

Review  
**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 has produced ceramic parts that have no cracks or large pores and have mechanical properties close to those of 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. Finally, 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 the single-step direct AM processes can produce ceramic parts more rapidly.

*Keywords:* Additive manufacturing, ceramics, selective laser sintering®, selective laser melting, stereolithography

**I. 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”<sup>1</sup>. According to the standard, seven 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 seven 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*”<sup>1</sup>. During powder bed fusion, different consolidation phenomena, i.e. binding mechanisms, can be distinguished<sup>2</sup>. 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) have only been investigated for metal-matrix composites<sup>3</sup> and not for pure ceramic materials. As depicted in Table 1, the thermal laser energy irradiating the powder particles can initiate either full 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®).

In the literature, different layer deposition systems can be distinguished to process ceramics by means of powder bed fusion, different 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).

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**Table 1:** Overview of AM processes to shape ceramics.

| classified by ISO/ASTM      |                   |                          |                                   |                    |                  |                |                             |                               |                            |              | not (yet) classified by ISO/ASTM |                 |              |               |               |
|-----------------------------|-------------------|--------------------------|-----------------------------------|--------------------|------------------|----------------|-----------------------------|-------------------------------|----------------------------|--------------|----------------------------------|-----------------|--------------|---------------|---------------|
| Single step                 |                   | Multi-step               |                                   |                    |                  |                |                             |                               |                            |              |                                  |                 |              |               |               |
| Directed energy deposition  | Powder bed fusion | Vat photo-polymerization | Material jetting                  | Material extrusion | Sheet lamination | Binder jetting | Electro-phoretic deposition | Electro-photographic printing |                            |              |                                  |                 |              |               |               |
| Powder bed fusion           |                   |                          |                                   |                    |                  |                |                             |                               |                            |              |                                  |                 |              |               |               |
| multi-step / single step    | single step       |                          |                                   |                    |                  |                |                             |                               |                            |              | multi-step                       |                 |              |               |               |
|                             | 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                  | electro-phoretic deposition   | conventional               | conventional | slurry coater                    | ring blade      | conventional | slurry coater | slurry coater |

In this review paper, the different AM technologies to produce ceramics are detailed in Section II. Section II 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 means of AM technology and the consequences of producing ceramics with single-step and multi-step AM technologies are discussed in Section III.

## II. Additive Manufacturing Technologies to Produce Ceramics

### (1) Material jetting

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

#### (Direct) inkjet printing (IJP)<sup>4–7</sup>

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)<sup>8,9</sup>

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 droplets containing fine ceramic particles in a gas.

### (2) Material extrusion

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

#### Fused deposition of ceramics (FDC)<sup>10–12</sup>

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<sup>13–16</sup>

In robocasting, also called three-dimensional fibre deposition (3DFD<sup>17</sup>) or Micropen<sup>18</sup>, 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 substrate<sup>19</sup>. In this way, alumina samples could be produced by Dr. M. C. Leu *et al.*<sup>20,21</sup> (Missouri University of Science and Technology).

### (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*”<sup>1</sup>, used to shape macroscopic ceramic parts can be categorized as follows:

#### (Traditional) directed energy deposition<sup>22</sup>

Direct energy deposition is also widely known as laser cladding. The printing head of a directed energy deposition system consists of a nozzle that 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<sup>23</sup>

At the University of Birmingham, Wang *et al.* managed to combine the FDM and the directed energy deposition process into a hybrid process. Ti<sub>6</sub>Al<sub>4</sub>V-TiC composite parts

could be fabricated by feeding powder (TiC) and wire (Ti<sub>6</sub>Al<sub>4</sub>V) material into the focus of a CO<sub>2</sub> laser.

#### (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*”<sup>1</sup>. 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 that deposits green ceramic tape-cast layers. These layers are unrolled onto the working bed where a CO<sub>2</sub> 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 layer<sup>4</sup>. The high ceramic powder load in the cast 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 silica<sup>24</sup>, or glass-ceramic<sup>25</sup>) 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 the layers being stacked and then cut, 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 produced<sup>4</sup>.

#### (5) Binder jetting

Binder jetting processes, defined as “*additive manufacturing processes in which a liquid bonding agent is selectively deposited to join powder materials*”<sup>1</sup>, 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 powder<sup>26</sup>. Generally, two different 3DP methods can be distinguished.

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

This is the traditional method to produce ceramic parts by means of 3D printing. Sequential depositing of powder particles with a roller or scraper system and printing of binder material by ink-jet printing yield the layers, resulting 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 at the Massachusetts Institute of Technology (both co-inventors of the binder jetting technology<sup>26</sup>) demonstrated this technology by preparing complex-shaped cores and shells with high dimensional tolerance to produce castings of high temperature<sup>27</sup>. In this study, sequential layers of

alumina powder particles were deposited and selectively glued with a colloidal silica binder.

Formerly, the company Soligen had an exclusive licence for 3D printing of ceramics<sup>28</sup>. Nowadays, ExOne<sup>29</sup> and 3D Systems<sup>30</sup> offer 3DP machines for AM of ceramics.

##### Slurry-based three-dimensional printing (S-3DP)<sup>4</sup>

In order to be able to process fine powders (< 20 μm) and improve the furnace sintering characteristics of the green part, research into 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.

#### (6) Single-step powder bed fusion by full melting

During single-step powder bed fusion by full melting (i.e. Selective Laser Melting, SLM), the laser beam causes the irradiated ceramic powder material to heat and fully melt. In the 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 μm) powder particles. During powder deposition the gravity forces overcome the electrostatic attraction forces, enabling the flow 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-TCP<sup>31</sup>) and micro-crack-containing zirconia<sup>31,32</sup> parts were produced using a CO<sub>2</sub> laser. In order to reduce the amount of micro-cracks caused by thermal gradients, a high-temperature preheating system was developed. This system used a CO<sub>2</sub> laser to preheat the powder layers (temperature controlled by means of a pyrometer) and a Nd:YAG laser to locally melt the ceramic.

Although pure ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub> (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. ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, 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 μm<sup>33</sup>.

In order to obtain SLM ceramics with a fine microstructure (i.e. grain sizes up to 10 μm), a eutectic zirconia-alumina (ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) powder ratio had to be chosen (Fig. 1). The starting powder was produced by means of dry mixing of 41.5 wt% spherical ZrO<sub>2</sub> powder with 58.5 wt% spherical Al<sub>2</sub>O<sub>3</sub> powder. The zirconia component was partially stabilized with 3 mol% yttria Y<sub>2</sub>O<sub>3</sub>. Both powders, sup-

plied by Innalox BV (the Netherlands), had a spherical shape and a monomodal size distribution of 50  $\mu\text{m}$ .

The SLM parameters for the 41.5 wt%  $\text{ZrO}_2$  - 58.5 wt%  $\text{Al}_2\text{O}_3$  powder comprised a preheating temperature of 1730  $^\circ\text{C}$ , a layer thickness of 50  $\mu\text{m}$ , a scanning velocity of 200 mm/s, a laser power of 60 W and a scan spacing of 50  $\mu\text{m}$ <sup>34</sup>. Owing to the preheating temperatures close to the melting point of the eutectic powder ratio (1860  $^\circ\text{C}$ ) a large melt pool evolved, which positively influenced the density of the obtained part. On the other hand, a poor surface quality was determined since the low-viscous melt pool exceeded the boundaries of the scanned part and wetted and impregnated the surrounding powder<sup>34–36</sup>.

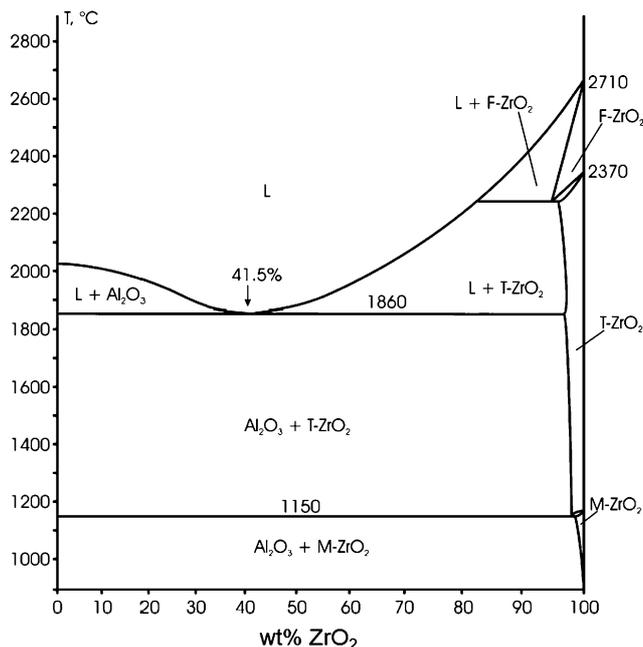


Fig. 1: Alumina-zirconia phase diagram<sup>37</sup>.

In order to improve this patented<sup>38,39</sup> SLM process, the preheating device was modified. Since specimens with a height > 3 mm could not be processed with the original setup, which only heated the powder surface, a bottom-up preheating system using inductive heating technology was developed<sup>34</sup>. In combination with the inductive preheating system, a selective preheating strategy was developed. This setup used two laser sources, in which a fibre laser with a focused spot size of ~ 200  $\mu\text{m}$  was used for selective melting while a diode laser-beam was coaxially superpositioned by a dichroic beam splitter, resulting in selective preheating with a focused spot size of ~ 5 mm<sup>34</sup>. In this way parts with a height up to > 10 mm could be produced<sup>40</sup>.

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 with SLM. Shishkovsky *et al.*<sup>41</sup> reported the use of a Phenix PM-100 machine to obtain SLM powder mixtures, prepared from yttria-stabilized zirconia, YSZ ( $\text{ZrO}_2$  90 wt%,  $\text{Y}_2\text{O}_3$  10 wt%, Zircar Zirconia Inc.), and aluminium (ADC4 grade, in some experiments alumina  $\text{Al}_2\text{O}_3$  from Baikovsky Inc. was used) in the ratio 4:1 in oxygen and argon atmosphere. The resulting surface

macro- and microstructures examined by means of optical metallography were relatively smooth, but contained pores and cracks. Probably, the microstructures were not only formed as a result of 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 coater<sup>42</sup>. In the literature the term ceramic laser fusion (CLF) is used to describe 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 the building process. During laser scanning, the dried silica-clay layer is fully melted and parts with 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 by means of SLM of the non-preheated slurry-coated layers<sup>43–46</sup>.

#### Aerosol-assisted spray deposition

Wu *et al.*<sup>47</sup> 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 densification by means of 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 Fig. 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 invented<sup>48</sup>) was one of the pioneers in laser-sintering ceramics. Under his supervision, alumina-ammonium phosphate<sup>49,50</sup> and alumina-boron oxide<sup>50</sup> ceramics were produced. Both ammonium phosphate (melting point: 190  $^\circ\text{C}$ ) and boron oxide (460  $^\circ\text{C}$ ) acted as structural material as well as binder to glue the alumina particles.

At Ecole Nationale d'Ingénieurs de Saint-Etienne (ENISE), Bertrand *et al.*<sup>51</sup> produced yttria-stabilized zirconia by means of 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, five different starting powders were selected: atomized and crushed yttria-zirconia (4 mol%) sup-

plied by Baikowski, atomized ZYP30 (10 mol%) powder from Zircar, atomized YZB5 powder from Tioxide and atomized YZ3P powder (3 mol%) from ENSME. Since the melted powder could not fill all the gaps between the powder particles that had not melted, only low-density ceramics could be produced.

At the University of Leeds, Lorrison *et al.*<sup>52</sup> produced hydroxyapatite -phosphate glass. In this case too, the glass acted as structural material as well as binder. By using metal as a binder and structural material, Gu and Shen<sup>53</sup>, Nanjing University of Aeronautics and Astronautics, produced WC-10Co/Cu ceramic-metal composites.

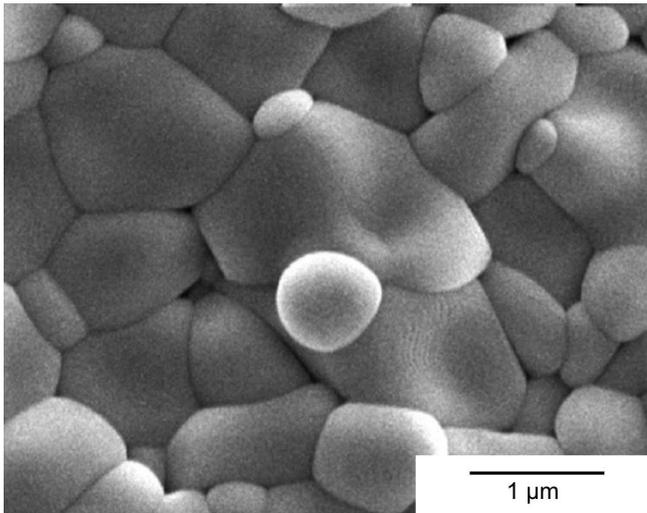


Fig. 2: SEM micrographs of the surface of an alumina sample, prepared by SLM of aerosol-assisted spray -deposited layers<sup>47</sup>.

### Slurry coating

At 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. 66 wt% solid phase<sup>2,54</sup>) are deposited with this system or another colloidal-processing-based deposition system, the packing density of the particles can be much higher (i.e. > 50 vol%<sup>55</sup>) compared to the packing density of conventionally deposited particles (i.e. estimated to be about 20 vol%<sup>56</sup>).

Through SLS® of the slurry-coated layers, hydroxyapatite<sup>57</sup>, porcelain<sup>58–60</sup> and alumina-silica<sup>54,61</sup> 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 in 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 produced<sup>62</sup>.

### Slurry spraying

At the Fraunhofer Institute of Production Technology (IPT) in Aachen, Klocke *et al.*<sup>63</sup> produced yttria-stabilized zirconia by means of 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 that 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 that had not melted.

### Ring blade

In 2002, the Laserinstitut der Hochschule Mittweida (LHM) developed the micro SLS® process, which is able to accurately produce ceramic and metal parts<sup>64–66</sup>. The process was internationally patented in 2004<sup>67</sup>. It consists of a ring blade<sup>68</sup>, also called ‘powder rack’, which is able to deposit dry non-agglomerated submicrometer powder particles. It is also possible to micro SLS® a part consisting of two segments of a different material (e.g. Cu and Ag)<sup>69</sup>. Further, a compacting system can be used to increase the packing density of the deposited layers and consequently that of the fabricated parts too<sup>70</sup>.

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 mode<sup>71</sup>.

Partial melting of submicrometer powders using the micro SLS® device has been applied to the following ceramic materials: alumina-feldspar<sup>72</sup>, alumina-silica<sup>71,73–75</sup>, feldspar<sup>71</sup> and silicon/silicon carbide/carbon (Si-SiC-C)<sup>68,69,71,74–77</sup>. 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 submicrometer-sized ceramic powder layer with a high packing density, preheated to a uniform and high ( $\pm 800$  °C) temperature. To achieve this, an experimental setup was designed, constructed and tested for Al<sub>2</sub>O<sub>3</sub> 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  $\pm 50$  °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 depo-

sition 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 the production of alumina ceramic parts with a density up to 85 % and a microstructure with a grain size below 5  $\mu\text{m}$ <sup>78,79</sup> (Fig. 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.

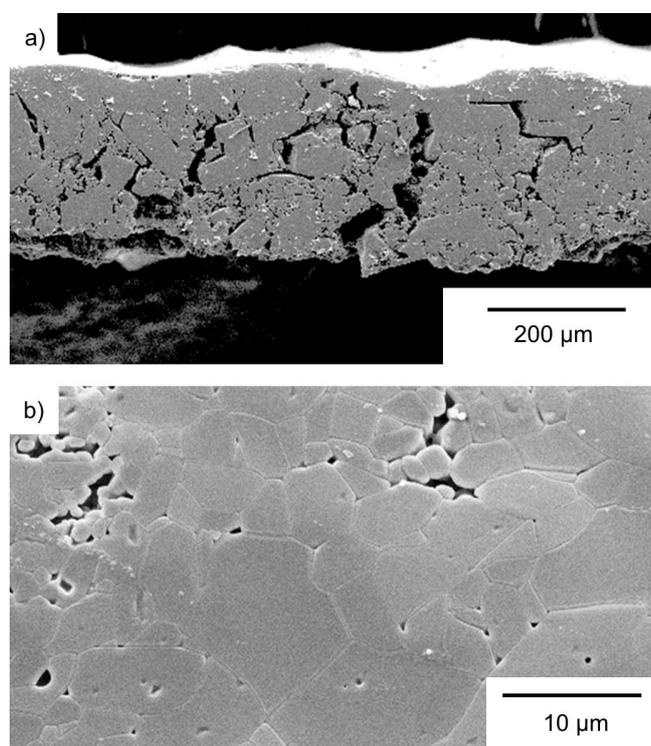


Fig. 3: Cross-section at low (a) and high (b) magnification of a part/sample produced by means of SLS®/SLM of submicrometer powder at 800 °C<sup>78,79</sup>.

### (8) Single-step powder bed fusion by solid-state sintering

#### Conventional deposition system

Bertrand *et al.*<sup>2,81</sup> 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 owing to the extra energy contribution of a Nd:YAG laser source. To obtain the desired characteristics, a post-sintering operation was necessary.

### (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 that

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)<sup>82</sup>.

#### 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 at the University of Texas in Austin SLSed Si powder in a  $\text{NH}_3$  atmosphere to produce  $\text{Si}_3\text{N}_4$ <sup>82</sup>. F. Klocke and H. Wirtz at the Fraunhofer Institute of Production Technology (IPT) SLSed SiC starting powder in an argon atmosphere. During laser irradiation, SiC decomposed into Si and C. Despite the inert argon atmosphere, the Si atoms reacted with  $\text{O}_2$  and formed  $\text{SiO}_2$ , which glued the SiC particles<sup>83</sup>. 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 silica<sup>84</sup>. The process, which is also called Ceramic Laser Sintering (CLS), was based on an irreversible chemical reaction of slurry containing aluminium phosphate and silica at a temperature above 250 °C.

#### Ring blade

The Laserinstitut der Hochschule Mittweida (LHM) used the patented micro SLS® device<sup>67</sup> to produce Si-SiC parts by means of 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<sup>71,74–77</sup>.

### (10) Multi-step powder bed fusion by partial melting

#### Conventional deposition system

A method for producing high-temperature parts by means of low-temperature selective laser sintering® was patented in 1993<sup>85</sup>. Ever since, this method has been 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 out and a ceramic part is obtained. As depicted in Table 2, many different ceramics are already produced with this process, including:  $\text{Al}_2\text{O}_3$ <sup>56,86–92</sup>,  $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ <sup>93</sup>,  $\text{Al}_2\text{O}_3\text{-glass-B}_2\text{O}_3$ <sup>94</sup>,  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-TiC}$ <sup>95</sup>, apatite-mullite<sup>96</sup>, graphite<sup>97</sup>,  $\text{K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ <sup>98</sup>,  $\text{SiO}_2$ <sup>24</sup>, SiC<sup>99–101</sup>,  $\text{ZrO}_2$ <sup>24,102</sup> and  $\text{ZrB}_2$ <sup>103–105</sup>.

If the binder is inorganic, it cannot be burned. During the thermal treatment, the inorganic binder (e.g.  $\text{HBO}_2$ ) chemically reacts and becomes part of the structural ceramic (e.g.  $\text{B}_2\text{O}_3$ )<sup>93,94</sup>. Different types of organic binders have been examined to fabricate ceramic parts via SLS®

like long-chain fatty acids (e.g. stearic acid<sup>86, 103–105</sup>), waxes (carnauba wax<sup>88</sup>), thermosets<sup>24, 98–101</sup> and thermoplastics<sup>56, 89–92, 96, 102</sup>. Sometimes, a combination of binders is used: e.g. a thermoset in combination with semi-crystalline PA-11 (or nylon 11) to produce graphite<sup>97</sup>, or a wax in combination with amorphous thermoplast PMMA to produce the composite ceramic Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiC<sup>95</sup>.

If the polymer-ceramic composite starting powders have an irregular shape (e.g. as a result of ball milling), craters are formed during layer deposition. As a result, no complex-shaped objects can be SLSed<sup>56</sup>. Shahzad<sup>106</sup> and Deckers<sup>107</sup> have demonstrated that, besides dispersion polymerization<sup>91, 108</sup>, 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<sup>87, 92</sup>, polypropylene<sup>89, 102</sup> and carnauba wax<sup>88</sup>) and ceramics (alumina<sup>87, 89, 92</sup>, zirconia<sup>102</sup> and hydroxyapatite-tricalcium\_phosphate) could be processed.

Indirect SLS® with the use of a sacrificial binder phase allows the production of 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 %<sup>104, 107</sup>. 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 Deckers<sup>107</sup> and Shahzad<sup>106</sup>: (i) irradiating the powder layers multiple times instead of only once (i.e. laser re-melting), (ii) cold, quasi and warm isostatic pressing of the SLSed parts and (iii) infiltrating the parts obtained at different stages of the PM process. As a result, freeform-shaped alumina parts (Fig. 4) with densities up to approximately 90 % could be obtained. In order to produce higher quality ceramic parts with 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 Hon<sup>109</sup> investigated SLS® of SiC-PA ceramic-polymer composites. Evans *et al.*<sup>110</sup> infiltrated SiC preforms with molten Si, creating SiC-Si cermets.

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

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

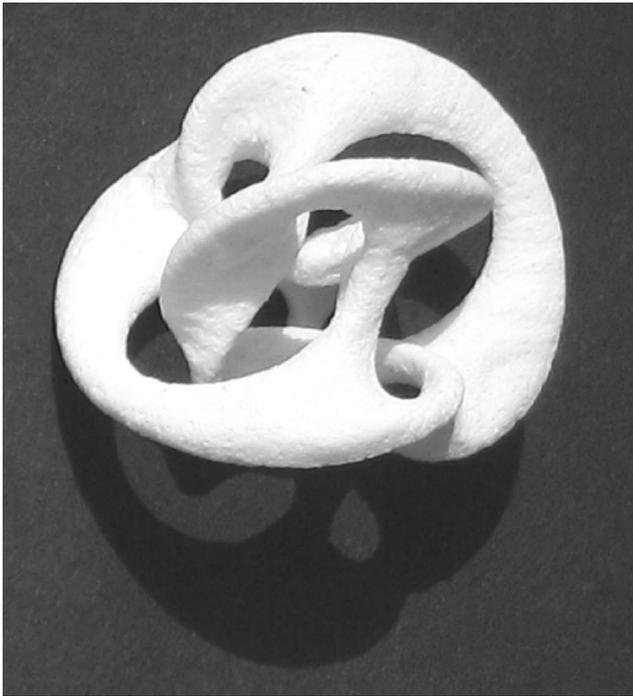


Fig. 4: Example of a freeform-shaped alumina part obtained with indirect SLS®.

#### 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 with the so-called ceramic laser sintering (CLS) process<sup>46, 111–113</sup>. 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 by means of slurry-based SLS®<sup>114</sup>. Both sub-partially hydrolysed polyvinyl alcohol PVA(BC) and fully hydrolysed polyvinyl alcohol PVA(BF) were used as a binder. As depicted in Fig. 5a 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 Al<sub>2</sub>O<sub>3</sub> ceramic parts (Fig. 5b), free from delamination and cracks, with a homogeneous microstructure, a density of 98 % and a mean flexural strength of 363.5 MPa were obtained.

#### (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, CO<sub>2</sub> 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.*<sup>115</sup> used slurry that mainly consisted of Al<sub>2</sub>O<sub>3</sub> powder, silica sol and deionized water to fabricate alumina-silica parts. Owing 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 with the CLG process (Fig. 6). The maximum green part strength after CLG was 4.7 MPa. After heat treatment at 1200 °C for 1.5 hours, the flexural strength increased up to 12.5 MPa. No density values were reported<sup>116–118</sup>.

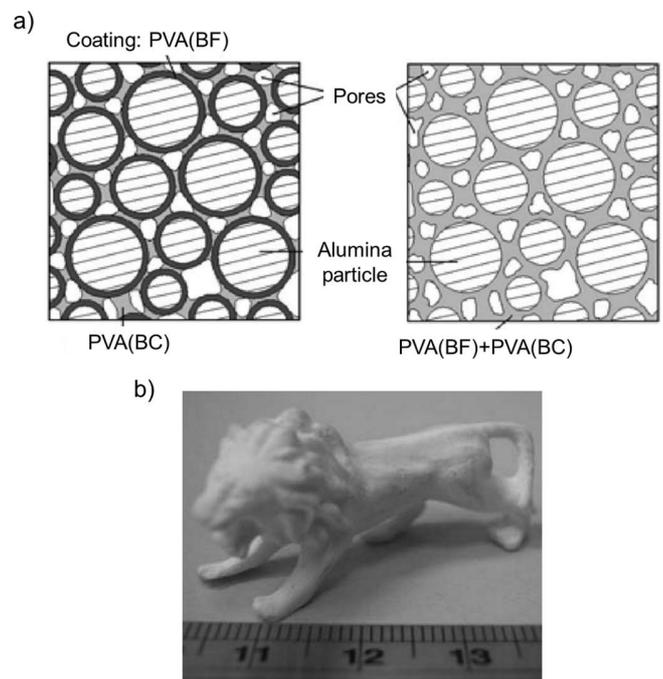


Fig. 5: The slurry-based indirect SLS® process<sup>114</sup>.

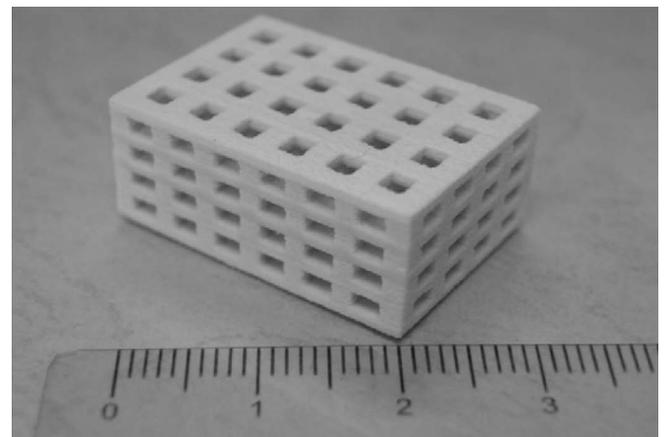


Fig. 6: A silica part with inner channel structure made with ceramic laser gelling<sup>117</sup>.

### (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*”<sup>1</sup>.

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.

#### (Macro) SLA

In the literature, SLA of ceramics is described under different names and abbreviations such as ceramic stereolithography (CerSLA<sup>119</sup>, CSL<sup>120</sup>) and lithography-based ceramic manufacturing (LCM<sup>121</sup>). Different research teams have investigated the fabrication of ceramics with SLA. The polymerization reaction is mostly performed by an UV laser. However, Griffith and Halloran<sup>19, 122</sup> 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)<sup>123</sup>. During LAMP, each layer is rapidly patterned by UV exposure in the pattern of a bitmap defined by a spatial light modulator.

Many patents have already described different suspensions or specific applications for SLA of ceramics<sup>124–129</sup>. 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<sup>120, 130</sup>. It is also possible to use a medium that consists of an UV-curable resin as an organic binder and methanol as a solvent and a dispersant. After the solvent-based slurry has been paved, the solvent is vaporized using a fan. This results in shrinkage of the slurry volume of the deposited layer<sup>131</sup>.

Another route to produce the resin was developed by De Hazan *et al.*<sup>132</sup>. In this case, surfactants were adsorbed in aqueous media under controlled pH conditions on Al<sub>2</sub>O<sub>3</sub>, ZnO and Al<sub>2</sub>O<sub>3</sub>/ZnO particles. After drying, the particles were transferred to an UV-curable organic medium, which mostly consisted of 2-hydroxyethyl acrylate (HEA, Rahn, Switzerland) and polyethylene glycol 200 diacrylate (M282, Rahn, Switzerland) in a 14:1 ratio.

The extent of the photopolymerization reaction during laser irradiation can be described with the following equation which P.F. Jacobs derived, starting from the Beer-Lambert equation<sup>133</sup>.

$$\delta_c = D_p \cdot \ln\left(\frac{E_1}{E_2}\right) \quad (1)$$

where  $\delta_c$  is the cured depth, i.e. the polymerized thickness,  $E_1$  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 have used this equation to describe the hardening of a ceramic suspension under UV radiation<sup>119, 120, 123, 134–138</sup>. The cured depth  $\delta_c$  is influenced by extra photoactive components in the light curable medium and the ceramic particles<sup>123</sup>. 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 Fig. 7a<sup>134</sup>, 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 SiO<sub>2</sub>. On the other hand, the refractive index of the ceramic filler is increasingly higher than the refractive index of the organic medium for respectively Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> 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 SiO<sub>2</sub><sup>139, 140</sup> or Al<sub>2</sub>O<sub>3</sub><sup>141</sup> to be easier, compared to SLA of ZrO<sub>2</sub> or SiC.

As depicted in Fig. 7b<sup>134</sup>, 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 concentration<sup>134</sup>.

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<sup>123, 135</sup>:

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

where  $\eta_r$  is the relative viscosity of the suspension,  $\eta$  is the viscosity of the suspension,  $\eta_0$  is the viscosity of the medium,  $\phi$  the volume fraction of ceramic powder,  $\phi_0$  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<sup>124–127, 129</sup> have been filed.

SLA of ceramics from high-viscosity paste slurries is commercially exploited by 3DCERAM<sup>142</sup> and Sirris<sup>143</sup>. At Sirris in Belgium, a special coater that can deposit pastes, containing up to 60 vol% ceramic (or metal) powder, was developed<sup>144</sup> and patented<sup>124</sup>. The paste-coater

is used in combination with an Optoform SLA machine to produce ceramic parts. 3DCERAM uses a similar setup to AM ceramics.

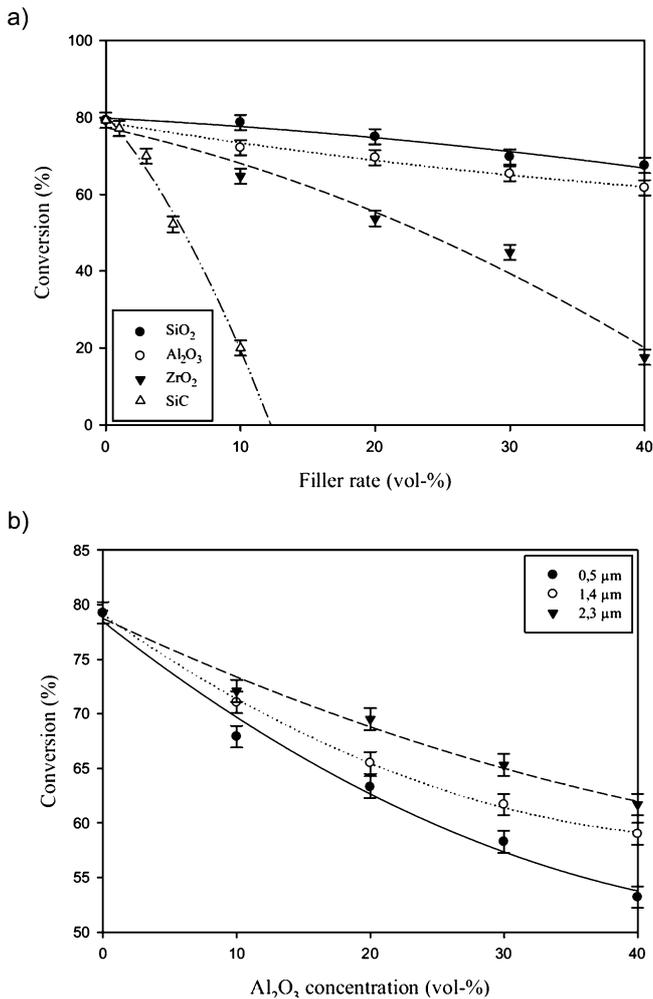


Fig. 7: Influence of the refractive index (refractive index of SiO<sub>2</sub> < Al<sub>2</sub>O<sub>3</sub> < ZrO<sub>2</sub> < SiC) and solid loading of the ceramic filler (a) and alumina particle size and solid loading (b) on the photo polymerisation conversion of a ceramic filler containing acrylate<sup>134</sup>.

SLA of ceramics from low-viscosity slips is commercially exploited by Admatec Europe BV<sup>145</sup>, a subsidiary of Formatec<sup>145</sup>, and by Lithoz GmbH<sup>121</sup>, a spin-off from the Technische Universität Wien (TU Wien<sup>146</sup>) that closely co-operates with Ivoclar Vivadent AG<sup>125, 127, 147</sup>. 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 (Fig. 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 at TNO<sup>148</sup> 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 with the SLA process (Fig. 8b). Owing to the relative large amount of polymer in the produced sample, overly 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 parameters<sup>119</sup> and avoiding the presence of uncured monomer material after the SLA process<sup>149</sup>, 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 with SLA is quite uniform and about 10 % in all directions, usually somewhat smaller in the z-direction, compared to the x-y direction<sup>149</sup>.

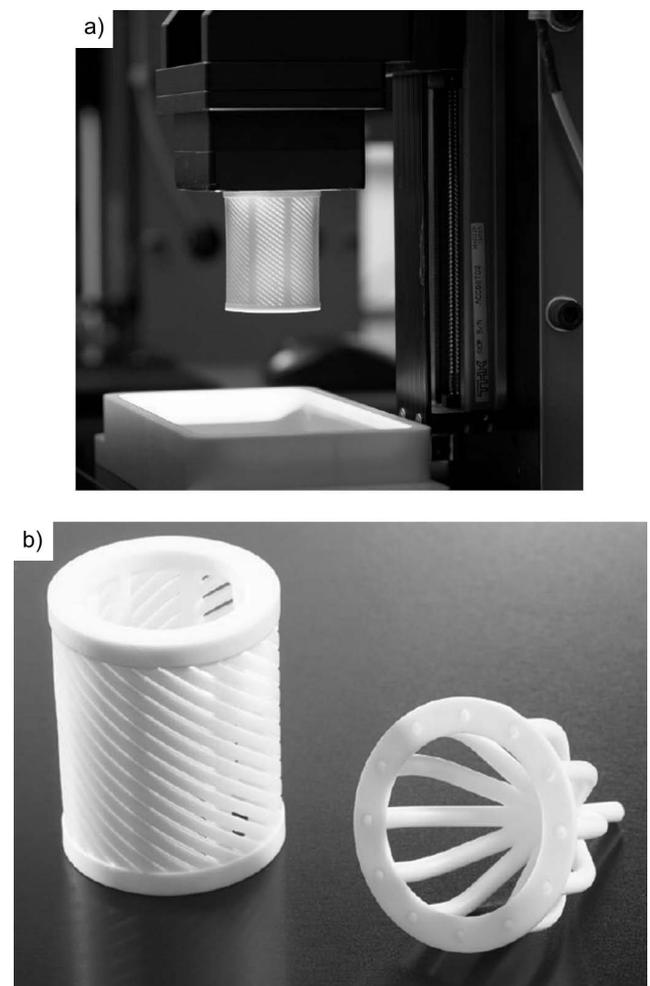


Fig. 8: SLA machine from Admatec producing a composite ceramic part (a). After debinding and furnace sintering, the ceramic components are obtained (b)<sup>150</sup>.

#### 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<sup>130, 151, 152</sup>. 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. with a DLP projector, or with laser vector-by-vector scanning. If specialized lasers and optics are used, the micro SLA technology allows the production of ceramic components with submillimeter resolution<sup>130</sup>.

### (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)*<sup>153</sup>

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)*<sup>4</sup>

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.

## III. Discussion

### (1) Single-step vs. multi-step AM processes

Taking a closer look at the discussed AM processes, the following trends can be observed with regard to the production of ceramic parts in single- 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 ceramic parts more rapidly 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.

### (2) Part quality

Section II 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 photopolymerization<sup>19</sup>.

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 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. Wilkes<sup>33</sup> and Hagedorn<sup>35</sup> (Fraunhofer ILT) proved that preheating the ceramic powder before laser irradiation and/or material considerations, i.e. by using 41.5 wt% ZrO<sub>2</sub> - 58.5 wt% Al<sub>2</sub>O<sub>3</sub> powder eutectic powder composition, are possible ways to overcome these cracks during single-step powder bed fusion. Also, as a result of joint work between the University of Connecticut and Dalian University of Technology in China (Prof. B. Zhang), Niu *et al.*<sup>154</sup> could also successfully produce crack-free ceramics by directed energy deposition. Also in this study, crack-free ceramics were obtained by preheating and using ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in eutectic proportions. During multi-step processes, cracks are generally caused during the furnace treatment. In this context, especially the polymer binder burnout (i.e. debinding) step needs to be well controlled<sup>91,155</sup>.

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 into the ceramic part owing to the nature of the AM process.

Extrusion-based processes exhibit specific defects arising owing to the use of filaments. However, the optimization of processing parameters resulted in structural parts almost matching the properties (strength, density) of conventionally produced ceramics<sup>19</sup>. For example, as a result of DARPA-funded research, supported by Professor S.C. Danforth, Iyer *et al.*<sup>156</sup> produced bending strength Si<sub>3</sub>N<sub>4</sub> samples by means of FDC. The fracture strength results were categorized 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 bending 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.*<sup>56,87,91</sup>, Shahzad *et al.*<sup>89,102,156</sup> and Rombouts *et al.*<sup>88</sup>, who investigated the production of ceramics by means of 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 %<sup>104</sup> if

no special scanning strategies were used during the SLS® process<sup>105</sup>, or no extra steps to densify the ceramic component (i.e. densification steps) were introduced after the SLS® process. Yoo *et al.*<sup>157</sup> at 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 that 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 base-plate’, a sacrificial plate separated from the main parts, Dr M.C. Leu (Missouri University of Science and Technology) could produce ZrB<sub>2</sub> parts that had an average relative density of 87 % and an average flexural strength of 250 MPa after furnace sintering<sup>103,105</sup>. By warm isostatic pressing (WIP) the part produced with P-3DP, Yoo *et al.* could increase the density of the alumina up to 99.2 %, resulting in an average flexural strength of 324 MPa<sup>157</sup>. 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 MPa<sup>89</sup>.

It can be concluded that ceramic parts without cracks or large pores have mechanical properties close to those of 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 with 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 means of LOM<sup>158</sup>. For example, Griffin *et al.*<sup>19,159</sup> produced Al<sub>2</sub>O<sub>3</sub> samples with a bending strength of 311 MPa. Rodrigues *et al.*<sup>160</sup> produced Si<sub>3</sub>N<sub>4</sub> 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 MPa·m<sup>1/2</sup>. Klosterman *et al.*<sup>161</sup> produced unpolished SiC specimens, which had a 4-point bending strength of about 150 MPa (142–165 MPa) and a Weibull modulus ‘m’ varying from 5.2 to 17.5. Finally, Weisensel *et al.*<sup>162</sup> 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 applying LOM to produce ceramic parts with mechanical properties close to those of conventionally produced ceramics, LOM has the draw-

back of very poor surface qualities, especially at round or angular surfaces as the individual layers are cut by laser beams (or hauling blades)<sup>19</sup>. Further, as the company Helisys, which formerly commercialized the LOM process for ceramics<sup>28,163</sup>, is no longer in business, this process is not currently commercially exploited.

As illustrated in Section II(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 those of conventionally produced ceramics. For example, Wang produced Al<sub>2</sub>O<sub>3</sub> parts with a mean sintered density of about 98 % and a mean tensile and flexural strength of about 327 and 476 MPa<sup>131</sup>. Currently Lithoz offers Al<sub>2</sub>O<sub>3</sub> parts with densities of 3.96 g/cm<sup>3</sup> and 4-point bending strengths of 430 MPa<sup>121</sup>.

Besides vat photopolymerization, other AM processes, making use of slurry based deposition systems, are also able to produce crack- and pore-free ceramic parts. For example, as illustrated in II(10) and Fig. 5b, Tang *et al.* could produce Al<sub>2</sub>O<sub>3</sub> parts free from delamination and cracks, with a homogeneous microstructure, a density of 98 % and a mean flexural strength of 363.5 MPa.

#### IV. Conclusions

This paper has provided a survey of the AM methods reported in the 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 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 those of 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 with 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 as a starting point for further R&D in the coming decades and to expand the applicability of AM for ceramics.

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