

Title

Additive Manufacturing of Ceramics: A Review

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Abstract

Additive manufacturing (AM) of ceramics is coming to an era where the first industrial applications are becoming economically profitable. This review paper provides a survey of AM methods reported in literature to shape ceramic components. It demonstrates that AM produced ceramic parts that have no cracks or large pores, have mechanical properties close to conventionally produced ceramics. Crack- and pore-free ceramics can be manufactured by optimizing the AM process parameters or performing extra densification steps after the AM process. It is also advisable to incorporate colloidal processing techniques in the AM process. At last, the paper demonstrates that, especially for AM of ceramics, the multi-step indirect AM processes are more appropriate to shape different types of ceramics, while to single-step direct AM processes can produce ceramic parts more rapidly.

Keywords

Additive manufacturing, ceramics, selective laser sintering®, selective laser melting, stereolithography

1. INTRODUCTION

The ISO/ASTM 17296 standard on Additive Manufacturing (AM) Technologies defines AM as the “process of joining materials to make objects from three-dimensional (3D) model data, usually layer by layer, as opposed to subtractive manufacturing and formative manufacturing methodologies.”¹ According to the standard, 7 types of AM processes can be differentiated: material jetting, material extrusion, direct energy deposition, sheet lamination, binder jetting, powder bed fusion and vat photopolymerization (Table 1). These 7 AM technologies can all be applied to shape ceramic components, starting from usually submicrometer sized ceramic powder particles.

There are basically two different categories of AM process according to the ISO/ASTM standard: (i) the single-step processes (also called ‘direct’ processes), in which parts are fabricated in a single operation where the basic geometrical shape and basic material properties of the intended product are achieved simultaneously and (ii) the multi-step processes (also called ‘indirect’ processes), in which the parts are fabricated in two or more operations where the first typically provides the basic geometric shape and the following consolidates the part to the intended basic material properties. Most of the AM processes to shape ceramics are multi-step (indirect) processes, which make use of a sacrificial binder material to shape ceramic powder particles. This binder is usually removed in a subsequent ‘debinding’ furnace treatment. The only single-step processes to shape ceramics are direct energy deposition and single step powder bed fusion. The latter process comprises Selective Laser

Melting (SLM) and single step Selective Laser Sintering® ('direct' SLS®, in contrast to 'indirect SLS®').

Powder bed fusion processes are defined as “*additive manufacturing process in which thermal energy selectively fuses regions of a powder bed*”¹. During powder bed fusion different consolidation phenomena, i.e. binding mechanisms, can be distinguished². Generally, the thermal energy irradiating the powder particles comes from a laser beam or an electron beam. However, to the best of our knowledge, electron beam processes (i.e. Electron Beam Melting, EBM) are only investigated for metal-matrix composites³ and not for pure ceramic materials. As depicted in Table 1, the thermal laser energy irradiating the powder particles, can initiate either fully melting of the powder particles, partial melting of the powder particles, solid state sintering of the powder, a chemical reaction of the powder particles, or a gelation reaction (i.e. the formation of a three-dimensional network that entraps the powder particles). If the powder is fully melted by the laser beam, the process can be categorized as Selective Laser Melting (SLM). All other laser based powder bed fusion processes can be categorized as Selective Laser Sintering® (SLS®) process.

In literature, different layer deposition systems can be distinguished to process ceramics through powder bed fusion, differentiating conventional deposition systems, slurry based deposition systems (i.e. a slurry coater, slurry sprayer, aerosol sprayer or electrophoretic deposition) and ring blade deposition systems (Table 1).

In this review paper, the different AM technologies to produce ceramics are detailed in section 2. Section 2 differentiates the powder bed fusion processes

further according to single step / multi-step processes and binding mechanisms to fuse the powders. The quality of the ceramic parts produced by AM technology and the consequences of producing ceramics through single step and multi-step AM technologies are discussed in section 3.

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Single step			Multi-step													
Directed energy deposition	Powder bed fusion		Vat photo-polymerization		Material jetting	Material extrusion		Sheet lamination	Binder jetting	Electrophoretic deposition		Electro-photographic printing				
multi-step / single step	Powder bed fusion															
	single step											multi-step				
binding mechanism	full melting			partial melting						solid state sintering	chemically induced binding			partial melting		gelling
powder deposition mechanism	conventional	slurry coater	aerosol assisted spray deposition	conventional	slurry coater	slurry sprayer	ring blade	electrophoretic deposition	conventional	conventional	slurry coater	ring blade	conventional	slurry coater	slurry coater	

Table 1: Overview of AM processes to shape ceramics.

2. ADDITIVE MANUFACTURING TECHNOLOGIES TO PRODUCE CERAMICS

2.1 Material jetting

The material jetting methods, defined as “*additive manufacturing processes in which droplets of build material are selectively deposited*”¹, that can be used to shape macroscopic ceramic parts are:

*(Direct) inkjet printing (IJP)*⁴⁻⁷

During (direct) inkjet printing (IJP), a suspension containing ceramic powder particles is deposited (directly) from a print nozzle. The print nozzle selectively

deposits individual droplets of the suspension onto a substrate. Upon contact, the droplets undergo a phase change, creating a solid part.

Aerosol jet printing (AJP)^{8, 9}

Instead of using individual liquid ink droplets as printing media (cf. IJP), an aerosol jet printer uses a focused aerosol, i.e., a suspension of fine ceramic particle containing droplets in a gas.

2.2 Material extrusion

The material extrusion methods, defined as “*additive manufacturing process in which material is selectively dispensed through a nozzle or orifice*”¹, that can be used to shape macroscopic ceramic parts are:

*Fused deposition of ceramics (FDC)*¹⁰⁻¹²

Fused deposition of ceramics (FDC) is also known as multiphase jet solidification (MJS) or extrusion free forming (EFF). Ceramic particles are first densely (up to 60 vol%) dispersed into a thermoplastic (or wax) filament. Layer by layer, the flexible filament is partially melted and extruded from a moving deposition head onto a static worktable.

*Robocasting*¹³⁻¹⁶

In robocasting, also called three-dimensional fibre deposition (3DFD¹⁷) or Micropen¹⁸, a concentrated sol is extruded through a nozzle to form a filament that is directly deposited in a controlled pattern to assemble complex, three-dimensional structures in a layer-by-layer sequence. In contrast to FDC, no polymer material is (partially) melted. A special kind of robocasting technique is Freeze-Form Extrusion Fabrication (FEF). During FEF, a suspension or colloidal gel is deposited and frozen on a cooled substrate¹⁹. In this way,

alumina samples could be produced by dr. M.C. Leu et al.^{20, 21} (Missouri University of Science and Technology).

2.3 Directed energy deposition

The direct energy deposition methods, defined as “*additive manufacturing processes in which focused thermal energy is used to fuse materials by melting as they are being deposited*”¹, used to shape macroscopic ceramic parts can be categorized as follows:

*(Traditional) directed energy deposition*²²

Direct energy deposition is also widely known as laser cladding. The printing head of a directed energy deposition system consists of a nozzle which feeds ceramic powder particles to the focal point of a laser beam. The powder melts and solidifies on a substrate.

*Hybrid fused deposition modelling – Directed energy deposition*²³

At the University of Birmingham, Wang et al. managed to combine the FDM and the directed energy deposition process into a hybrid process. Ti6Al4V-TiC composite parts could be fabricated by feeding powder (TiC) and wire (Ti6Al4V) material into the focus of a CO₂ laser.

2.4 Sheet lamination

Sheet lamination processes, also called Laminated Object Modelling (LOM) processes, are defined as “*additive manufacturing process in which sheets of material are bonded to form an object*”¹. Basically, two LOM technologies can be differentiated: traditional LOM and Computer-Aided Manufacturing of Laminated Engineering Materials (CAM-LEM).

Traditional LOM

The traditional LOM process consists of a system which deposits green ceramic tape casted layers. These layers are unrolled onto the working bed where a CO₂ laser cuts the outline of each layer of the part. A heated roller is passed over the layer to thermally activate the tape's binder system and to laminate the sheet to the previous layer⁴. The high ceramic powder load in the casted tapes (>40 wt%) requires the use of an adhesive agent, such as double-side adhesive tape or a diluted binder solution, to promote the interconnection between the adjacent tapes. The boundary between the tapes should be undetectable after compression by the roller. After debinding and sintering in a furnace, the final ceramic (e.g. alumina and silica²⁴, or glass-ceramic²⁵) parts are obtained.

Computer-Aided Manufacturing of Laminated Engineering Materials (CAM-LEM)

Another embodiment of this process is the CAM-LEM method. This process is identical to that of LOM, but instead of stacking the layers and then cutting them, each layer is pre-cut and robotically stacked onto the working part for lamination. This method has some advantages over traditional LOM, e.g. internal voids within each layer can be easily produced⁴.

2.5 Binder jetting

Binder jetting processes, defined as “*additive manufacturing processes in which a liquid bonding agent is selectively deposited to join powder materials*”¹, are also known as three-dimensional printers (3DP) and consist of a printing head and a powder deposition device. A 3DP device can shape ceramic components by first depositing a layer of ceramic powder and then jetting binder material to

selectively bind the ceramic powder²⁶. Generally, two different 3DP methods can be distinguished.

3DP of dry powder agglomerates (P-3DP)

This is the traditional method to produce ceramic parts through 3D printing. Sequential depositing of powder particles with a roller or scraper system and printing of binder material by ink-jet printing, yields the layers and results in a solid part. After binder burnout and sintering, a consolidated ceramic part is obtained.

Already in 1991, M.J. Cima and E.M. Sachs of Massachusetts Institute of Technology (both co-inventors of the binder jetting technology²⁶) demonstrated this technology through preparing complex-shaped cores and shells with high dimensional tolerance to produce castings of high temperature²⁷. In this study, sequential layers of alumina powder particles were deposited and selectively glued by a colloidal silica binder.

Formerly, the company Soligen had an exclusive license on 3D printing of ceramics²⁸. Nowadays, ExOne²⁹ and 3D Systems³⁰ offer 3DP machines for AM of ceramics.

Slurry based three-dimensional printing (S-3DP)⁴

In order to be able to process fine powders (< 20 µm) and improve the furnace sintering characteristics of the green part, research of ceramic 3DP shifted away from working with dry powders to working with a slurry-based material (S-3DP). During S-3DP, each powder bed layer is created by jetting ceramic slurry onto a substrate. The as-cast layer is subsequently dried and a binder is selectively deposited in the desired pattern to cement the ceramic particles.

2.6 Single step powder bed fusion by fully melting

During single step powder bed fusion by fully melting (i.e. Selective Laser Melting, SLM), the laser-beam causes the irradiated ceramic powder material to heat and fully melt. In literature, three different powder layer deposition systems can be distinguished for SLM of ceramics: conventional deposition (i.e. a scraper or a counter current roller system), slurry based deposition and aerosol assisted spray deposition (Table 1).

Conventional deposition system

Conventional deposition systems are able to deposit 'heavy' and thus relatively large (e.g. $> 5 \mu\text{m}$) powder particles. During powder deposition the gravity forces overcome the electrostatic attraction forces, enabling the flowing of the powder particles.

SLM with a conventional powder deposition system was thoroughly investigated at the Fraunhofer Institute of Laser Technology (ILT) in Aachen and TNO Eindhoven. In the initial research, porous silica-tricalcium-phosphate (silica-TCP³¹) and micro-crack containing zirconia^{31, 32} parts were produced using a CO₂ laser. In order to reduce the amount of micro-cracks which were caused by thermal gradients, a high temperature preheating system was developed. This system used a CO₂ laser to preheat the powder layers (temperature controlled by a pyrometer) and a Nd:YAG laser to locally melt the ceramic.

Although pure ZrO₂, Al₂O₃ and MgAl₂O₄ (spinel) ceramics could be processed in this way, a large amount of micro-cracks were present in the parts. It was also concluded that SLM of single phase ceramics, e.g. ZrO₂ and Al₂O₃, resulted in large grained microstructures. In example, grain sizes of about 100 μm were

obtained for SLM of alumina at a preheating temperature of 1850°C, an Yb:YAG laser power of 70 W, scan speed of 200 mm/s, scan spacing (i.e. space between adjacent scan tracks) of 50 µm and layer thickness of 200 µm³³.

In order to SLM ceramics with a fine microstructure (i.e. grain sizes up to 10 µm), a eutectic zirconia-alumina (ZrO₂-Al₂O₃) powder ratio had to be chosen (Figure 1). The starting powder was produced through dry mixing of 41.5wt% spherical ZrO₂ powder with 58.5wt% spherical Al₂O₃ powder. The zirconia component was partially stabilized by 3 mol% yttria Y₂O₃. Both powders, supplied by Innalox BV (The Netherlands), had a spherical shape and a monomodal size distribution of 50 µm.

The SLM parameters for the 41.5wt% ZrO₂ - 58.5wt% Al₂O₃ powder comprised a preheating temperature of 1730°C, a layer thickness of 50 µm, a scanning velocity of 200 mm/s, a laser power of 60 W and a scan spacing of 50 µm³⁴. Due to the preheating temperatures close to the melting point of the eutectic powder ratio (1860°C) a large melt pool evolved, which positively influenced the density of the obtained part. On the other hand, a poor surface quality was examined since the low viscous melt pool exceeded the boundaries of the scanned part and wetted and impregnated the surrounding powder³⁴⁻³⁶.

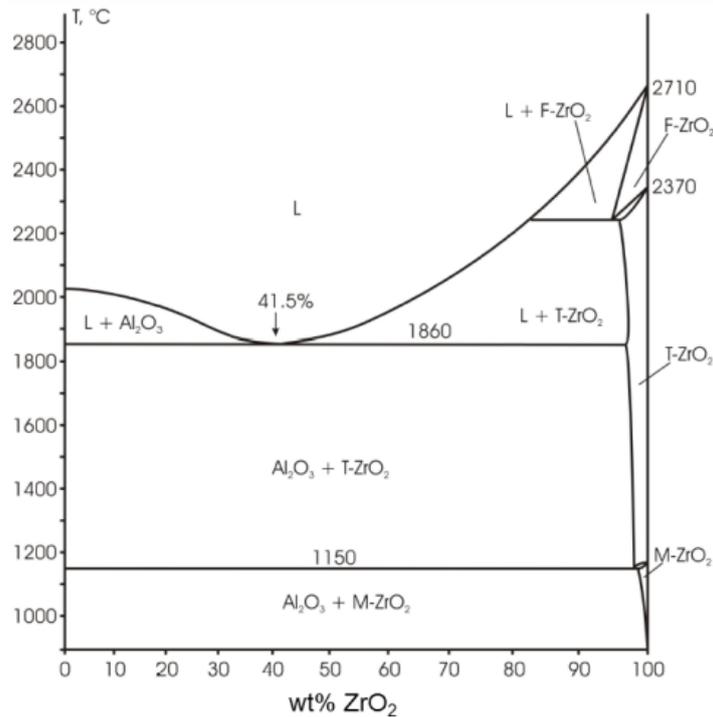


Figure 1: Alumina-zirconia phase diagram.³⁷

In order to improve this patented^{38, 39} SLM process, the preheating device was modified. Since specimens with a height > 3 mm could not be processed by the original setup, which only heated the powder surface, a bottom up preheating system using inductive heating technology was developed³⁴. In combination with the inductive preheating system, a selective preheating strategy was developed. This setup used two laser sources, in which a fiber laser with a focused spot size of ~200 μm was used for selective melting while a diode laser-beam was coaxially superpositioned by a dichroic beam splitter, forming a selective preheating with a focused spot size of ~5 mm³⁴. In this way parts with a height up to > 10 mm could be produced⁴⁰.

Besides ILT Aachen and TNO Eindhoven, the AM research group at Ecole Nationale d' Ingénieurs de Saint-Etienne (ENISE) in France attempted to

produce ceramic parts through SLM. Shishkovsky et al.⁴¹ reported the use of a Phenix PM-100 machine to SLM powder mixtures, prepared from yttria-stabilized zirconia, YSZ (ZrO_2 90 wt.%, Y_2O_3 10 wt.%, Zircar Zirconia Inc), and aluminium (ADC4 grade, in some experiments alumina Al_2O_3 of Baikowsky Inc. was used) in the ratio 4:1 in oxygen and argon atmosphere. The resulting surface macro- and microstructures examined by optical metallography were relatively smooth, but contained pores and cracks. Probably, the microstructures were not only formed through melting, but also chemical reactions at elevated temperatures.

Slurry coating

At the National Taipei University of Technology in Taiwan, H.H. Tang developed an SLM device with a slurry coater⁴². In literature the term ceramic laser fusion (CLF) is used to depict this technology. SLM in combination with slurry coating is mainly applied to produce silica-clay parts. Water based slurries of silica, clay and silica sol (silica:clay:silica sol:deionized water weight-compositions of 100:7:3:80, 100:7:9:80 and 100:3:7:80 were used) are paved by a slurry coater and dried afterwards. The clay is used as an inorganic binder for the silica powder during drying. In this way a ceramic green layer substrate is created which can minimize balling and give the part a solid support during building. During laser scanning, the dried silica-clay layer is fully melted and parts with a reduced porosity are obtained. However because silica is a brittle material and the deposited layers are not preheated, high-energy laser scanning easily induces thermal cracks. As a result, no high strength parts can be produced through SLM of the non-preheated slurry coated layers⁴³⁻⁴⁶.

Aerosol assisted spray deposition

Wu et al.⁴⁷ applied aerosol assisted spray deposition of a suspension to prepare powder beds for subsequent laser scanning. In this way single layer ceramics were fabricated. The alumina suspensions were prepared by adding 5 wt% alumina powder (Alcan Chemicals) to an ethanol solvent (Aldrich, 99.5%) with an optimized content of 0.2 wt% of polyacrylic acid (PAA, Aldrich, M_w 2000) dispersant. During the laser irradiation of the alumina powder beds, the PAA evaporated and the submicrometer sized alumina particles were melted to form a liquid-phase, which facilitated the densification through liquid-phase sintering. With increasing laser energy density, the microstructure of the laser sintered alumina powder beds varied from open to closed porosity to a fully densified microstructure, as shown in Figure 2.

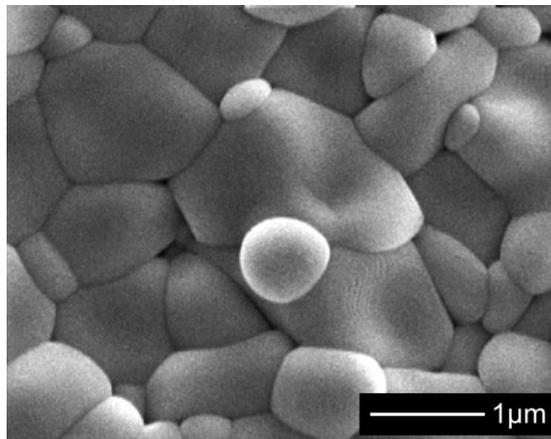


Figure 2: SEM micrographs of the surface of an alumina sample, prepared by SLM of aerosol assisted spray deposited layers⁴⁷.

2.7 Single step powder bed fusion by partial melting

Conventional deposition system

Prof. H. Marcus of the University of Texas at Austin (i.e. the university where powder bed fusion was invented⁴⁸), was one of the pioneers in laser sintering ceramics. Under his supervision, alumina - ammonium phosphate^{49, 50} and alumina – boron oxide⁵⁰ ceramics were produced. Both ammonium phosphate (melting point: 190°C) and boron oxide (460°C) acted both as structural material as well as binder to glue the alumina particles.

At Ecole Nationale d' Ingénieurs de Saint-Etienne (ENISE), Bertrand et al.⁵¹ produced yttria stabilized zirconia through direct SLS®. In order to do so, a Phenix PM-100 machine, equipped with a Nd:YAG laser and a conventional powder deposition system was used. In this study, 5 different starting powders were used: atomised and crushed yttria-zirconia (4 mol%) of Baikowski, atomized ZYP30 (10 mol%) powder of Zircar, atomized YZB5 powder of Tioxide and atomized YZ3P powder (3 mol%) of ENSME. Since the melted powder could not fill all the gaps between the powder particles which were not melted, only low density ceramics could be produced.

At the University of Leeds, Lorrison et al.⁵² produced hydroxyapatite - phosphate glass. Also in this case, the glass acted as structural material as well as binder. By using metal as a binder and structural material, Gu and Shen⁵³ of the Nanjing University of Aeronautics and Astronautics, produced WC-10Co/Cu ceramic-metal composites.

Slurry coating

At the Clausthal University of Technology (TU Clausthal), a layer-wise slurry deposition (LSD) system has been developed. A powder containing slurry layer is deposited and dried afterwards. When highly solid loaded slurries (e.g. 66wt% solid phase^{2, 54}) are deposited by this system or another colloidal processing based deposition system, the packing density of the particles can be much higher (i.e. >50 vol%⁵⁵) compared to the packing density of conventionally deposited particles (i.e. estimated to be about 20 vol%⁵⁶).

Through SLS® of the slurry coated layers, hydroxyapatite⁵⁷, porcelain⁵⁸⁻⁶⁰ and alumina-silica^{54, 61} parts were successfully produced at TU Clausthal. The produced parts however still contained open porosity. As an example, after the SLS® process alumina-silica parts could be obtained with densities of 86-92%. Subsequent thermal post treatment in air in a conventional sintering furnace led to additional phase reactions and caused an increase of density to about 96%.

At the National Taipei University of Technology in Taiwan, Hsiao-Chuan Yen deposited slurry layers composed of silica particles, silica sol and polyvinyl alcohol (PVA). During drying, PVA and silica gel bound the silica particles and a uniform gelled layer was formed. During SLS®, the PVA degraded and a cristobalite silica part was produced⁶².

Slurry spraying

At the Fraunhofer Institute of Production Technology (IPT) in Aachen, Klocke et al.⁶³ produced yttria stabilized zirconia through direct SLS®. High density powder layers were formed by spraying (instead of layer deposition) a ceramic suspension before the drying step. The SLSed layers contained cracks which

were caused by contraction during cooling after laser irradiation. The amount of open porosity in the final parts was 24-32%. Despite the high packing density of the deposited green layers, the melted powder could not fill all the gaps between the powder particles which were not melted.

Ring blade

In 2002, the Laserinstitut der Hochschule Mittweida (LHM) developed the micro SLS® process, which is able to produce accurately ceramic and metal parts⁶⁴⁻⁶⁶. The process has been internationally patented in 2004⁶⁷. It consists of a ring blade⁶⁸, also called 'powder rack', which is able to deposit dry non-agglomerated submicrometer powder particles which are not agglomerated. It is also possible to micro SLS® a part consisting of two segments of a different material (e.g. Cu and Ag)⁶⁹. Further, a compacting system can be used to increase the packing density of the deposited layers and as a result of the fabricated parts⁷⁰.

During micro SLS®, a near-infrared (NIR) laser is used to partially melt the deposited powder particles. In order to control and prevent overheating of the scanned material, the laser is mostly used in a pulsed (q-switched pulses of about 20 ns) instead of a continuous mode⁷¹.

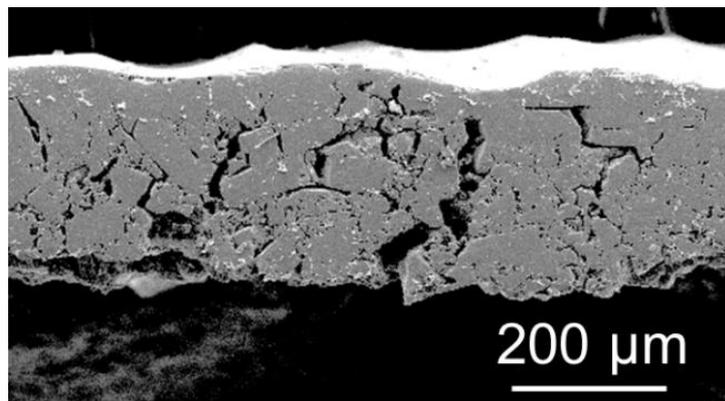
Partial melting of submicrometer powders using the micro SLS® device has been applied to the following ceramic materials: alumina-feldspar⁷², alumina-silica^{71, 73-75}, feldspar⁷¹ and silicon/silicon carbide/carbon (Si-SiC-C)^{68, 69, 71, 74-77}. However, the resulting ceramic parts still contained pores.

Electrophoretic deposition (EPD)

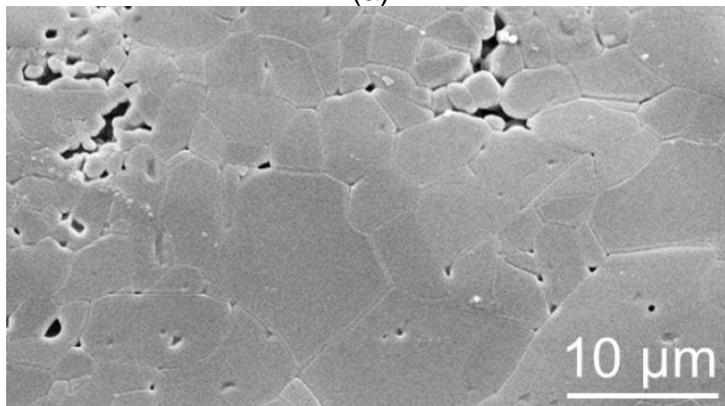
In order to selective laser sinter (SLS®) fine grained alumina directly, i.e. without organic or inorganic binder addition, a low laser energy density should be applied on a high packing density submicrometer sized ceramic powder layer, preheated to a uniform and high ($\pm 800^{\circ}\text{C}$) temperature. To achieve this, an experimental setup was designed, constructed and tested for Al_2O_3 ceramics at KU Leuven.

The experimental setup consisted of a vertical tube furnace and a deposition mechanism. In the furnace, a cylindrical zone could be homogeneously heated within a range of $\pm 50^{\circ}\text{C}$ up to a temperature of 800°C . The layer deposition process consisted of two steps. In a first step, a powder layer was deposited on the deposition electrode by the EPD process in a so called EPD cell. The EPD cell consisted of a positively charged alumina suspension. At the bottom of the cell a counter electrode was mounted. At the top of the cell the deposition tool was placed. During the EPD process, a DC power supply negatively charged the deposition electrode and positively charged the counter electrode. As a result, submicrometer alumina particles moved from the suspension to the deposition electrode. In this way, a highly packed (about 60%) powder layer of controlled thickness was formed on the deposition electrode. In a second step, the deposition tool with EPD deposited powder layer was removed from the EPD cell and mounted into a gearbox to deposit the powder layer in the vertical tube furnace. Optimizing the layer deposition and laser scanning parameters allowed producing alumina ceramic parts with a density up to 85% and a microstructure with a grain size below $5\ \mu\text{m}$ ⁷⁸⁻⁸⁰ (Figure 3).

The main consolidation mechanism of this process seemed to be partial melting. However, since several mechanisms (partial melting, full melting and solid state sintering) might act together, it is sometimes not clear what consolidation/binding mechanism is active. Therefore, the laser consolidation was designated as direct Selective Laser Sintering®/Melting or direct SLS®/SLM.



(a)



(b)

Figure 3: Cross-section at low (a) and high (b) magnification of a part/sample produced through SLS®/SLM of submicrometer powder at 800°C.⁷⁸⁻⁸⁰

2.8 Single step powder bed fusion by solid state sintering

Conventional deposition system

Bertrand et al.^{2, 81} of ENISE reported solid state sintering (SSS) as consolidation mechanism during SLS® of ceramic materials using the high temperature process chamber of a Phenix PM-100 machine at 800°C. The powder, which was preheated close to the onset temperature of sintering, was sintered due to the extra energy contribution of a Nd:YAG laser source. To obtain the desired characteristics, a post-sintering operation was necessary.

2.9 Single step powder bed fusion by chemically induced binding

During chemically induced binding (CIB), the heat of the laser beam is used to initiate a chemical reaction which results in binding of the powder particles. The following powder deposition systems are used to investigate the production of ceramic parts through this process, which is also known as selective laser reaction sintering (SLRS)⁸².

Conventional deposition system

Different research groups investigated SLS® of ceramic parts through CIB using a conventional deposition system. B.R. Birmingham and H.L. Marcus of the University of Texas in Austin SLSed Si powder in a NH₃ atmosphere to produce Si₃N₄⁸². F. Klocke and H. Wirtz of the Fraunhofer Institute of Production Technology (IPT) SLSed SiC starting powder in argon atmosphere. During laser irradiation, SiC decomposed into Si and C. Despite the inert argon atmosphere, the Si atoms reacted with O₂ and formed SiO₂, which glued the SiC particles⁸³.

Since the melting temperature of Si is 1420°C, the SiC particles were probably also bound by melted Si.

Slurry coating

At the National Taipei University of Technology in Taiwan, H.H. Tang deposited slurry layers, consisting of aluminium phosphate and silica⁸⁴. The process, which is also called Ceramic Laser Sintering (CLS), was based on an irreversible chemical reaction of slurry containing aluminum phosphate and silica at a temperature above 250°C.

Ring blade

The Laserinstitut der Hochschule Mittweida (LHM) used the patented micro SLS® device⁶⁷ to produce Si-SiC parts through SLS® of SiC. A Nd:YAG laser with a wavelength of 1064 nm was used in a continuous mode to decompose a fraction of the irradiated SiC powder. This yielded elementary silicon, which became the matrix or bridging material for unreacted SiC grains^{71, 74-77}.

2.10 Multi-step powder bed fusion by partial melting

Conventional deposition system

A method for producing high temperature parts by low temperature selective laser sintering® was patented in 1993⁸⁵. Ever since, this method is extensively studied at different universities.

A conventional SLS® machine is used to selectively sinter composite powders, which consist of ceramic particles and sacrificial binder material. During SLS®, the binder phase melts and glues the ceramic particles together. After a furnace cycle, the binder material is usually burned and a ceramic part is obtained. As

depicted in Table 2 **Error! Reference source not found.**, many different ceramics are already produced through this process: a.o. Al_2O_3 ^{56, 86-92}, $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ ⁹³, $\text{Al}_2\text{O}_3\text{-glass-B}_2\text{O}_3$ ⁹⁴, $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-TiC}$ ⁹⁵, apatite-mullite⁹⁶, graphite⁹⁷, $\text{K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ ⁹⁸, SiO_2 ²⁴, SiC ⁹⁹⁻¹⁰¹, ZrO_2 ^{24, 102} and ZrB_2 ¹⁰³⁻¹⁰⁵.

If the binder is inorganic, it cannot be burned. During the thermal treatment, the inorganic binder (e.g. HBO_2) chemically reacts and becomes part of the structural ceramic (e.g. B_2O_3)^{93, 94}. Different types of organic binders have been examined to fabricate ceramic parts via SLS® like long chain fatty acids (e.g. stearic acid^{86, 103-105}), waxes (carnauba wax⁸⁸), thermosets^{24, 98-101} and thermoplastics^{56, 89-92, 96, 102}. Sometimes, a combination of binders is used: e.g. a thermoset in combination with semi-crystalline PA-11 (or nylon 11) to produce graphite⁹⁷, or a wax in combination with amorphous thermoplast PMMA to produce the composite ceramic $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-TiC}$ ⁹⁵.

If the polymer-ceramic composite starting powders have an irregular shape (e.g. by producing them through ball-milling), craters are formed during layer deposition. As a result, no complex shaped objects can be SLSed⁵⁶. Shahzad¹⁰⁶ and Deckers¹⁰⁷ have demonstrated that, besides dispersion polymerization^{91, 108}, temperature induced phase separation (TIPS) is a very promising process to produce polymer-ceramic composites for SLS® applications. Firstly, the agglomerates produced by the TIPS process have a (near) spherical shape and can be well deposited by a conventional powder deposition system. Secondly, the TIPS process seemed to be very flexible, as composite agglomerates containing different binders (nylon 12^{87, 92}, polypropylene^{89, 102} and carnauba

wax⁸⁸) and ceramics (alumina^{87, 89, 92}, zirconia¹⁰² and hydroxyapatite-tricalcium_phosphate).

Indirect SLS® with the use of a sacrificial binder phase allows producing crack free ceramic parts, but the final density, i.e. the density of the part after debinding and before furnace sintering, is generally low and limited to 39-80%^{104, 107}. The low density is caused by the occurrence of voids between the 10-100 µm sized powder particles/agglomerates, after layer deposition during the SLS® process. Since these voids do not disappear during debinding and solid state sintering, they reside in the final part.

In order to reduce the inter-agglomerate voids, the possibility to include the following steps into the PM process chain was explored by Deckers¹⁰⁷ and Shahzad¹⁰⁶: (i) irradiating the powder layers multiple times instead of only once (i.e. laser re-melting), (ii) cold, quasi and warm isostatic pressing the SLSed parts and (iii) infiltrating the parts obtained at different stages of the PM process. As a result, freeform shaped alumina parts (Figure 4**Error! Reference source not found.**) with densities up to approximately 90% could be obtained. In order to produce higher quality ceramic parts through indirect SLS®, the inter-agglomerate pores should be avoided or eliminated.

Indirect SLS® by partial melting composite agglomerates has been used not only to produce pure ceramics, but also composite ceramics. Gill and Hon¹⁰⁹ investigated SLS® of SiC-PA ceramic-polymer composites. Evans et al.¹¹⁰ infiltrated SiC preforms with molten Si, creating SiC-Si cermets.

		Binder				
		inorganic	organic			
			acid	wax	thermoset	thermoplast
Ceramic	Al ₂ O ₃		stearic acid ⁸⁶	carnauba wax ⁸⁸		nylon 12 ^{56, 87, 92} , polypropylene ⁸⁹ , polystyrene ⁹¹ , PMMA ⁹⁰
	Al ₂ O ₃ -B ₂ O ₃	HBO ₂ ⁹³				
	Al ₂ O ₃ - glass-B ₂ O ₃	HBO ₂ ⁹⁴				
	Al ₂ O ₃ - ZrO ₂ -TiC			unspecified ⁹⁵		PMMA ⁹⁵
	Apatite- mullite					unspecified acrylic binder ⁹⁶
	Graphite				phenolic resin ⁹⁷	nylon 11 ⁹⁷
	K ₂ O-Al ₂ O ₃ - SiO ₂				epoxy resin ⁹⁸	
	SiO ₂				unspecified ²⁴	
	SiC				phenolic resin ⁹⁹⁻¹⁰¹	
	ZrO ₂				unspecified ²⁴	polypropylene ¹⁰²
	ZrB ₂		stearic acid ^{103- 105}			

Table 2: Sacrificial binders used to produce different ceramic parts using a conventional SLS® system.



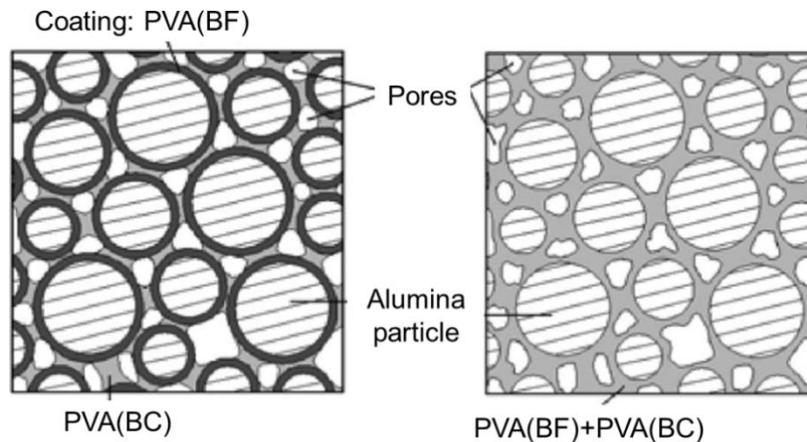
Figure 4: Example of a freeform shaped alumina part obtained through indirect SLS®.

Slurry coating

At the National Taipei University of Technology in Taiwan, a slurry coating device was used to investigate the indirect production of ceramic parts. Silica parts were produced through the so called ceramic laser sintering (CLS) process^{46, 111-113}. The water based slurries used in CLS consisted of high melting point of silica powder (~1720°C) and silica sol (melting point ~1700°C) as a structural material and low melting point (melting point: ~1200°C) clay as inorganic binder. Slurries with following silica:clay:silica_sol:water weight compositions were investigated: 100:7:3:80, 100:7:9:80 and 100:3:7:80. The slurry was deposited and dried. During laser scanning, the clay particles were melted. The melted clay bridged the silica particles to build an interconnected porous structure.

In later experiments, organic polyvinyl alcohol (PVA) was used as binder material to produce alumina parts through slurry-based SLS®¹¹⁴. Both sub-partially hydrolysed polyvinyl alcohol PVA(BC) and fully hydrolysed polyvinyl alcohol PVA(BF) were used as a binder. As depicted in Figure 5**Error! Reference source not found.**a the submicrometer alumina particles were first coated with the water insoluble PVA(BF). The coated particles and the water soluble PVA(BC) were used to form a water based slurry, which was deposited and dried. After laser scanning, the ceramic particles were bound by a PVA(BF)-PVA(BC) mixture that is water insoluble. After thermal debinding and solid state sintering, complex shaped Al₂O₃ ceramic parts (Figure 5**Error! Reference source not found.**b), free from delamination and cracks, with a

homogeneous microstructure, a density of 98% and a mean flexural strength of 363.5 MPa were obtained.



(a) Schematic of the PVA- Al_2O_3 mixture: before (left) and after (right) laser irradiating.



(b) 3D sintered Al_2O_3 part

Figure 5: The slurry based indirect SLS® process¹¹⁴.

2.11 Multi-step powder bed fusion by gelling

At the National Taipei University of Technology in Taiwan, a slurry deposition device was also used to investigate the ceramic laser gelling (CLG) process. During CLG, the heat induced by the laser beam initiates the chemical or physical gelling of a colloidal suspension (i.e. a sol). When a sol is gelled, it first becomes more viscous, then develops rigidity, and finally crosslinks forming a

three-dimensional network. For example, when a thin film is deposited by a slurry coater, CO₂ laser irradiation can be used to dry a portion of the deposited layer, forming a physically gelled solid particle network. The portion of slurry film that is not scanned by the laser beam remains in the slurry state.

Yen et al.¹¹⁵ used slurry which mainly consisted of Al₂O₃ powder, silica sol and deionized water to fabricate alumina-silica parts. Due to the expulsion of water and part of the ceramic powder during laser scanning, the density of the final parts after furnace sintering was only 75%.

By mixing a silica sol with silica powder, pure silica parts could be obtained through the CLG process (Figure 6**Error! Reference source not found.**). The maximal green part strength after CLG was 4.7 MPa. After a heat-treatment at 1200°C for 1.5 hours, the flexural strength increased up to 12.5 MPa. No density values were reported¹¹⁶⁻¹¹⁸.

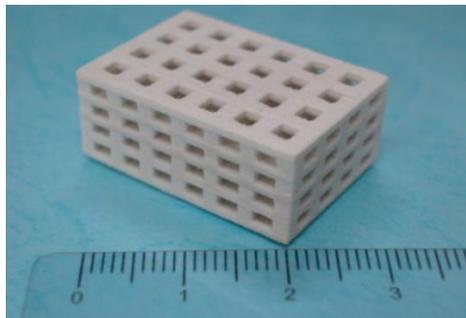


Figure 6: A silica part with inner channel structure made by ceramic laser gelling¹¹⁷.

2.12 Vat photopolymerization

Vat photopolymerization processes are defined as *“additive manufacturing processes in which liquid photopolymer in a vat is selectively cured by light-activated polymerization”*¹.

During stereolithography (SLA) of ceramics different ceramic containing slurry layers are scanned by ultraviolet (UV) radiation. The UV radiation causes a chemical reaction (in contrast to a thermal reaction during powder bed fusion processes) which results in the polymerization, i.e. chemical gelling, of the slurry layers with incorporation of the ceramic particles. After debinding the resulting polymer and sintering the structural material in a furnace, the final ceramic part is obtained. A distinction can be made between the systems which produce macroscopic and microscopic ceramic parts.

2.12.1 (Macro) SLA

In literature, SLA of ceramics is described under different names and abbreviations such as ceramic stereolithography (CerSLA¹¹⁹, CSL¹²⁰) and lithography based ceramic manufacturing (LCM¹²¹). Different research teams have investigated the fabrication of ceramics through SLA. The polymerization reaction is mostly performed by an UV laser. However, Griffith and Halloran¹⁹,¹²² demonstrated that the laser can be replaced by LEDs or halogen lamps when transferring a desired pattern on the photocuring liquid. This technology is called Large Area Maskless Photopolymerization (LAMP, also called ‘digital light projection’ or DLP)¹²³. During LAMP, each layer is rapidly patterned by UV exposure in the pattern of a bitmap defined by a spatial light modulator.

Many patents already described different suspensions or specific applications for SLA of ceramics¹²⁴⁻¹²⁹. The suspensions are prepared by dispersing different powders in an UV curable medium (also called photopolymer), consisting of monomers and/or oligomers, and photoactive components. In most cases, the medium is a resin-based acrylate or water-based acrylamide^{120, 130}. It is also possible to use a medium which consists of an UV curable resin as an organic binder and methanol as a solvent and a dispersant. After paving the solvent-based slurry, the solvent is vaporized using a fan. This results in a shrinkage of the slurry volume of the deposited layer¹³¹.

Another route to produce the resin was developed by De Hazan et al.¹³². In this case, surfactants were adsorbed in aqueous media under controlled pH conditions on Al₂O₃, ZnO and Al₂O₃/ZnO particles. After drying, the particles were transferred to an UV curable organic medium, that mostly consisted of 2-hydroxyethyl acrylate (HEA, Rahn, Switzerland) and polyethyleneglycol 200 diacrylate (M282, Rahn, Switzerland) in a 14:1 ratio.

The extent of the photopolymerization reaction during laser irradiation can be described through the following equation which P.F. Jacobs derived, starting from the Beer-Lambert equation¹³³.

$$\delta_c = D_p \cdot \ln \left(\frac{E_i}{E_c} \right) \quad \text{Equation 1}$$

where δ_c is the cured depth, i.e. the polymerized thickness, E_i the energy density delivered at the surface of the resin, E_c the critical energy density of photopolymerization which is the minimum input energy necessary to trigger the curing process, D_p the penetration or sensitivity of the laser beam (the distance at which the laser intensity is reduced by 1/e).

Many authors used this equation to describe the hardening of a ceramic suspension under UV radiation^{119, 120, 123, 134-138}. The cured depth δ_c is influenced by extra photoactive components in the light curable medium and the ceramic particles¹²³. The photoactive components include: (1) a photo initiator, which is a dye that decomposes to form free radicals upon absorption of an UV photon, thereby initiating polymerization reactions, (2) inert dyes, which absorb photons without forming free radicals and (3) inhibitors which react with free radicals to inhibit polymerization.

As depicted in Figure 7a¹³⁴, the ceramic particles reduce the photopolymerization reaction, i.e. conversion, by diluting the photoactive medium and attenuating the UV light by scattering. The light scattering is essentially the reflection of the UV light by the ceramic particles. Reflection of the UV light will not occur when the refractive index of the ceramic filler is almost equal to the refractive index of the organic matrix, as is the case for SiO₂. On the other hand, the refractive index of the ceramic filler is increasingly higher than the refractive index of the organic medium for respectively Al₂O₃, ZrO₂ and SiC. The higher the refractive index, the more UV light will be absorbed by the ceramic filler material, reducing the curing depth. This causes SLA of SiO₂^{139, 140} or Al₂O₃¹⁴¹ to be easier, compared to SLA of ZrO₂ or SiC.

As depicted in Figure 7b¹³⁴, smaller particles also reduce the photopolymerization reaction. The deterioration of the final conversion by lowering of the particle size while keeping the vol% of the suspension constant, could be allocated to an increase in scattering centres for a given volume concentration¹³⁴.

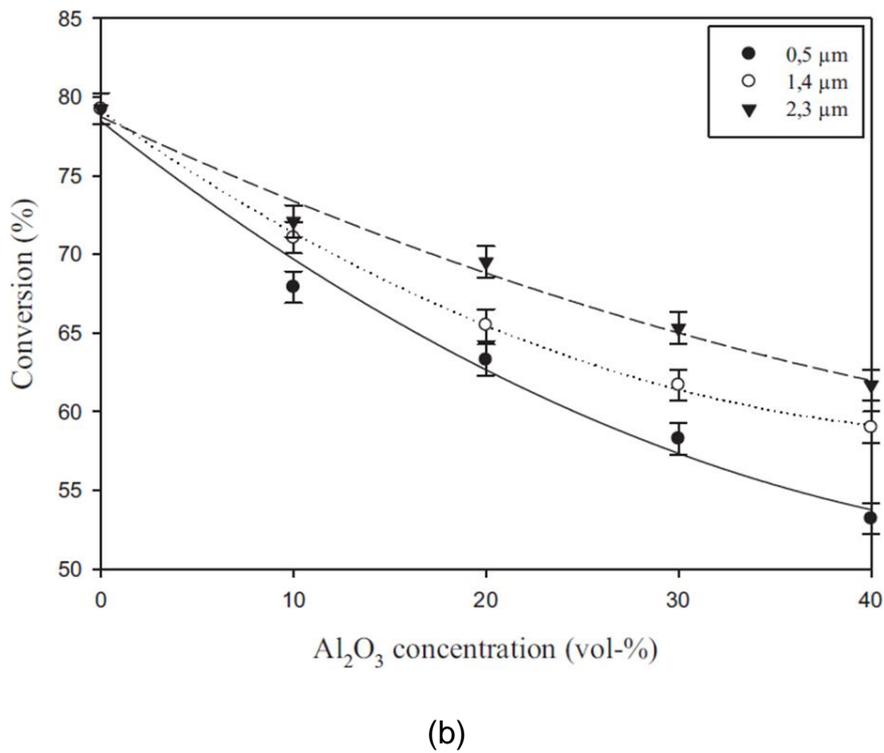
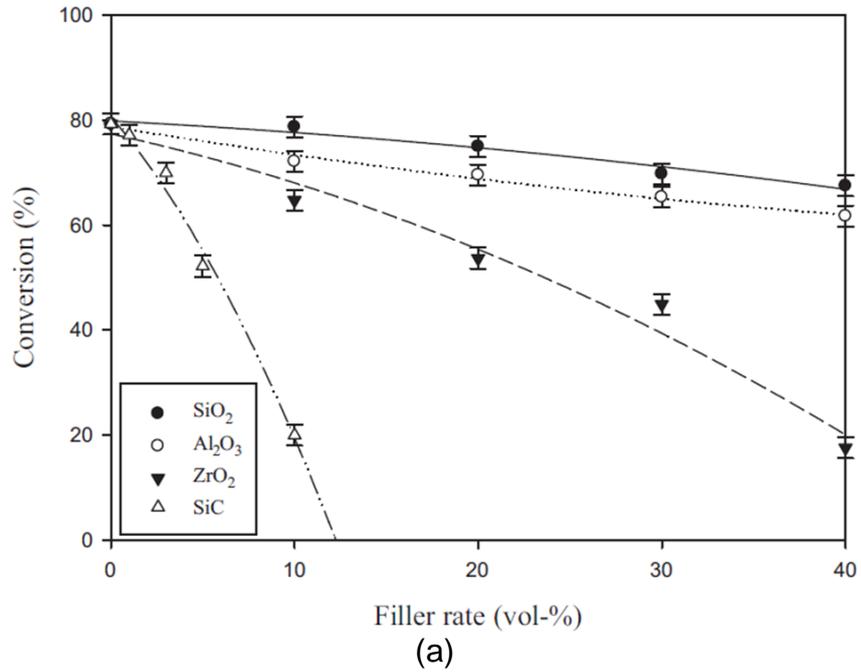


Figure 7: Influence of the refractive index (refractive index of SiO₂ < Al₂O₃ < ZrO₂ < SiC) and solid loading of the ceramic filler (a) and alumina particle size and solid loading (b) on the photo polymerisation conversion of a ceramic filler containing acrylate¹³⁴.

When the suspensions are highly loaded with ceramic particles and interaction between the particles is not negligible, the viscosity usually has a shear thinning rheological behaviour that follows the Krieger-Dougherty equation^{123, 135}:

$$\eta_r = \frac{\eta}{\eta_0} = \left(1 - \frac{\phi}{\phi_0}\right)^{-[\eta]\phi_0} \quad \text{Equation 2}$$

where η_r is the relative viscosity of the suspension, η is the viscosity of the suspension, η_0 is the viscosity of the medium, ϕ the volume fraction of ceramic powder, ϕ_0 the volume fraction of the filler for close-packed particles corresponding to an infinite viscosity (no flow) and $[\eta]$ the hydrodynamic shape factor which depends on the shape of the particles ($[\eta]$ is 2.5 for spheres).

The suspensions commercially used for SLA of ceramics are either high viscosity pastes or low viscosity slips. Both types of suspensions are commercialized by different companies and several patents^{124-127, 129} have been filed.

SLA of ceramics from high viscosity paste slurries is commercially exploited by 3DCERAM¹⁴² and Sirris¹⁴³. At Sirris in Belgium, a special coater which can deposit pastes, containing up to 60 vol% ceramic (or metal) powder, was developed¹⁴⁴ and patented¹²⁴. The paste-coater is used in combination with an Optoform SLA machine to produce ceramic parts. 3DCERAM uses a similar setup to AM ceramics.

SLA of ceramics from low viscosity slips is commercially exploited by Admatec Europe BV¹⁴⁵, a daughter company of Formatec¹⁴⁵, and by Lithoz GmbH¹²¹, a spin-off from the Technische Universität Wien (TU Wien¹⁴⁶) that closely cooperates with Ivoclar Vivadent AG^{125, 127, 147}. The SLA machines used by

Admatec and Lithoz, use a lifting mechanism to deposit layers of powder suspension. The part being produced touches a glass support. The layers are deposited through lifting the part from the glass support, so the suspension can flow underneath. The laser or digital light processing (DLP) projector then irradiates the bottom of the part through the glass support (Figure 8a).

Besides TU Wien, the Netherlands Organisation for Applied Scientific Research (TNO) is also very active on SLA using a lifting mechanism to deposit powder suspension layers. Maalderink of TNO¹⁴⁸ illustrated that the green parts produced with such a layer deposition method, can contain a small amount of pure photopolymer material (no ceramic particle) between every layer. The resulting inhomogeneities can cause the parts to crack during debinding and solid state sintering. If only one type of binder is used, only relatively thin (maximum 2.5 mm thickness) ceramic parts can be produced through the SLA process (Figure 8b). Due to the relative large amount of polymer in the produced sample, too thick parts are likely to crack during the debinding process, similar as during the debinding of injection moulded parts. By choosing low debinding rates, multiple binder systems, appropriate building parameters¹¹⁹ and avoiding the presence of uncured monomer material after the SLA process¹⁴⁹, cracking of the parts can be minimized and ceramic parts with a thickness of about 1 cm can be produced. The shrinkage during debinding and furnace sintering of parts produced through SLA is quite uniform and about 10% in all directions, usually somewhat smaller in the z-direction, compared to the x-y direction¹⁴⁹.

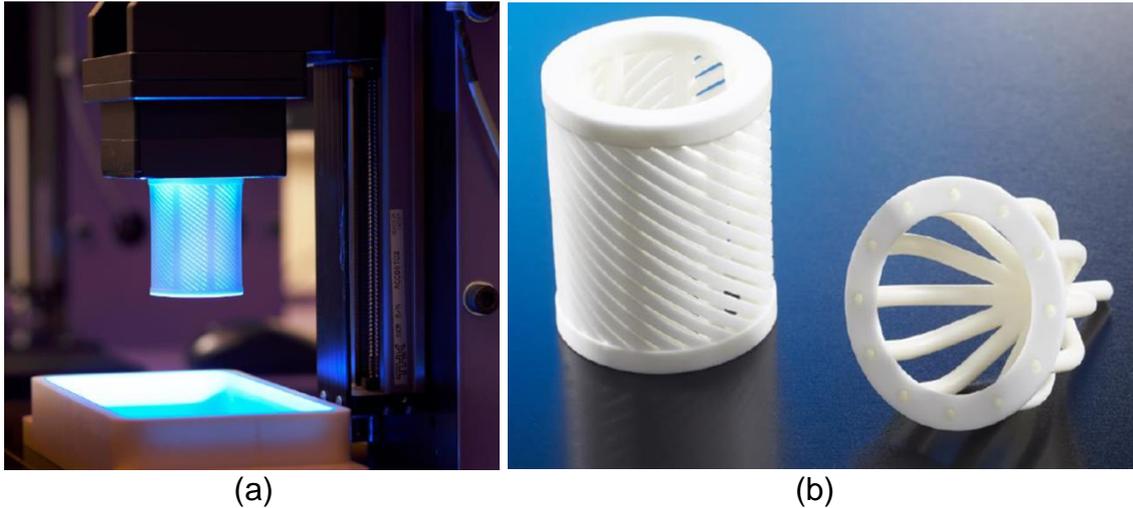


Figure 8: SLA machine of Admatec producing a composite ceramic part (a). After debinding and furnace sintering, the ceramic components are obtained (b)¹⁵⁰.

2.12.2 Micro SLA

Powder based micro-stereolithography uses the SLA process to produce as small as possible complex three-dimensional (3D) components. By starting from suspensions which contain a photo polymerizable medium and ceramic filler material, polymer-ceramic composite parts can be fabricated. After debinding and furnace sintering, ceramic parts can be obtained^{130, 151, 152}. As is the case for macro SLA, UV radiation can be performed at the top surface or at the bottom surface. Also similar to macro SLA, UV radiation can be performed by illuminating deposited layers integrally, e.g. by a DLP projector, or by laser vector-by-vector scanning. If specialized lasers and optics are used, the micro SLA technology allows the production of ceramic components with a submillimeter resolution¹³⁰.

2.13 Alternative methods

Some AM processes to shape ceramic particles, are difficult to classify within the ISO/ASTM framework. As depicted in Table 1, these AM processes are electrophoretic deposition (EPD) and electro photographic printing (EP) and can be described as follows:

Electrophoretic deposition (EPD)¹⁵³

Charged colloidal particles suspended in a liquid medium migrate (electrophoresis) and are deposited in a controlled manner to shape a three-dimensional part using an electrical field created between electrodes.

Electro photographic printing (EP)⁴

A photoreceptor plate, containing an electrostatic image of the part layer, is aligned over a powder bed. The electrostatic charge causes the powder to be attracted to the plate in the exact shape of the part layer (or the negative shape of the part layer if support material has to be printed). After sequentially charging and depositing powder layers, the printed layers are compacted and sintered to produce the ceramic part.

3. DISCUSSION

3.1 Single step vs. multi-step AM processes

When having a closer look to the discussed AM processes, the following trends can be observed, concerning the production of ceramic parts through single step and multi-step processes.

The multi-step (indirect) AM processes, which make use of a binder material, are able to produce different types of ceramics. However, the multi-step

processes require the time consuming binder removal step. Therefore, multi-step AM processes cannot rapidly produce ceramic parts.

The single step (direct) AM processes, which do not use a binder material, do not require the time consuming binder removal step. Therefore, single step AM processes can produce more rapidly ceramic parts compared to indirect AM processes. However, the single step processes (powder bed fusion and directed energy deposition) are not (yet) able to produce as many different types of ceramics as the multi-step AM processes.

3.2 Part quality

Section 2 described the different additive manufacturing technologies to produce ceramic parts. However, not all of these technologies resulted in high quality ceramic parts. This section discusses the quality of the parts, with a main focus on commercialized AM methods: i.e. sheet lamination, binder jetting, powder bed fusion and vat photopolymerization¹⁹.

The strength of a ceramic part is determined by its largest flaw. A ceramic can be regarded as a chain in which each elemental volume with a flaw corresponds to a link in the chain and the volume-element with the critical flaw is the weakest link. As a result, the statistical nature of the strength of ceramics is usually handled by the use of Weibull statistics, where the Weibull modulus 'm' describes the flaw size distribution and is a measure for the controllability of the ceramic production process. When $m > 20$, the material can be considered to have an unique strength. Typically, m is 5-20 for ceramics, indicating that it is only possible to determine how likely failure will be at some given stress.

For some AM processes producing ceramic parts, cracks are still the most critical flaws that compromise the mechanical strength. During single step processes, i.e. direct energy deposition and single step powder bed fusion processes, thermal cracks are generally caused by thermal shocks introduced by the laser beam heating. Wilkes³³ and Hagedorn³⁵ (Fraunhofer ILT) proved that preheating the ceramic powder before laser irradiation and/or material considerations, i.e. by using 41.5wt% ZrO₂ - 58.5wt% Al₂O₃ powder eutectic powder composition, are possible ways to overcome these cracks during single step powder bed fusion. Also, as a result of a joint work between the University of Connecticut and Dalian University of Technology in China (prof. B. Zhang), Niu et al.¹⁵⁴ could also successfully produce crack-free ceramics by directed energy deposition. Also in this study, crack-free ceramics were obtained through preheating and using ZrO₂ and Al₂O₃ in eutectic proportions. During multi-step processes, cracks are generally caused during the furnace treatments. In this context, especially the polymer binder burnout (i.e. debinding) step needs to be well controlled^{91, 155}.

Except for non-structural ceramic parts where part strength is not a major issue (e.g. for the production of scaffolds), pores can be considered as the second largest flaws. Pores are generally introduced in the ceramic part due to the nature of the AM process.

Extrusion based processes, exhibit specific defects arising through the use of filaments. However, the optimization of processing parameters resulted in structural parts almost reaching the properties (strength, density) of conventionally produced ceramics¹⁹. For example, as a result of DARPA funded

research, supported by professor S.C. Danforth, Iyer et al.¹⁵⁶ produced bending strength Si_3N_4 samples through FDC. The fracture strength results were censored into two groups: one representing the 'volume' defect failure mode (i.e. failure due to internal pores: Weibull modulus 'm' of 3.9) and the other resulting from the 'surface' defect failure mode (i.e. failure due to surface pores: Weibull modulus 'm' of 11.7) as detected by fractography. The average four-point bend strength was 908 MPa.

AM processes using conventional deposition systems, such as a counter current roller or scraper system, to deposit dry powder agglomerates of 10-100 μm generally lead to low density ceramics. As described by Deckers et al.^{56, 87, 91}, Shahzad et al.^{89, 92, 102} and Rombouts et al.⁸⁸, who investigated the production of ceramics through indirect SLS® (multi-step powder bed fusion by partial melting), the inter-agglomerate pores which were in the powder bed after powder deposition remained in the part after furnace sintering. As a result the relative density of the ceramic parts could not (yet) exceed 80%¹⁰⁴ if no special scanning strategies were used during the SLS® process¹⁰⁵, or extra steps to densify the ceramic component (i.e. densification steps) were used after the SLS® process. Yoo et al.¹⁵⁷ of the Massachusetts Institute of Technology produced alumina parts with a density of 62.5% during binder jetting of dry powder agglomerates (P-3DP) if no extra densification steps were applied. The authors believe that also in this case the inter-agglomerate pores which were in the powder bed after powder deposition, remained in the part after furnace sintering. Generally, the inter-agglomerate pores could be reduced/eliminated by applying optimized processing strategies during AM, or extra steps after AM

to densify the ceramic components. For example, by laser sintering a 'sacrificial baseplate' sacrificial plate separated from the main parts, dr. M.C. Leu (Missouri University of Science and Technology) could produce ZrB_2 parts which had an average relative density of 87% and an average flexural strength of 250 MPa after furnace sintering^{103, 105}. By warm isostatic pressing (WIP) the part produced through P-3DP, Yoo et al. could increase the density of the alumina up to 99.2%, resulting in an average flexural strength of 324 MPa¹⁵⁷. By infiltrating laser sintered parts and WIPing them afterwards, Shahzad et al. could increase the density of alumina parts from 37% up to 88%. The resulting flexural strength was 148 ± 20 MPa⁸⁹.

It can be concluded that ceramic parts that have no cracks or large pores, have mechanical properties close to conventionally produced ceramics. As illustrated above, this can be realized by optimizing the AM process parameters or performing extra densification steps (e.g. infiltration, WIP) after the AM process. In order to produce crack- and pore-free ceramics through AM, it is also advisable to incorporate colloidal processing techniques into the AM process. Through the use of colloidal processing techniques, the packing of the initial ultrafine ceramic power particles can be improved. This leads to an improvement of the density and quality of the final ceramic components. The following examples illustrate this:

Sheet lamination processes (such as LOM and CAM-LEM) use ceramic tapes, produced by tape casting, which is a colloidal processing technique. Since tape casting has a well-established manufacturing history, almost any ceramic material can be processed by LOM¹⁵⁸. For example, Griffin et al.^{19, 159} produced

Al_2O_3 samples with a bending strength of 311 MPa. Rodrigues et al.¹⁶⁰ produced Si_3N_4 parts with a density of 97%, resulting in an average bending strength at room temperature of 918 MPa and an average fracture toughness of $7.45 \text{ MPa}\cdot\text{m}^{1/2}$. Klosterman et al.¹⁶¹ produced unpolish SiC specimens, which had a 4-point bend strength of about 150 MPa (142-165 MPa) and a Weibull modulus 'm' varying from 5.2 to 17.5. At last, Weisensel et al.¹⁶² produced SiSiC parts with an average four point bending strength and Young's modulus of ~150 MPa and ~210 GPa, respectively.

Despite the successes of producing ceramic parts through LOM having mechanical properties close to conventionally produced ceramics, LOM has the drawback of very poor surface qualities, especially at round or angular surfaces as the individual layers are cut by laser beams (or hauling blades)¹⁹. Further, as the company Helisys, that formerly commercialized LOM of ceramics^{28, 163}, is currently no longer in business, this process is currently not commercially exploited.

As illustrated in section 2.12, vat photopolymerization processes are currently the most commercially exploited processes (e.g. by Admatec and Lithoz) for the fabrication of ceramic functional parts. As the ceramic slurry layers are produced by colloidal processing techniques, vat photopolymerization processes are able to produce crack- and pore-free oxide ceramics having mechanical properties close to conventionally produced ceramics. For example, Wang produced Al_2O_3 parts with a mean sintered density of about 98% and a mean tensile and flexural strength of about 327 and 476 MPa¹³¹. Currently

Lithoz offers Al_2O_3 parts with densities of 3.96 g/cm^3 and 4 point-bending strengths of 430 MPa ¹²¹.

Besides vat photopolymerization, also other AM processes, making use of slurry based deposition systems, are able to produce crack- and pore-free ceramic parts. For example, as illustrated in 2.10 and Figure 5b, Tang et al. could produce Al_2O_3 parts free from delamination and cracks, with a homogeneous microstructure, a density of 98% and a mean flexural strength of 363.5 MPa .

4. CONCLUSIONS

This paper has provided a survey of the AM methods reported in literature to shape ceramic components. It has been demonstrated that, especially for AM of ceramics, the multi-step (indirect) AM processes are more appropriate to shape different types of ceramics, while to single step (direct) AM processes can produce parts more rapidly. Further, it can be concluded that ceramic parts that have no cracks or large pores, have mechanical properties close to conventionally produced ceramics. Such parts can be fabricated by optimizing the AM process parameters or performing extra densification steps after the AM process. In order to produce crack- and pore-free ceramics through AM, it is also advisable to incorporate colloidal processing techniques into the AM process. Herewith the paper has given a summary of the state-of-the-art for further R&D in the coming decades and to expand the applicability of AM of ceramics.

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