Making Binder Jetting Really Work for Technical Ceramics – Additive Manufacturing of Technical Ceramics*

As an alternative shaping method to the traditionally used processes, Additive Manufacturing (AM) can produce economical ceramic components in small lot sizes and/or with complex geometries. Powder-based AM processes like binder jetting are popular in the field of metal AM. One reason is the increased productivity compared to other AM technologies. For ceramic materials, powder-based AM technologies result in porous ceramic parts, provided they are not infiltrated. CerAMing GmbH unites the advantages of powder-based processes with the production of dense ceramic by means of the Layerwise Slurry Deposition (LSD). By using a suspension, a high packing density of the powder bed is achieved which leads to high green body densities. Due to this advantage the approach overcomes the problems of other powder-based AM technologies. Furthermore, a very economical debinding time allows the production of parts with high wall thicknesses.

Fundamentals

Shaping equipment like moulds and pressing tools play a basic role in the manufacturing process of the conventional (technical) ceramic industry as major production methods like uniaxial and isostatic pressing need pressing tools, and injection moulding and slip casting need moulds of different kinds. This limits the design freedom of the final components and puts a high fixed cost burden on small series as the production of for example moulds is expensive. Here, Additive Manufacturing (AM) or 3D-printing is changing the production paradigm already at an industrial level by enabling the economical production of components with complex geometries and/or in small lot sizes since it is a tool-free production method.

Keywords
additive manufacturing, binder jetting, layerwise slurry deposition, lithography-based technologies, technical ceramics

There are different ceramic AM technologies available for industry applications [1, 2] which can satisfy different market needs. Advantages and limitations of the two most widely used ceramic AM technologies are outlined along with the introduction of the Layerwise Slurry Deposition (LSD) technology commercialized by CerAMing GmbH that is preparing to fill a gap in the AM landscape for industry applications of technical ceramics.

Invented originally in the 1990s for polymers, lithography-based technologies were adapted for the needs of ceramics [3] and are now the most widely spread industrial AM technologies in this field. The casted material in the moulding process is directly replaced here by a polymer matrix which encloses ceramic particles. The process iterates two steps to build up a part consisting of this polymer matrix. The starting material is a resin mixed with ceramic particles of preferred kind. The first process step spreads this material onto a building platform.

In the next step, the geometry of the CAD file is inscribed within the spread layer by crosslinking the polymer resin via light illumination. Dark materials like silicon carbide are challenging to process here since they absorb the radiation and impede the crosslinking of the surrounding resin to build the polymer matrix. The emerg-

Boris Agea Blanco, Sebastian Walzel, Jörg Lüchtenborg, Jinchun Chi

*CerAMing GmbH (i.G.) hosted by Bundesanstalt für Materialforschung und -prüfung (BAM)
14195 Berlin, Germany*

*E-mail:
boris.agea@ceraming.de;
sebastian.walzel@ceraming.de
https://en.ceraming.de*

**Paper will be presented at ceramitec conference 2021*

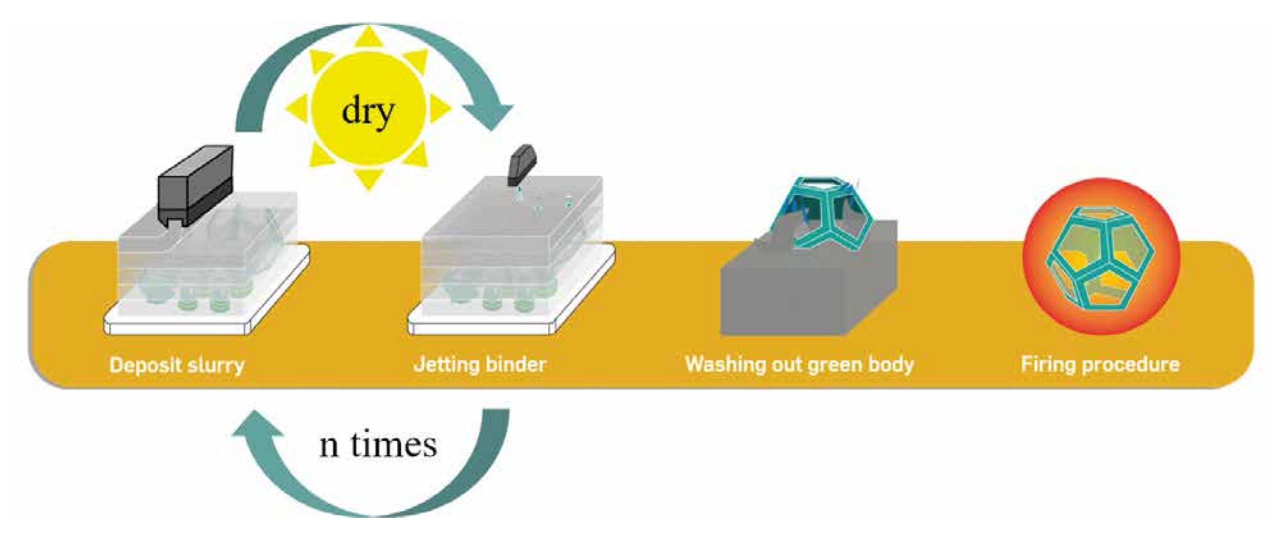

Fig. 1
Schematic workflow of CerAMings' LSD

ing preliminary product (called green body) is characterised by a high stability and precision due to this shaping matrix. However, this comes at a cost. To obtain a fully dense monolithic final ceramic, the part must be fired slowly (called thermal debinding) to burn out the large organic quantities including the polymer. In the thermal debinding process, the organic content (namely carbonaceous molecules) is generally oxidised into gaseous carbon dioxide that will slowly diffuse out of the printed body. The firing time grows here in a non-linear relation to the volume of the polymer matrix as cracks can only be avoided by gentle burning. This leads to non-economical firing times (partly weeks are necessary) for parts with a high effective volume. Lithography-based technologies address a market from tiny to medium size ceramic components that have complex geometries and request high precision and accuracy. Here, the achieved results are unmatched.

Meanwhile, powder-based processes such as binder jetting have become increasingly popular in the field of metal AM. The advantages are the scalability of the printing area and the very fast part inscription technology. This leads to higher effective part volumes and very productive manufacturing.

In powder-based binder jetting, a thin layer of flowable powder is spread onto the building platform. The sliced data of the part's CAD model is loaded into an inkjet printhead which jets selectively the binder onto the powder bed to glue the particles together. This glue shapes the object and replaces the function of a mould. Via repeating these steps, a part surrounded by loose powder is created. After removing the powder, the part can be accessed and used for further processing. For Technical Ceramics, however, binder jetting is challenging because the low packing density of the powder bed leads to highly porous fired ceramic parts, in working areas where porosity is typically not desired. In some cases, the material system can be infiltrated with an external component to achieve full density like for instance silicon-infiltrated silicon carbide. For material systems where infiltration is not possible, this porosity lowers the performance of the ceramic component and the superb physio-chemical properties of the ceramic are not fully reached.

CerAMing GmbH brings the LSD technology to the market for overcoming the shortcomings of both mentioned technologies. It increases the productivity and effective part volume using the merits of powder-based binder jetting processes while producing dense ceramic components like stereolithography. Furthermore, dark materials like silicon carbide can be processed as easy as light ones.

Layerwise Slurry Deposition (LSD)

In LSD, a slurry, which is the technical term used for a water-based ceramic suspension, is used as feedstock material. All powders that can be stabilised in a suspension form can be employed. This leads to a very broad potential material portfolio also beyond ceramics (e.g. hard metal). Even submicron particles can be employed which has another positive effect on the firing time for reaching the final ceramic properties. Submicron powders lack flowability and are not processable in conventional powder-based technologies.

The process is summarised in Fig. 1. A layer of the slurry with thickness of 20–200 µm is deposited onto the building platform.

Subsequently, the layer is dried to create a powder bed. A sliced image of the desired CAD geometry is inscribed inside of the now dried layer with the help of an inkjet printhead by gluing together the particles, like in powder-based binder jetting. Iterations of those three steps builds up a solid powder bed, wherein the printed part is found. The part is washed away from the block with water since the green body is water insoluble, whereas the powder bed is dispersible in water. After that, like in conventional manufacturing techniques, the green body is fired. The relative green body density of the reached parts is higher than that of purely powder-based pro-

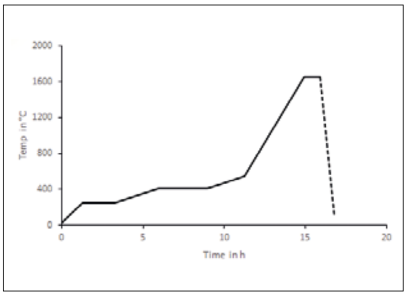

Fig. 2
Exemplary firing curve (including thermal debinding and sintering) for a given alumina part with wall thicknesses up to 10 mm; sintering scheme: heating ramp of 5 K/min up to 1650 °C

Fig. 3
Examples of printed alumina parts (f.l.t.r.): a rectangular 3D-grid (75 mm × 29 mm × 10 mm), two laser mirror-like structures (66 mm × 47 mm × 11 mm), a dental bridge (35 mm × 12 mm × 11 mm), a rotor-like structure (41 mm × 11 mm), and a test artifact adapted from NIST (66 mm × 41 mm × 10 mm)

cesses (about 15 % higher relative density) which ultimately affects obtaining a dense final ceramic. Because of that, the green strength is higher as well. Furthermore, since the powder bed is solid, no support structure is needed at all, in case for example a part with overhangs is to be printed.

As was described in the paragraph on lithography-based technologies, the duration of the debinding time is a non-linear function of the organic content contained by the green body. The ink that is used to glue together the particles in the powderbed of CerAMing's technology provides a stable green body but reduces its organic content to an optimal point. With a maximum amount of 5 mass-% of organics in our green bodies, compared to about 25 mass-% for stereolithography [4], the overall firing time can be significantly reduced without inducing cracks in the ceramic [5]. The LSD technology helps to reduce energy consumption significantly and carbon dioxide emissions here by a factor of four. This makes parts with much higher wall thicknesses and effective volume economically and environmentally reasonable. Fig. 2 shows an exemplary sintering curve for a given alumina part with wall thicknesses up to 10 mm. The overall firing time is less than 18 h. The combination of little organic content and larger effective volume allows for an economical serial production of batches with industrial technical ceramics.

Fig. 3 gives an impression of medium size alumina geometries. From left to right, a rectangular 3D-grid, two laser mirror-like structures, a dental bridge, a rotor-like structure, and a test artifact are displayed.

Fig. 4
CerAMing Shapefinity®: the layer thickness can be adjusted between 20–200 µm, all powders than can be made a suspension from, are processable with this machine

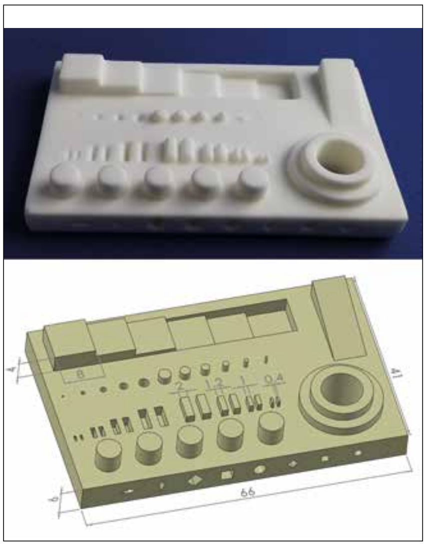

Fig. 5
The test artifact adapted from NIST which contains different features to show the capability of the process (top) sintered part; (bottom) CAD file

All these parts have been printed with the LSD technology using the CerAMing's printer from Fig. 4 using 50 µm layer thickness. The parts have a relative density of 99,6 % (Archimedes method).

To elucidate the optimal application area of LSD, the printing result of the shown test structure shall be discussed here in more detail. Fig. 5 shows again the printed test structure and below the original CAD file. The test artifact has been adapted from the "NIST Additive Manufacturing Test Artifact" [6]. It was printed with a CerAMing standard 96 % alumina slurry that was not optimised for a certain application but is used instead as a basic slurry for target-oriented development. The part was only washed out of the powderbed and fired. No post-processing scheme was implemented. It is the raw, non-optimised outcome of the printing itself. It contains different features starting with five cylindrical pins at the bottom. With this repeated cylindrical pin, a statement about reproducibility can be made. The theoretical 4,94 mm diameter of the feature resulted in a printed embodiment with diameters in the range of 5,02–5,10 mm. In relative terms this corresponds to a maximal deviation from the theoretical value of 3,2 % before any optimisation or post-processing scheme was implemented. There is room for improvement but as the printing technology will leave the deviation in absolute terms quite stable, the LSD is a candidate for industrial applications with higher effective part volume and bigger lot sizes.

Above the repeated cylindrical pins there are rectangular and round holes and pins. The rectangular bars have a thickness after firing of 2,0 mm, 1,2 mm, 1,0 mm and 0,4 mm and a height of 1,7 mm. Rectangular holes with the same dimensions were printed adjacent to the bars. The round pins have diameters of 2,0 mm down to 0,4 mm and a height/depth of 1,7 mm. The printed features show that for small structures with high resolution (below 1,0 mm), lithography-based technologies are still the remedy of choice.

The bigger the features get, the better is the performance of LSD. This applies in particular for cavities that contain inner sharp edges which is also shown in other geometrical inner features in the lateral of the test artifact. Shared with most of AM technologies, cavities with no or too narrow connection to the outside cannot be fully cleaned and the building material will become part of the final product. The ramp on the upper right corner of the test artifact is utilised to elucidate the effect of manufacturing a part additively that is layer by layer. Generally, whenever a part is 3D-printed, the steps denoting the layer thickness are somehow detectable. Most notably, however, the printed test structure shows no visible steps meaning the ramp is observed as a continuous inclined plane. Hence, the 50 µm layer thickness, with which the part was printed, has no negative effect on the surface quality. As a matter of fact, the final parts show no layer interface when made a cross-sectional study.

The positive and negative staircases on the upper side and the cylindrical structure with hole on the lower right side of the artifact, strengthen the elaborated statements from above. These two sets of structures are in good alignment with the theoretical design and bring out the strength of LSD.

In connection with the advantage of the economical firing time that was described before, the drawn conclusion is that the technology is not competing against lithography-based technologies. It can serve a market segment that focuses on bigger ceramic components with larger wall thickness. The recommendation is to use LSD in cases of gently complex parts with wall thickness of above 5 mm that lack the possibility of cost-efficient shaping methods or low lot size manufacturing needs where a shaping e.g. mould production is cost-intensive.

CerAMing has access to different LSD machines where the biggest has a building platform area of 600 cm^2. The current material portfolio consists of alumina and zirconia. A research proof-of-concept for silicon carbide has been achieved [7]. CerAMing is open to inquiries or validation projects with the target of commercial exploitation.

Conclusion

In summary, CerAMing's new AM technology can fill the gap that binder jetting technologies have left so far by producing dense technical ceramic components. Like in AM of metal, binder jetting is a scalable technology. With the usage of suspensions instead of loose powder, now, also Technical Ceramics which cannot be infiltrated can be binder jetted densely. With this technology it is possible to produce monolithic Technical Ceramics out of any powder which can be stabilised in a suspension form. Since no optical process step is involved, also dark materials like silicon carbide can be processed. Additionally, the low organic content reduces debinding time and makes it feasible to produce dense ceramic parts with wall thicknesses over 5 mm in an economic time. In general remarks, structures with details of down to 1 mm can be successfully printed.

The technology is not in competition with lithography-based processes as the strengths lie in different market segments. The recommendation is to use LSD in cases of gently complex parts that have features larger than 1,0 mm and body volumes of at least 500 cm^3 that lack the possibility of mould-based production or low lot size manufacturing needs where a mould production is cost-intensive.

CerAMing is searching at the moment for validation projects in connection to real industry needs.

References

[1] Zocca, A.; Colombo, P.; Gomes, C.M.; Gunster, J.: Additive manufacturing of ceramics: Issues, potentialities, and opportunities. J. Amer. Ceram. Soc. **98** (2015) [7] 1983–2001

[2] Chen, Z.; et al.: 3D printing of ceramics: A review. Europ. Ceram. Soc. **39** (2019) [4] 661–687

[3] Chartier, T.; Chaput, C.; Doreau, F.; Loiseau, M.: Stereolithography of structural complex ceramic parts. J. Mater. Sci. **37** (2002) [15] 3141–3147

[4] Mitteramskogler, G.; Gmeiner, R.; Felzmann, R.; Gruber, S.; Hofstetter, C.; Stampfl, J.; Ebert, J.; Wachter, W.; Laubersheimer, J.: Light curing strategies for lithography-based additive manufacturing of customized ceramics. Additive Manufacturing (2014) [1–4] 110–118

[5] Pfaffinger, M.; Mitteramskogler, G.; Gmeiner, R.; Stampfl, J.: Thermal debinding of ceramic-filled photopolymers. Mater. Sci. Forum **825–826** (2015) 75–81

[6] Moylan, S.P.; Slotwinski, J.A.; Cooke, A.L.; Jurrens, K.K.; Donmez, M.A.: Proc. of the 23rd International Solid Free Form Symposium – An Additive Manufacturing Conference, Austin, TX, USA, 2012, 902–920

[7] Zocca, A.; Lima, P.; Diener, S.; Katsikis, N.; Gunster, J.: Additive manufacturing of SiSiC by layerwise slurry deposition and binder jetting (LSD-print). J. Europ. Ceram. Soc. **39** (2019) 3527–3533