Additive Manufacturing of Ceramic Components Using Powder Bed and Suspension Methods

The present design of ceramic parts is limited by the opportunities of the conventional shaping techniques so far. In contrast, AM offers the possibility to produce ceramic components of extremely complex geometries as individualized or customized products in efficient single component or small scale production.

Fig. 1
Demonstration components of hydroxyapatite made by 3D-powder bed printing; left: petrous bone (data from Phacon GmbH), right: part of mandible

Introduction
Additive Manufacturing (AM) methods gain more and more in importance for ceramics. However, in contrast to metals and polymers, the AM of ceramics stands right at the beginning of technical implementation.
According to ASTM, AM is a "process of joining material to make objects from 3D-model data, usually layer upon layer" [1]. In a similarly matter, the VDI defines AM as a "manufacturing process in which the workpiece is built up in successive layers or units" [2]. The term 3D-printing is increasingly used as synonym for AM methods, not only in popular science.
Ceramic materials have been studied in AM processes ab initio with the development of the different AM technologies since about 25 years, see for example [3, 4]. All common AM technologies – formerly referred as Rapid Prototyping (RP) or Solid Free Form Fabrication (SFF) – have been tested for ceramic materials too.
The present design of ceramic parts so far is limited by the opportunities of the conventional shaping techniques. In contrast, AM offers the possibility to produce ceramic components of extremely complex geometries as individualized or customized products in efficient single component or small-scale production. In case of expensive raw materials also the waste avoiding (e.g. from green machining of dry pressed components) is an important advantage of the use of AM processes.
AM technologies can be classified according to the state of the material that is used [5] – powder materials, liquid materials and solid materials. It is also possible to classify the AM technologies according the dimensional order [6] – point, line or plane. With regard to ceramics considering the well-known AM process groups: a) Fused Deposition Modelling (FDM) and direct printing (including robocasting), b) lithography-based methods and other Digital Light Processing (DLP) methods, and c) 3D-(Powder) Printing (3DP) and Laser Sintering (LS), it can be stated that either a powder or a suspension perform the initial state to build up the component in layers or units.
Therefore, the AM of ceramic components can be roughly divided into powder-based and suspension based methods. Examples for both methods are given in this paper.
Aside from some special cases of LS, the use of AM processes for ceramics results

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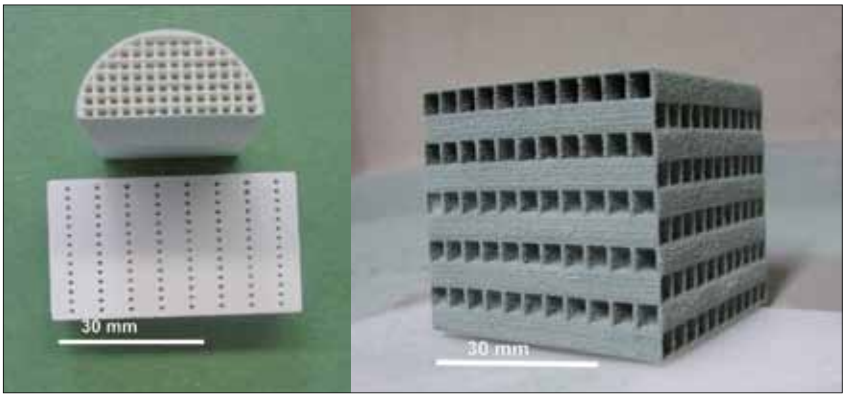

Fig. 2
Porous structures of Al_2O_3-based material (l.) and glass-bonded SiC (r.) made by 3D-powder bed printing

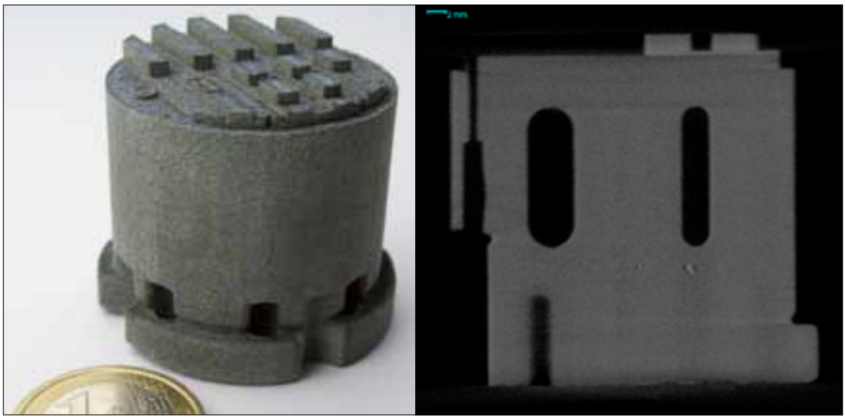

Fig. 3
Laser-sintered SiC, green component (tool insert) and CT cross-section image after Si-infiltration, visualizing the inner channels

in a ceramic green body, which is processed subsequently according the conventional ceramic processing steps up to the sintered component.

Powder-based AM processes

3D-Printing

The 3D-Printing (3DP) or better 3D-powder bed printing is a well-known powder-based AM process. A thin powder layer is applied by a doctor roller and selectively hardened. With one or more printing heads a liquid (ink) is printed on the powder layer. The selective hardening of the powder occurs by interaction between liquid, binder and powder. The binder is either solved in the printing liquid or dry mixed in the powder.
In general, the density of the powder layers is low, and therefore the green density are too low to reach high density (>90 %) after sintering. Typical application of 3D-powder bed printing is focused on the production of porous ceramic components. For example, complex individual bioactive components based on calcium phosphates [7, 8] and porous glass-ceramic [9] have been produced by 3D-powder bed printing.
Another way to utilize the 3D-powder bed printing is the infiltration of the 3D-printed and sintered porous ceramic component with liquid metal [10]. It is also possible to use a ceramic particle-filled ink in powder bed printing to adjust the composition and the green density of the printed sample [11].
For the experiments, the printer Z510 from the former Z Corporation (now 3D systems) was used. The minimum possible layer thickness of the machine is 87 µm. The used ceramic powder must be free flowing for spreading with the doctor roller. Furthermore, the system binder/powder/printing liquid has to be adapted to each different ceramic powder, so that a fast solidification of the respective powder layer, an adequate bond between the powder layers and a sufficient green strength of the printed body is ensured.
Fig. 1 shows 3D-printed structures of hydroxyapatite, a bioactive Ca-phosphate ceramic material. Channels and macropores, which are one of the main requirement for cell growth and existence, are realized via the printing process according to the CAD model. The selected raw powder and the sinter conditions determine likewise the required microporosity.
The manufacturing of filter structures or catalyst support structures is another promising application of 3D-powder bed printing. Fig. 2 presents as an example a honeycomb structure with perforated walls and a so-called cross-channel filter structure. Both can be produced only by an AM method.

Laser Sintering

In Laser Sintering (LS), the powder layer is applied by a doctor roller or blade too. The selective powder solidification by means of laser beam can result in a ceramic body with high density if a liquid phase forming powder composition is used. It was verified for example for an Al_2O_3/feldspar mixture [12] and for an eutectic Al_2O_3/ZrO_2 mixture [13].
Similar to 3D-powder bed printing, the powder layers have a relatively low density. If a ceramic suspension is used as the starting material and then the suspension layer is dried before laser application, a higher density is reached [14].
Another way of using LS is directed to the production of porous ceramic structures, which can be consolidated by post-treatment processes, for example by reaction infiltration or glass infiltration.
A typical example is the LS of SiC to form a complex green body and the post-processing to SiSiC by infiltration, pyrolyses and silicon reaction infiltration. At Fraunhofer-IKTS, the authors worked on process and material development for LS of SiC and post-processing to SiSiC since about 15 years.
Different laser sinter equipment from EOS GmbH with CO_2 laser have been used. The achieved mechanical properties of the material have been increased nearly to the

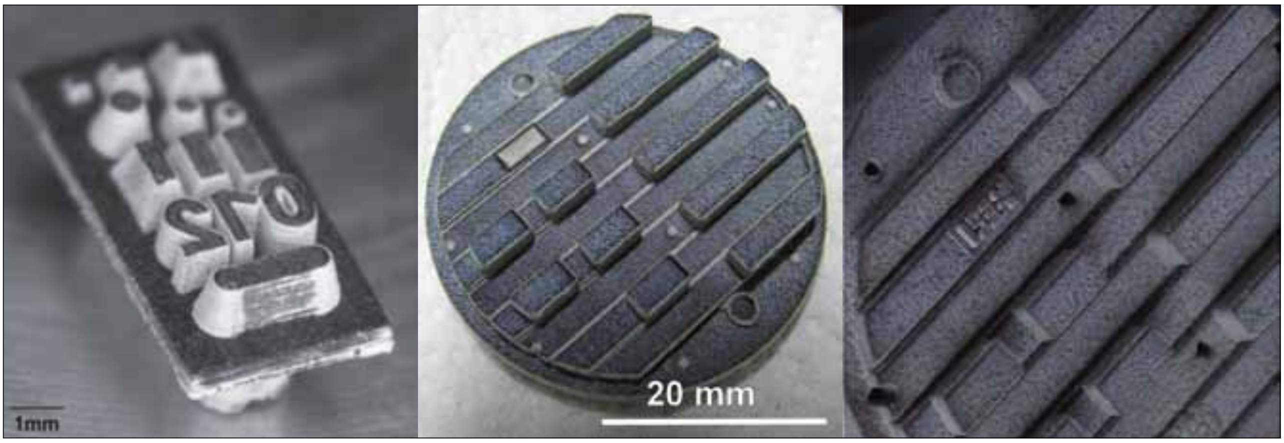

Fig. 4
Laser-sintered hybrid tool insert made of SiSiC –
left: laser micro-sintered SiC part (from University of Applied Science Mittweida);
middle: laser-sintered "macro" part; right: hybrid part after Si-infiltration to SiSiC

level of conventionally produced SiSiC by optimization of process conditions and material composition (starting powder, carbon content). The material and process development for producing complex-shaped SiSiC components via LS is described in detail in [15, 16]. Demonstrator parts for diverse applications have been realized ranged from optical elements via engine components to tool components.
For example, Fig. 3 shows a tool insert with inner cooling channels for injection moulding. Only the AM process allows the production of this complex geometry otherwise additionally joining and finishing processes would be required.
Furthermore, promising results were gained by combination of laser sintering and laser micro-sintering (Fig. 4). This could be a future concept for cost-effective production of laser-sintered SiC components.
Large complex-shaped structures can be generated by "macro" laser-sintering with layers of e.g. 25 µm or 50 µm and filigree shaped details can be formed by laser micro-sintering [17] with very low layer thickness of e.g. 5 µm. Of course a finer SiC powder has to be used for the micro-part. Both parts can be connected during the high-temperature reaction infiltration process.
Certainly a SiC green body can be produced by 3D-powder bed printing too. Using the above-mentioned printer Z510, the experiments with the same powder like that used for LS have shown, that the green density of the 3D-printed parts is significantly lower compared to laser sintered SiC. Moreover, the minimum layer thickness in 3DP is much larger than the possible layer thickness of 25 µm in LS.

Suspension-based AM processes
Lithography-Based Ceramic Manufacturing

For producing dense materials structures with a high level in mechanical properties, AM methods have to be used that based on suspensions and pastes allowing a very homogeneous distribution of ceramic particles and a possibly high volume content of powder as high as possible in the suspension media.
A very promising method for attaining dense ceramic components is the Digital Light Processing (DLP). Initially, the ceramic powder is homogeneously dispersed in a photo-curable organic binder system. Via selective exposure of this suspension by means of a micro-mirror system, a ceramic green body according to the CAD model is built.
The DLP principle described above is adapted by the equipment CeraFab7500 from Lithoz GmbH/AT, which is used at Fraunhofer-IKTS. This technology has been developed especially for AM of ceramic components and it is called Lithography-Based Ceramic Manufacturing (LCM). In the machine CeraFab7500 machine, the layer thickness of the suspension can be varied between 25 – 100 µm, the lateral resolution is 40 µm.
A radical polymerization of the binder system is initiated by selective exposure with blue light by means of the DLP modulus. All regions of a layer necessary for constructing the desired component are cured simultaneously by this method. In this way, the productivity of this technique can be increased in comparison to the dot-wise exposure by means of a UV laser beam in stereolithography. The principle of LCM is explained in detail in [18, 19].
The suspensions used for LCM have a relatively high solid content allowing green densities up to 55 %. Since the components are made upside down in hanging position, the suspension volume necessary for the production process is relatively low, which is important for resource-efficient processing.
After curing the bottom most layer close to the bottom of the glass vessel containing the suspension, the component is raised by a distance corresponding to the thickness of the next layer. A novel suspension layer is now applied by a doctor blade, which is exposed in the next processing step.
Beside the LCM equipment itself, the development of the particular ceramic powder suspension containing the photosensitive component and the adaption of debinding process of the green body play a key role in AM of ceramic using LCM. At present, three different ceramic materials can be processed using the LCM machine: alumina, zirconia and tricalciumphosphate.

Fig. 5
Al_2O_3 honeycomb with triangular-like protuberances in the walls made by LCM, outer diameter 15 mm, channels 1,9 mm × 1,9 mm, wall thickness 0,2 mm

Fig. 6
Al_2O_3 mixer structure alternating channel width made by LCM, channel diameter 1,6 – 3,5 mm, wall thickness 0,25 mm

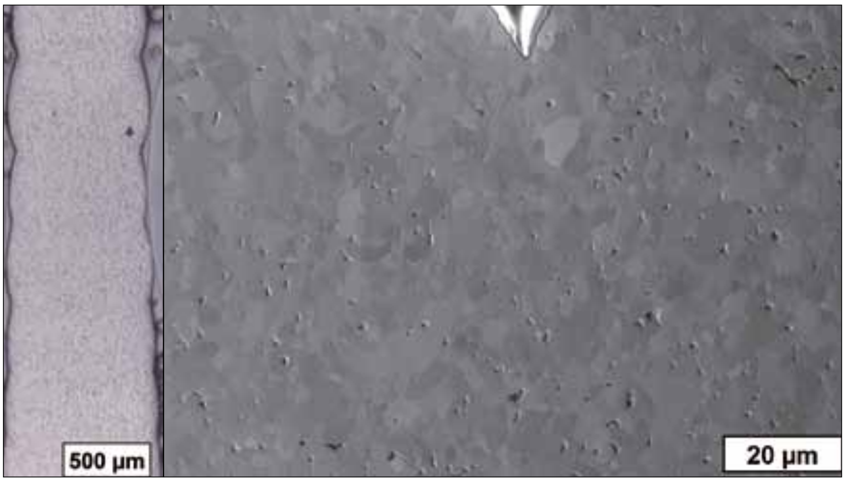

Fig. 7
Microstructure of Al_2O_3 sample made by T3DP, light-microscopic images of seven layers (l.) and FESEM cross-section image of two layers (r.)

For alumina, a standard-suspension to demonstrate the potential of LCM for tool-free, cost-effective production of complex-shaped parts was used. With AM, geometries and designs are possible, that are determined by the aimed function of the ceramic part and not by producibility with the particular (conventional) ceramic shaping method.
Fig. 5 shows an example of alumina honeycomb components made by LCM. For application as mixer structure or catalyst support, the perforated walls with the triangular-like protuberances in the walls effects a gas exchange between the channels and therefore a better mixing. Besides the mixer structure in Fig. 6, other innovative micro-mixer structures have already been presented in [20].

The density achieved after sintering of the debinded alumina green samples is 99,4 % of theoretical density. It corresponds very well to the identified density in [18]. Furthermore, for zirconia samples we achieved a sinter density of 99 % of the theoretical density.
The LCM process has a high potential for producing monolithic dense ceramics. For effective curing of the binder by exposure to blue light, the ceramic particles dispersed in the binder must not absorb the light radiation. For that reason, dark powders are limited for use in this process.

Thermoplastic 3D-Printing

Thermoplastic 3D-Printing (T3DP) is a new approach Fraunhofer-IKTS pursues, which does not have limitations concerning powder colour [21]. This approach bases on highly particle-filled thermoplastic feedstocks with relatively low melting temperatures (80–100 °C). The thermoplastic feedstocks are based on binder systems that are known from low-pressure injection moulding [22]. The viscosity of the molten feedstock (= suspension) is relatively low compared to thermoplastic feedstocks that are used in conventional fused deposition modelling.
In T3DP, the material is only locally applied on the needed positions for construction. A heatable dispensing unit assessable in three axis is moving over a fixed platform carrying a metallic or glassy plate as carrier for the ceramic part.
The thermoplastic feedstock is molten in the dispensing unit for attaining a flowable suspension and it solidifies immediately when cooling down. For that reason, the solidification takes place almost independently from the physical properties of the ceramic powders. First experiments started with thermoplastic feedstock with 67 vol.-% alumina. Using a dispensing nozzle with a diameter of 400 µm simple structures were produced, which consisted of a different number of filaments on top of each other.
Fig. 7 illustrates the complete bond between the layers. An interface between the layers is not visible in the microstructure, rather grain grow occurs across the primary layers. Using two or more dispensing units, different materials can be applied. Therefore, the method is predestined for producing multi-material components.
First results have been attained for producing of zirconia/stainless steel composites using the T3DP [21]. Recent work is focused on utilization of micro-nozzles and dispensing systems creating small single droplets to improve the local resolution.

Conclusion

AM methods open new horizons in design, construction and material composition of ceramic components. Due to the tool-free shaping technology and the layer-wise or point-wise assembly of materials, AM methods work most of all resource- and cost-efficient and almost without waste. For producing ceramic components with high material density, suspension based methods have to be used.

Up to date, LCM is the most-suitable method to produce dense complex ceramic parts with high level of the material properties. T3DP, actual developed in lab-scale also enables producing components with improved material properties. Moreover, this method opens new prospect for producing multi-material composites. The powder-based 3DP is suited for manufacturing porous ceramic components for biomedical and technical application. Relatively low equipment cost, also related to the building space will be a relevant motivation for further development of the 3D-powder bed printing of ceramics.

LS ideally should result in a stable ceramic component that is ready for application. However, using LS for producing complex green parts and followed by conventional thermal processes is a promising way for special materials like SiSiC.

Independently from the particular AM process, by further work on material and technological development, it will be possible to exploit the huge innovation potential of AM also for ceramics and to promote its industrial application.

References

[1] ASTM-Standard F2792-l 2a: Standard terminology for additive manufacturing technologies, March 1, 2012. ASTM international distributed under ASTM license by Beuth publisher

[2] VDI3404, VDI-Richtlinie Additive Fertigung, Entwurf Mai 2014

[3] Lakshminarayan, U.; Ogrydiziak, S.; Marcus, H.L.: Selective laser sintering of ceramic materials. 1st Solid Free-Form Fabrication Symposium Proceedings, Austin, TX, 6–8 August 1990, 16–26

[4] Lauder, A.; et al.: Three-dimensional printing: Surface finish and microstructure of rapid prototyped component. Mater. Res. Soc. Symp. Proc. **249** (1992) 331–336

[5] Chartier, T.; Badev, A.: Rapid prototyping of ceramics, in: Handbook of Advanced Ceramics. Oxford, UK, 2013

[6] Travitzky, N.; et al.: Additive manufacturing of ceramic-based materials. Advanced Engin. Mater. **16** (2014) 729–754

[7] Gbureck, U.; et al.: Preparation of tricalcium phosphate/calcium pyrophosphate structures via rapid prototyping. J. Mater. Sci.: Mater. Med. **19** (2008) 1559–1563

[8] Deisinger, U.; et al.: 3D-printing of HA-scaffolds for the application as bone substitute material. cfi/Ber. DKG **83** (2006) E75–E78

[9] Zocca, A.; et al.: LAS glass-ceramic scaffolds by three-dimensional printing, J. Europ. Ceram. Soc. **33** (2013) 1525–1533

[10] Melcher, R.; et al.: 3D printing of Al2O3/Cu-O interpenetrating phase composite. Mater. Sci. **46** (2011) [5] 1203–1210

]11] Polsakiewicz, D.; Kollenberg, W.: Highly loaded alumina inks for use in a piezoelectric print head. Mater. Sci. Engin. Technol. **42** (2011) 812–819

[12] Exner, H.; et al.: Laser micro sintering of ceramic materials, cfi/Ber. DKG **83** (2006) [13] E45–E52

[13] Hagedorn, Y.C.; et al.: Net shaped high performance oxide ceramic parts by selective laser melting. Physics Procedia **5** (2010) 587–594

[14] Mühler, T.; et al.: Slurry-based powder beds for the selective laser sintering of silicate ceramics. J. Ceram. Sci. Tech. **6** (2015) [02] 113–118

[15] Lenk, R.; et al.: Material development for laser sintering of silicon carbide. cfi/Ber. DKG **83** (2006) [13] E41–E43

[16] Ahlhelm, A.; Richter, H.-J.; Haderk, K.: Selective laser sintering as an additive manufacturing method for manufacturing ceramic components. J. Ceram. Sci. Techn. **4** (2013) [1] 33–40

[17] Regenfuss, P.; et al.: Laser micro sintering of ceramic materials, Part 2. Interceram **57** (2008) [1] 6–9

[18] Schwentenwein, M.; Homa, J.: Additive manufacturing of dense alumina ceramics. Int. J. Appl. Ceram. Technol. **12** (2015) [1] 1–7

[19] Felzmann, R.; et al.: Lithography-based additive manufacturing of cellular ceramic structures. Advanced Engin. Mater. **14** (2012) [12] 1052-1058

[20] Moritz, T.; et al.: Novel functional structures and structural combinations by additive manufacturing. Ceramic Applications **3** (2015) [2] 44–47

[21] Scheithauer, U.; et al.: Additive manufacturing of metal-ceramic-composites by thermoplastic 3D-printing. J. Ceram. Sci. Tech. **6** (2015) [02] 125–132

[22] Cetinel, F.A.; et al.: Influence of dispersant, storage time and temperature on the rheological properties of zirconia-paraffin feedstocks for LPIM. J. Europ. Ceram. Soc. **30** (2010) [6] 1391–1400