

How Can CIM Benefit from Additive Manufacturing?

In the field of ceramic processing, there is a strong need for the introduction of additive manufacturing (AM) technologies. Tools for ceramic injection molding (CIM) are expensive and require significant lead times which severely restrict the suitability of CIM for the production of small scale series or customized products. These are actually perfect conditions for the implementation of AM technologies; however, so far no adequate prototyping technology was available. The main reason for that are the high demands on high-performance ceramics – these materials are used where other materials fail, thus the quality and the reliability of the parts are crucial.

Abstract

In this paper a novel AMT-approach is presented, which is capable of producing strong, dense and accurate ceramic parts via a photopolymerization process, namely the Lithography-based Ceramic Manufacturing (LCM). For alumina a theoretical density of over 99,4 % and 4-point bending strength of 430 MPa could already be realized.

Moreover, due to its layer-by-layer approach, the LCM technology provides the opportunity to shape highly complex and intricate geometries that cannot be realized by conventional means. Holes with a diameter of 200 µm and a wall thickness of down to 150 µm could be realized by this technology to date. These characteristics render the LCM technology a capable addition to conventional processing techniques in the field of ceramics.

Introduction

Additive Manufacturing (AM) has created a regular hype in recent years; some people even see the next industrial revolution in this technology and predict a future with 3D-printers in almost every household.

Keywords

additive manufacturing, alumina, photopolymerization

While some of these expectations will not be fulfilled in the foreseeable future, AM has begun to play an integral role in today's research and also became an important methodology in industry. AM technologies have seen a huge rise in importance in the last few years. These technologies started to emerge in the late 1980s and beginning 1990s and were not noticed by a wider public until first machines were developed for the home user market [1]. But how does AM work and what distinguishes them from established fabrication techniques? AM produces parts by attaching volume elements which is in contrast to conventional erosive methods like milling or turning. Almost all AM-processes work according to a layer-by-layer concept, which means they attach 2-dimensional contours with a given thickness. The specialty of AM is that physical models can be manufactured directly from computer aided design (CAD) data and that no tools or molds are needed for fabrication of the part.

Industrial applications of AM

But how important are these AM technologies for the industry? According to the Wohler's report, a market report for AM, the benefit and the impact in industry is huge and will gain even more importance. Parts made by AM are employed in all different

industries ranging from aerospace, automotive and jewelry to toys, furniture and medical applications. Especially the latter has already been taking advantage of this kind of technology for some time. In particular it is the hearing aid industry that serves as an example for the potential of AM as a new production technology. The majority of all customized hearing aids are produced by AM nowadays. The shells of the hearing aids have to be customized to fit perfectly into the patient's ear. Since the auditory canal of each person varies, it is necessary to provide customized solutions – and AM is the tool that delivers them. And AM will continue to play an integral role in this field; customized prostheses, implants or scaffolds can be made using this approach, ensuring that the influence and importance of AM for biomedical applications will continue to grow.

Benefits for the ceramic industry

Another field that could significantly benefit from the implementation of AM is high-performance ceramics. A more widespread use

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of technical ceramic parts is often limited by the costly and laborious fabrication of prototypes and test parts. The main factor within this process chain is usually the fabrication of the respective mold. In this context, AM technologies enable a significantly faster time-to-market in combination with a shorter product life cycle. Unlike in conventional fabrication routes with the need for molds and/or laborious machining and mechanical finishing, AM provides a fabrication methodology to directly convert the digital file into the three dimensional (3D) object. The elimination of lead and machining times enables a much faster production of first parts or prototypes. AM produces parts by attaching volume elements which is in contrast to conventional erosive methods like milling or turning. Thus AM allows the efficient fabrication of complex 3D structures with high feature resolutions directly from a geometric computer model, which is virtually sliced into very thin layers. The respective parts are built upon the selective addition of material by stacking the individual cross-sections of the object in a layer-by-layer manner.

Another important opportunity of this fabrication methodology is the freedom of design. Due to the layer-by-layer building principle it is possible to produce highly complex shapes without any additional effort. In this manner AM can be the key technology to enable a transition from manufacturing-oriented design towards design-oriented manufacturing. Neither production time nor cost significantly rise with the complexity of part in question – printing out a cylinder or a cuboid requires the same time and labour as a complex cellular scaffold, a defined catalyst carrier or an entangled structure. This can be a huge advantage for the construction of lightweight parts or parts with integrated functionality. It also leads to significant savings in terms of the used material and provides new possibilities in the design of the parts.

Prototypes

Another interesting benefit of AM is the customization of the part designs. It is possible to produce new designs or alter and improve existing designs by only changing the respective CAD drawing. AM is especially well-suited for the application in the context of sustainable industrial production. Due to the potential for highly efficient material usage, AM can play an instrumental

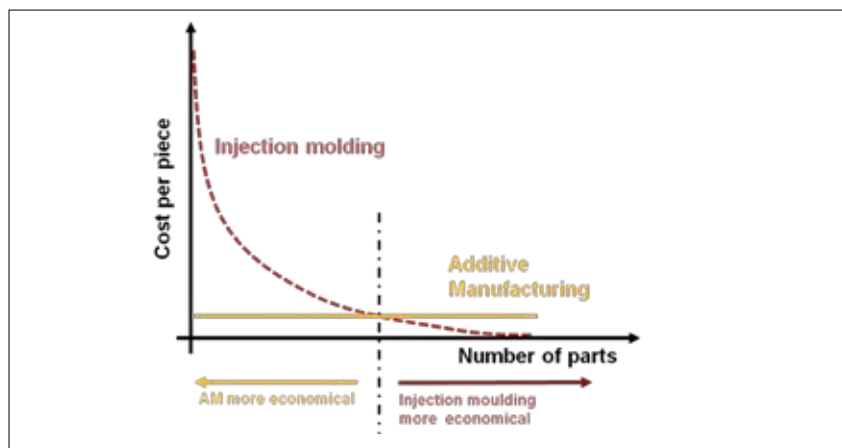


Fig. 1
Comparison of the cost effectiveness of CIM and AM

role in making the manufacturing industry more energy efficient.

In view of these circumstances it is no surprise that research in the direction of AM of ceramics has been an intriguing topic for the relevant industry and academia in recent years.

Additive manufacturing as complement to CIM

The advantages of AM technologies will also have an impact on the fabrication of high-performance ceramic parts in general. Especially for CIM, with its significant lead times and costly tools, AM can act as capable complement to this production means. The opportunity of the fast and cost efficient production of prototypes will also yield benefits to the CIM industry; it is possible to provide the customer much faster and cheaper with first parts for a screening or tests. If a given design has been chosen or the prototypes have been evaluated by the customer, the respective mold is fabricated and the production means is changed to CIM to enable higher throughput.

AM also provides the possibility to carry out design studies or to implement design variations. But AM is not only the preliminary step to CIM; it can also already be the adequate manufacturing means. While with AM each part approximately causes the same production costs, in CIM there is a significant dependency on the given lot size as illustrated by Fig. 1.

The fabrication of ceramic parts using CIM always requires the previous acquisition of the respective mold which causes significant expenses. For the price of the mold it

does not matter if one or 100 000 parts are to be made; thus, from an economical viewpoint, CIM is highly unfavorable for small scale series or even individual parts. For AM the only prerequisite is the respective CAD drawing making the costs for each part that is produced by this means almost equal. Hence, especially in the case of small scale series or individual parts, switching to CIM would be unfavorable.

Of course an approach like the one described above has one crucial requirement: the parts produced by AM have to be fully functional.

There must be no significant deviation between the performance of the AM produced part and the one made by CIM. This point leads to main limitation AM of high-performance ceramic materials used to suffer from – inadequate mechanical characteristics.

Limitations

But while there are a lot of intriguing opportunities with AM technologies, this relatively young manufacturing discipline still has to face some limitations. None of the currently established AM technologies is able to provide excellent geometric quality and excellent materials quality at the same time. Geometric quality involves precision and surface quality while materials quality refers to the mechanical properties of the processed compounds.

This dilemma is one of the main reasons, why AM has not yet found a stronger foothold in the ceramic manufacturing industry: the necessary manual post-processing steps and inferior material quality in are in

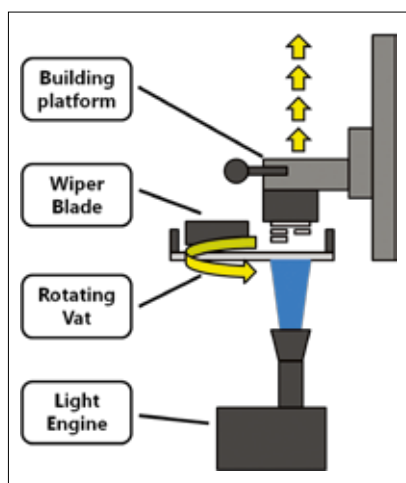


Fig. 2
Schematic illustration of the CeraFab 7500

many cases a severe limitation for a more wide-spread use of AM.

State of the art

AM technologies applicable for the shaping of ceramic objects can be divided into two categories: direct AM techniques and indirect AM techniques.

Direct AM techniques

As their name suggests, direct AM techniques immediately give the sintered ceramic parts without the need for further thermal postprocessing. These methods are powder-based. The underlying principle is the connection of the individual particles using thermal energy input by means of a laser. Due to the locally increased temperature in the zones where the laser interacts with the powder, the ceramic particles melt together. The associated techniques are referred to as laser sintering (LS) or laser melting (LM) [2]. Problems associated with this approach are internal stresses that are built up during the melting by temperature gradients or the very rough surfaces that are also a consequence of the melt pool.

Indirect AM techniques

Indirect AM techniques require a subsequent second process step to obtain the sintered ceramic bodies meaning that the shaping is an individual process and the debinding and sintering another. This methodology includes all disciplines where the shaping of the objects involves a combination of ceramic powder and an organic binder. This can either mean that the feed-

stock already includes the binder or that the binder is added to the ceramic particles during the shaping process. The first concept is the case for laminated object manufacturing (LOM) [3], extrusion-based techniques such as robocasting [4] and fused deposition modeling (FDM) [5], methods that rely on the concept of lithography [6] like stereolithography and digital light processing (DLP), inkjet-based techniques using an ink which already comprises the ceramic powder together with the binder (direct inkjet printing) [7] or so-called indirect SLS-methods where binder is also present in the powder bed of the feedstock. The latter approach involves indirect inkjet printing where the binder alone is used as an ink and is ejected onto a bed of ceramic particles [8]. These techniques have in common that after the shaping a green part consisting of the ceramic particles and the organic binder is formed. The further treatment is very similar to conventionally shaped ceramic components, the green parts are debinded to eliminate the organic components and subsequently sintered to give the ceramic bodies.

Lithography-based AM techniques

Since techniques based on lithography provide the best feature resolution these methods have the potential to open new possibilities for the fabrication of ceramic objects, especially regarding intricate and complex shapes as well as fine details. Lithography-based techniques are based on the underlying principle of photopolymerization where a liquid formulation is transferred into a polymer material upon selective space-resolved exposure to light. During this event the low molecular monomers are consumed to give long polymer chains or a 3D polymer network causing the initially liquid formulation to solidify.

Lithography-based ceramic manufacturing

The following section focuses on a dedicated methodology for high-performance ceramic parts, the so-called Lithography-Based Ceramic Manufacturing (LCM process). All parts discussed within this contribution were produced by means of LCM-technology using a CeraFab 7500-system by Lithoz.

The assembly of the CeraFab 7500-system comprises a rotating vat that is filled

with the photocurable suspension. The bottom of the vat is transparent; thus, the light source can illuminate the suspension from below through the vat. The projected image is generated via a digital micromirror device (DMD). The resolution of the DMD is 1920×1080 pixels. Using a dedicated optical system the resolution in x/y-plane is adjusted to $40 \mu\text{m}$; thus, the building envelope of the CeraFab 7500 is $76 \text{ mm} \times 43 \text{ mm} \times 150 \text{ mm}$. The building platform is above the vat and moves upwards the z-axis during the fabrication process. Fig. 2 shows a photograph of the actual CeraFab 7500-system and also gives a schematic overview of the machine.

The layer thickness can be adjusted in the range between 25 and $100 \mu\text{m}$ resulting in a building speed of typically between 2,5 – 10 mm/h.

The LCM-process relies on the concept of photopolymerization. Ceramic powder is dispersed into a mixture of photocurable monomers to give the photocurable suspension. A thin layer of this suspension is automatically coated onto the vat, the building platform approaches the vat, only leaving a small gap of a couple of microns which is filled with slurry. The photosensitive compounds comprised within this slurry are then cured by selective exposure with light of a certain wavelength. Where light hits the ceramic-filled slurry the monomers photopolymerize into a 3-dimensional network which then acts as a cage for the ceramic filler as it is schematically shown in Fig. 3. After completing the layer, the building platform is elevated and the whole sequence is repeated all over again.

Materials

In general, different resin systems with varying filler content and crosslink density of the organic matrix are applicable for this process; thus, it is possible to realize a broad range of different geometries from fine and delicate features to rather massive and bulky parts. The materials processed by the LCM-technology presented within this work were suspensions comprising a photopolymerizable monomer mixture filled with ceramic powders in typical concentrations between 75 and 85 mass-%. In order to ensure proper processability the formulation has to be highly homogeneous, stable towards sedimentation of the fillers and must exhibit a viscosity within the working

window of the machine. Depending on the produced geometry different resin systems varying in filler content and crosslink density of the organic matrix have to be chosen to give the green part the sufficient mechanical strength. The used suspensions for this work were on the basis of alumina (LithaLox HP 500), zirconia (LithaCon 3Y 610 Purple) and tricalcium phosphate (TCP; LithaBone TCP 200).

Post-processing

After the structuring using the CeraFab 7500-system the green parts were cleaned from the excess slurry by immersing the part in an appropriate solvent capable of dissolving the slurry without damaging the cured structure.

Subsequent processing involved the de-binding of the green part where the organic matrix was removed by treating the parts at elevated temperatures. The hereby obtained white parts were then sintered in a high-temperature furnace to give the final dense ceramic parts.

Results

The systematic characterization presented within this paper focused on the parts composed of alumina made from the LithaLox HP 500 slurry. The density measurements for the sintered alumina parts by the Archimedes method gave values of $3,96 \text{ g/cm}^3$ which are equivalent to a relative density of 99,3 %. The linear shrinkage from the manufactured structure in the green state to the sintered ceramic was 19,7 % for the respective suspension. The characterization of the mechanical strength of the alumina ceramics was determined by 4-point-bending (4PB) experiments. With a measured strength of 426,8 MPa and a Weibull-modulus of 11,2 the sintered ceramic parts produced by LCM exhibit very similar values to those of conventionally produced alumina [9]. These values are perfectly acceptable for the use of these compounds as functional parts in numerous areas of application. The results are also affirmed by the examination of the fracture surface of the 4PB parts that underline the similarity of the LCM-fabricated parts to conventional manufactured ceramics as can be seen in Fig. 4. The deviation of the reproduction accuracy of these and other parts was determined to be considerably below 1 % with respect to the underlying CAD data.

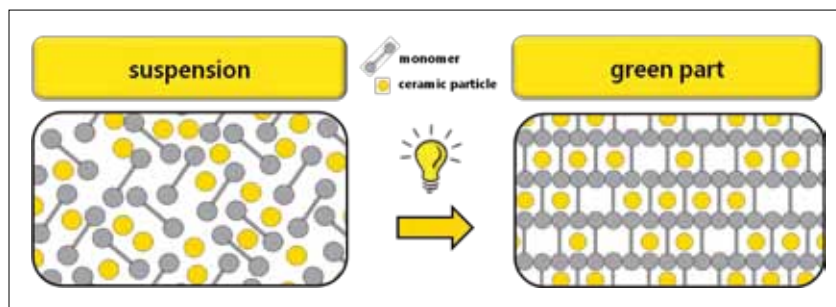


Fig. 3
Schematic illustration of the curing of the ceramic suspension

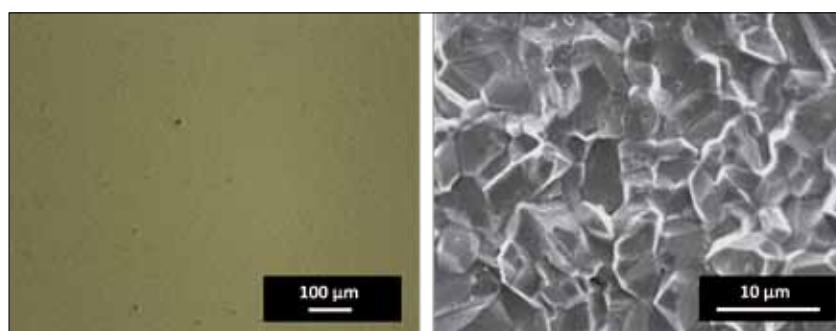


Fig. 4
Micrograph (l.) and SEM image (r.) of LCM fabricated alumina samples

The appearance of the polished surface in the microstructure is in good correspondence with the material's high density that was determined by the Archimedes method. The SEM image shows the fracture surface of a 4PB testing bar. These specimens were fabricated in a manner that the load during the subsequent bending tests was applied in the direction along the layer boundaries, which was expected to be the weakest orientation possible. Nonetheless, it can be seen that the fracture does not take place at the boundary between the two adjacent layers but randomly throughout the part. This behavior confirms a highly homogeneous microstructure upon sintering and that the interlaminar boundaries from the layer-by-layer fabrication process do not act as predetermined breaking points. Also the green bodies exhibit sufficient mechanical strength and stiffness to be handled or machined if this should be necessary. This is due to the three-dimensional network of the organic matrix which is formed upon photopolymerization during the shaping of the material. In this manner, using the LCM-process on the CeraFab 7500-system it was possible

to realize highly accurate reproductions of the underlying CAD-geometries. The variety of different parts that is feasible using the LCM approach is broad ranging from delicate cellular scaffolds to more massive and bulky hulls, mountings or housings. Fig. 4 shows exemplary parts for prototypes, small scale series and complex structures. Using the LCM-process on the CeraFab 7500-system it was possible to realize highly accurate reproductions of the underlying CAD-geometries. Fig. 5 shows photographs of some exemplary structures built by the CeraFab system using photocurable suspensions on the basis of alumina, zirconia and TCP.

Conclusion

AM must not be seen as a competitor to CIM, it is a complementary technology that broadens the range of ceramic parts that can be fabricated – from an economic point of view, but also in general terms. AM technologies in general provide a number of intriguing opportunities. Their straightforward methodology eliminates the necessity of lead-times as well as laborious post-machining for fabricated parts. A paradigm

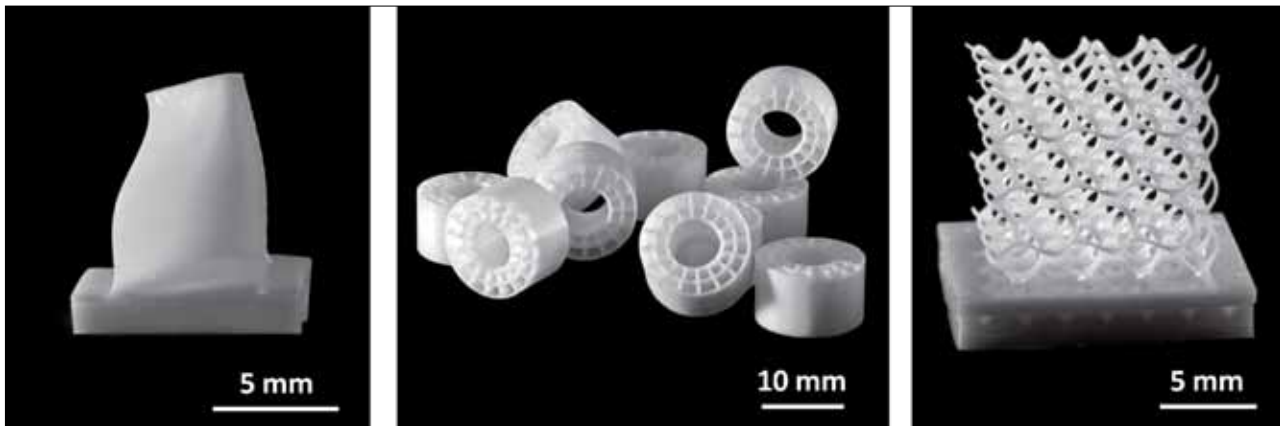


Fig. 5
Turbine blade (l.), extrusion profiles (center) and a cellular lightweight structure (r.) made from alumina

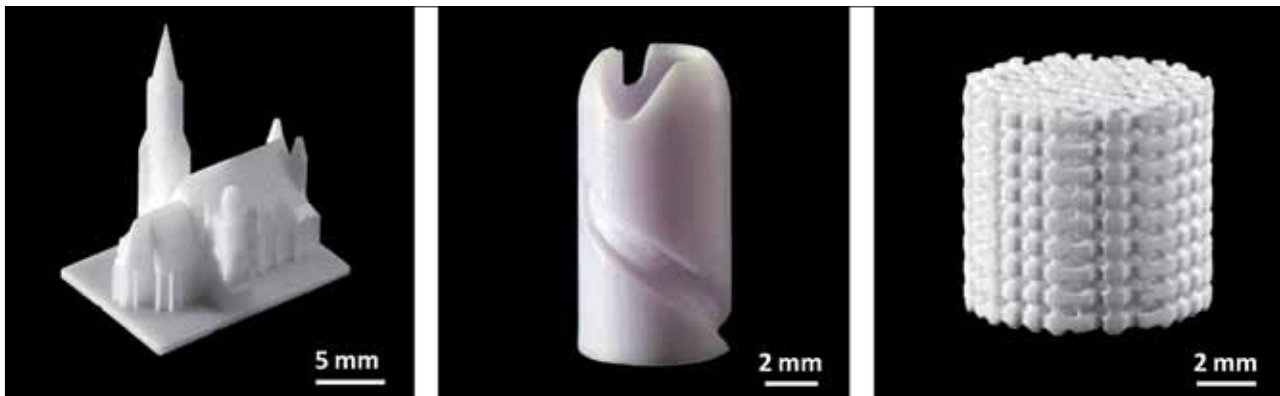


Fig. 6
Exemplary sintered ceramic objects made by LCM technology: miniature of the St. Stephen's Cathedral in Vienna made from alumina (l.); hull made from zirconia (center); scaffold made from TCP (r.)

shift from manufacturing-oriented design towards design-oriented manufacturing is possible. The different AM disciplines can cover the whole range of technical ceramic materials, but not each approach is suitable for each product. While e.g. FDM-based

processes deliver good results for larger structures, porous bodies and foams, these techniques do not lead to satisfactory results for dense and strong objects. In this respect, the recently developed LCM technology is currently the only commercially

available AM technology for the production of dense and precise ceramic objects. This fabrication technique allows combining the material properties of high performance ceramics with completely new possibilities in terms of design freedom.

References

- [1] Wohlers T.: Wohlers Report 2013. Wohlers Associates, 2013
- [2] Gahler, A.; Heinrich, J.G.; Günster, J.: Direct laser sintering of $\text{Al}_2\text{O}_3\text{-SiO}_2$ dental ceramic components by layer-wise slurry deposition. *J. Amer. Ceram. Soc.* **89** (2006) [10] 3076–3080
- [3] Götschel, I.; et al.: Processing of preceramic paper and ceramic green tape derived multilayer structures. *Advances in Applied Ceramics* **112** (2013) [6] 358–365
- [4] Miranda, P.; et al.: Mechanical properties of calcium phosphate scaffolds fabricated by robocasting. *J. Biomed. Mater. Res. A* **85** (2008) [1] 218–227
- [5] Novakova-Marcincinova, L.; et al.: Special materials used in FDM rapid prototyping technology application, 2012 IEEE 16th Int. Conf. Intell. Eng. Syst. INES. (2012) 73–76
- [6] Chartier, T.; et al.: Stereolithography process: Influence of the rheology of silica suspensions and of the medium on polymerization kinetics – Cured depth and width. *J. Europ. Ceram. Soc.* **32** (2012) [8] 1625–1634
- [7] Ebert, J.; et al.: Direct inkjet printing of dental prostheses made of zirconia. *J. Dent. Res.* **88** (2009) [7] 673–676
- [8] Leukers, B.; et al.: Biocompatibility of ceramic scaffolds for bone replacement made by 3D printing. *Mater. Werkst.* **36** (2005) [12] 781–787
- [9] Informationszentrum Technische Keramik: *Brevier Technische Keramik*. 4th ed., Lauf 2003