Lithography-based Ceramic Manufacturing: A Novel Technique for Additive Manufacturing of High-Performance Ceramics

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Abstract. Albeit widely established in plastic and metal industry, additive manufacturing technologies are still a rare sight in the field of ceramic manufacturing. This is mainly due to the requirements for high performance ceramic parts, which no additive manufacturing process was able to meet to date.

The Lithography-based Ceramic Manufacturing (LCM)-technology which enables the production of dense and precise ceramic parts by using a photocurable ceramic suspension that is hardened via a photolithographic process. This new technology not only provides very high accuracy, it also reaches high densities for the sintered parts. In the case of alumina a relative density of over 99.4 % and a 4-point-bending strength of almost 430 MPa were realized. Thus, the achievable properties are similar to conventional manufacturing methods, making the LCM-technology an interesting complement for the ceramic industry.

Introduction

Ceramic materials are extensively used in a vast number of technological processes as well as in everyday life. They are usually considered as the material of choice for applications where other materials such as plastic and metal fail to deliver the required performance. Their outstanding characteristics include corrosion resistance, the ability to withstand very high temperatures as well as their exceptional mechanical properties like hardness, stiffness and wear resistance. Those properties make ceramics ideal for the use in demanding environments such as furnaces, heating units or in chemical reactors.

Other applications of ceramics involve electric and thermal insulators, gear wheels, nozzles and watch housings. There is also an increasing demand for high performance ceramics for medical applications such as tooth- and bone replacement materials or in artificial hip-joints.

Ceramics consist of inorganic non-metallic compounds such as oxides, nitrides or carbides and are typically prepared with the help of an organic binder component which allows the shaping of the material into the so-called green bodies. Those green bodies are then transformed into the final ceramic parts over a two-staged heat treatment. The first stage is the so-called debinding step where the organic binder component is burned out. This is followed by the second step the so called sintering where the material is heat treated at much higher temperatures as during the debinding step. During sintering the material undergoes a massive densification which leads to the excellent mechanical properties of the finished part.

Limitations for an even wider field of application lie in the high costs and efforts to produce small series and individual parts as well as the geometrical limitations of conventional production techniques such as pressing, extrusion or even more advanced techniques like ceramic injection molding (CIM).[1] Additive manufacturing (AM) technologies have the potential to be a remedy to those constraints. These technologies are already established in the metal and plastic industry but have yet to gain a significant foothold in the ceramic industry. The reluctance to implement AM processes in ceramic manufacturing until now was due to incapability of the technology to meet the necessary high quality requirements of the ceramic industry.[2]

However, especially the ceramic industry would benefit from this approach since it would allow the manufacturing parts with unseen geometrical complexities as well as a more economical fabrication for small scale series. Also design changes in the prototype stage could be implemented fast and efficient, making this method a very interesting route for the ceramic industry and researchers in this field.

Experimental

Metallic or ceramic parts processed via AMTs are often fabricated by selective laser sintering (SLS). However, the resulting ceramic parts lack the mechanical properties of conventional manufactured counterparts, mainly due to the insufficient densities or the rough surfaces of the sintered parts, and therefore the applicability of those materials for the ceramic industry is severely limited.[3]

To overcome this shortcoming, Lithoz introduced a new methodology where the ceramic powder is distributed in a photocurable monomer formulation in presence of a photoinitiator. This slurry is crosslinked upon irradiation of light to form green bodies with adequate mechanical strength for further processing. This approach eliminates the handling of the fine powders which enhances the work safety and allows the yielding of higher densities after sintering due to the improved powder compaction.

Machine Principle. The CeraFab 7500-system provides the technology to produce 3D-parts directly from a Computer Aided Design (CAD)-file. The CeraFab system virtually slices the CAD-file into a large number of very thin layers and then sequentially cures those slices by a mask exposure process. Thus, the CAD-file is converted into the physical 3D object in a layer-by-layer manner.

The ceramic slurry is poured into the vat and through a vat rotation in combination with the static wiper blade a thin and leveled slurry film is applied. After that the building platform is moved downwards into the slurry and the layer is cured through irradiation from the bottom side of the vat by a light engine based on light emitting diodes (LEDs) and a digital micro-mirror device (DMD). The cured layer attaches to the building platform which is then moved upwards to enable the recoating of the vat. These steps are repeated numerous times until the fabrication process is completed and the finished green part is obtained.

The resolution of the DMD is 1920 x 1080 pixels. Using a dedicated optical system the resolution in x/y-plane is adjusted to around 40 µm which results in a building envelope of 76 x 43 mm for the CeraFab-system. The thickness of the individual layers can be adjusted between 25 and 100 µm resulting in an average building speed within a range of 2.5 and 10 mm per hour.

Materials. The feedstock suitable for processing with the CeraFab-system are photocurable ceramic suspensions in which the ceramic powder is homogenously distributed. The organic components of the matrix are based on acrylate and methacrylate chemistry and the photoinitiator-system is chosen in accordance to the wavelength of the LED-based light source.

The suspensions have to be extremely homogenous and stable in terms of filler sedimentation to ensure proper processability and also the viscosity must be adjusted to match the working window of the system. Depending on the geometry of the desired green parts different slurry systems are available, varying in filler content and crosslink density of the organic matrix in order to achieve sufficient mechanical green strengths. The used suspensions for this work were on the basis of alumina (LithaLox HP 500), zirconia (tetragonal zirconia polycrystal, LithaCon 3Y 610 Purple) and tricalcium phosphate (TCP; LithaBone TCP 200).

Characterization. The density of the parts was determined according to the Archimedes method using a Denver Instruments SI-234A scale equipped with a Denver Instruments SA3013771 density determination kit and the 4-point-bending tests were conducted on a Zwick/Roell Z010-machine. The fracture surface was examined by scanning electron microscopy (SEM) using a FEI Philips XL 30.

Results and Discussion

After the building process in the CeraFab 7500 the green parts are obtained. These composites of ceramic particles in a photopolymer matrix have to be cleaned in an appropriate cleaning fluid to ensure that no excess slurry remains on the parts before debinding and sintering. It is important to choose a cleaning fluid capable of dissolving the slurry without damaging the cured structure. Fig. 1 depicts the building platform with differently designed impellers as exemplary green parts which were fabricated in a single run. This shows the possibility of simultaneously fabricating different parts. Due to the mask exposure process, the necessary time for the fabrication run is only determined by the height of the parts; thus, the production time of the shown assembly is the same as it would have been for a single impeller.

Fig. 1 Building platform of the CeraFab 7500-system with structured green parts: left – uncleaned parts directly after building process; right – green parts cleaned in an adequate cleaning fluid

After structuring and cleaning the green parts undergo a two-staged heat treatment in order to convert them into dense ceramic parts. In the first step the organic binder components are removed at temperatures up to 500 °C. The hereby obtained white parts are then sintered in a high temperature furnace at optimized heating rates and holding times to ensure maximum densification and ideal mechanical properties in the resulting ceramic parts. Fig. 2 shows finished ceramic parts composed of the three standard materials that are currently manufactured by Lithoz: alumina, zirconia and TCP.

Fig. 2 Sintered ceramic parts made from the three standard materials currently available at Lithoz: left – St. Stephen's cathedral in Vienna at a scale of approximately 1 : 6500 made from LithaLox HP 500 (Al_2O_3); middle – hull made from LithaCon 3Y 610 Purple (TZP); right – cellular scaffold made from LithaBone TCP 200 (TCP)

The systematic characterization focused on the parts composed of alumina made from the LithaLox HP 500 slurry. The density measurements gave values of 3.96 g/cm³ which is equivalent to a relative density of 99.4 %. The densification is aligned with a volume shrinkage of approximately 20 % of the sintered part compared to its green state. The bending strength from 4-point-bending tests was determined to be 426.8 MPa with a Weibull-modulus of 11.2 which is in same range as conventional manufactured alumina ceramics.[4] The examination of the fracture surface indicate even more the equality of the material to conventional manufactured ceramics as can seen in Fig. 3.

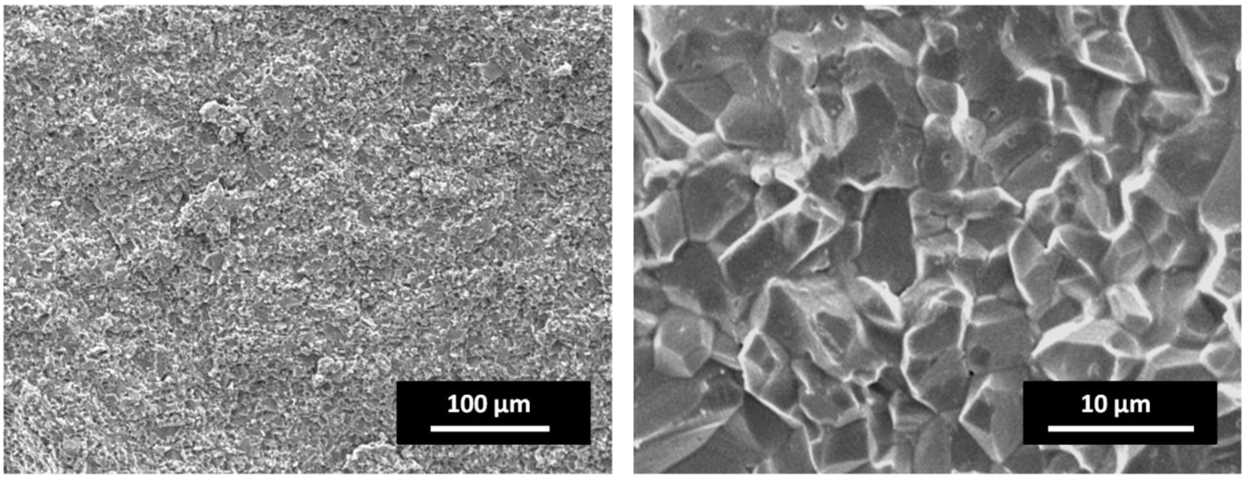

Fig. 3 Fracture surfaces of a 4-point-bending test bar

The parts fabricated by the CeraFab 7500 system show properties very similar to conventional manufactured ceramics. Due to the crosslinked photopolymer matrix the green bodies show excellent properties in terms of stiffness and mechanical resilience. The bending strengths of the sintered material is well above 400 MPa. In combination with a determined Weibull modulus of around 11 the LCM technology is absolutely competitive to conventional production methods.

The precision of the CeraFab-system is below 100 µm and the achievable minimum feature size is around 150 µm. Thus, holes down to 200 µm in diameter as well as cellular structures with strut thicknesses around 150 µm could be realized and are reproducible. The high precision and accuracy in combination with the high density of the sintered parts makes it possible to manufacture geometrically complex ceramic parts with excellent mechanical properties unmatched by any other ceramic manufacturing technology.

Outlook

Future work concerning the LCM technology will concentrate on the development of new ceramic suspensions to expand the currently available range of materials. This includes new powders based on the already available alumina, zirconia and TCP as well as other technical ceramic materials. Another priority in future research will be the further optimization of the organic matrix compounds to improve debinding behavior and green strength. In this manner the fabrication of even smaller and finer structures shall be enabled.

Summary

The introduction of the LCM-technology for the production of ceramic parts enables the fabrication of dense and accurate structures of high complexity. The parts manufactured using the CeraFab 7500-system exhibit mechanical properties very similar to conventional manufactured ceramic materials. This methodology shows high potential for time- and cost savings when it comes to the development of new ceramic products as design changes can much easier be implemented and realized then in any conventional technique. Moreover, the LCM-technology offers tremendous opportunities regarding the fast and simple fabrication of highly complex geometries where other methods often cannot deliver the same results or require major efforts in terms of mechanical postprocessing.

References

[1] W. Kollenberg, A. Kindtner, and M. Kindtner, Rapid Prototyping keramischer Komponenten (Rapid Prototyping of Ceramic Components), Keram. Z. 58 (2006) 76–79.

[2] R. Knitter and W. Bauer, Ceramic microfabrication by rapid prototyping process chains, Sadhana, 28 (2003) 307–318.

[3] W. Kollenberg, Technische Keramik (Technical Ceramics), second ed., Vulkan, Essen, 2009.

[4] Informationstentrum Technische Keramik, Brevier Technische Keramik (Brevier Technical Ceramics), fourth ed., Fahner Verlag, Lauf, 2003.