Lithography-Based Ceramic Manufacturing for 3D-Printing of Si_3N_4-Based Ceramics and Cermets

LITHOZ/AT succeeded in the development of silicon nitride as a standard material for its Lithography-based Ceramic Manufacturing (LCM) process and has mastered the challenge to overcome the reduced light penetration for darker powders.

Introduction

Additive Manufacturing (AM) of ceramics has grown out of its infancy and a lot of new applications are emerging in this field. These new ideas often also require development of novel materials for AM. Among others, silicon nitride-based ceramics are receiving a great deal of attention as high potential materials for additive manufacturing.

For the first time in history LITHOZ, system provider of AM systems for ceramics, succeeded to make silicon nitride with the same material properties as in conventional forming methods available for the ceramic AM community by providing a stable process for printing, debinding, and sintering of so-called SiAlON materials. This article presents the advances concerning AM of these SiAlON ceramics and marks out various fields of application which open up new opportunities and benefits for the ceramic industry.

AM, often also referred to as rapid prototyping or 3D- printing, is becoming a common and reliable production method in the ceramic industry. State-of-the-art 3D-printers for ceramics are meeting the high standards of the ceramic industry and are already used for different applications. AM is a cost-effective production method for prototypes and small scale series and has also the potential for mass manufacturing for certain applications. It allows the realization of advanced designs which cannot be realized with conventional production methods.

If everything is applied correctly, AM parts can achieve the same material properties as in conventional forming technologies. Due to their excellent surface quality additive manufactured parts can be used without post processing such as polishing or grinding. State-of-the-art 3D-printers are characterised by their reliability to produce high-precision parts and offer greater flex-

Fig. 1
Photograph of CeraFab 7500 (l.), and schematic principle of CeraFab (r.): (1) building platform, (2) rotating vat filled with resin, (3) optical system, and (4) light source

Keywords
Additive Manufacturing, silicon nitride, SiAlON, lithography-based ceramic manufacturing, vat polymerization processes

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ibility in part design in order to enhance the functionality of products.

AM system providers are continuously working on the improvement of their systems and the expansion of the range of ceramic materials for their systems. In collaboration with their customers, they identify high-potential materials for new fields of application. While materials such as alumina, zirconia and tricalcium phosphate are already available as standard materials for AM, system providers are engaged in research and development of new materials which have the potential to open up new markets and applications for their customers.

One very promising and high-performance material for many interesting applications is silicon nitride. It exhibits superior material properties such as high strength, high toughness, thermal shock resistance and good chemical resistance to corrosion by many acids and alkalis. Besides that, silicon nitride parts can be used at temperatures up to 1200 °C and has an outstanding ratio of strength versus density and is therefore suited for many aerospace applications.

Silicon nitride is also used for a wide range of applications such as insulators, springs, impellers, bearings, forming tools etc. Additionally, it also offers great possibilities for medical purposes due to its osteointegrative potential and anti-infective properties for medical implants and devices where high strength and wear resistance are required. Its anti-infective properties exceed even well established materials as titanium and PEEK (poly ether ether ketone) and therefore can potentially reduce implant failure due to infection. Several studies have shown that silicone nitride has favorable properties regarding the attachment of cells which supports the ingrowth of bone cells. This makes the material a great candidate for implants where osseointegration is crucial, as in spinal implants or as treatment of nonunion, which are permanent failures of healing following a broken bone. Potential other applications are screws, plates but also acetabular cups, knee joint replacements and many more.

Among all different AM techniques for ceramics, especially vat-polymerization-based processes stand out due to their high precision, homogeneous as well as isotropic microstructure, excellent surface quality and last but not least due to their comparable mechanical properties which provides special benefits for the industry.

In order to make silicon nitride accessible for these lithography-based AM processes, system providers need to overcome some serious issues. Silicon nitride belongs to the group of non-oxide ceramics which are typically darker in color and hence, show a high level of light absorption, which is not favourable for lithographic processes. Due to the problem associated with light absorption of dark powders, lithography-based AM processes for ceramic materials until now were not able to process silicon nitride.

By intensive research, LITHOZ succeeded in the development of silicon nitride as a standard material for its Lithography-based Ceramic Manufacturing (LCM) process. LITHOZ has mastered the challenge to overcome the reduced light penetration for this darker powder. Furthermore by using their LCM process it is possible to print and pressureless sinter SiAlON components with the same mechanical properties as parts made by conventional manufacturing. With a relative density of 99,8 %, a hardness of 1500 (HV) and a biaxial bending strength of 760 MPa the tested composition is at eye-level with conventionally processed analogues 1500 (HV) and 765 MPa for isostatically pressed sialon material). These material properties in combination with the high precision of the LCM process allow the production of highly complex components that have not been feasible before and that are fully functional.

The novel vat polymerization process introduced by LITHOZ enables the industry to combine the favourable characteristics of silicon nitride with the benefits of 3D-printing in a completely new way. The developed concepts for lithographic printing of SiAlON are also transferable to other material systems; here, the processing of an exemplary cermet system based on aluminium oxide and molybdenum is described. Other cermet combinations are under development and even the processing of pure metals could already be demonstrated successfully using the described approach. The subsequent text describes the used process for lithographic printing and sintering of SiAlON and cermet materials as well as the final properties of the resulting parts.

Materials and concept

All sample parts discussed and presented here were fabricated using CeraFab 7500 and 8500 printing systems from LITHOZ GmbH using its LCM technology. 3D-parts are printed starting from a CAD file and converted directly into the physical object based on the principle of vat polymerization. LCM is an indirect AM technique; in a first step the so-called green part is produced. This green part is a composite of ceramic particles homogeneously dispersed in a photopolymer matrix which acts as a scaffold. In a second subsequent process this green parts undergoes a thermal post-process (debinding and sintering) and is converted into the final dense ceramic part. The viscous starting material is polymerized from below by a high-performance projection unit. The building platform with the green parts is layer-by-layer lowered according to the set layer thickness. For the described SiAlON and cermet materials a layer thickness of 20 µm in the green state was chosen. After the curing of a layer, the combination of a rotating vat and a static wiper blade applies a fresh film of material. The size of the available building platforms was 75 mm x 43 mm (CeraFab 7500) or 115 mm x 64 mm (CeraFab 8500) and the coressponding resolution in x- and y-direction was 40 µm (CeraFab 7500) or 60 µm (CeraFab 8500). Fig. 1 shows the setup of the printing system used for all experiments discussed within this paper.

The debinding of printed green parts is performed in ambient atmosphere until 500 °C. The decomposition of the organic components takes place by diffusion and evaporation of small gaseous molecules. The rate of debinding has to be controlled to avoid the build-up of internal pressure to avoid possible cracks and deformation. The overall duration of the temperature cycle strongly depends on the thickness of the walls of the green parts. Particularly critical zones during the debinding are regarded with dwell times and slower temperature rates. Sintering was done under inert or reducing conditions (nitrogen for SiAlON and hydrogen for the cermet system) to avoid oxidation.

Fig. 2
Printed and sintered SiAlON demonstrators

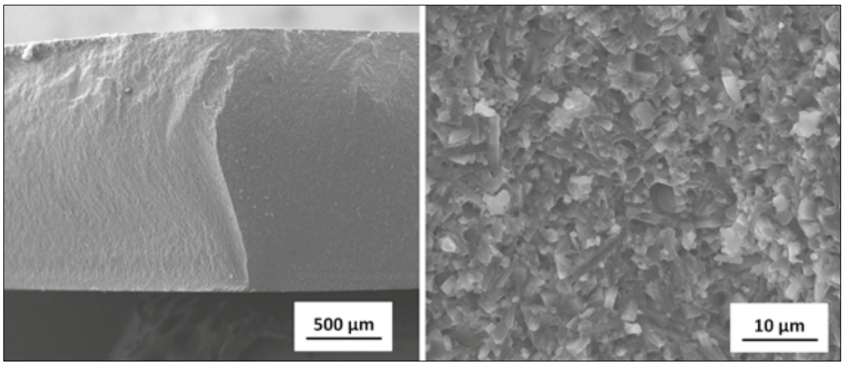

Fig. 3
Fracture surface of broken SiAlON disc from biaxial bending tests in two different magnifications

The materials processed by the LCM technology are slurries comprising a photopolymerizable monomer mixture filled with ceramic powders in typical concentrations between 40 – 55 vol.-%. The photoinitiator-system is chosen in accordance to the characteristics of the emitted wavelength of the LED-based projection system. In order to ensure proper processability the used formulations have to be completely homogeneous, stable towards sedimentation of the ceramic particles and must exhibit a viscosity within the working window of the machine (< 100 Pa·s).

In the case of the sialon material a silicon nitride-based powder blend with a glassy phase content < 10 vol.-% was used.

For the tested cermet systems, a mixture of aluminum oxide as ceramic and molybdenum as metal compound was used; the Mo-phase was 20 mass-% (8,7 vol.-%).

Mechanical properties

To characterize the mechanical properties of the printed SiAlON materials biaxial bending tests were performed. For this purpose, 7 discs with a diameter of 21 mm and a thickness of 2 mm were fabricated, preparated (polishing) and tested. To evaluate the quality of the laminar structure all discs were printed standing on the cylinder jacket so that the load during testing was introduced in the direction of the layer boundaries. For the sintered samples, density was determined according to the Archimedean principle and the strength by conduction biaxial bending tests. These characterizations showed that the printed and sintered samples had a density of 3,24 g/cm³ (99,8 % relative density) and the resulting bending strength was at an average of 764 MPa (770 MPa for isostatically pressed test parts). Fig. 2 shows pictures of sintered demonstrator designs manufactured by LCM. The mechanical strength data could be verified by fractography. Fig. 3 shows the fracture surface of a broken biaxial bending disc. No artifacts from the layerwise build-up are visible after sintering.

First simple thermal shock experiments were also conducted. For this purpose a printed sialon impeller was heated to 800 °C in air and then quenched by immersing it in a water bath at room temperature. Subsequent optical inspection did not show any effects of the quenching on the integrity and quality of the parts; the described experiment can be watched under https://www.youtube.com/watch?v=IxcVGufLsLs . Fig. 4 shows a picture from the tested impeller immediately after the experiment.

Based on the successful proof-of-principle for silicon nitride-based ceramics the LCM concept was tested for other non-oxide materials. As an exemplary cermet material, the system aluminum oxide/molybdenum was investigated. A possible application of such a cermet is for example in heat sinks due to the increased thermal conductivity coming from the metallic phase. There a mixture with 20 mass-% Mo-content (8,7 vol.-%) was found as best candidate in offering both reasonable metal loading high photoreactivity, and good curing depth. Moreover, at this molybdenum content printing was possible without any major modifications of the printing setup and parameters. Fig. 5 shows printed cylindrical test geometries in the green state. Higher metal contents, even purely metallic parts, are also feasi-

Fig. 4
SiAlON impeller after thermal shock experiment

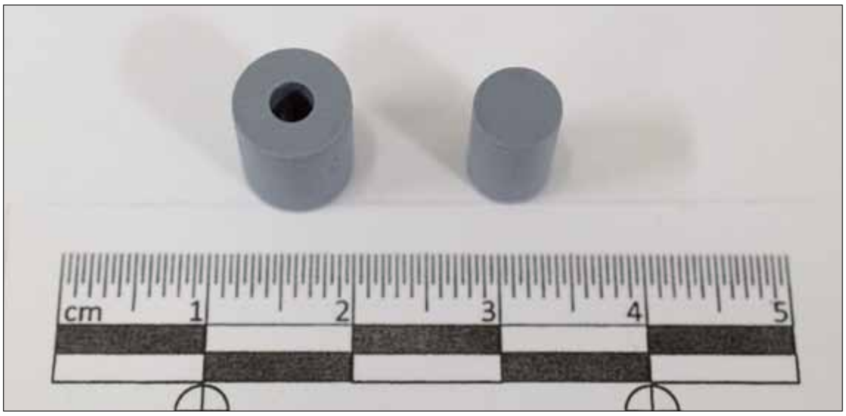

Fig. 5
Photograph of printed cermet (aluminium oxide/molybdenum) green parts

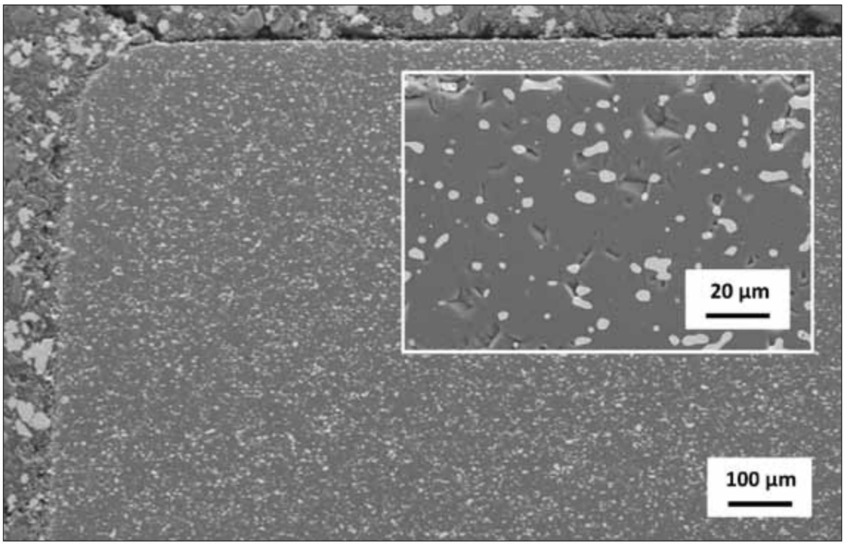

Fig. 6
Polished cross-section of a sintered alumina/molybdenum-cermet in two different magnifications

ble but require significantly different process parameters [1].
Thermal post-processing of the parts printed from this system could be realized under hydrogen atmosphere to give the sintered cermet parts. Fig. 6 shows polished surfaces of the sintered cermet.
It can be seen that the molybdenum is homogenously dispersed within the alumina matrix, thus no sedimentation occurred during the printing process. The material looks homogeneous without any indication of artifacts from the layer-by-layer printing (e.g. pore concentrations at the layer boundaries).

Summary and outlook

Among AM techniques, vat-polymerization-based processes stand out due to their high precision, homogeneous as well as isotropic microstructure and excellent surface quality. However, one limitation associated with this approach are problems arising from high light absorption of dark materials. This paper presents a novel vat polymerization process for the shaping of highly complex green parts for the shaping of non-oxide materials. Especially for silicon nitride-based systems it could be shown that lithography can be used as powerful tool to produce parts having properties as known from conventional processes. Further investigations confirmed that these concepts can also be transferred to other powders that are rather dark in color. Within this work, the feasibility of printing cermets (aluminium oxide/molybdenum) was also performed successfully.
This first results show great potential for this novel process to be used as a complementary technology to conventional fabrication techniques. In general, lithographic techniques show a great advantage when focusing on smaller, more complex parts, which require a high feature resolution and improved surface quality. The presented process can be used to directly produce parts in a small-scale series or to manufacture prototypes prior to a CIM- (Ceramic Injection Molding) -based mass series production. Since the final geometry of the part is developed by means of a sintering process, the same similar microstructural properties compared to conventional processes can be achieved.
Lithographic printing of complex and precise parts from non-oxide ceramics and cermets bears a great potential. The transferability of the developed concepts to other types of non-oxide ceramics (e.g. silicon carbide), cermets, and even metals (e.g. titanium- and aluminium-based alloys) will be topic of future investigations.

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Reference

[1] Schwentenwein et al.: Lithography-based Ceramic Manufacturing for Printing of Non-Oxide Ceramics, Proceedings of the Fraunhofer Digital Manufacturing Conference DDMC 2018, in press