Additive Manufacturing of Ceramics: Stereolithography versus Binder Jetting

S. Nachum, J. Vogt, F. Raether

Stereolithography and Binder Jetting are two promising Additive Manufacturing techniques for the fabrication of complex ceramics components. The Fraunhofer Center for High Temperature Material and Design HTL/DE has experience in the fabrication and development of ceramic and metallic components with both technologies. This paper describes and compares the respective process setups as well as the advantages and disadvantages of both techniques, and discusses future challenges and developments expected in Additive Manufacturing methods of ceramic components.

1 Introduction

Additive Manufacturing (AM) is a relatively new technique for manufacturing complex ceramic components directly from a CAD file. A major advantage of this technique is to respond quickly to new designs of next generation parts.

Development started in the 1990ies when AM was used mainly to produce form study prototypes. Later on porous ceramic components were produced by AM, e.g. bioceramics or filters. Due to the rapid improvement of AM technologies within the last decade it is now possible to produce dense ceramic functional prototypes or even small series. With ceramic components the intrinsic disadvantage of all AM technologies, the long production time, is compensated by the elimination of moulding tools, which are especially costly and time consuming if made for ceramic production.

To obtain high-level mechanical properties of AM components, the same basic requirements are to be met as with customary ceramic production:

1) The microstructure, i.e. particle arrangement and pore distribution, in the green state has to be homogenous and porosity has to be sufficiently small.
2) During the heat treatment, temperature and pressure gradients, which lead to stresses and cracks, are to be avoided.
3) Surfaces must be smooth and may not have flaws or notches.

The first requirement gives a strong argument to start from suspensions or pastes in the AM process and to avoid dry powders. The latter are used in the widespread powder bed printers. Van der Vaals forces between dry powder particles lead to particle sticking and inhomogeneous particle arrangement in a powder bed printer when particle diameters are below 20 µm.

Different from dry pressing processes, where the problem of insufficient powder flow is overcome by using granules, granules do not help in powder bed AM processes. Since no significant pressure can be applied in the powder bed, the granules remain essentially spherical. During sintering the granules achieve full density, but the intergranular pores prevent full densification of the compacts. If coarse ceramic powders are used as raw material, their flowability is fine, but the large pores between the coarse particles inhibit complete densification as well.

The second requirement urges to separate the forming process from the heat treatment. Local heating is used in AM techniques like Selective Laser Melting (SLM) or Selective Laser Sintering (SLS).

Although a tremendous effort was taken in SLM/SLS processing of ceramics during the last two decades by many groups, the outcome was rather poor showing incomplete densification and cracks. This can be explained by the short time periods available for the local heating process preventing sufficient material transfer by diffusion – as it is usually required for the densification of crystalline ceramics. In addition, strong temperature gradients occur during local laser heating.

To avoid cracks the laser treatment is limited to very small components or thin surface layers (compare e.g. [1]). Improvements were obtained using extensive preheating of the entire components to decrease temperature gradients. In addition, special sintering additives were introduced to shorten densification time by utilizing melt phases. However, both measures create so many restrictions that we do not see a large potential for AM of ceramics by SLM/SLS techniques.

The third requirement is often difficult to be fulfilled by AM processes using pastes. Pastes are applied either as layers or as filaments.

The most important AM technique based on layers, i.e. ceramic green tapes, is Laminated Object Manufacturing (LOM) and the one based on filaments is filament extrusion 3D printing. The latter comprises techniques like robocasting, direct ink writing and fused deposition modelling.

In spite of an intensive research work carried out worldwide to reduce temporarily

Sarig Nachum, Joachim Vogt, Friedrich Raether
Fraunhofer Institute for Silicate Research ISC, Center for High Temperature Materials and Design HTL
95448 Bayreuth
Germany

Corresponding author: S. Nachum
E-mail: sarig.nachum@isc.fraunhofer.de
www.htl.fraunhofer.de

Keywords: additive manufacturing, stereolithography, binder jetting, powder bed printing, 3D printing

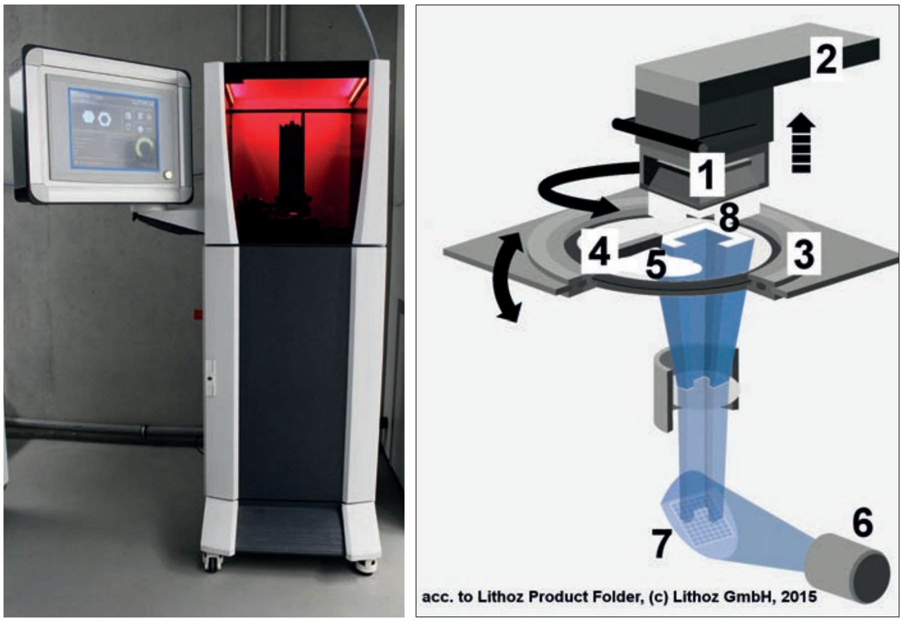

Fig. 1 **Stereolithographic printer (CeraFab 7500) at Fraunhofer HTL (l.) and its building chamber (r.)**

the viscosity of the pastes during the forming process, the minimal diameters of the layers respectively filaments are still in the order of some hundred microns.

Therefore, texturing of the surfaces is unavoidable and leads to deterioration of mechanical and other properties. It becomes apparent that the most interesting AM processes for ceramic manufacturing are based on suspensions.

There are three suspension based AM processes, which have achieved the commercialization state:

- Inkjet Printing (IJP)
- Aerosol Jet Printing (AJP)
- Stereolithography (SL or SLA).

Fig. 2 **Examples of high purity alumina parts manufactured via the stereolithography process**

IJP and AJP directly deposit the ceramic suspension on a substrate in the desired shape. They suffer from poor dimensional control – especially in the direction perpendicular to the substrate – and/or from small solid content of the inks respectively aerosols. The remaining SL process will be described in more detail in the following chapter.

In spite of the difficulty to achieve full densification by sintering we have selected a powder bed printing technique to be compared with SL. This is due to the large success of powder bed techniques using other materials than ceramics.

Taking into account the second requirement, a binder jetting technique – also termed 3D Printing (3DP) – is chosen among the numerous powder bed based AM methods. Details of 3DP are given in chapter 3. The reader is referred to recent reviews on AM techniques for more information about the other AM methods [2–3].

2 Stereolithography

In the SL process, a ceramic green part is manufactured by layer-wise curing of a light-sensitive ceramic slurry through selective irradiation and photopolymerization. After removing the excess slurry, the green part is debinded and sintered to an almost fully dense ceramic part.

At Fraunhofer Center HTL, a CeraFab 7500 printer manufactured by Lithoz GmbH/AT is used for SL printing (Fig. 1a). The setup of the CeraFab is illustrated in Fig. 1b. It consists of a building platform (1) on a vertically movable axis (2), a rotatable slurry vat (3) with a transparent base plate and a doctor knife (4). The slurry vat holds the slurry (5) which is selectively cured upon light irradiation.

In order to form a layer of a green body (8), the building platform is lowered into the slurry until a defined gap of slurry is left, and an LED unit (6) irradiates a micro-mirror-array (7). The latter projects the pattern of the respective slice onto the base plate of the slurry vat, which causes the slurry to selectively cure and thus form a layer on the building platform.

By iterating this process, various filigree and complex parts can be fabricated simultaneously and with only little waste of material. The parts are subsequently

TECNARGILLA 2016

25th International exhibition of technology and supplies for the ceramic and brick industries

The future of ceramics

26th-30th SEPTEMBER 2016

RIMINI - ITALY

CLAYTECH KROMATECH KERMAT

Organized by RiminiFiera business space | In cooperation with ACIMAC Association of Italian Manufacturers of Machinery and Equipment for Ceramics | With the support of Ministero dello Sviluppo Economico, ITA Italian Trade Agency ICE - Agenzia

tecnargilla.it

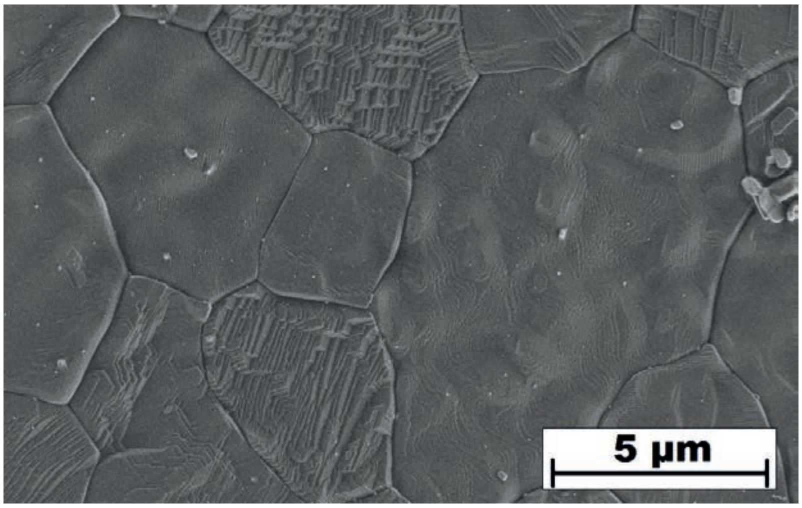

Fig. 3 Cross-section of a stereolithography-printed alumina part, illustrating an almost fully dense microstructure

relieved from the fundamental layer, cleaned and finally debinded and sintered. Fig. 2 shows a selection of parts made of high purity alumina fabricated by this technique.

The building volume in the CeraFab is 76 mm × 43 mm × 150 mm (x, y, z). The printing resolution is ~40 µm in the x- and y-axis, and between 25–100 µm in the vertical z-axis, depending on the parameters used. The layer thickness is usually set to 25 µm in order to maximize the cohesion between the layers and the stability of the part. Minimum and maximum wall thicknesses are ~0,15 mm and 10 mm respectively. Depending on the settings used, the production speed per green layer varies between 30–90 s, or considering green part height between 2–12 mm/h.

A major advantage of this fabrication method besides the high resolution resulting from stereolithographical processing, is based on the use of a suspension which provides a homogenous arrangement of small ceramic particles. The photo-polymeric binder is burnt off before the ceramic powder particles are sintered and does not affect end product properties.

As suspensions are used, no flowability issues have to be addressed, which restrict powder-based fabrication processes to large particle sizes. On the other hand, the suspensions used in the SL process require a careful design of colloidal, rheological and optical properties. The penetration of the UV light into the suspension must ensure sufficient photo polymerization in a layer of at least 25 µm.

The light intensity exponentially decreases by scattering and absorption processes within the suspension. A large difference in refractive index of ceramic particles and solvent or a small size of the ceramic particles drastically increases scattering. The resultant decrease of penetration depth of the light leads to poor adhesion of the layers and delamination during drying or binder burnout.

Up to now only few suspensions are commercially available for SL printing: alumina, zirconia and tricalcium phosphate. Parts manufactured via the SL process exhibit nearly full theoretical density (up to ~99,4 % theoretical density for high purity alumina and 99,1 % for partly stabilized zirconia).

Fig. 3 shows an SEM image of an SL printed and sintered alumina part, demonstrating a dense corundum microstructure. The nearly dense state of the printed parts results in excellent mechanical properties, e.g. 430 MPa for high purity alumina, determined by four-point bending tests [2]. Furthermore, the parts show an exceptionally low surface roughness of ~1 µm in the direction perpendicular to the layer plane, which reduces post-processing cost on functional surfaces of the part.

Good dielectric and tribological properties and a high creep resistance are also a consequence of the high density of the sintered parts. These are the reasons why the SL process is a favourable AM technique for the fabrication of prototypes for both design and high technical performance purposes.

Despite the simple setup and the excellent properties of the fabricated parts, the SL technique requires support structures which have to be attached to largely overhanging areas of the part.

These support structures have to be removed manually after the printing process, which leaves a rough surface and ridges on the joints. However, this issue can be mitigated by optimizing the part orientation during the printing process focusing on the functionality of the surfaces.

Another problem related to the SL technique is the high volume fraction of binder in the green parts (up to 40 vol.-%). To avoid damages during binder burnout, the heating process must be conducted very carefully.

It can take up to 8 days, depending on wall thickness and geometry of the green parts. Speeding up the debinding cycle is crucial for obtaining higher fabrication rates and lower production cost. For that, at Fraunhofer HTL the method of maximum safe debinding rates [4] is used, which is based on thermal analysis and thermooptical measurements of the debinding process. In this way, the authors managed to reduce the debinding time of SL printed green parts, 1 cm^3 cubes and 1 cm diameter cylinders, from about 6,5 days to only 2 days.

3 Binder Jetting

In the Binder Jetting (3DP) process, liquid binder droplets are selectively deposited by a print-head into a powder-bed to join loose powder particles. The interaction of the binder droplets and the powder forms primitives (smallest building elements created by the interaction of a single droplet and loose powder) which are bonded together to form a cross-sectional layer.

At Fraunhofer HTL, a 3D printer of type M-Flex manufactured by company ExOne/US is used (Fig. 4a). Once a layer has been printed, the deposited binder droplets are partially cured (at ~60 °C) for a short time by an infrared heater to give the printed layer sufficient strength. The powder-bed is then lowered and fresh powder is spread on top of the previous layer followed by leveling through a rotating roller. This step is called recoating process. It provides some improvement in particle arrangement by applying small vertical pressure.

The print-head consecutively deposits binder to form the subsequent layer and to bond

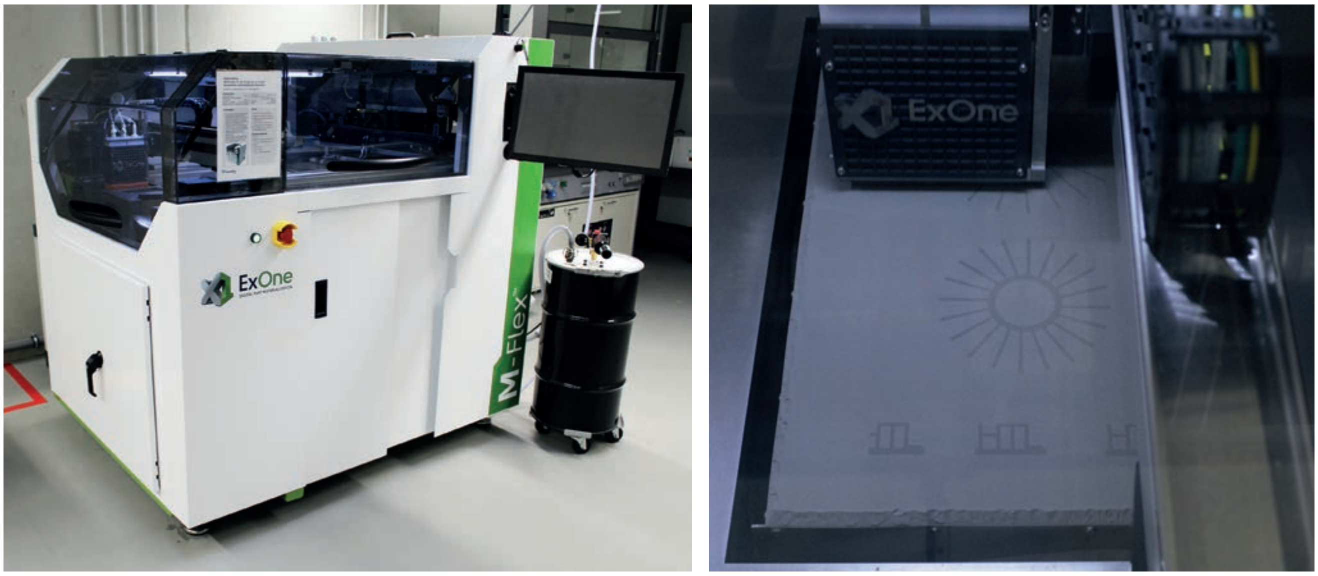

Fig. 4 **Binder Jetting printer (M-Flex) (l.), and a view on its print-head and powder-bed during operation (r.)**

it to the previous layer (Fig. 4b). This layer-by-layer process is repeated until the part is completed.

Once the parts have been printed, the powder-bed (including printed parts and loose powder) is then placed in a furnace at ~200 °C to cure the binder and to give the parts sufficient strength for handling when the loose powder is removed. Debinding and sintering are then performed like in customary ceramic processing.

The Binder Jetting technique, like other powder-bed AM techniques, requires a flowable powder typically of a spherical shape and of size above 20 µm. The powder-bed density following the recoating process of a flowable powder is typically >50 %.

The powder-bed size of the M-Flex is relatively large with dimensions of 400 mm × 250 mm × 250 mm (x, y, z). The lateral resolution is approximately 60 µm and the resolution in the building direction (z) depends on the layer thickness. The layer thickness is commonly set to above 50 µm. It should be larger than the largest particle in the powder and smaller than the primitive size. The minimum stable wall thickness is about 1 mm and depends on the dimensions of the part.

Depending on the printing parameters, the maximum printing speed of the M-Flex is approximately 1000 cm^3/h corresponding to a thickness of 1 cm/h.

The main advantages of this method are that it is adaptable to a wide-range of metallic and ceramic powders; it has a large printing envelope – which can be easily extended to produce even larger parts – and it offers a high throughput due to the large number of nozzles in the print-head. Consequently large and complex parts are easily created.

Fig. 5 illustrates a number of complex parts printed with the M-Flex using martensitic stainless steel powder. In comparison to other AM technologies, like for example stereolithography, the unprocessed powder in the binder jetting method supports the printed part.

The primarily challenge in 3DP is to produce dense components during the heat treatment of the porous green parts. Due to the large particle size and relatively low green density, sintering activity is poor and sintered densities of ceramic parts are usually below 90 % of theoretical density.

If a fully dense part is required, the green part can be infiltrated with a lower melting point material. As an example, Fig. 6 shows a polished and etched cross-section of a part printed with a martensitic stainless steel powder, which was then infiltrated with bronze.

An additional advantage of the melt infiltration route is the absence of shrinkage. So, net shape forming is already achieved in the green state. Note that unlike SLS/SLM printing, 3DP offers the opportunity for melt in-

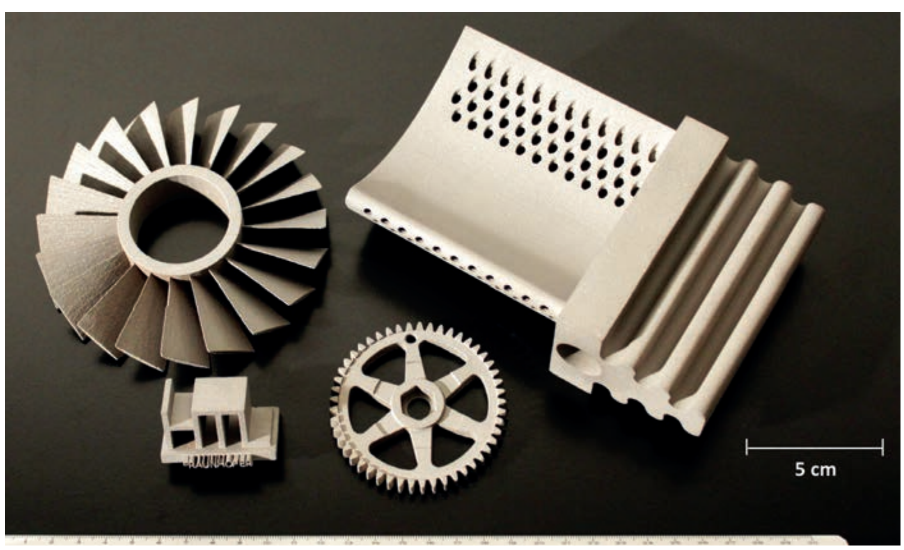

Fig. 5 **Examples of a number of printed components using martensitic stainless steel powder fabricated using the binder jetting technique**

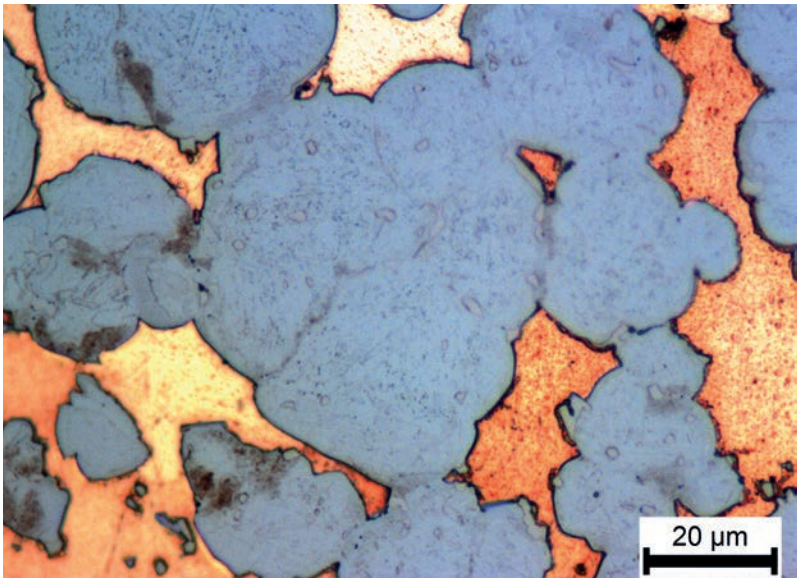

Fig. 6 Cross-section of a part printed by binder jetting using stainless steel powder infiltrated by bronze (stainless steel – blue, bronze – orange)

filtration because forming process and heat treatment are clearly separated.

Compared to SL the melt infiltration is easier in 3DP due to the larger pore channels. Both techniques, SL and 3DP, obtain significant improvement in throughput and flexibility, because the heat treatment can be performed simultaneously with many parts in large and/or customized furnaces independent from the AM process.

4 Future challenges

Stereolithography and binder jetting are two complementary and successful AM techniques. Nevertheless, both require further development in order to be able to compete with the performance, reliability and material composition of parts made by traditional ceramic manufacturing techniques.

In stereolithography, R&D is mainly focused on expanding the spectrum of materials which can be processed. Developments of new materials have been recently published, which show that this technique is not only restricted to the commercially provided materials [5].

In order to extend the processable material spectrum for the SL process, we follow a systematic approach of matching the suspension's optical, colloidal rheological and drying properties. Furthermore, a significant enlargement of the printing envelope would improve the possible uses of SL. This should not be a principal problem considering the large waver diameters used in microlithographic processing of semiconductor components.

With Binder Jetting, the main challenge is to obtain either better sintering activity of the green parts or to identify other strategies for achieving full densification. The former is realized by sintering additives which form melt phases and lead to liquid phase sintering.

However, end product material composition and properties are modified by the additives. An interesting new idea is the combination of powder bed and colloidal processing. Slurries can be deposited layer-wise upon a powder bed by wet chemical techniques like spraying or doctor blade methods. The dried powder beneath the slurry provides rapid drying of the slurry by absorbing the solvent. Thereafter a local binding of the new layer can be performed [3].

Challenges with these routes are the homogenous distribution of the slurry on the powder bed and the subsequent removal of excess slurry. Thus, other strategies have to be investigated in order to achieve full densifications.

The combination of Binder Jetting with melt infiltration is actually the most promising route to obtain dense components from 3DP. Melt infiltration is already well established in 3DP of metal components.

With ceramics, a successful development was presented recently by company Schunk using liquid silicon infiltration (LSI) into 3DP preforms of silicon carbide for manufacturing complex SiSiC parts.

The advantage of the densification by melt infiltration is that it is already well established in ceramic manufacturing. Besides SiSiC, also cermets and cemented carbides have been produced by melt infiltration. Even oxide ceramics like dental crowns are produced by this process using a crystallizing glass for the infiltration of alumina or zirconia preforms [6].

Due to the large porosity of 3DP preforms, the melt fraction is rather high after melt infiltration. Melt infiltration can be combined with crystal forming reactions within the melt or between melt and solid reactants, already present in the preform, to increase the amount of crystalline ceramics.

Also a well-aimed pre-sintering before infiltration can be used to reduce the pore fraction. Careful control of process parameters is required to obtain the desired microstructures without flaws. To ensure proper control of the reaction kinetics and the microstructure the authors use in situ monitoring of the relevant process parameters during melt infiltration and pre-sintering, as well as performing 3D computer simulations of the entire process.

It is worth pointing out that the careful control of the quality of the green parts manufactured by AM techniques is the key to obtain proper end product properties after sintering or melt infiltration. This control requires quantitative measurements of particle and pore arrangements on the micro-scale, identification of flaws on the meso-scale and detection of density gradients on the macroscale.

While the material structure on the microscale controls sintering behaviour and overall material properties, defects on the mesoscale deteriorate strength and reliability and density gradients on the macroscale led to shape deviations during thermal processing. Specific methods are required for these measurements, which have already been described in a previous publication in this journal [7].

References

[1] Baber, J.; Raether, F.: Production of oxide ceramic coatings on glass by laser sintering. Glastechn. Ber. Glass Sci. Technol. **73** (2000) 211–215

[2] Deckers, J.; Vleugels, J.; Kruth, J.-P.: Additive manufacturing of ceramics: A review. J. Ceram. Sci. Tech. **5** (2014) [4] 245–260

[3] Zocca, A.; et al.: Additive manufacturing of ceramics: Issues, potentialities, and opportunities. J. Amer. Ceram. Soc. **98** (2015) [7] 1983–2001

[4] Raether, F.; Klimera, A.: Methods of measurement and strategies for binder removal in ceramics. Special edition of cfi: Thermal process engineering in the ceramics industry; M. Herrmann, R. Clasen (eds.). Baden-Baden 2008, 5–11

[5] Zanchetta, E.; et al.: Stereolithography of SiOC ceramic microcomponents. Adv. Mater. 2015

[6] Raether, F.; Durschang, B.; Thiel, N.: Microstructural design of a CAD/CAM machinable infiltration ceramic with high strength and near net shape performance. Proceedings of Materials Week 2002, Munich, Germany

[7] Raether, F.: Energy efficiency during production of ceramics. cfi/Ber. DKG **90** (2013) [10] E27–E30