

Towards a debinding-free additive manufacturing of ceramics: A development perspective of water-based LSD and LIS technologies

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ABSTRACT

Ceramic additive manufacturing (AM) requires a complex process chain with various post-processing steps that require expensive machines and special expertise. The key to further market penetration is AM that makes it possible to integrate into an already established ceramic process chain. Most successful AM technologies for ceramics are, however, based on processes that initially have been developed for polymeric materials. For ceramics AM, polymers or precursors are loaded with ceramic particles. This strategy facilitates the entry into AM, however the introduction of organic additives into the ceramic process chain represents a considerable technological challenge to ultimately obtain a ceramic component after additive shaping. In the present communication, two technologies based on ceramic suspensions will be introduced, the “layerwise slurry deposition” (LSD) and “laser induced slip casting” (LIS) technology. Both technologies take advantage of the high packing densities reached by conventional slip casting and moreover enable the processing of fines, even nanoparticles.

1. Introduction

Additive manufacturing (AM) of ceramics is on one hand a field of active research and development, on the other it has found its way into the market. The field of application of advanced ceramics is very wide and encompasses products in a size range from millimeters to meters. Examples of applications vary from millimeter-sized medical devices [1] to meter-sized supports for telescope mirrors and optical devices for the semiconductor industry [2,3]. So far, no single AM technology has been demonstrated to be able to cover such a wide size range for advanced ceramic materials.

Fig. 1 provides an overview of ceramic AM technologies (or technology classes), currently capable of providing dense ceramic parts, showing their range of applications regarding both typical part sizes and printing resolution that can be achieved. This graph and the following paragraphs are not intended to be a comprehensive review of individual technologies or equipment, but rather to serve as a guide to discuss the potential and limitations of different technology classes. For a detailed description of the working principle and state-of-the-art of ceramic AM several review articles are available in the literature [4–7].

A rather obvious trend can be observed in that there is a trade-off between typical part size and print resolution. Currently, at the

research stage, the highest print resolution can be achieved by **two photon polymerization (2 PP)**. Originally developed for polymeric materials, the 2 PP working principle is based on photocuring a resin by the absorption of two photons with a wavelength typically in the infrared (IR) [11]. The resins used have very low linear absorption in the selected IR region, which allows focusing a laser inside the volume of the material. Due to the quadratic dependence of the 2 PP polymerization rate on light intensity, photopolymerization can be achieved in a very small volume of material, leading to a high spatial resolution down to 100–200 nm [12]. Research work demonstrated that 2 PP can be applied not only to polymer-derived glasses [13], but also to silica glass [14] and recently to polycrystalline advanced ceramics starting from a particle suspension [15].

Fig. 1 shows as example of the latter a complex 3D model made of polycrystalline ZrO₂ manufactured at BAM (Berlin, Germany). Although 2 PP polymeric parts larger than 1 cm have been demonstrated, most 2 PP printed parts are limited to sizes < 1 mm, lastly due to the slow build-up rates (<1 mm³/h) [16].

At a larger size scale than 2 PP, **vat photopolymerization (VPP)** is one of the first and most commercially successful ceramic AM technologies, also using an organic photosensitive resin which can be locally crosslinked and, thus, consolidated by light. This technology was

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adapted from the polymer processing stereolithography (SL) and its related technologies, now grouped in the category of vat photopolymerization (VPP) technology by ISO/ASTM 52900:2022-03 [17]. Ceramic VPP uses photosensitive resins highly filled with ceramic particles as feedstocks, which are layer-by-layer consolidated by photopolymerization, achieved by means of a point laser source or of a projector. Pioneer work was done by Griffith and Halloran [18], by Chartier et al. [19] and later by the group of J. Stampfl [20], the latter two activities leading to the foundation of companies (3D Ceram and Lithoz GmbH, respectively) which are successfully operating since more than 10 years in the field of AM of ceramics. Finding appropriate photocurable ceramic feedstocks can be regarded as the key achievement for adapting the VPP technology to ceramics AM.

Micro-stereolithography can achieve a resolution of a few μm and a part size up to 1 cm [21,22], whereas common ceramic VPP commercial systems typically have a lateral resolution of 40–60 μm and use a layer thickness of 25–100 μm [23–25]. Laser top-down systems can be easier to scale up maintaining the same lateral resolution, e.g. up to a printable area of 600 mm \times 600 mm with four lasers [26]. Digital light processing (DLP) systems using a digital micromirror device with a fixed number of pixels instead have a resolution that depends on the projected area, e.g. 25 μm for an area of 64 mm \times 40 mm and 75 μm for 192 mm \times 120 mm [27].

However, as shown in Fig. 1, in the ceramic VPP the limiting factor often is the part's wall thickness rather than the maximum building

envelope. Process-wise, this approach has added an additional step in the ceramic powder processing chain, the debinding. Like injection molding, the green part contains excessive amounts of organics, and this organic matrix must be removed before sintering.

Even for thin-walled parts, this approach necessitates a long debinding step of tens of hours. For thick-walled parts (5–10 mm) debinding can take up to several days and is not feasible above a certain thickness (15–20 mm) without introducing defects in the part [28]. Thermal debinding technologies are applied in this context, and debinding has become a key technology for the successful use of VPP in ceramics manufacturing. Currently VPP is one of the most successful AM technologies for the manufacture of advanced ceramics. Nevertheless, due to the time-consuming debinding process step and associated restrictions to the geometry of the parts, like limited wall thickness, VPP is not able to exploit the full potential of AM of ceramics.

Material jetting (MJ) is a wide class of AM technologies including several processes able to generate high-quality advanced ceramic components. The working principle is the selective deposition of droplets of build material. Depending on the dispensing apparatus and on the feedstock used, a wide window of part size and printing resolution can be realized by MJ, as shown in Fig. 1.

At the lower end of the spectrum, low-viscosity suspensions of sub-micrometric ceramic particles can be printed with an in-plane resolution up to 1200 DPI (approx. 47 μm lateral resolution). Building on the theoretical work of Fromm [29], the groundwork for ceramic MJ was set

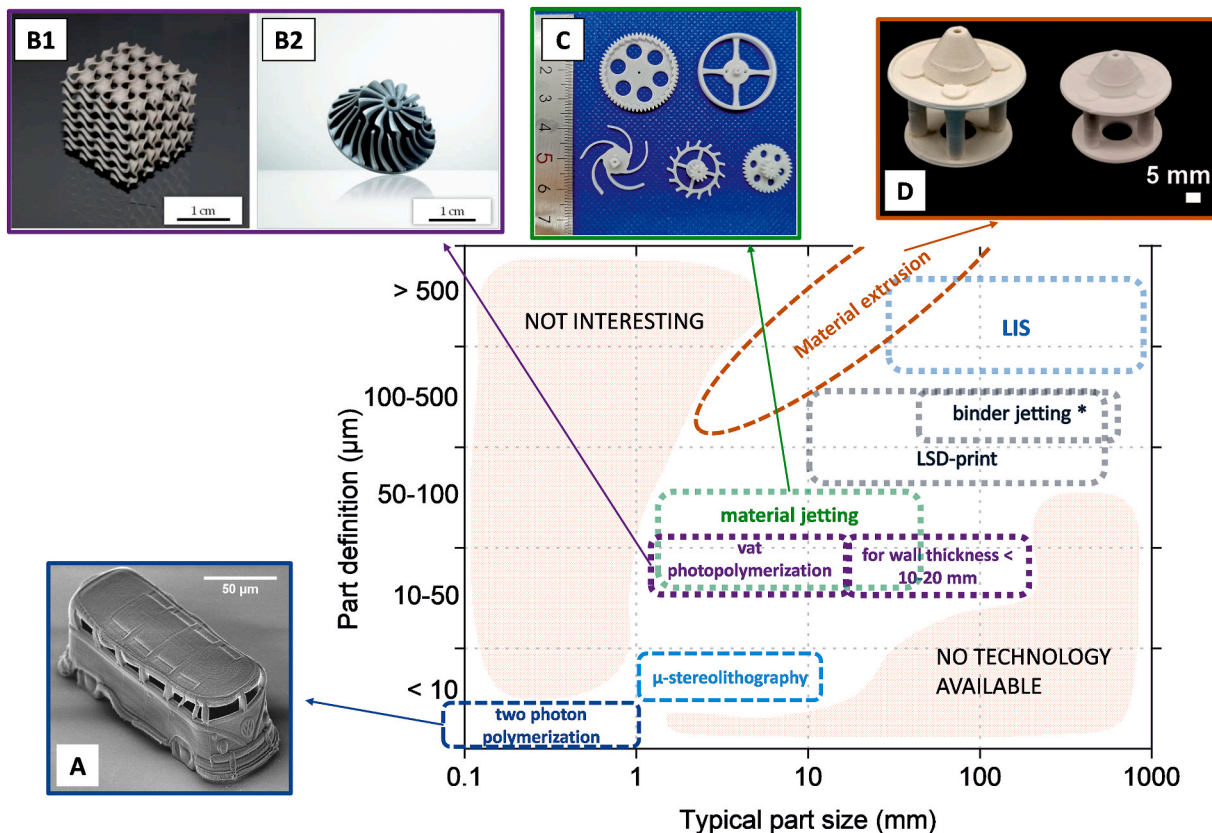


Fig. 1. Overview of AM technologies for dense advanced ceramics showing their ranges of application concerning the typical part size and the part definition that can be achieved.

* Powder-based binder jetting finds application to dense advanced ceramics only for specific ceramic material systems, e.g. silicon-infiltrated silicon carbide, but due to its limitation in handling very fine powders, it is generally not providing green bodies with sufficient sintering activity to be sintered to dense ceramics. A: Zirconia structure made by two photon polymerization (2 PP). Source: BAM, Berlin. B1, B2: Silicon nitride parts made by lithography-based ceramic manufacturing, in the technology class of vat photopolymerization (VPP). Reproduced with permission from Ref. [8]. C: Zirconia parts made by nanoparticle jetting (NPJ), in the technology class material jetting (MJ). Reproduced with permission from Ref. [9]. D: Structure made by infrared-assisted direct ink writing (DIW), in the technology class material extrusion. Reproduced with permission from Ref. [10]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

by researchers including Reis and Derby [30], defining printability criteria for the inkjet printing. Alongside the evolution of drop-on-demand inkjet technologies for 2D-printing [31], the development of ceramic ink formulations recently allowed pushing the ceramic MJ to the market. Israeli company XJET currently commercializes a platform with a 500 mm × 140 mm build area, using piezoelectric printheads to print organic solvent-based nanoparticle inks at a resolution of 1200 DPI [32]. The use of water-based inks and thermal printheads has also been developed, amongst others by Telle's group at RWTH Aachen [33], for printing technical ceramics using a carbon-based ink as support material. For both these approaches a lengthy debinding is not necessary, since the liquid phase (organic solvents or water) is evaporated during the printing process and only a small amount of organic additives needs to be burnt off in the post-processing. Despite leveraging the high throughput of drop-on-demand printheads for in-plane printing, the build-up rate of these MJ technologies is limited by the small layer thickness (5–10 μm) and by the time needed to dry and level each layer. Typical build rates are in the range of 0.5–1 mm per hour, making these technologies better suitable for printing high-precision parts rather than tall parts. MJ can however be adapted to increase the build-up rate and the flexibility in terms of processable particle sizes, at the compromise of a reduced printing resolution. As an example, AMAREA, a spin-off of Fraunhofer IKTS (Dresden, Germany), announced the commercialization of the CerAM Multi-Material Jetting (CerAM MMJ) technology [34]. MMJ uses micro-dosing heads to eject drops with a diameter between 200 and 1000 μm and uses a layer thickness of 70–300 μm to print up to four materials [35]. Since the technology uses thermoplastic feedstocks based on a mixture of molten paraffin and beeswax, the printed parts have to undergo a dedicated debinding process (e.g. approx. 120 h up to 900 °C in Ref. [36]).

Newly, company D3-AM (part of Durst group, Bolzano, Italy) announced a Micro Particle Jetting technology (MPJ) able to print water-based inks with increased layer thickness and with less limitations in terms of particle size used [37]. Although technical specifications have not been released yet, this technology indicates a development of MJ in the direction of larger and thicker parts with increased productivity, at the expense of a reduced printing resolution.

The medium resolution (100–200 μm) area of the diagram in Fig. 1 is occupied by **binder jetting (BJ)**. BJ is a class of processes in which layers of a flowable powder are deposited and selectively printed with a liquid binder, which is dispensed by an inkjet printhead. At the end of the process, the green parts are de-powdered and removed from the surrounding powder bed, debinded and sintered. In the field of advanced ceramics, BJ is not limited by the printhead resolution (which can be comparable to MJ, typically up to 1200 DPI, although 300–600 DPI is common in large-area printers [38]), but rather by the choice of powders and materials. Sintering of advanced ceramics requires the use of fine particles (often <1 μm diameter), and such fine powders are usually not sufficiently flowable for the layer deposition in BJ. Still, some advanced ceramic materials can be manufactured starting from coarser powders and these can be successfully used in BJ. The most relevant system is arguably silicon-infiltrated silicon carbide (SiSiC), also known as reaction-bonded silicon carbide (RB-SiC). SiSiC is fabricated by shaping a green body made of relatively coarse SiC powder (in the tens of μm range) mixed with carbon sources and other additives. After shaping, the green part is heat treated to convert the carbon sources into reactive carbon, followed by infiltration with liquid silicon at high temperature [39]. BJ of SiSiC has become a successful example of ceramic AM on the market, with commercial products such as *IntrinSiC*® by Schunk (Willich, Germany) and research activities dedicated to BJ of SiSiC [40,41] and of RB-SiC/B₄C [42]. One of the advantages of BJ is the possibility to manufacture large components at high productivity. The process chain to produce SiSiC is also favorable for large components, since the silicon infiltration process is near net-shape [43]. Schunk for example reports a maximum size of 1.8 m × 1.0 m × 0.7

m. The restrictions of BJ however come into play for most sintered advanced ceramics. The printed green parts generally have low density, leading to a low density after sintering, which rules out an application for dense advanced ceramics. It should be noted that there are interesting potential applications of porous ceramics manufactured by BJ (e.g. Ref. [44]) which however are not going to be discussed in this context. Active research is being dedicated to increase the density of sintered BJ ceramics. A promising approach is the use of inks filled with nanoparticles of the same material as the powder bed [45–47]. The sintered relative density using these approaches, however, rarely exceeds 90 %, thus restricting the field of application for most advanced ceramics.

The top-right corner of Fig. 1 is occupied by **material extrusion (MEX)**. In MEX, the build material is extruded and selectively deposited on the building platform. The trade-off between resolution and part size in MEX is related to the diameter of the nozzle used, which can vary between <100 μm for ceramic inks [7] to centimeters for construction materials [48]. For this reason, MEX is one of the most diverse and versatile AM classes. Focusing on advanced ceramics there are two main sub-classes of MEX: (i) technologies using a ceramic paste (visco-elastic ink made of particles and additives in a liquid medium) which is cold-extruded and (ii) technologies using thermoplastic feedstocks that are processed in the form of pellets or filaments, melted to be extruded through a nozzle and consolidated upon cooling. The first category includes processes known as robocasting and direct ink writing (DIW), which use water-based (or solvent-based) inks relying on their complex viscoelastic behavior and/or on their drying kinetics to retain the shape of the extruded structure [49]. The printed structures typically require careful drying, but do not need a complex debinding before sintering. On the other hand, technologies of the second category (known e.g. as fused filament fabrication, FFF, or fused deposition of ceramics, FDC) take advantage of the know-how, feedstocks and equipment which are widely available for the AM of polymers. Differently to DIW, these technologies generate a green part made of ceramic particles in a polymeric matrix, which requires a dedicated debinding procedure before sintering. The matrix often is composed of two phases, i.e. a polymer which is eliminated in a first debinding step and a backbone polymer that helps retaining the part's shape until the second debinding step and sintering. In such systems, the first debinding is often performed by immersing the part in a solvent bath [50] or by catalytic debinding [51], while the second debinding is thermally activated [52]. Although this two-steps debinding is a lengthy and complex process, the related know-how can be adapted from the established ceramic injection molding. Although both FFF and DIW are well suited to produce lattice structures or parts with a porous infill, dense advanced ceramic components can in principle be manufactured [53]. Research and development efforts are focusing on the characterization and reduction of typical process defects, e.g. gaps between extruded lines [54,55].

2. Ceramic process chain and thermal post-processing

Different to polymeric and metallic materials, ceramic AM requires a complex process chain with various post processing steps engaging expensive machinery and dedicated know-how. Post processing can ideally be reduced to a thermal treatment, that is, debinding and sintering, of the additively manufactured green part. Fig. 2 summarizes the differences in the debinding and sintering (or infiltration) processes between AM technologies by showing the microstructural evolution from the green to the final part.

In addition to the complexity of the debinding and sintering (or infiltration) processes, green and hard machining (after sintering) is often required. This together makes the consumer market inaccessible, and it significantly raises the threshold for industrial users to successfully enter the market of ceramics AM. Moreover, ceramic processing has to deal with a severe shrinkage of the part upon densification during sintering, which is in case of AM rarely uniform, due to the layerwise build-up up of the part. This is a problem common to all ceramic

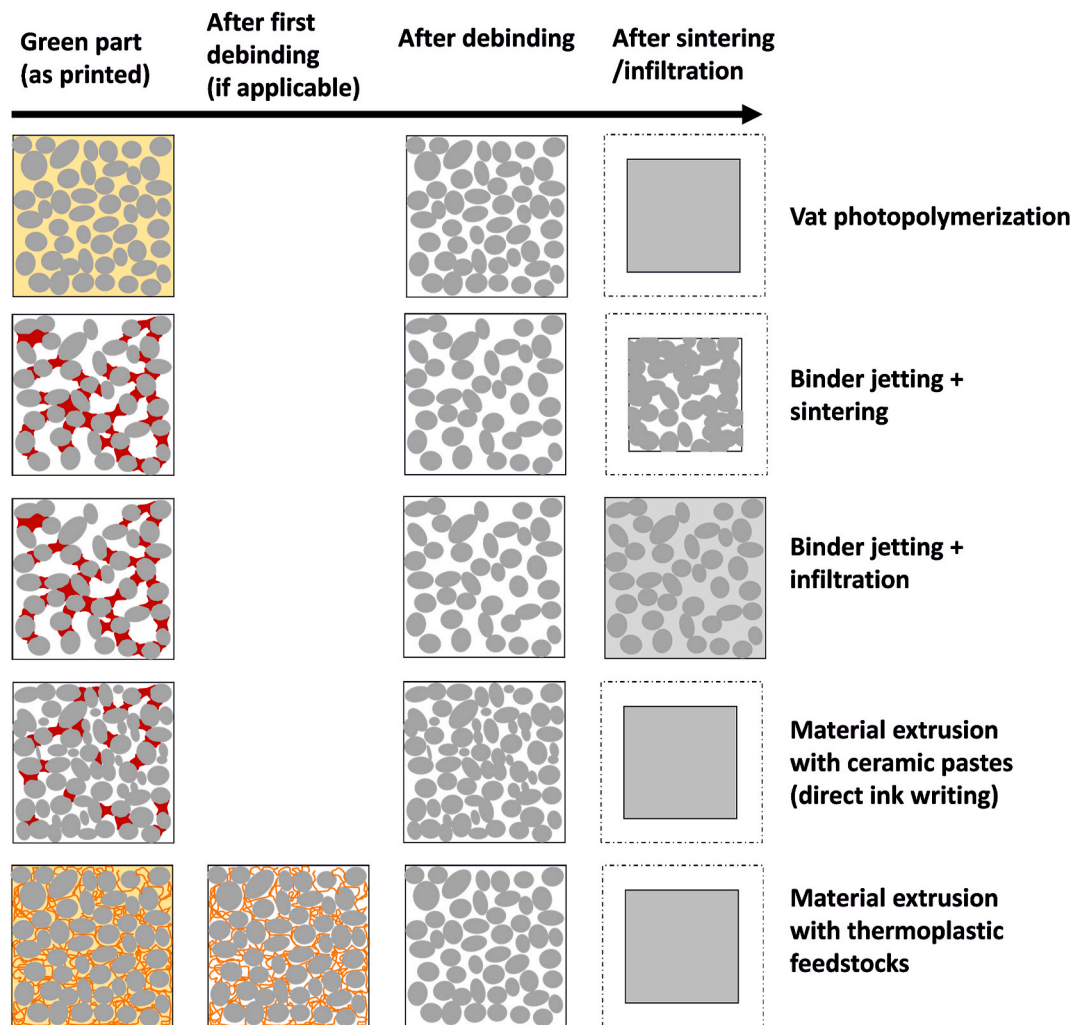


Fig. 2. Microstructural evolution from the additively manufactured ceramic green part to the final part after sintering/infiltration for different AM technologies. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

industry, but it is an additional burden when it comes to single parts manufacturing and complex geometries.

From this perspective, the development of processes and materials for ceramic AM was initially driven more by the enthusiasm of research than by applications. For making additive manufacturing more attractive for the ceramic industry, it needs to be considered that the ceramic industry is based on a long-standing know-how combining process and material expertise to manufacture parts with the desired quality. Minimal changes of raw materials or only slight adaptations of process parameters will directly affect the parts quality. Even worth is the fact that the relations between material, process and parts quality are often founded on an empirical base. This explains why the ceramic industry is very reluctant when it comes to changes in their material base or process chain, and it builds up an immense threshold for the introduction of AM technologies. Consequently, the market entry of AM for ceramics manufacture is driven by start-ups and companies originally not exactly members of the ceramic community. On the other hand, making AM of ceramics more attractive to established ceramic manufacturers can be realized, by introducing AM as a new shaping technology ideally having minimal influence on the process chain. This strategy allows the parallel use of materials and equipment for conventionally shaped and additively manufactured parts which is most beneficial concerning the process step sintering, as capital expenditures for sintering equipment and energy costs are high. Moreover, having minimal changes in the process chain provides an advantage regarding parts quality against start-ups

and newcomers in this industry.

To achieve this goal, the corresponding AM technology must be able to produce green parts with comparable properties to conventional parts, i.e. with a high particle packing density and low organic additive content. It must also be able to process the finest powders in the sub micrometer range and be easily adaptable to an existing raw material base.

3. Perspectives towards a debinding-free additive manufacturing of ceramics

A conventional shaping technology which delivers without any costly and complex equipment green parts with high powder packing density, up to 60 % of the theoretical density (T.D.), low organic content, typically 2 wt%, and which is capable of processing a broad range of particle sizes, is the slip casting process. It seems therefore logical to take inspiration from slip casting, one of the oldest forms of ceramic shaping, to develop concepts applicable to ceramics AM. In the following, 2 AM technologies will be introduced, which are taking advantage of the slip casting technology. These are the layerwise slurry deposition (LSD) and the laser induced slip casting (LIS).

3.1. Layerwise slurry deposition (LSD)

Powder bed AM technologies such as binder jetting and powder bed

fusion play an important role in the AM market, especially for metal AM [56]. It may therefore come as a surprise that these technologies only cover a small area of the diagram in Fig. 1, also limited to a handful of ceramic material systems. One of the critical aspects in this context lies with the processable particle size, which must be larger than typically 10–20 μm to ensure sufficient flowability of the deposition of defect free layers. Moreover, the finer the particles are, the lower is the particle packing density in the deposited layers and, thus, in the powder bed [57, 58]. This in stark contrast with the conventional process chain for the manufacture of ceramic parts, in which the use of fine powder particles and a powder compact of high green density helps to accomplish densification during sintering. Different approaches have been proposed to increase the packing density of powder beds in AM, as recently reviewed by Diener et al. [59] and by Du et al. [45]. In this regard, one effective method is the use of a liquid feedstock, which was originally suggested in the patent by Sachs et al. at MIT describing the binder jetting technology [60]. A technical solution for the deposition of powder layers from a ceramic slurry is offered by the layerwise slurry deposition (LSD), which was patented in the year 2002 at Clausthal University of Technology (Germany) [61] in combination with selective laser sintering.

In the meanwhile, the feasibility of this technology for the manufacturing of silicate ceramic parts has been demonstrated [62–64]. Fig. 3 is showing a coffee cup made by the LSD-laser process from porcelain.

In the year 2012, the LSD-print process has been developed, as a logic improvement of the classical BJ process substituting the deposition of dry powders by the slurry-based deposition technology. LSD-print has been patented in the year 2012 at BAM, Berlin, Germany [65], followed by two additional patents devoted to process details: in 2016, a continuous deposition of layers on a rotating platform for increasing productivity [66], and in 2017 a new deposition unit [67]. The LSD-print process provides green bodies with a higher density than the conventional powder-based BJ technology and very fine powders, as typically used for the manufacture of advanced ceramics, can be processed, also.

Fig. 4 illustrates the basic concept of the LSD process chain. Step one is the slurry preparation. Water-based slurries are prepared from ceramic powders and organic additives, which need to be optimized for layer deposition. Most critical in this context is the cracking of layers after subsequent drying. Also, the viscosity and solid content of the slurry need to be adapted for the deposition of defect- and bubble-free layers. Only in the case of silicate ceramics, industrial slurries for conventional slip casting can be directly used in the LSD process.

The unique feature of the LSD process is related to the build-up of the



Fig. 3. Coffee cup, about 100 mm tall made from porcelain by the LSD-laser process, that is, local laser sintering in combination with a slurry-based layer deposition. Image courtesy of QEP3D GmbH. Cup design by Daniel Becker Design Studio.

powder layers, combining features of tape casting and slip casting technologies: similar to tape casting, a doctor blade is used for spreading a ceramic slurry (slip) to a thin layer; similar to slip casting, this layer is bound to the previously deposited and dried layers, acting as a porous mould. Powder beds generated by LSD have a final green density comparable to conventional powder compacts prepared by slip casting. Drying of a freshly deposited layer can be achieved in less than 30 s, even though the slurry is water-based. Desiccation of a deposited layer is associated to two major mechanisms: first, the liquid water is drawn by capillary forces into the supporting powder compact formed by previously deposited and dry layers, and second, due to a rapid evaporation, facilitated by a mild heating of the powder bed and by a flow of warm air. For both mechanisms, the temperatures of the powder bed and air are generally not exceeding 100 °C.

After layer deposition and drying, the powder bed is locally consolidated in each layer by means of a laser beam or by binder jetting. Both technologies are applied in a manner comparable to the well-established selective laser sintering, respectively, binder jetting (BJ) technology and do not need a further introduction at this point. However, somewhat different is the depowdering process step. In case of conventional selective laser sintering or BJ, the part is embedded in a powder bed of dry and loosely packed powder and the separation of the powder from the final part is relatively easy. In case of the LSD based processes, the powder bed is comparable in strength and density to a ceramic green body, and it needs to be washed away. This washing process must already be considered in the choice of the organic additives in the slurry preparation. The powder bed must be re-dispersible in water, while the part printed should be chemically and mechanically stable in water. A major benefit of the strong and compact powder bed is, however, the good support it provides for the parts during buildup, making support structures obsolete.

For the buildup of 3D structures, the process steps layer deposition, drying, and laser sintering or binder jetting are then repeated. Typical layer thicknesses are between 50 and 100 μm . The width of the layer stack is defined by the width of the doctor blade in use, while the length is controlled by the movement of the blade parallel to the supporting surface. Thus, within the boundaries of the supporting platform, the width of the doctor blade and the trajectory of its movement determine the area of material deposition. A freestanding powder bed is generated by the layerwise slurry deposition technology. This enables a further development of the LSD technology, namely the realization of a continuous process through the build-up of parts on a rotary platform. While the disc shaped platform is rotating, the doctor blade is lifted by one layer thickness each revolution of the platform [68]. Fig. 5 is showing the powder bed in the continuous LSD-print process.

3.1.1. Post-processing of parts made by laser sintering LSD and by LSD-print

Fig. 6 shows the microstructural evolution of AM parts produced by LSD technologies.

A major difference between LSD-print and powder-based BJ is in the green density of the printed parts. Fig. 7 compares the fracture surface of alumina green parts produced by powder-based BJ (A, B) and by LSD-print (C, D). It is evident that BJ results in an aggregate of loosely packed granules, while the alumina particles in the LSD-printed green body are finely distributed. The reason for this is the fact, that BJ can simply not handle very fine powders, due to their poor flowability for layer deposition. It should be pointed out, that powder deposition technologies for BJ are improving over time and modern machines can handle finer powders in the μm range, but still there is a significant gap to the sub-micron to nano-powders, generally required for the manufacture of advanced ceramics. Slurry-based processes on the contrary do not show this limitation.

LSD-print is however similar to BJ in that the green part contains a significant amount of printed ink (named “binder” in BJ terminology, but not to confuse with binders used in the slurry in this context).

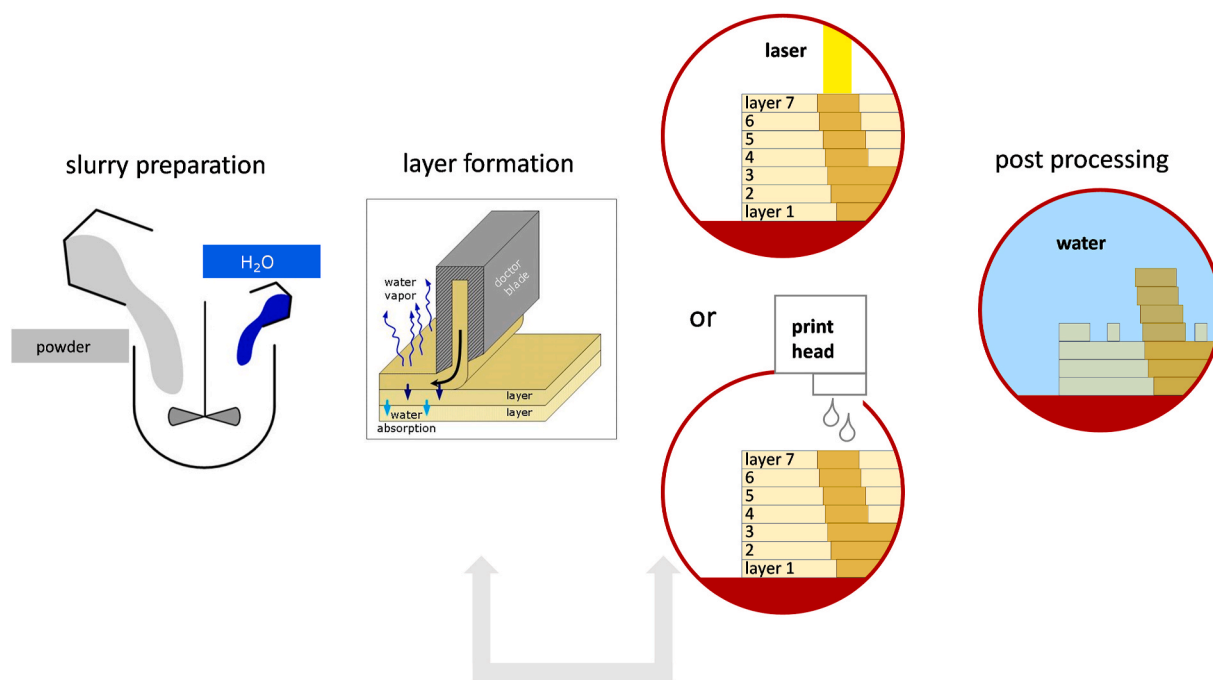


Fig. 4. Illustration of the layerwise slurry deposition process in combination with selective laser sintering (LSD-laser process) or binder jetting (LSD-print process).

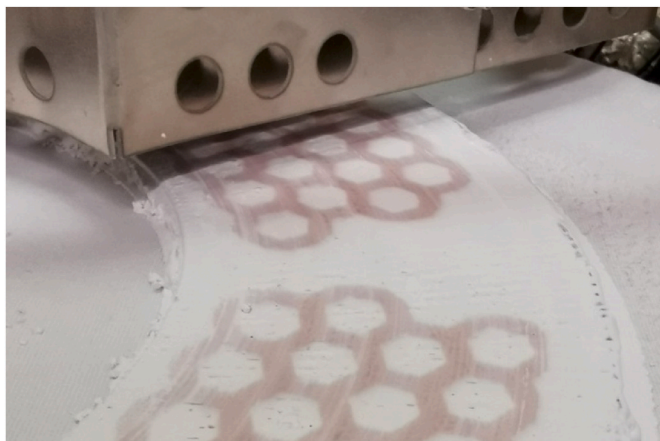


Fig. 5. View into an LSD-print machine showing the circular powder bed, which is continuously fed with slurry to build up layers in a continuous rotation. Image courtesy of CerAMing GmbH.

Typically, the ink content is up to 6 vol % [70], which requires a dedicated debinding step before sintering in a kiln. Nevertheless, LSD-print green parts still have $\geq 20\%$ open porosity [70], which allows for a relatively fast debinding. The presence of open channels is key to an efficient debinding, because it allows the release of gases developed during the burn-out of organics from the inside to the part's surface.

A simplified debinding curve which can be applied to most LSD-printed oxide ceramic parts up to a wall thickness of 10 mm is shown in Fig. 8(A).

For large and complex parts and/or for wall thickness >10 mm an optimized debinding curve is presented in Fig. 8(B).

Depending on wall thickness and part complexity, debinding can be achieved in 4–10 h, followed by a standard sintering curve.

Recent results (not yet published) indicate that parts with a wall thickness of few millimeters can be debinded during the heating ramp of a standard sintering curve (2–5 K/min) without a dedicated, lengthy debinding treatment.

The alumina parts shown in Fig. 9 for example were debinded and sintered in a single step with the temperature schedule shown in Fig. 8 (C) (the cooling ramp is not shown).

For small parts, e.g. dental restorations, debinding and sintering of LSD-printed green bodies can even be performed in a fast sintering furnace with a full cycle (debinding, sintering, cooling) below 45 min.

Fig. 10 shows as an example a 3-unit fixed dental prosthesis made by LSD-print in the green state (Fig. 10(A)) and after firing (Fig. 10(B)). Debinding was performed in air in approx. 18 min up to 500 °C and firing in approx. 25 min with a maximum temperature of 1190 °C under vacuum. It should be noted that this part is shown as a technological demonstrator of the fast debinding and firing cycle. The material used is a feldspathic glass-ceramic, which is not suitable for bridges in dental applications due to the limited material strength, but is rather indicated for small restorations (veneers, inlays, onlays etc.).

The LSD-print process can have potential advantages even for material systems that can normally be processed by powder-based BJ, such as silicon-infiltrated SiC (SiSiC). As shown in the schematic in Fig. 6 and in Fig. 11, complex parts can be manufactured by LSD-print of SiSiC having a dense microstructure with a minimized amount of residual silicon.

LSD-print can be seen as an extension of powder-based BJ for material systems in which the flowability of fine powders is challenging, while taking advantage of the scalability and medium-high resolution typical of BJ (see Fig. 1), obviously with the compromise of an increase of process complexity due to the management of the slurry deposition and drying.

Despite being a step towards a simplification of debinding processes for AM parts, the LSD-print cannot be considered a debinding-free process. Additionally, most organic ink systems such as phenolic resins require a backing step overnight at 100–150 °C for full consolidation, followed by washing of the parts and drying [72]. While the whole post-processing can be realized within 24–48 h, a multi-step process is still necessary.

Considering ceramic AM, laser sintering technologies arguably have the highest potential to minimize post-processing. The selective laser sintering of ceramic powders is an active field of research [73], but still, it is difficult to manufacture ceramic parts with reasonable mechanical

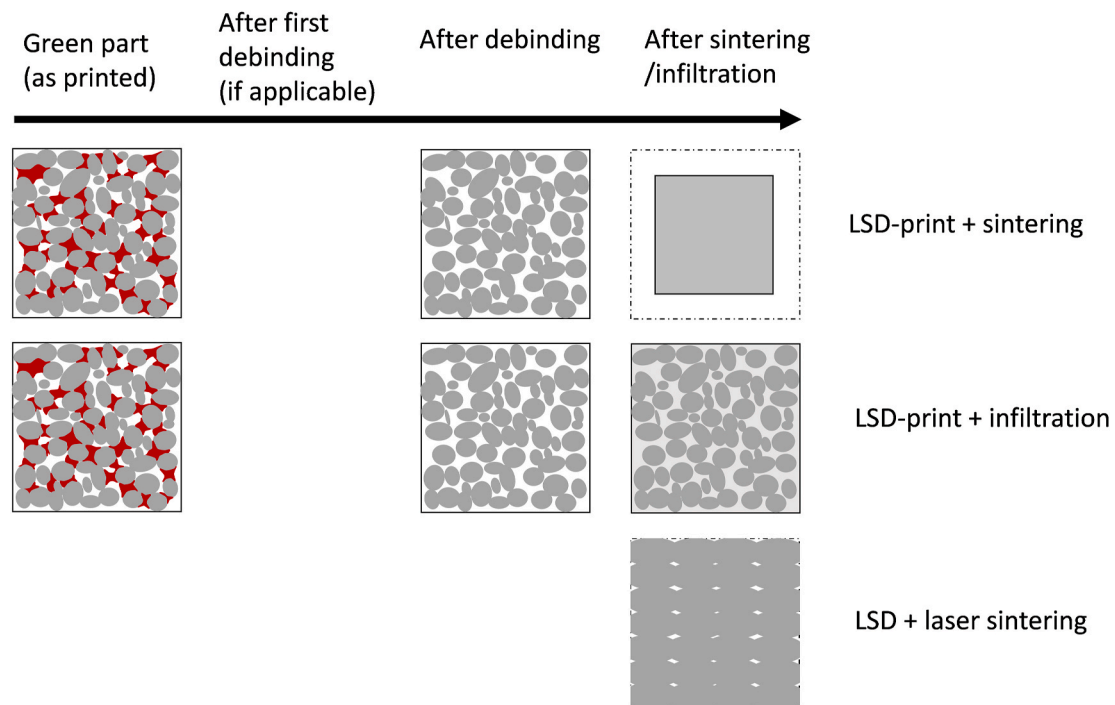


Fig. 6. Microstructural evolution from the additively manufactured ceramic green part to the final part after sintering/infiltration for LSD technologies. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

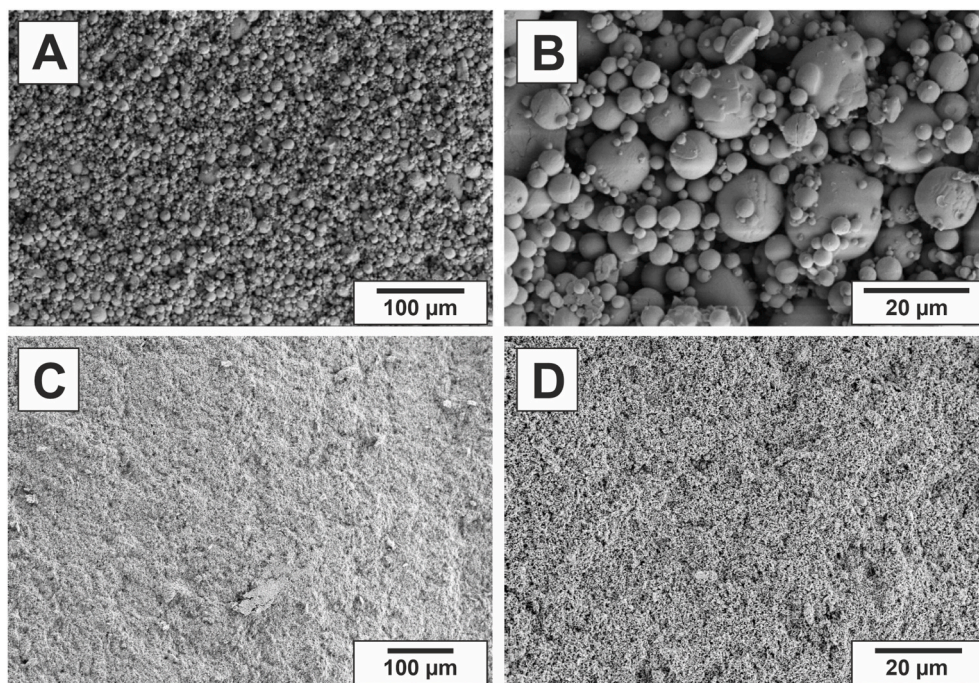


Fig. 7. Comparison between the green body microstructure of (A,B) powder-based binder jetting of alumina and (C,D) slurry-based binder jetting of alumina by LSD-print. (A,B) reproduced with permission from Ref. [69]. The larger aggregates in A,B are granules from spray drying, for giving the fine powders the required flowability.

properties. The generation of defects, as a result of the rapid local annealing of the powder bed, can be regarded as the main cause. Still, laser sintering can be optimized either for ceramic parts not requiring full densification such as for metal casting molds [74], or for specific material systems forming a liquid phase [63,75] or forming phases with low thermal expansion coefficient [76]. All these considerations also hold when laser sintering is used for the consolidation of the powder and

sintering to a dense part is achieved in an additional conventional sintering step. Once defects, such as, cracks and bubbles, are introduced by the fast local annealing within the laser spot, they generally cannot be healed by subsequent sintering. Formation of a liquid phase and a high powder packing density of the powder bed in particular help to densify the material in the short time span in which the laser is annealing the material. Therefore, LSD-laser of silicate ceramics like porcelain or fine

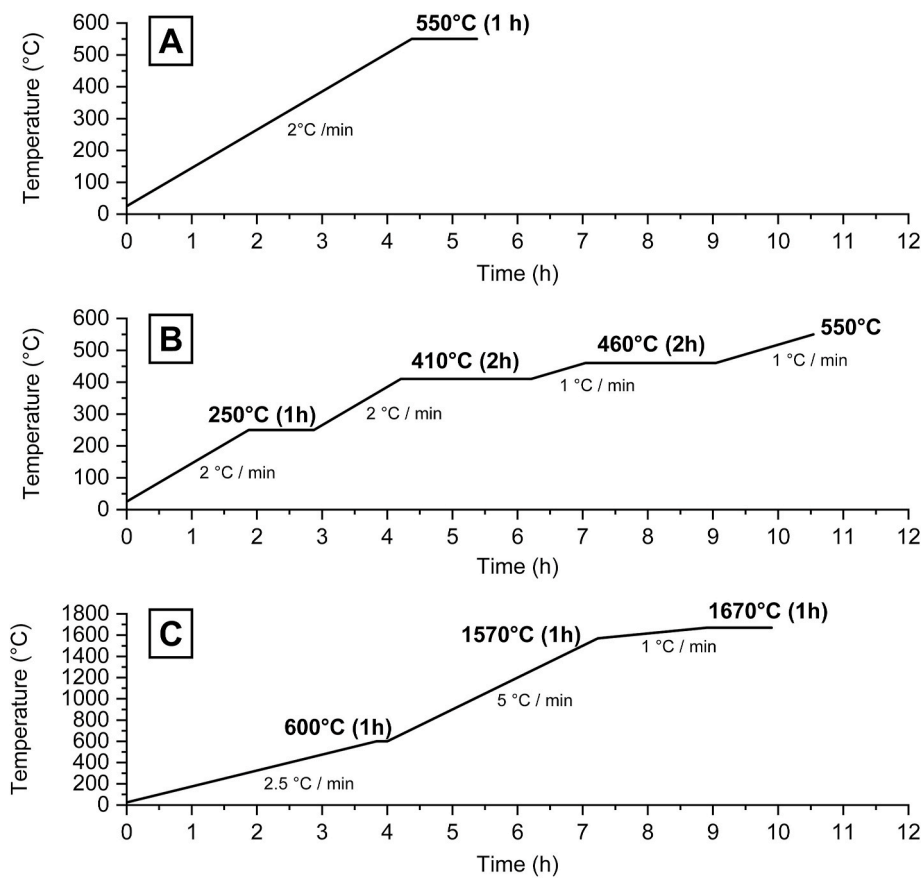


Fig. 8. (A) Simplified debinding schedule of LSD-printed parts with wall thickness up to 10 mm. (B) Optimized debinding schedule of LSD-printed parts with wall thickness >10 mm. (C) Debinding and sintering schedule for the alumina parts shown in Fig. 9.

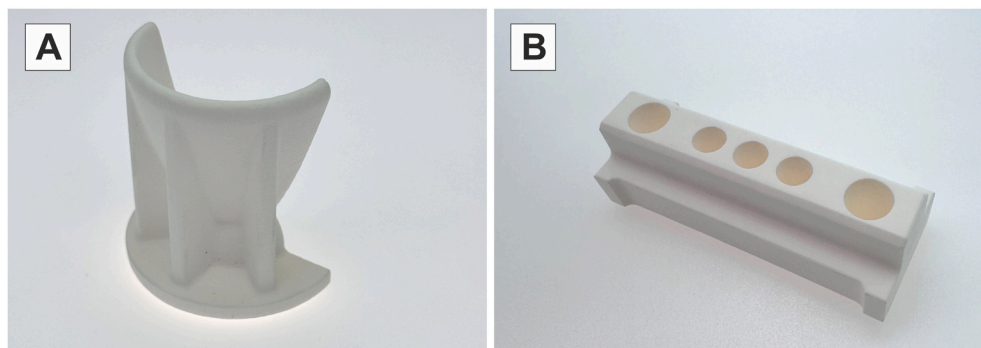


Fig. 9. Sintered alumina components manufactured by the continuous LSD-print process. Source: images courtesy of QEP3D GmbH.

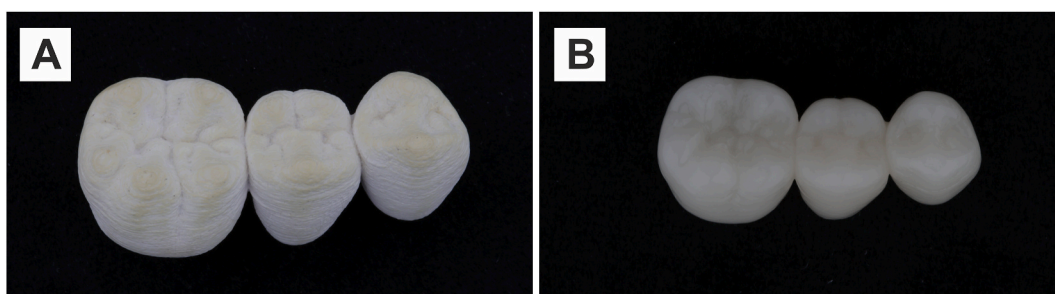


Fig. 10. 3-unit fixed dental prosthesis made by LSD-print in the green state (A) and after debinding and firing (B). The bridge has a length of ca. 26 mm in the as-printed state (A). Source: part printed at BAM by LSD-print; debinding and firing at the Department of Prosthetic Dentistry, Ludwig-Maximilians-University, Munich (Germany).

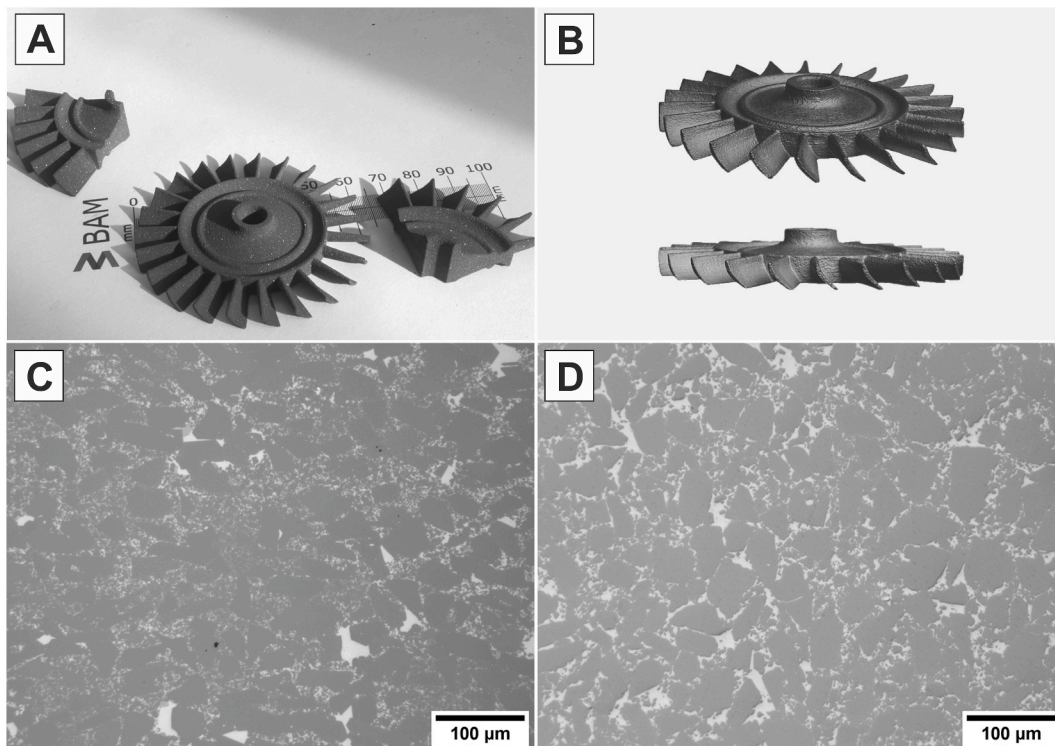


Fig. 11. (A) Silicon carbide green turbine wheel manufactured by LSD-print (b) SiSiC turbine wheel after silicon infiltration (c) microstructure of the LSD-printed and infiltrated SiSiC turbine (d) reference microstructure of SiSiC material produced by isostatic pressing and infiltration. Reproduced with permission from Ref. [71].

fire clay is a promising approach for the AM of table and sanitary ware. In comparison to BJ technologies, laser-based technologies have an additional big advantage, as the laser optics do not degrade as fast as print heads, in particular, when the machine is not running 24/7.

Layers deposited in the LSD process contain < 2 wt% organics derived from the additives in the slurry, which however do not have any noticeable influence on the laser sintering process. In that sense, LSD-

laser is comparable to conventional slip casting. Laser sintered porcelain parts are in a semi-finished, sintered state comparable to a biscuit fired porcelain body, however, presenting still half of the mechanical strength in comparison to a conventional biscuit fired body. On the other hand, the mechanical strength has been verified to be sufficient for post-treatments, such as glazing and gloss firing [63]. Also, for raw materials such as Al_2O_3 and SiO_2 mixtures, as well as for lithium aluminosilicate

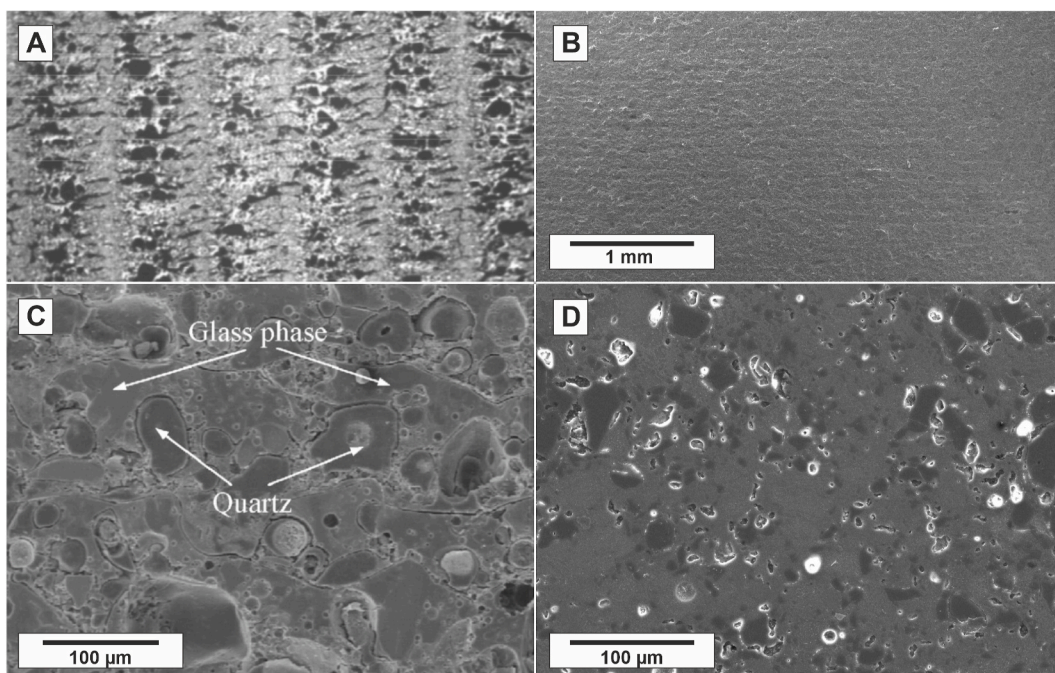


Fig. 12. Cross sections of a porcelain part in the LSD process, (A,C) laser sintered with the cross section perpendicular to the laser tracks and (B,D) manufactured by LSD-print and sintered (1h at 1250 °C). D reproduced with permission from Ref. [79].

glasses and glass ceramics, this technology has been successfully used [64,77].

Fig. 12 compares cross sections of a porcelain part manufactured by laser sintering LSD-laser (A,C) and by LSD-print (B,D). Clearly noticeable is the generation of pores and the coarser microstructure in the laser sintered part. It was found [78] that the laser sintered material has a density comparable to a biscuit fired porcelain, however, with significantly larger pores. This effect is a result of the rapid and local annealing of the material within the laser spot. The material is not uniformly annealed and local overheating results in viscous flow and densification, but, on the other hand, also in the formation of bubbles. Subsequent conventional sintering is not improving the microstructure significantly. However, it improves the mechanical properties to values acceptable for the use as tableware. Meanwhile, the LSD-print results in a cleaner interface between layers and the controlled sintering in the thermal post-process results in a finer and more homogeneous microstructure.

An interesting alternative technology to take advantage of modern lasers' high electrical efficiency, high power output and high scanning velocity, while avoiding defects induced by sintering/melting, is the laser induced slip casting (LIS), which is introduced in the following paragraph.

3.2. Laser induced slip casting (LIS)

A different approach for slurry-based AM of ceramics is the laser induced slip casting (LIS) process. In this process, water-based slurries are spread as thin layers and the water is extracted from the slurry by local evaporation, as illustrated in Fig. 13. The process was patented in the year 2015 at BAM, Berlin, Germany [80]. In the meanwhile, Lithoz GmbH, Vienna, Austria, has a commercial machine based on the LIS technology in its product portfolio. In comparison to the LSD process, the drying of the freshly deposited layers is not required, and consolidation of parts is induced by local evaporation of water directly in the slurry. The local drying of the slurry is realized by intense laser radiation. By subsequent repetition of the steps layer deposition and laser drying, a part is built [81]. The formed part is a stable green body, which is immersed in its ceramic slurry during the building process. After extraction from the slurry, the part can be dried and sintered like a green body made by conventional slip casting. The build-up rate can be varied by the thickness of the deposited layers: increasing layer thicknesses generally results in higher build-up rates. Layer thicknesses up to 0.5 mm can easily be realized. Hence, the build-up rate of the LIS process is

higher than for the LSD process, due to the possibility of forming layers of large thickness, but LIS is not that precise regarding the final contour of the parts.

While the LSD technology is a logic improvement of BJ, with the previously mentioned pros and cons, the LIS technology is a completely new development, which aims to satisfy the gap between the additive manufacturing of large parts, see also Fig. 1, with feedstocks which allow the related industry to use established ceramic raw materials and sintering technologies. In particular, LIS requires minimum adaptation of ceramic slurries, as compared to conventional slip casting slurries, and consequently, after shaping, that is AM, drying and sintering can be achieved in line with conventionally shaped products. Nonetheless, still appropriate applications and products for LIS need to be identified. In the following some examples will be introduced.

Fig. 14 shows silicon nitride green parts shaped by LIS, manufactured with a layer thickness of 300 μm . The square part in Fig. 14(A) has a height of 60 mm.

Fig. 15 demonstrates a possible approach to improve the surface definition of LIS parts. Since LIS green bodies have properties similar to slip cast bodies, green machining is possible followed by a standard firing procedure without dedicated debinding. The part in Fig. 15 was debinded at 5 $^{\circ}\text{C}/\text{min}$ until 300 $^{\circ}\text{C}$ and 3 $^{\circ}\text{C}/\text{min}$ to 600 $^{\circ}\text{C}$ with 30 min dwell, followed by a standard sintering at 1600 $^{\circ}\text{C}$.

4. Conclusions and future perspectives

While the AM of small and precise ceramic components is starting to consolidate around technologies such as vat photopolymerization VPP and material jetting MJ (see Fig. 1), several new research and industry developments are focusing on enabling the AM for the manufacture medium-large parts.

For medium-large porous or lightweight parts, material extrusion MEX technologies are in continuous development especially for applications that do not require a smooth surface finish and ultimate mechanical properties. Few such examples are filters, catalyst carriers or furnace components (sintering plates, trays, crucibles etc.). For medium-large dense components, laser induced slip casting (LIS) can be a viable alternative. LIS offers high build-up rates with layer thicknesses of up to 1 mm, however, at the expense of surface quality. Green machining is a possible solution for improving surface quality of LIS parts, while retaining a high build-up rate.

For the AM of medium-sized (e.g. 20–200 mm diameter) and/or thick walled (>10 mm) dense ceramic parts with medium printing

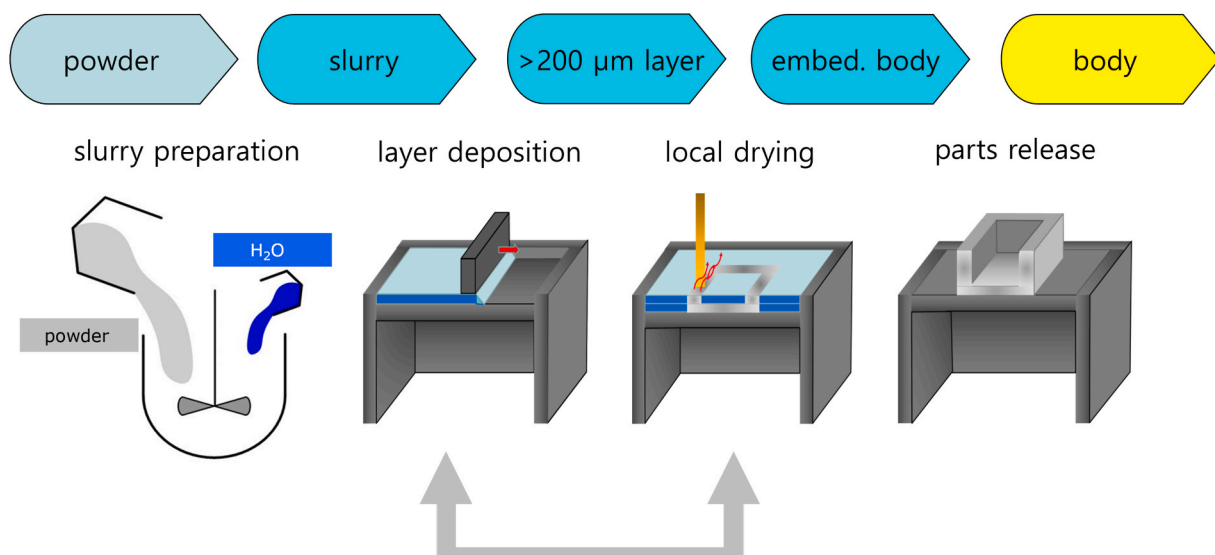


Fig. 13. Illustration of the laser induced slip casting (LIS) process.

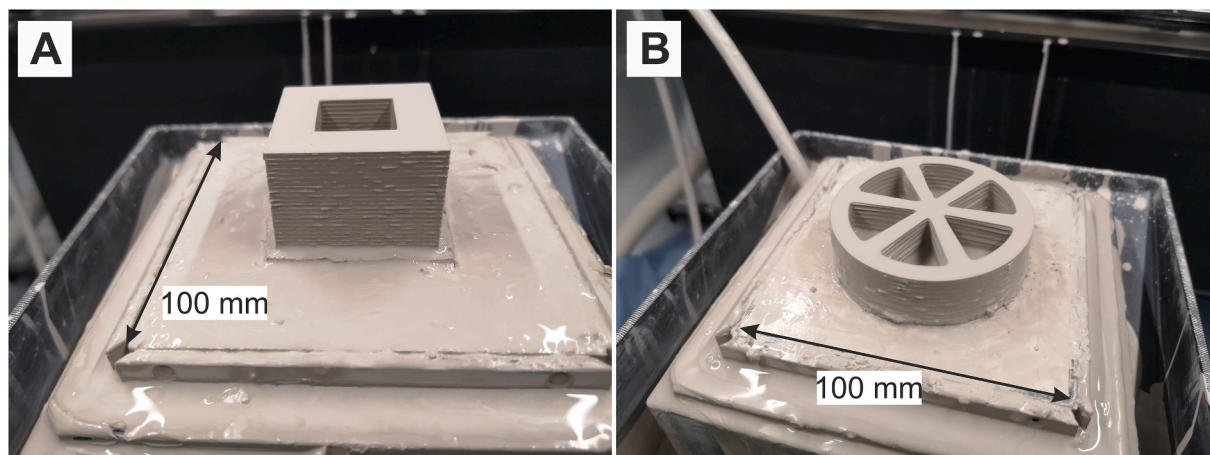


Fig. 14. (A,B) Silicon nitride green parts shaped by LIS. Images courtesy of QEP3D GmbH. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

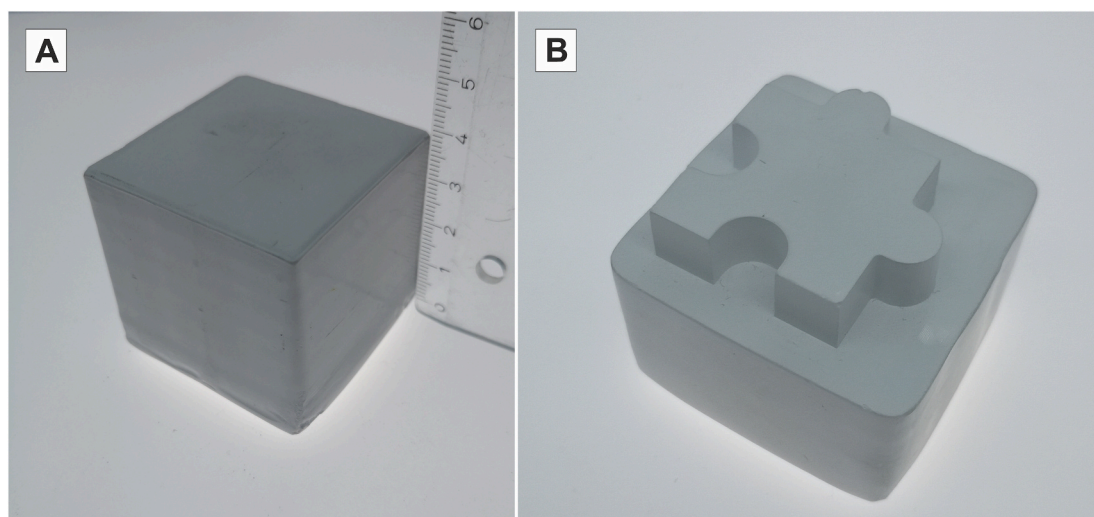


Fig. 15. (A) Alumina block shaped by LIS and (B) Puzzle piece-shaped green part machined from the block. Images courtesy of QEP3D GmbH. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

resolution (around 100 μm) there currently isn't any single technology capable of covering the whole range of ceramic materials and applications. Rather, depending on the ceramic raw materials (particle size and shape, physico-chemical and optical properties) and object geometry (size, wall thickness, overhangs, tolerances) different technologies should be considered. In this context, the LSD-print technology has been introduced in detail as a slurry-based extension of BJ, which enables processing of technical ceramics. Similarly, technologies such as multi material jetting (MMJ, AMAREA, Germany) and multi particle jetting (MPJ, D3-AM, Italy) can be seen as natural evolution of MJ, pushing the boundaries of productivity and material flexibility with the compromise of a reduced printing resolution.

Interestingly, understanding the limits of the traditional AM technology classes is leading to the invention and development of new and hybrid processes. The MoldJet technology (Tritone, Israel) for example uses material jetting for printing a mold layer-by-layer, which is filled with a metal or ceramic paste and scraped by a blade. This approach takes advantage of the printing resolution and high throughput of polymer MJ (for the mold) while achieving high green density of the part by using a slurry feedstock.

LIS is another process that cannot be clearly classified in one of the AM categories defined in ISO/ASTM 52900:2022-03. While its setup

(Fig. 13) resembles VPP, its consolidation mechanism is based on drying of water-based slurries rather than on selective photopolymerization. As a result, the obtained ceramic green bodies contain very little organic additives, comparable to conventional slip casting, and can be sintered parallel with conventionally shaped products.

In conclusion, the ceramic AM market for medium-sized components is far from consolidated. Successful processes in the future might be established through evolution of existing technology classes or may emerge from new ideas and concepts. A key factor for the industrialization success will be the ability of these technologies to be integrated in the existing process chains in the ceramic industry.

CRediT authorship contribution statement

Andrea Zocca: Conceptualization, Visualization, Writing – original draft, Writing – review & editing. **Jens Günster:** Conceptualization, Writing – original draft.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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