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Ceramics 3D printing: State-of-the-Art

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Bachelor's thesis

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Additive manufacturing (AM), or 3D printing, is a production method creating parts in a layer-by-layer fashion. AM enables an enhanced design freedom, being able to produce highly complex geometries. The use of ceramics in 3D printing is an increasing trend, and a high amount of research and development is focused on it. Ceramics have many different use cases because of their unique properties in comparison to metals and polymers. High strength, resistance to wear and corrosion as well as mostly being good electric and thermal insulators make ceramics a suitable material for use in aerospace, automotive, electronics and biomedical fields. This thesis explores the processes of ceramics 3D printing as well as their differences compared to traditional ceramics production. AM of ceramics include multiple different production methods, all with their advantages and disadvantages. In addition, the applications and future prospects of ceramics AM are studied.

Key words: Additive manufacturing, 3D printing, ceramics.

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1 Introduction

Ceramics have unique characteristics in comparison to other materials like polymers and metals. The high resistance to wear and corrosion, coupled with high thermal resistance and hardness makes ceramics lucrative options for many applications in extreme conditions. The same characteristics also make ceramics difficult to manufacture reliably and cost effectively [1].

There are multiple conventional ways of ceramics production, such as different forms of casting, moulding and pressing. While these methods have their benefits, they also come with limitations, such as limited complexity of possible parts, high costs of production and difficult and costly postprocessing [2]. Additive manufacturing (AM), also known as 3D printing, of ceramics includes multiple different manufacturing methods with different processes. While AM of ceramics can address some of the issues rising with conventional methods, AM also comes with its own limitations.

1.1 Aim, scope and structure of thesis

The goal of this thesis is to compare the conventional and additive manufacturing methods of ceramics, and to study the impact of additive manufacturing within ceramics applications. The processes of different AM methods and applications of them will be studied, and advantages and disadvantages will be addressed. This thesis seeks to address the following key research questions:

- What are the fundamentals of ceramics AM processes?
- What are the benefits of ceramics AM?
- What challenges and limitations do ceramics AM behold?

1.2 Methodology

This thesis was written as a literature review, utilising Scopus and ScienceDirect for finding suitable scientific literature. Material from journals and books from the past 5 years was prioritised, but no material older than 10 years was used, to ensure an up-to-date review. The use of artificial intelligence, in the form of Scopus AI, was used to find suitable material and to generate search phrases for wanted subjects.

2 Manufacturing of ceramics

2.1 Conventional manufacturing of ceramics

There are multiple conventional methods of manufacturing ceramics, such as different forms of moulding, casting and pressing. The ceramic material is in powder form mixed with a polymeric binder material. The binder can be in powder, liquid or wax form, depending on the forming method used. A dry powder mix of ceramic and binder material is used when pressing. The ceramic powder can also be mixed with a liquid binder, forming a ceramic slurry for shaping with slip casting and gel casting, while a wax-based binder is used for injection moulding. The production process of ceramics is generally divided into 6 steps, as depicted in Figure 1: making the powder, mixing the powder with a binder, forming, debinding, sintering and finally machining [2]. All steps, such as machining, might not always be necessary, depending on the desired precision and tolerances.

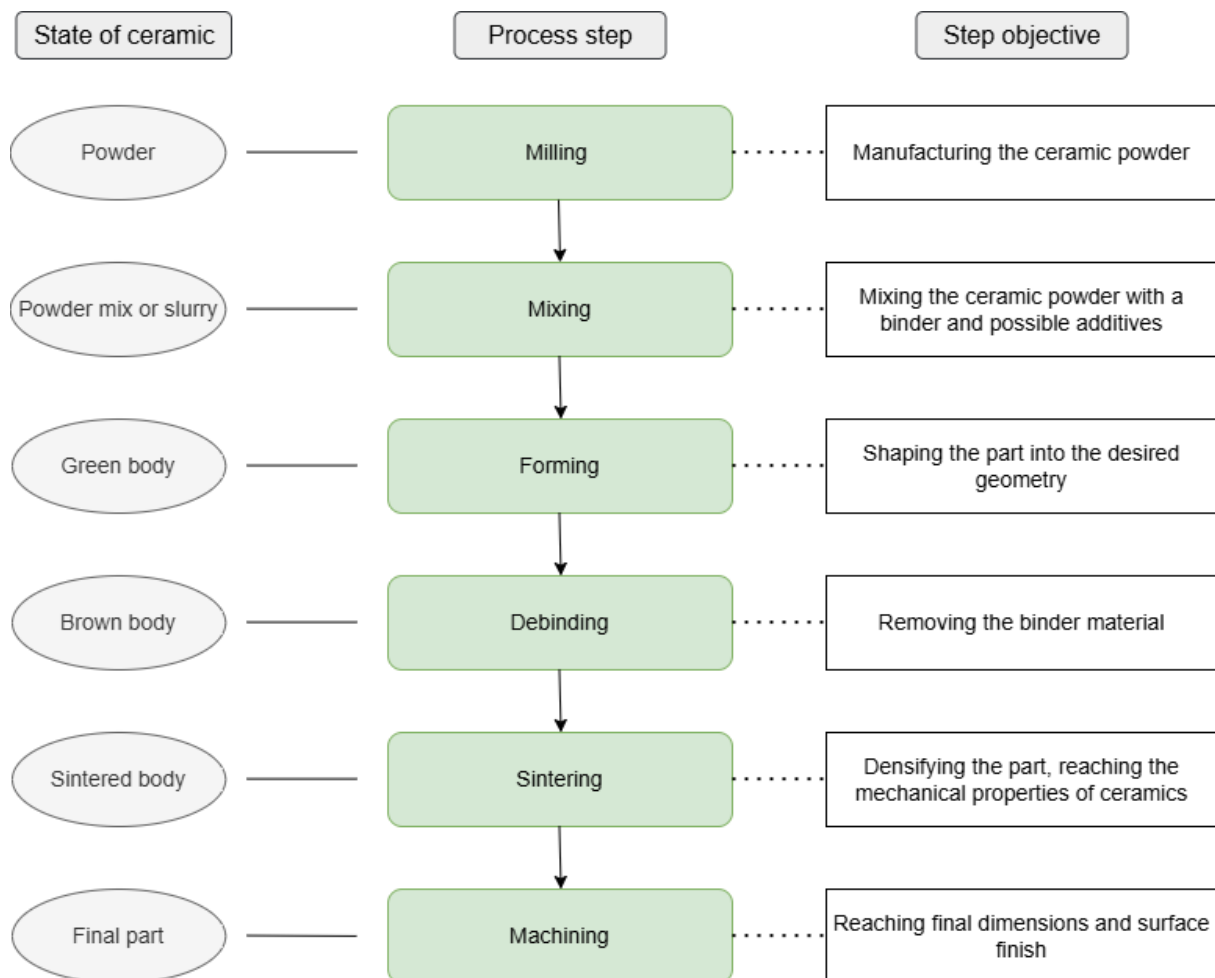


Figure 1. Flow chart of the production process of ceramic parts. Modified from ref. [2].

Debinding is the process of removing the binder material from the green body. The term “green body” refers to the ceramic part after it has attained its intended shape, before the process of debinding and sintering. Thermal and solvent debinding are the most common methods of debinding. Solvent debinding is based on dissolving and diffusion, and the green body is usually submerged in a liquid which dissolves the binder material [3]. Thermal debinding removes the binder by slowly heating it. The binding polymer slowly evaporates, and the resulting gas diffuses out of the part. If the heating is too fast, the gasses can't diffuse through the material quickly enough, and pressure will build up in the part, possibly leading to fractures [4]. After debinding the part goes through sintering at a high temperature, usually to around 70% to 90% of the melting point of the material. Sintering increases the density and the ceramic particles bond together, reaching the desired mechanical properties of the ceramic material [3], [5].

Conventional powder pressing (CPP), also known as dry pressing, is a process where dry powder is compacted in a mould to form into the desired shape, forming the so-called green body. Different forms of CPP can be distinguished by the method of compacting the powder, e.g. uniaxial and isostatic pressing. Uniaxial pressing involves a load being applied in one direction to compact the powder in the mould while isostatic pressing applies the pressure uniformly via a liquid surrounding the deformable mould. The CPP processes are considered to be the simplest production methods of ceramics, and are thus widely used, but limited by the simple geometries that can be achieved. Because of the lack of complexity in possible parts, machining of the green body might be necessary [6].

In high pressure injection moulding of ceramics, the feedstock made up of a wax-like polymer and ceramic powder is fed into the barrel of the machine by a screw. The feedstock is heated, typically to 130-200°C, where it becomes a semi-fluid mass. The feedstock is then forced into the mould cavity and a pressure of 50-150 MPa is held until the part has cooled, usually around 10 to 300 seconds later, depending on the volume of the moulded part. The moulded part is then released from the mould and debinded and sintered. The most common debinding process consists of a solvent debinding to remove soluble binder and create porosity after which a thermal debinding takes place. The porosity created by the solvent helps the remaining polymers to diffuse easier during the thermal debinding process [7].

Different forms of casting ceramics, such as slip casting and gel casting use liquid and gel-like binders, respectively. The mould in slip casting is made of a porous plaster, and when the

ceramic-polymer slurry is poured into the mould, the liquid is absorbed into the edges of the mould, creating a coating of ceramic particles on the inside walls. In contrast, gel casting uses a non-porous mould, where a ceramic-polymer mix is poured. The polymer is then solidified through either thermally or chemically induced gelation [6]. The curing can be done in a vacuum to ensure there are no air bubbles trapped in the slurry. The gelled part is then removed from the mould and taken to sintering. Debinding is not necessarily needed with some biopolymers because of the small amount needed to achieve proper strength to the green body. Since gel casting is a relatively low temperature process (usually no more than 80°C), the range of materials for the mould is large, including metals, plastics and wax-like materials. For complex shapes the removal of the gelled part can cause issues, so the use of softer materials for the mould that can be dissolved, molten or broken off can turn out to be the most suitable option [8].

2.2 Additive manufacturing of ceramics

Additive manufacturing, commonly also called 3D-printing, is a production method in which an object is manufactured based on a three-dimensional Computer Aided Design (CAD) model by adding material in layers on top of each other. The model is sliced into thin slices by computer software into a format that the 3D-printing apparatus can decipher [9]. Since its inception in the 1980s, AM has evolved from a method used mainly for prototyping to a viable manufacturing method with a plethora of use cases [10].

There are many different methods of AM, providing different solutions to how the desired part is built. When it comes to 3D printing ceramics, the main methods are stereolithography (SLA), powder bed fusion (PBF), material extrusion (ME), binder jetting (BJ) and directed energy deposition (DED) [11]. Each method has its own set of properties, including material compatibility, resolution of possible parts and speed of manufacturing [1].

The AM process can be either a single- or a multi-step process. In a single-step process the manufactured part gets both its intended geometrical shape and basic material properties at once. In a multi-step process the object first gets its shape, forming a green body, after which additional treatment, such as debinding and sintering, is needed to gain the desired material properties. The debinding and sintering process causes shrinkage of the part, which has to be taken into consideration when planning and designing the part for a multi-step AM method. The only methods of AM to achieve single-step ceramics production are PBF and DED [11].

2.2.1 Stereolithography

Stereolithography was the first commercialised form of AM and is a type of Vat photopolymerization (VPP), which is a process where radiation sensitive liquid polymers, known as photopolymers, react to provided radiation and solidify. The process directs radiation to the photopolymer in specific patterns corresponding to the desired object's cross sections, curing layers onto each other, as depicted in Figure 2. A platform is lowering as layers are added, making sure the top of the object always remains just below the surface of the resin. SLA, like most VPP methods, uses an ultraviolet (UV) laser to harden the liquid resin [9].

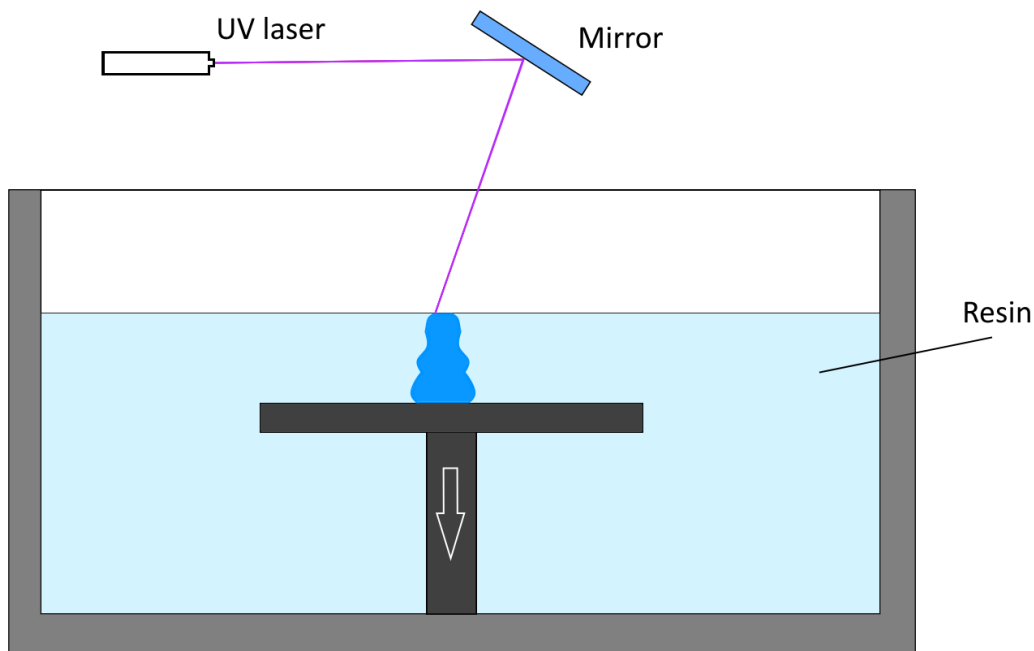


Figure 2. Model of SLA working principle.

AM of ceramics can be achieved with SLA by using a ceramic-resin slurry, made of a photosensitive resin, ceramic powder and dispersant. The dispersant makes sure the ceramic powder is mixed evenly in the resin. The resin is cured by the UV laser, creating a polymer cross-linked network, forming the ceramic particles to a 3D object, the so-called green body. The green body then must undergo post processing in the form of debinding and sintering at high temperatures to obtain the desired properties of ceramics [5].

SLA can achieve high resolution and surface finish, but is limited by the need of extensive post processing compared to other AM technologies [1].

2.2.2 Powder bed fusion

In the PBF process, a thin layer of powder is bonded by a high-energy source, after which a new layer of powder is spread by a roller or blade [12], as shown in Figure 3. The energy source used to bond the powder divides PBF technology into two main categories: electron beam melting and laser powder bed fusion. As electron beam melting needs the building material to be electrically conductive, and most ceramics are good electrical insulators, laser PBF is the method mostly used with ceramics. A few different processes fall under the laser PBF term, including processes such as selective laser sintering (SLS) and selective laser melting (SLM) [13].

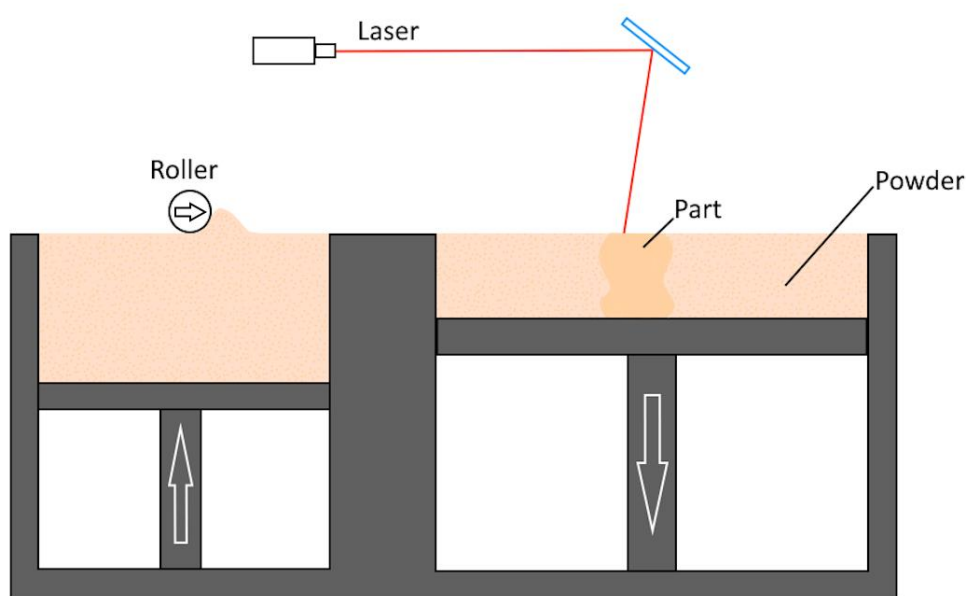


Figure 3. Model of PBF working principle.

In the SLS process the laser heats the powder to around 70% of its melting point, sintering the material. The sintering process is based on solid-state diffusion of the powder particles across grain boundaries, forming strong bonds between adjacent particles. Once the roller/blade spreads a new layer of powder onto the bed, the laser sinters the next cross section onto the object. As opposed to SLS, SLM heats the powder to its melting point, followed by rapid cooling, forming solid layers of ceramic material. As SLM heats the particles to a higher temperature, it is a more energy intensive process [5], [14].

The high melting point of ceramics causes challenges for the PBF process, needing high powered lasers to reach such temperatures. The rapid heating and cooling of the layers also causes issues, leading to internal stresses and possible cracking of the ceramic material. The

low thermal shock resistance of ceramics makes them challenging materials to use in PBF, but the single-step nature of the process makes it a lucrative option [1].

2.2.3 Material extrusion

Material extrusion is one of if not the most recognizable forms of AM. The core principle of ME is the continuous feeding and heating of material through a moving nozzle at a temperature just above the melting point of the material, solidifying as soon as it has been extruded [3]. Figure 4 shows the three types of ME, classified by the method of extrusion used: plunger-, filament- and screw-based extrusion.

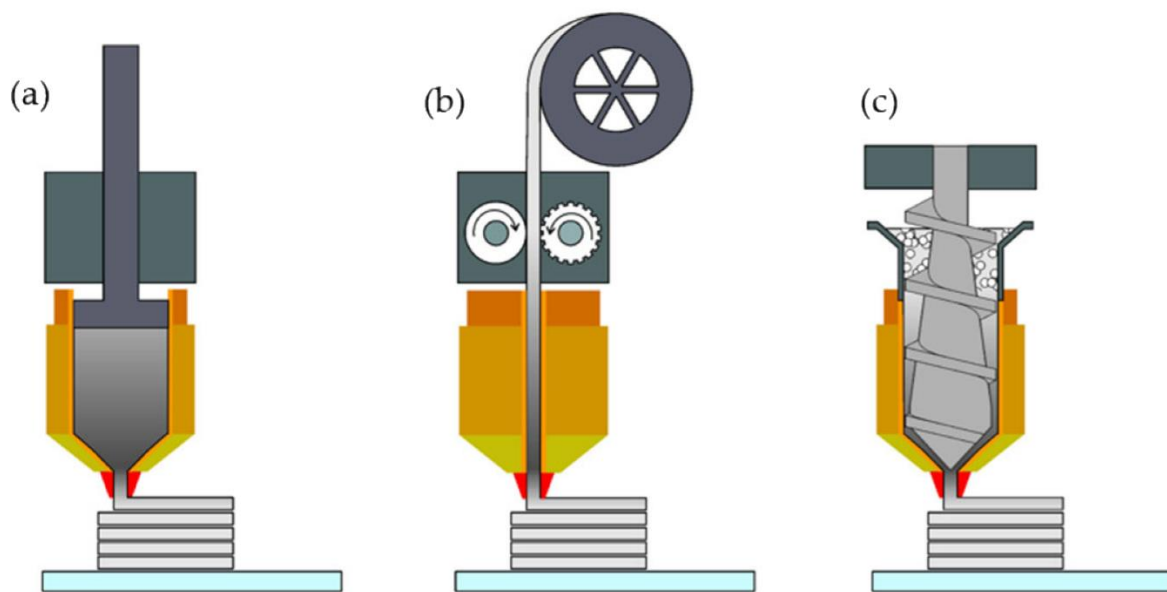


Figure 4. Three methods of material extrusion: a) plunger-based b) filament-based c) screw-based. Reproduced from ref. [15].

Ceramics can be printed with a polymer binder. Compared to other AM methods used for ceramics, ME benefits from a fast and simple process and low investment costs to achieve strong green bodies. However, limitations emerge with the resolution of small parts and a long post-processing time required for larger geometries [16]. The nozzle size directly affects the resolution achievable by ME. The diameter of the nozzle is the smallest possible shape that can be achieved, but a smaller nozzle leads to a longer fabrication time.

In contrast to the powder bed-based AM techniques, where the part is generally supported by surrounding powder, parts manufactured by ME often need support structures when printing complex or overhanging geometries[6].

2.2.4 Binder jetting

Binder jetting, like PBF, is a powder-based AM method. Figure 5 visualises the BJ working principle, where a liquid adhesive is sprayed onto a bed of powder to bind the powder together, and onto the previous layer. Like in the PBF process, the build platform is lowered, and a new layer of powder is spread on the bed by a roller or blade. The speed of manufacturing in BJ can be increased by utilising multiple nozzles spraying the adhesive at once, completing each layer more quickly [9].

In contrast to PBF, BJ needs post processing in the form of debinding and sintering before reaching its final properties [5]. BJ is a suitable for virtually any powdered material, meaning it has one of the widest ranges of possible materials to print with, especially in the realm of ceramics [17]. The powder used in BJ has relatively larger particle sizes than with the PBF method. This leads to limited resolution, rougher surface finish and a difficulty to achieve fully dense final parts. Post processing steps can be taken to increase the density of the parts, however, at the expense of additional labour, manufacturing time and overall costs [2].

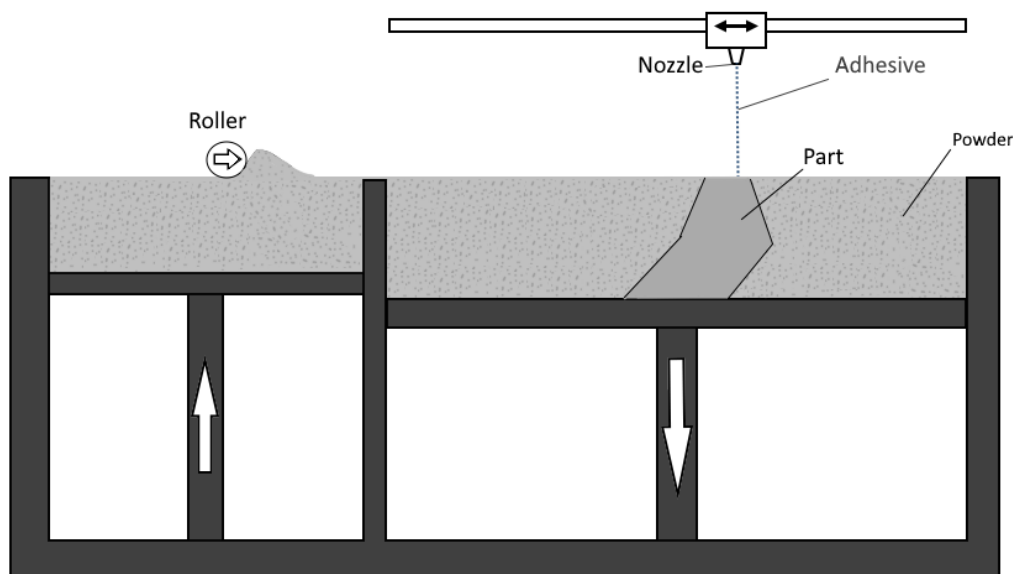


Figure 5. Working principle of BJ visualised.

2.2.5 Directed energy deposition

DED is in addition to PBF the only AM process capable of single-step ceramics production. DED directs energy, usually in the form of a laser or electron beam to melt the printing material as it is being deposited. The material can be delivered either as a powder or a wire.

As Figure 6 depicts, lasers are utilized for ceramics and a ceramic powder is deposited into the melt pool the laser provides [9].

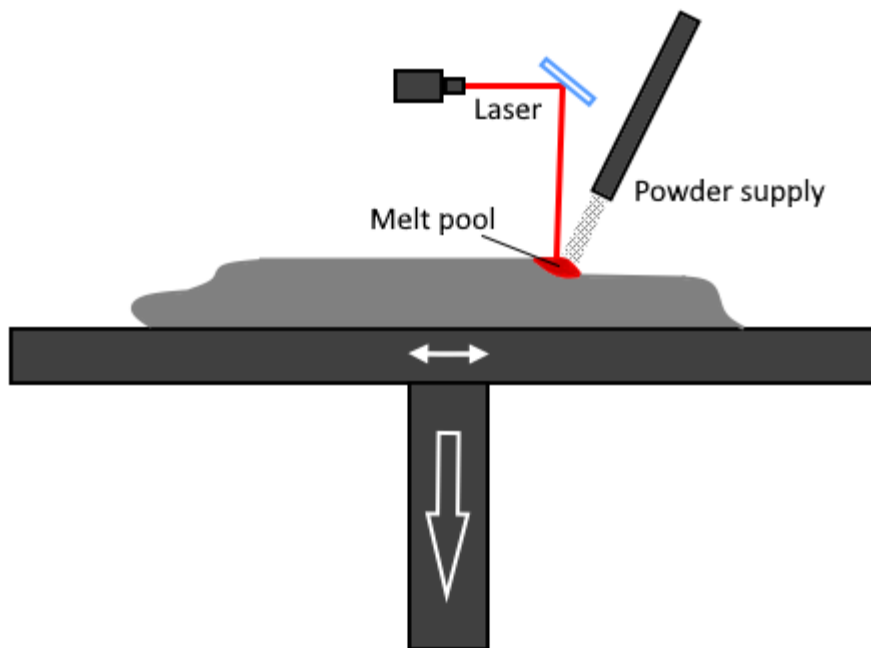


Figure 6. Schematic of DED working principle.

In comparison to SLS and SLM, DED has a lower precision and can produce less complicated parts. In addition, the surface finish is poorer than what can be achieved with the PBF process, leading to DED being utilized with larger, less complex parts [11].

2.2.6 What ceramic materials can be printed?

The different methods of AM have different material selections when it comes to ceramics.

Error! Reference source not found. Table 1. The most common ceramic materials for each AM method. shows the most common ceramic materials used for each AM method. The most common ceramic materials for AM are alumina (Al_2O_3), silica (SiO_2), zirconia (ZrO_2) and silicon carbide (SiC). Composites of these materials are also often used to enhance wanted properties [1], [2], [14].

The most research for ceramic materials for AM has been done for alumina, mainly for its versatility and low price, and zirconia because of its high toughness and wide range of industrial applications. The relatively low sintering temperature of these ceramics also make them desirable for production [2].

Table 1. The most common ceramic materials for each AM method.

AM method	Materials	References
SLA	Alumina (Al_2O_3) Silica (SiO_2) Zirconia (ZrO_2) Silicon carbide (SiC) Titanium carbide (TiC) Silicon oxycarbide ($SiOC$) Silicon nitride (Si_3N_4)	[1], [14]
PBF	Alumina (Al_2O_3) Silica (SiO_2) Zirconia (ZrO_2) Silicon carbide (SiC) Tri-calcium phosphate (TCP)	[1],[2],[14]
ME	Alumina (Al_2O_3) Silica (SiO_2) Zirconia (ZrO_2) Silicon nitride (Si_3N_4)	[1],[14]
BJ	Alumina (Al_2O_3) Silica (SiO_2) Zirconia (ZrO_2) Magnesia (MgO) Calcium silicate ($CaSiO_3$) Calcium phosphate (CaP)	[1],[2],[14],[18]
DED	Alumina (Al_2O_3) Zirconia (ZrO_2) Silicon carbide (SiC) Magnesia (MgO) Titanium diboride (TiB_2)	[1],[2]

2.3 Conventional or additive manufacturing?

Both the traditional manufacturing methods of ceramics and the various forms of AM have their advantages and disadvantages. The selection of manufacturing method largely depends on the complexity and requirements of the part and the volume of production. The cost of manufacturing is always a critical factor when determining what method to use.

In general, AM is more cost effective when manufacturing small volumes, or when the complexity of the part exceeds a certain point. As shown in Figure 7, the cost per part for AM processes is not particularly affected by the amount of parts manufactured, while the very

high cost of the moulds used in injection moulding lead to high volumes being necessary for the injection moulding process to be more viable. The complexity of the part does not affect the cost of an AM part much either, since no modification of tools or machinery is needed when increasing complexity. In injection moulding however, increasingly complex shapes often need additional steps in the process, like extremely expensive machining. This gives AM a vastly enhanced design freedom with no added cost [2].

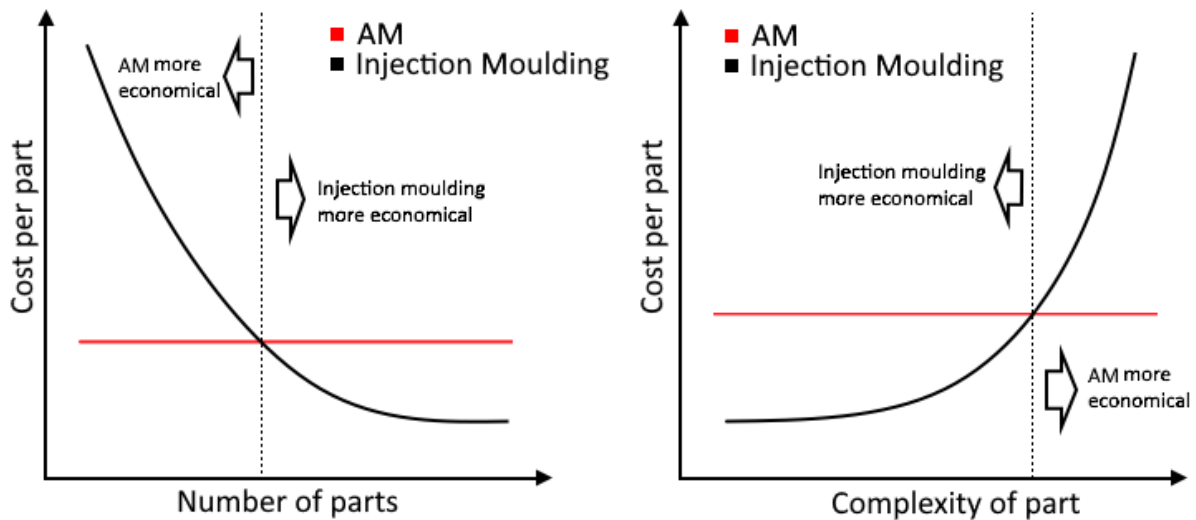


Figure 7. Graphs showing the relationship between cost of AM and Injection moulding with increasing production volume (left) and increasing complexity of part (right). Modified from ref. [2].

In contrast with injection moulding, the moulds of casting methods are relatively inexpensive, such as the plaster moulds used in slip casting. However, the limitation in part complexity of slip casting gives an advantage to AM in those circumstances [2]. For gel casting of complex ceramic parts, the sometimes-needed sacrificial nature of the mould makes it a challenging method to scale [6]. The dry pressing methods are the most used conventional techniques even if the wet powder processes offer the ability to make complex geometries and flexibility in feedstock handling. The removal of the moisture from the wet powder processes however, is energy intensive, time consuming and carry a higher proneness to defect generation [14].

Since AM is a mould-free manufacturing technique, the lead time, that is the time from the start of product design to a ready product, is much shorter than with the conventional manufacturing methods. The freedom in design and not needing moulds is also extremely beneficial in applications where customisation or personification is important [2].

3 Applications of ceramics AM

Ceramics have dramatically different properties compared to metals or polymers, which make them unique in certain applications. Advanced ceramic materials have exceptional characteristics like high mechanical strength, hardness, great wear and corrosion resistance as well as low thermal and electrical conductivity. These properties makes AM of ceramics lucrative in industries like biomedical, aerospace, automotive and electronics [1], [14].

3.1 Biomedical applications

The high biocompatibility, coupled with great wear resistance of ceramics make them good candidates for biomedical applications. The unique anatomy of each patient makes AM a suitable method for creating patient-specific implants, such as hip prosthetics. The quick lead time of the AM process ensures the patient gets faster care, coupled with the reduced cost of AM in comparison to traditional production methods, especially of customised or personalised parts. Especially alumina and zirconia ceramics are widely used in biomedical applications, because of their high strength and bioinertness, meaning they don't react with biological tissue [14]. Parts that mimic bones do not often need to be fully dense, making them easier to make by AM.



Figure 8. 3D printed dental crowns made of zirconia. Green body (right), after debinding (centre) and final sintered part (left). Reproduced from ref. [19].

Dental applications also benefit from the customisability of AM parts. Parts such as dental implants, crowns and veneers are well suited for AM, and not only is the demand of

mechanical properties of these applications, but also the demand for aesthetically pleasing parts, met by ceramics[12], [20]. Figure 8 shows a zirconia dental crown in three stages of the 3D printing process: the green body, the part after the debinding process and the final sintered part.

3.2 Aerospace & automotive applications

High temperatures and stresses in aerospace and automotive applications make ceramics good options with the addition of their light weight in comparison to metallic counterparts. AM enables improvements in part efficiency and easy manufacturing of parts like complex turbine and aerofoil components with internal cooling channels, reducing costs and shortening production times [14]. The properties of ceramics and the precision achievable by AM result in parts that can perform at a higher level in extreme conditions. The complexity of parts directly affects the cost of conventional production methods, but with AM, the difficulty of manufacturing can largely be ignored in the design process, as it does not drastically affect the production cost. Instead, engineers can focus on the performance of parts [21]. Figure 9 shows a turbine produced with the SLM method out of a zirconia-alumina mix.



Figure 9. Turbine of a turbocharger made with SLM out of 80% zirconia / 20% alumina. Reproduced with permission from ref. [22]. Copyright 2013, Emerald Group Publishing Limited.

3.3 Electronics applications

In electronics, AM of ceramics can be crucial for different reasons. The traditional manufacturing of Printed Circuit Boards (PCB) is time consuming and involves very repetitive milling and etching, while generating significant waste. The use of AM makes this process much easier and produces less waste, while enabling companies to produce PCBs in-house, avoiding supply chain issues. Since electronics are a very quickly evolving industry, rapid prototyping plays a key role in innovation [21].

4 Research & future of ceramics AM

Ceramic AM can achieve relatively good properties, such as density, mechanical properties, surface finish and complexity of shapes, compared to their traditionally manufactured counterparts. Research and development are still needed to overcome issues regarding scalability and production of bigger, fully dense parts [6].

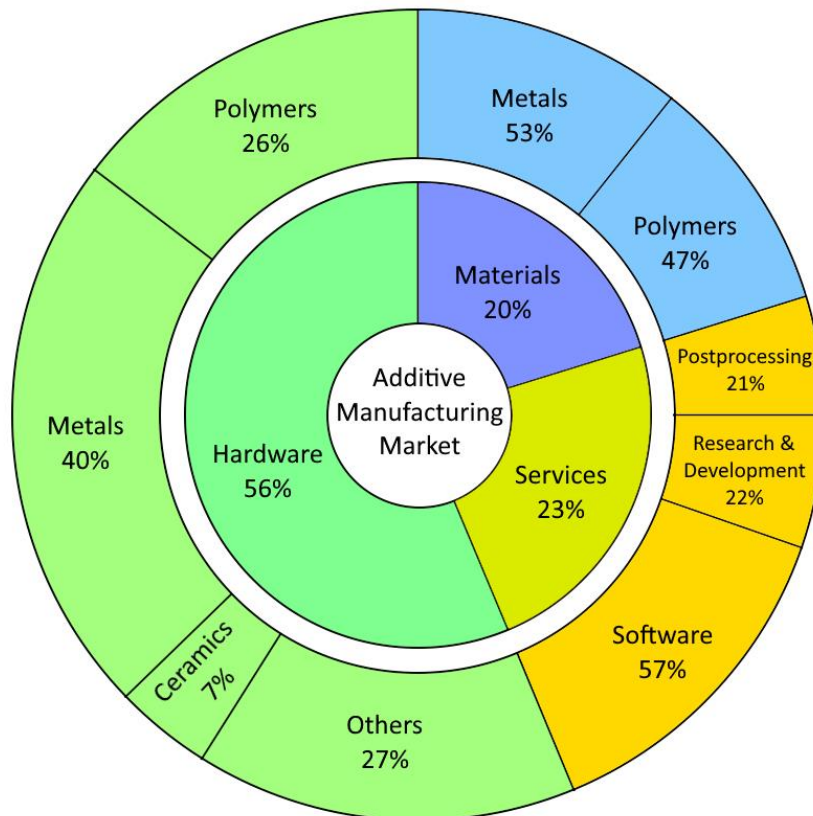


Figure 10. Diagram of the total AM market divided into sectors: hardware, materials and services (inner circle), and segments (outer circle). Modified from ref. [6].

As seen in Figure 10, ceramics only occupy a small fraction of the total AM market, only having a residual market share in the materials sector and a small sliver of the hardware sector. The hardware sector includes mainly the 3D printing machinery, while the services sector includes software, research and development as well as post processing [6]. The graph in Figure 10 may indicate a strong opportunity for research, development and new business endeavours within ceramic AM.

Research with different parameters of ceramic AM is done continuously. The challenges can be divided into relating to preprocessing, processing and postprocessing. Preprocessing challenges largely focus on the powders and slurries used in different AM processes. Choosing the right binder and particle size of the ceramic powder have big implications for

the final product. The research and selection of binder material and composition must be done for each material separately, since a slurry composition working with alumina might not work with SiC. Processing challenges, including tolerances, part size and support structures, are unique to each manufacturing method. Printing functional parts has been held back by software, since most slicing software used only accounts for shape, and not other parameters. Postprocessing challenges might be the most important ones when it comes to manufacturing competitive parts compared with traditional methods. Cracking and warping are common with 3D printed ceramics, and postprocessing steps often require long times. Longer debinding and sintering processes often lead to better, more predictable results, but lead to higher overall costs [14].

The total market for ceramics AM is estimated to reach around 3.7 billion USD in the year 2028, showing exponential growth. This would account to an around 14 times increase from a 2020 valuation of around 268 million USD. When dividing the market into four segments: materials, parts, services and hardware, the estimated growth rate of each segment is different. Until 2028, the market segment including printed parts is expected to have the strongest growth (around 30 times its 2020 valuation), utilizing the knowledge from metals and polymer 3D printing, while the services segment is expected to realise the slowest growth of the sectors (around 5 times its 2020 valuation). Materials and hardware segments are expected to be around 10 times their 2020 valuations in 2028 [6].

5 Conclusions

Conventional manufacturing methods of ceramics have many advantages like reliability, scalability and ease of use. Limiting factors, such as rapidly rising costs when increasing complexity and high production volumes needed for cost effectiveness, leaves a market gap for additive manufacturing.

AM of ceramics includes multiple different production methods, such as stereolithography, powder bed fusion, material extrusion, binder jetting and directed energy deposition. Each method has its own process parameters and advantages, but also disadvantages. The PBF and DED methods are particularly studied because of their single-step nature, enabling production of ceramic parts in a single process, without the need for postprocessing like debinding and sintering. While the different methods of ceramics AM are promising, there has not yet been large-scale industrial adoption of the technology. Difficulties in achieving reliable, fully dense parts hinder the adoption of AM. Ceramics AM can be implemented in fields such as aerospace, automotive, biomedical and electronics. The high stress, unique and complex shapes as well as need for biocompatible materials give ceramics AM a good advantage.

The ceramics AM field has seen exponential growth in past years, which is expected to continue. While ceramics still occupy only a small fraction of the total additive manufacturing market, it is expected to gain more market share and find more applications as the technology advances.

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