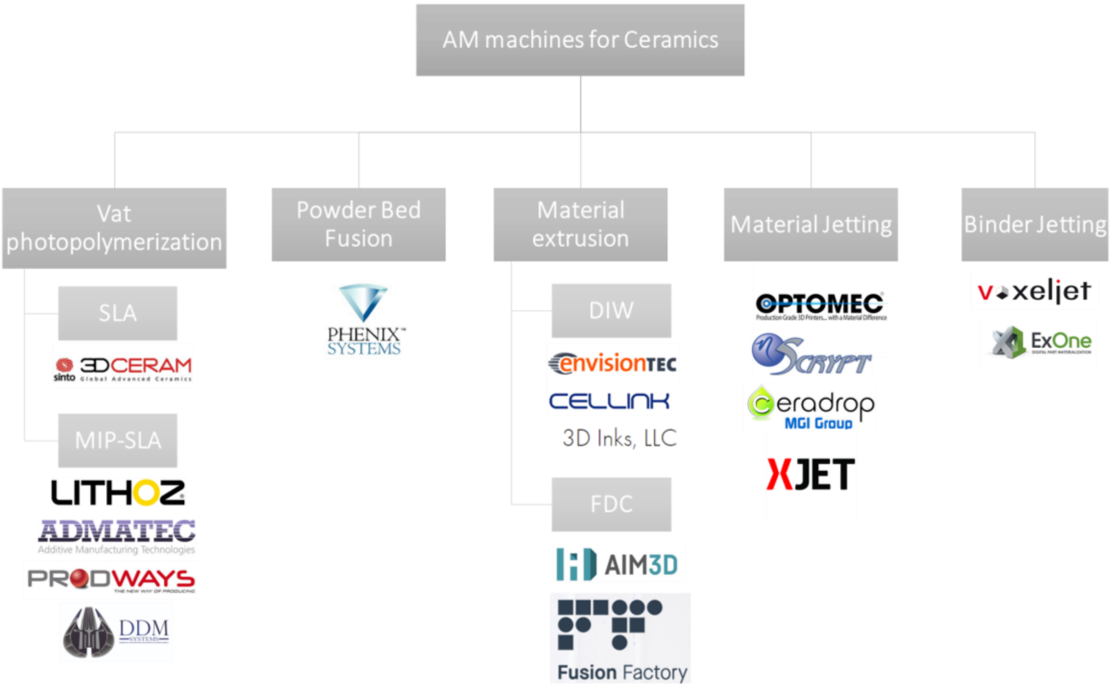

Figure 1.26 - Benchmarking of existent AM machines manufacturer for high performance ceramic materials

There are no commercially available machines for the Sheet Lamination and for the Direct Energy Deposition processes for ceramic applications. This fact is related to the limitation inherent to the technology in the case of Sheet Lamination. The Powder Bed Fusion processes are well implemented for polymeric and metallic materials, however it is much more complicated to use directly for ceramic materials, as seen before. The more promising technologies for ceramic material today are vat photopolymerization and material extrusion. In addition, material jetting could be used just for small pieces, and for multi-material printing.

1.5. MIP-SLA ceramic process

As shown previously, the technologies based on the vat photopolymerization processes are the ones where pieces with high complexity could be achieved with a high level of density and resolution. These processes give one more possibility to shape ceramic materials in the sense that the process step is practically the same as in the traditional suspensions-based techniques, such as wet pressing, slip casting, injection molding, gel molding, gel casting, and tape casting. As shown in Figure 1.27, the common steps of these technologies are based on the ceramic suspension preparation (formulation), shaping the green body, cleaning, the thermal treatment for the organic material removal (debinding), and the densification of the final part (sintering).

Figure 1.27 – Flowchart of ceramic manufacturing process based on suspensions.

In the case of AM methods, ceramic-based suspensions, the shaping step is performed by AM methods, increasing the range of geometrical possibilities. Along this work, each process step is described and analyzed for both material and machine perspective, resulting in three different chapters focused on the formulation of the ceramic suspension, printing, and thermal treatment of the printed parts.

As the MIP-SLA printer has a top-down configuration, the recoating of the layer along the printing process is achieved by a so-called deep dip system. [66] Under the influence of gravity, the liquid resin recoats the previous cured layer when the platform goes down. After this step, a recoating blade (wiper) is used to level the resin surface by sweeping the excess liquid resin. In this regard, by using this machine approach, the ceramic suspension must be fluid enough to ensure proper flow during the recoating step. Conventional liquid resins used in SLA machines usually have viscosities less than *5* Pa.s at low shear rates [66]–[68] which can be considered as the criterion for the further ceramic suspension formulations.

Apart from the viscosity, another important parameter is the solid load of the photocurable suspension. In order to avoid 1) deformations and cracking formation during the debinding process, 2) low dimensional shrinkage after the whole thermal treatment, and 3) to obtain homogenous and dense ceramic pieces after the sintering, the organic concentration must be minimized.[43],[69]. In this regard, the solid load should be higher than 40 vol.% [42], [43], [67], [68] However, in a highly loaded ceramic suspension the viscosity drastically increases, due to the interparticle attraction, thus a compromise must be achieved during formulation of the ceramic suspension.

The printing parameters are also related with the formulation, due to the interaction between the projected light with the ceramic particles and the photopolymer. At the same time, the defined parameters also influence the results after the thermal treatment.

The following scheme, shown in Figure 1.28, display the different stages of the process (which correspond to each results-related chapter) and the associated challenges, further explained and discussed throughout the dissertation.

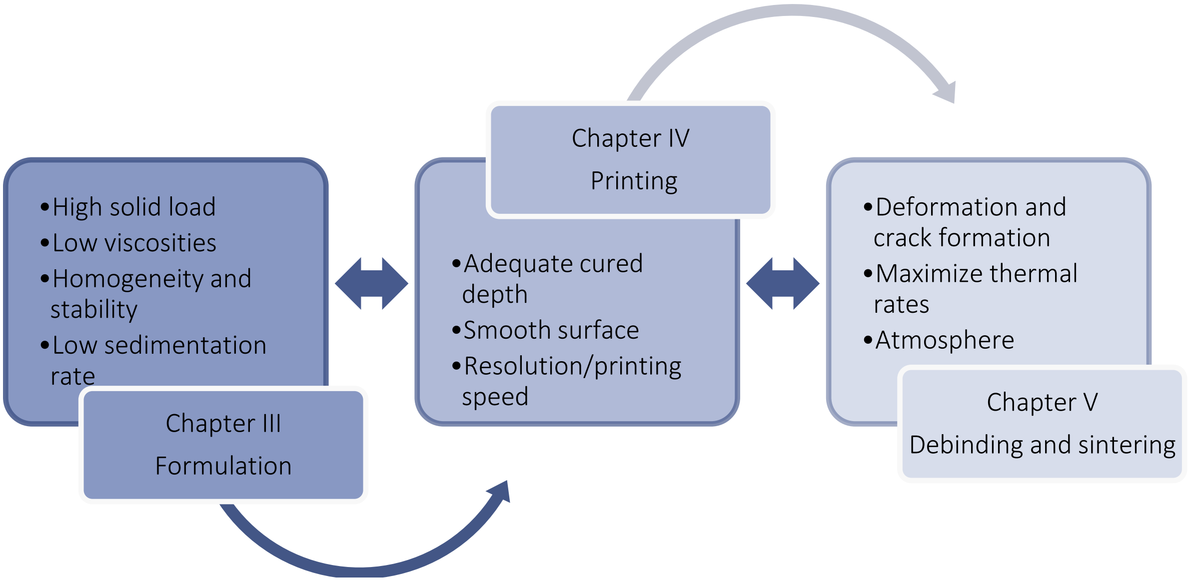

Figure 1.28 – Results related chapters with their associated challenges.

1.5.1. Traditional and AM processes

The traditional method used for complex shapes is Ceramic Injection Molding (CIM), where the forming cycle times could range from several seconds to several minutes, depending on the piece size.[70] A high production of pieces with the same geometry using vat photopolymerization processes are not competitive if they can be produced by CIM. Nevertheless, in AM processes, the platform can include a large number of parts and the cycle time per piece can be shorter (while it takes hours to construct). In addition, several geometries can be produced on the same platform, allowing for the production of highly customized pieces in just one printing process. Another advantage is for the piece re-design: even compared to a large production using traditional ceramic processes, AM reduces the time and mold cost for the re-design study.

Until now, the component shape was thought through regarding the existent technologies' capabilities; in this sense, AMT provides the possibility to re-design with less geometrical limitations which could improve the final performance. For example, a component which is formed by different pieces could be constructed as a whole piece, which reduces the assembling process of the different components and the issues related to the piece interfaces. In terms of weight, the piece geometry could be re-designed thinking about the weight reduction, maintaining or improving the performances with less material, resulting in a reduction of the cost of the material and of the weight of the final part.

1.5.2. Benchmarking of AM ceramic machines and materials

Table 1.5 shows the companies that are currently commercializing AM machines for ceramic materials, based on the vat photopolymerization process. All of them have their own materials with certain viscosities adapted to the technology. Almost all of them have customer-specific ceramic formulation services.

Table 1.5 - Benchmarking of existing companies which commercialize AM machines and materials based on the vat photopolymerization process.

Company	AM machine	Building area (X,Y,Z) mm	Commercial ceramic resins	Technology
3DCeram	CERAMAKER 100	100 x 100 x 100	Zirconia Silicon dioxide Silicon nitride Alumina Toughened Zirconia Hydroxyapatite Alumina Zirconia Customized service	SLA
	CERAMAKER 900	300 x 300 x 100		
Admatec	ADMAFLEX 130	96 x 54 x 120	Alumina Toughened Zirconia Hydroxyapatite Fused Silica Zirconium Oxide Aluminum Oxide Customized service	MIP-SLA with tape casting integration
Prodways	ProMaker V6000	120 x 150 x 150	Tricalcium Phosphate Hydroxyapatite Zirconia Alumina Customized service	MOVINGLight® ceramic 3D printing technology (MIP-SLA)
		120 x 350 x 150		
		120 x 500 x 150		
Lithoz	CeraFab 7500	76 x 43 x 170	Aluminum Oxide Zirconium Oxide Silicon nitride Tricalcium phosphate Customized services	Lithography-based Ceramic Manufacturing (LCM)-technology (MIP-SLA)
	CeraFab 8500	115 x 64 x 200		
Formlabs	Form 2	145 x 145 x 175	Ceramic Resin: silica-filled photopolymer	SLA
Tethon3D	-	-	Porcelite® Ceramic Resin Vitrolite® Glass-Ceramic Resin	FMIP-SLA SLA

Tethon3D is not a machine manufacturer but has two different ceramic resins which could be used in common and low-cost SLA or MIP-SLA machines. In 2018, Formlabs commercialized its first ceramic resin for their Form 2 machine. This resin has a high temperature resistance in comparison with the usual polymeric resins (up to 1000 °C). The highest temperature resistant material for this technology is High Temp Resin (Formlab), which has a heat deflection temperature (HDT) of 289 °C at 0.45 MPa. Nevertheless, there are many applications where this temperature resistance is not enough. In this regard, the commercialization of this ceramic resin represents a huge step for the implementation of this technology on the prototyping of functional components with affordable prices.

Among the ceramic AM manufacturers, 3DCeram, Admatec, Prodways, and Lithoz, there are differences in terms of printing strategies. 3DCeram has a top-down SLA configuration with a highly viscous paste, which allows printing without supports. Nevertheless, as the ceramic paste is too viscous, the time consumption for the cleaning of the printed pieces is higher when compared with a bottom-up configuration, where the pieces are not immersed into uncured material (in the case of Admatec and Lithoz). The Prodways system is similar to the 3DCeram one, the difference being the light projection which is based on the MIP-SLA concept. In addition, the projection could move (MOVINGLight®) allowing the printing of higher areas at a higher velocity compared with the 3DCeram system (if the platform is full of pieces). In the Lithoz and Admatec systems, the pieces are partially cleaned after the printing process, meaning that the cleaning process must be applied but not as meticulously as in the Prodways and 3DCeram systems. 3DCeram can obtain higher resolution than 300 µm, due to the cleaning process. Nevertheless, the high viscosity allows to increase the concentration of ceramic particles, resulting in less shrinkage and less materials to burn out during the thermal treatment. Admatec offers both advantages: cleanliness and high solid load. However, the bottom up approach could induce stresses on the ceramic part due to the separating movement from the bottom of the vat, something that does not happen in the top-down approach. The Admatec system integrates a tape casting system, which deposits the layer on a mylar carrier with a certain layer thickness; during the printing process the paste is polymerized in the desired zones and stacked on the previous layers; the uncured resin is recovered and could be reused for the next layers. This is a great advantage when compared with the other machines, since the recovering of the uncured paste is integrated in the printing process, resulting in a clean process. The viscosity of both cases (Lithoz and Admatec) must be lower than the previous ones for the layer recoating.

1.6. Low temperature co-fired ceramics and AMT hybridization

The Low Temperature Co-fired Ceramic (LTCC) materials are highly used for high frequency devices, required for high-speed data communications. The LTCC materials are glass–ceramic composites, where the main phase is a dielectric such as alumina which have a high sintering temperature (1650 °C). However, the addition of a glass phase to the dielectric material lowers the sintering temperature, below 950 °C, depending on the amount and type of the glass composition. In these materials, the main phase is the crystalline phase which makes a significant contribution to the dielectric properties. The addition of the glass phase lowers relative permittivity and increases the dielectric loss (loss tangent). Nevertheless, during the sintering, the glass recrystallizes to low loss phases and produces a low dielectric loss ceramic body. Thus, during the heat treatment, when the glass is transformed into a glass–ceramic material, not only complete densification should be obtained, but also sufficient crystallization must be achieved.[71]

In this regard, the low sintering temperature provided by the LTCC materials is one of the key issues of these materials when compared with the High Temperature Co-fired Ceramics (HTCC). The sintering process at low temperatures allows the fabrication of the embedded electronic components and transmission lines using highly conductive and inexpensive metals such as silver or copper with low conductive loss and low electrical resistance at high frequencies. In the case of HTCC materials, these metals can not be used since the sintering temperature must be lower than the melting point of the used metal. Apart from the low sintering temperature, LTCC materials have a lower dielectric loss at high frequencies when compared with polymeric materials or even with alumina, leading to a low loss of performance of the device. Furthermore, another important parameter is the dielectric constant - this must be low to achieve high speed transmission of signals.[72]

These electronic devices are commonly fabricated by multilayer ceramic substrate technology.[73], [74] The whole process is explained in Figure 1.29.

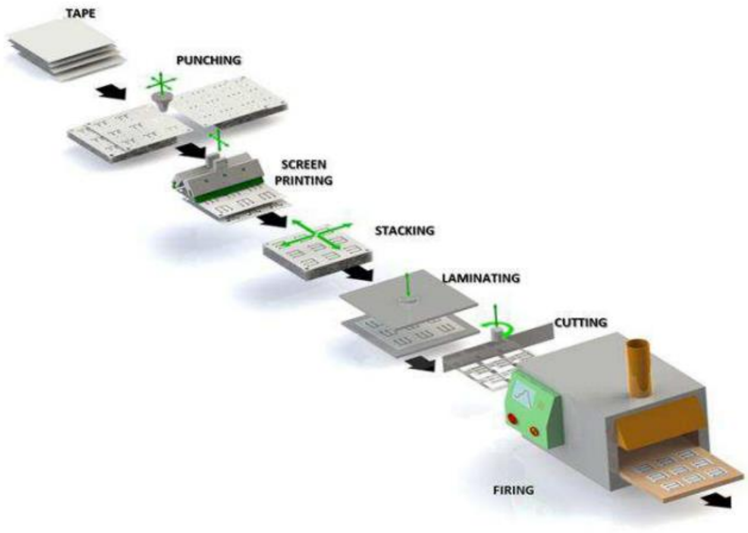

Figure 1.29 – Multilayer ceramic technology process. [74]

Currently, the design and manufacture of electronic components based on the LTCC process requires different technologies such as tape casting, screen printing, filling vias, stacking, cutting, and lamination, apart from the ceramic suspension preparation and the sintering of the green body. [74] Moreover, in the screen-printing step each re-design needs a new screen pattern, increasing the development costs and time-to-market. Thus, one possibility to improve this technological drawback can be AM of multi-material. For this to happen, the hybridization of AM technologies is a key strategy enhancing the individual technologies' capabilities.

Many efforts have been made during the last years in 3D printed electronics due to the possibility to manufacture high performance parts or build up parts with the electronics embedded on its structure. Furthermore, it could allow for the building up of highly customized 3D electronic devices. [75]–[77]

In this regard, the integration of multiple printing technologies in a single system has been investigated. For example, in 2010 F. Medina et al.[78]proposed the hybridization of a SLA system with a DIW, giving an enormous potential for the manufacture of complex geometries with embedded circuitry, which was optimized years later.[79] In 2016, Voxel8 announced the first low-cost commercial 3D printer combined with a pneumatic ink dispenser, a DIW system, with FDM of polymeric material. Voxel 8 has been ranked by the MIT Technology Review as the 17th smartest company in 2015 for having claimed to have created the first 3D electronic printer.

Although 3D printed electronics has appeared in the last years, their use has been mostly limited to printing electronics on a plastic substrate. Nevertheless, there are some AM manufacture companies which are now investigating multi-material printing to increase functionality, increasing its added value. 3DCeram have already announced the Ceramaker 900H, a hybridization of SLA and DIW systems. Ceradrop, another French company, presents some electronic devices based on LTCC materials printed by material jetting technologies in its products portfolio.

According to the SmarTech forecast, the AM of electronic devices with ceramic materials will be a reality in a few years. In this context, this work contributes to the development of suitable LTCC materials for MIP-SLA technology, demonstrating the proof of concept of the hybridization of MIP-SLA with an inkjet system. In this way, the number of steps in the manufacturing of electronic devices on ceramic substrate could be reduced by leveraging the benefits of AM. The time-to-market could be reduced once the whole device could be directly printed from the CAD, in a single hybrid machine. Moreover, smaller and more efficient new shapes could be obtained by taking advantage of freedom of design.

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