Additive Manufacturing of Ceramic-Based Functionally Graded Materials

Additive Manufacturing (AM) is a new group of shaping technologies, and nearly everybody is talking about AM because of the new degrees of freedom concerning the design of components for each area of application.

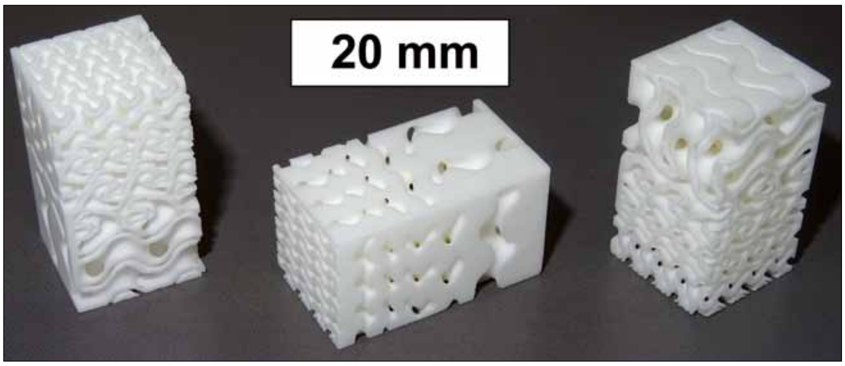

Fig. 1
Alumina components additively manufactured by CerAM VPP

Introduction

Starting in the 1980s with the development of polymer stereolithography by Hull [1], more and more different AM technologies were established which differs by the realisable product properties, such as used material, size, surface roughness or mechanical properties.

But not only polymer components can be manufactured additively. The market for AM of metals shows impressive economic growth and more and more metals can be processed to address manifold applications.

AM of ceramics is possible, too. Most of the common AM technologies were adapted for ceramic materials. Good summaries were given by Chartier [2] and Badev, Travitzky et al. [3] or Zocca et al. [4]. For Technical Ceramics, the AM technologies are only used as shaping technology for the green bodies (organic matrix, highly filled with ceramic particles), which have to be debinded and sintered complementary to conventional ceramic processing. Therefore, not only challenges exist concerning the preparation of the pre-products (powder, suspension, feedstock or filament) or process conditions, but regarding the defect- and deformation-free removing of the organic components (debinding) and sintering of the ceramic particles as well.

Mostly, the names used for the AM technology are not tied to the material. To highlight the complex processing which is needed for AM of ceramics (powder, suspension, feedstock or filament preparation, AM, debinding and sintering), the authors add the term CerAM to the commonly used acronyms like CerAM FFF (Fused Filament Fabrication of ceramic components), and pool these to CerAMfacturing (AM of ceramic components at Fraunhofer IKTS/DE, Tab. 1).

Further technologies are available at Fraunhofer IKTS, which can be used for AM of (functionalised) ceramic components like screen printing, Aerosol Printing or Inkjet Printing, as well.

Currently, AM of defect-free single-material ceramic components becomes state-of-the-art. But the portfolio of processable ceramic materials has to be enlarged all AM technologies. One of the authors goals is to enlarge the variety of processable ceramic materials (SiC, Si_3N_4, ATZ, ZTA, etc.) to allow the AM of ceramic components with complex geometries for manifold applications. Another goal is the development of AM technologies and materials for AM of Functionally Graded Materials (FGM), which will be focused in this paper.

FGM are materials with a variety of properties concerning transitions in the microstructure or in the material [5]. These transitions can be discrete or continuous. There are different types of FGM, such as components with material gradients, graded porosity as well as multi-coloured components.

Previously, they could be manufactured using conventional shaping technologies [6–11] or by a combination of these technologies, for example, by in-mould labelling as a combination of tape casting and injection moulding [12–13]. Tab. 2 summarizes different kinds of FGM, the resulting requirements on the AM technologies and the AM technologies which are used at Fraunhofer IKTS to manufacture FGM additively in one step.

Alternatively, a combination of different AM technologies like CerAM VPP and Aerosol printing or a combination of conventional shaping technologies like low and high pressure injection moulding with AM technologies like CerAM FFF or CerAM T3DP can be used to realise FGM.

Keywords
ceramics, additive manufacturing, functionally graded materials, CerAMfacturing, CerAM VPP, CerAM FFF, CerAM T3DP

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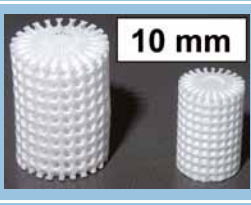
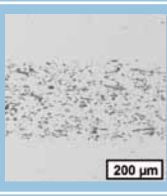
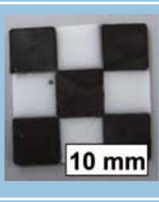
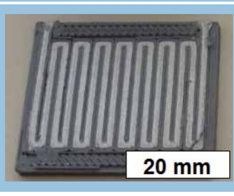
Tab. 1 CerAMfacturing: AM technologies for ceramic-based components at Fraunhofer IKTS Dresden

CerAM BJ	Binder Jetting of Ceramic Components	• powder bed based, indirect AM technology • binder printed into powder bed • focus on porous ceramic components or dense hard metal components
CerAM FFF	Fused Filament Fabrication of Ceramic Components	• basing on highly particle-filed thermoplastic filaments • selective deposition of molten filaments → direct AM method • solidification occurs because of cooling • no restrictions concerning processable materials • focus on big components and multi-material components
CerAM VPP	Polymerization of Ceramic Components	• basing on highly particle-filed photo curable suspensions • selective curing (DLP-module) with light (465 nm) initiate polymerization → indirect AM method • portfolio of processable materials limited because of light absorption • focus on very complex single-material components
CerAM SLS	Selective Laser Sintering of Ceramic Components	• powder bed based, indirect AM technology • selective pre-sintering of powder • focus on porous ceramic components or dense SiSiC (infiltration needed)
CerAM T3DP	Thermoplastic 3D-Printing of Ceramic Components	• basing on highly particle-filed thermoplastic suspensions • selective deposition of molten droplets → direct AM method • solidification occurs because of cooling and missing shear forces • no restrictions concerning processable materials • focus on multi-material components

Tab. 2 Different kinds of FGM, the resulting requirements, and the AM technologies which are used at Fraunhofer IKTS

FGM	Picture/Scheme	Process Requirements	Possible Technologies
Graded macroscopic porosity in one component		• fine resolution • usage of support materials or support-free manufacturing of the component	CerAM FFF CerAM VPP CerAM T3DP
Graded microscopic porosity in one component		• processability for different materials in one device (e.g. suspensions with different contents of pore forming agents)	CerAM FFF CerAM T3DP
Multi-colour component		• processability for different materials in one device (e.g. suspensions with different coloured powders)	CerAM FFF CerAM T3DP
Material gradient in one component (e.g. electrically conductive – non-conductive)		• processability for different materials in one device (e.g. suspensions with different powders)	CerAM FFF CerAM T3DP

Because of the selective deposition of the used material instead of the selective solidification of material placed on the entire layer, direct AM technologies are more suitable for AM of multi-material components than indirect AM technologies. For the latter ones, the areas which have not been solidified are occupied by non-solidified material which have to be removed before a second material can be deposited in these areas. Using direct AM technologies, a second material and further ones can be deposited directly beside the already deposited and solidified first material.

Nevertheless, indirect AM technologies can be used to manufacture FGM additively, especially if a graded macroscopic porosity has to be realised in one component.

CerAM VPP

Different kinds of vat photopolymerisation devices for ceramic components are available. The authors use a device of LITHOZ/AT, which established the term Lithography-based Ceramic Manufacturing (LCM) [14] It is a stereolithography based approach that employs a Digital Light Process (DLP) as light source containing a Digital Micro-Mirror Device (DMD chip), used to polymerize a resin which can be mixed with powders of different nature. LCM is based on the curing of a suspension containing ceramic material dispersed in photoactive polymers [15, 16].

The most commonly employed resins are based on mixtures of acrylate and/or urethane monomers. The CeraFab 7500 cures layers as follows: firstly, the tub bottom vat rotates to coat slurry by a small doctor blade. Then, the building platform is lowered down to a specific remaining gap between the platform and the tub's bottom which defines the thickness of the next layer (5–100 µm). The polymerization is induced by the reaction of a photoinitiator molecule (PI) with the light photons generated by the DMD chip. Therefore, the light device's engine (providing blue light, wavelength of 465 µm) irradiates the thin suspension layer by projecting a given contour onto the tub's bottom (pixel size: 40 µm × 40 µm). The photoactive polymers polymerize and the ceramic suspension cures upside down at the building platform. Finally, by raising the platform again, the consolidated thin ceramic layer is detached from the tub bottom.

Important parameters to the component quality during the LCM process are the light scattering effect produced when light (photons) crosses through different surfaces [17], the cleaning of the printed components [18] as well as the thermal debinding of the components, which extremely depends on the used resin formulation as well as printing parameters and the debinding strategy [19].

The fine resolution of the process results in a high surface quality and fine realisable geometries, which are needed to address different applications in the micro-scale [20, 21]. Fig. 1 shows sintered alumina components additively manufactured by CerAM LCM; 3 different fluidic systems interpenetrate each other in different scales. This geometry could be used as micro-reactor, heat exchanger or a combination of both.

CerAM FFF

Fused Filament Fabrication (FFF) is a direct AM method, known from thermoplastics like PLA, ABS, PC or slightly filled modifications of them. By means of this method, an endless filament is used as a semi-finished product, which is melted and deposited under a heated nozzle. The main advantages of this technique is the availability of comparatively cheap standard devices, a short production time and a large building space.

By rising the solid content to a level above 40 vol.-%, the filament route becomes interesting for powder metallurgical processing such as sintering of metals, ceramics or cermets. In this case, mostly ceramic particles are dispersed in a molten mixture of different thermoplastic binder components. After homogenization, a particle-filled filament is generated and used to manufacture additively a green component, which has to be debinded and sintered (CerAM FFF).

Compared to light curing AM methods like CerAM LCM, thermoplastic approaches can handle almost all types of sinterable powder or even the combination of them into one part. This can be a combination of ceramics or metal and ceramic for instance. The functional gradation will rise the variety of applications in a magnitude. Another interesting subject is the possibility to reinforce the filaments with carbon or ceramic fibres for AM of Ceramic Matrix Composites (CMC). This can be achieved by using ultra-short to endless fibres within the filament.

Fig. 2
Variety of filaments (d = 1,75 mm) made by Fraunhofer IKTS

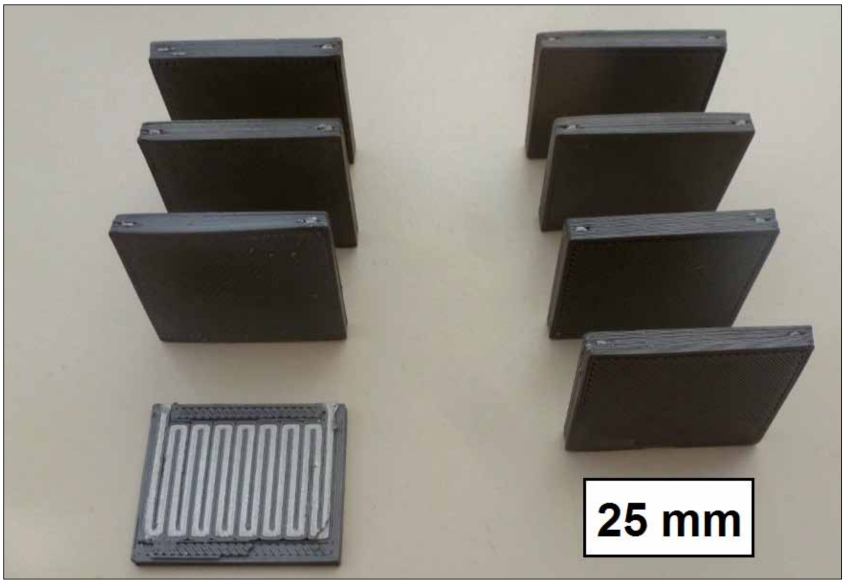


Fig. 3
Stainless steel – ceramic components additively manufactured by CerAM FFF

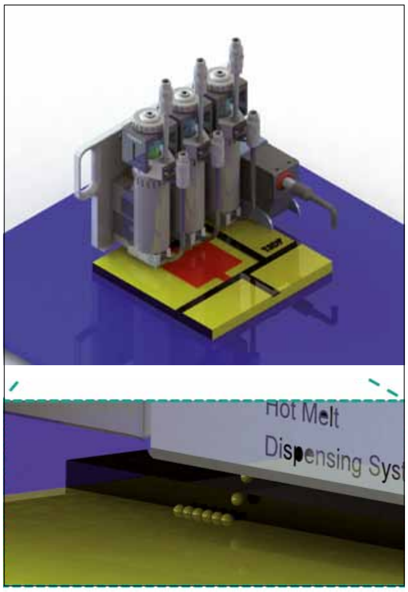


Fig. 4
Scheme of laboratory device with 3 different micro-dispensing systems and one profile scanner

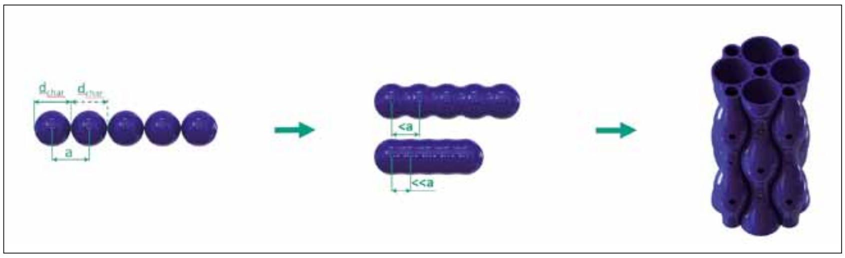


Fig. 5
Scheme of single droplets fused to 2D- and 3D-components

Fig. 6
CerAM T3DP test components, manufactured without support material: stainless steel, white zirconia, black zirconia (f. l. t. r.)

In this way, it is possible to print SiC/SiC or C/SiC components [22].
The filaments itself contain a solid loading ranging from 45–60 vol.-% to receive fully dense parts after the thermal treatment (debinding and sintering). The matrix contains thermoplastic polymers which provide a certain flexibility for spooling, a stiffness to be pushed through a heated nozzle and a high viscosity drop during melting at the same time.
This can be reached by using a binder blend having different polymer properties such as high and low melting points. The production of the filaments is done by using a twin screw extruder for high energy compounding and drawing at the same time. The resulting filaments have a desired diameter of 1,75 mm or 2,85 mm to be used in standard devices. A small variety of manufactured filaments is shown in Fig. 2.
Within the IKTS cerAMfacturing project, funded by the European Union (EU-Project CORDIS 678503: Fraunhofer IKTS, Montanuniversität Leoben, Hage Sondermaschinenbau, Inmatec, Ceramixx, Eye-D, Admatec, Ceramtec, Eurogrant), the task was to combine a ceramic with a stainless steel to realise a high temperature ceramic heating element. This approach combines both an electrical conductive (17–4 PH) and isolating (ZrO_2) phase as well as a weldable ductile join partner to integrate suchlike parts into metallic devices.
This heating structure was realised by CerAM FFF of zirconia, and stainless steel filaments. This combination requires the knowledge about the shrinking behaviour, and certain modifications of the metal powder to get suitable parts after sintering [23]. Fig. 3 shows the co-sintered multi-material components with an internal electrically conductive meander.

CerAM T3DP

Thermoplastic 3D-Printing is a direct AM process basing on the selective deposition of single particle-filled droplets of molten thermoplastic suspensions. It is used to produce green components, which still have to be debinded and sintered in order to preserve the final properties of the material. A special micro-dispensing unit, developed by Vermes/DE, which is based on the drop-on-demand principle, is used to manufactures the components drop by drop.
Because of the direct AM process, it is possible to deposit droplets of different materials side by side and manufacture multi-material green-components. The micro dispensing units work with a nozzle orifice diameter of 100 µm or 160 µm. The average deposition frequency for practical purposes is between 80–100 Hz, but a frequency up to 3000 Hz is possible with the used dispensing units.
Fig. 4 shows 3 micro-dispensing systems, and an implemented profile scanner, which is used to investigate the droplet characteristics.
Basic elements of the green components are single droplets with a defined characteristic diameter and distance between droplet centres. If the distance between the droplet centres is reduced, the droplets will overlap and form a line-like structure (Fig. 5). This way single- and multi-material components can be manufactured.
Powder-side limitation are only given by the used nozzle orifice diameter. Typically, pow-

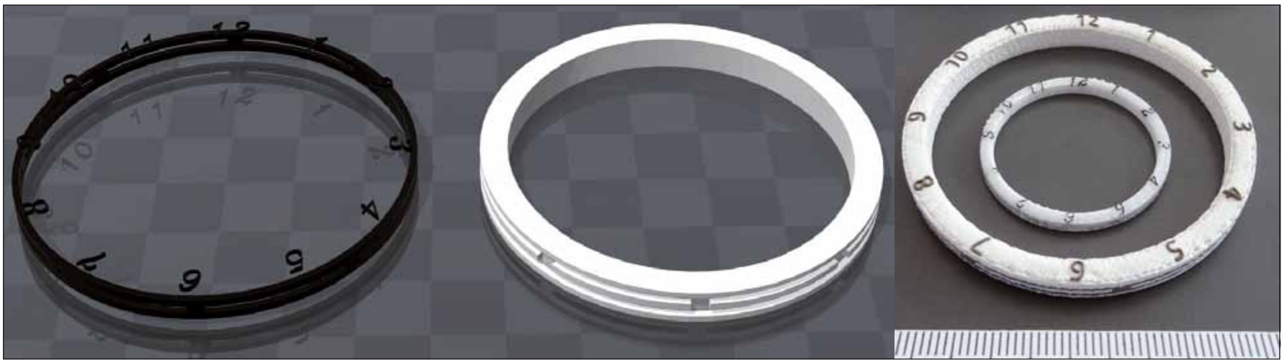


Fig. 7
Black-and-white component additively manufactured by CerAM T3DP; CAD-drawings (l.); green component (outside), and downscaled sintered component (inside) (r.)

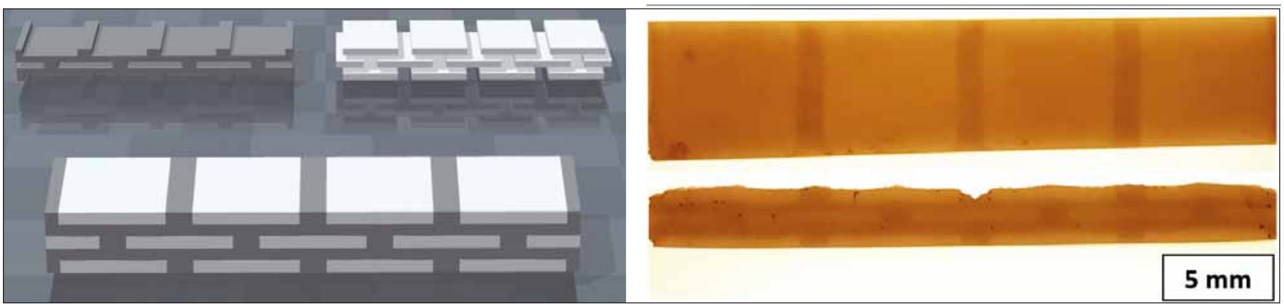


Fig. 8
Ceramic component with dense and porous volumes inside: CAD-drawings (l.); sintered zirconia component in front of a light source (r.)

ders with an average particle diameter of less than 5 µm are used. The solidification of suspensions is nearly unaffected by the physical properties of the used powders. So even metal, hard metal or glass suspensions can be fabricated and processed (Fig. 6).

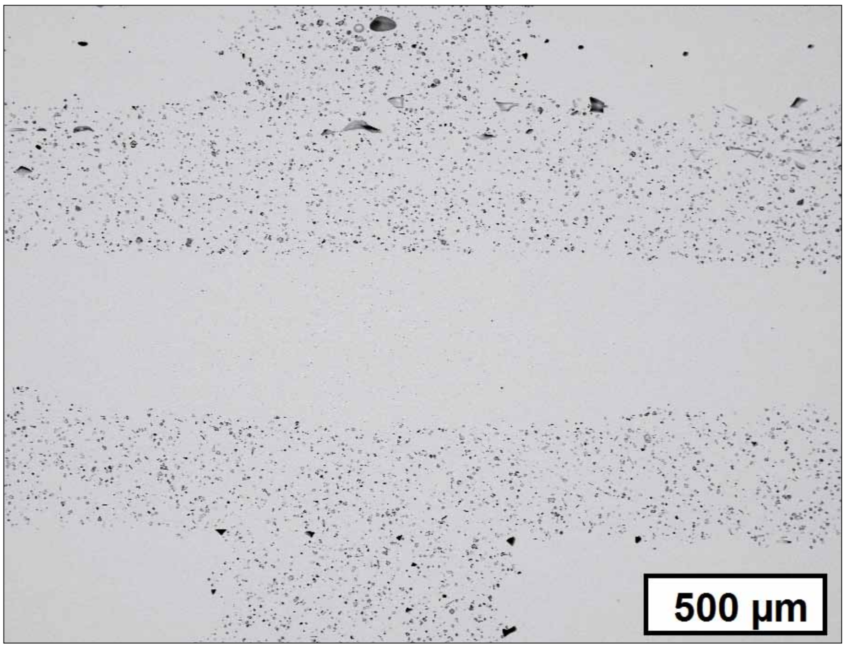


Fig. 9
Ceramic component with dense and porous volumes inside; FESEM-image of interface

Because of the selective deposition of single droplets and the material independent solidification, CerAM T3DP is highly suitable for AM of FGM. This could be demonstrated within the cerAMfacturing project for 3 different kinds of FGM, for multi-colour components, for multi-material components, and for components with graded microscopic porosity.

Multi-colour components were made of black and white zirconia. As black zirconia, powders TZ-Black of Tosoh/JP, and ZirPro ColorYZe Black of Saint Gobain/FR, were used and for the preparation of the white phase TZ-3Y-E of Tosoh, as well as ZirPro ColorYZe Arctic White of Saint Gobain.

Saint Gobain, as powder manufacturer, uses pigments (4,2 mass-%) for colouring the zirconia. Additionally, the high percentage of alumina (20,43 mass-%) contributes to the white colour. This way, both ColorYZe powders have the same sintering behaviour.

The Tosoh powders have a different composition, and therefore accordingly require a different sintering temperature for complete densification. In contrast to the TZ-3Y-E, the

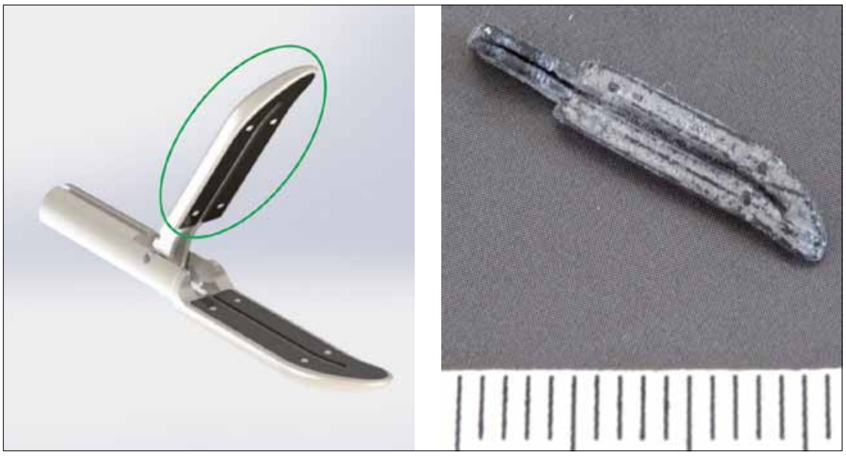


Fig. 10
Ceramic – stainless steel component: CAD-drawings (l.); under reducing atmosphere co-sintered zirconia – 316L component (r.)

TZ-Black consists of ≤5 mass-% pigments. The recommended sintering temperature of the TZ-Black is 1400 °C, the sintering temperature of the TZ-3Y-E is 1350 °C. By adding alumina, the sintering temperature can be approximated. To produce a multi-material component, each material requires its own CAD file (Fig. 7, l.). Before slicing, the materials are assigned to the 3D-models.

Starting with a new suspension appropriate dispensing parameters have to be investigated. The correlation between the dispensing parameters and the properties of the generated droplets and structures allowed the deduction of appropriate parameters for each suspension. Fig. 7 (r.) shows 2 printed clock bezels. In the centre, a sintered component with a scaling of 75 %, and on the outside a green body with a scaling of 100 %. The sintering-related shrinkage is about 18 % in one dimension.

The combination of dense and porous volumes in one component was realised for zirconia. For the dense volumes, pure zirconia TZ-3Y-E (Tosoh) was used. The porous areas were realised by a zirconia suspension with additional pore-forming agents such as polysaccharide. In this case, the content of zirconia particles had to be reduced from 40 vol.-% to 36 vol.-% within the suspension. With CerAM – T3DP it is possible to realise components like this brick-wall like structure (Fig. 8, l.).

The dense volumes are permeated fine porous volumes. FESEM images of cross-sections of these components show clearly distinguishable interface between the two former suspensions (Fig. 9). Thus, regardless of the drop-bound deposition of the material, the arrangement of the different microstructure can be realised very precisely [24].

Fig. 8 shows the sintered component in front of a light source. The dense volumes appear brighter than the porous ones because of the lower light scattering at the pore boundaries.

The last CerAM – T3DP application is the combination of electrically conductive with insulating materials. In this example, zirconia was combined with a 316L stainless steel (V4A). Essential for the combination of these 2 materials is the shrinkage adaptation of the metal powder to the zirconia powder. This is achieved by high energy milling. Fig. 10 shows an individualized metal-ceramic gripper for minimal invasive surgery. Another challenge in the processing of multi-material components is the thermal treatment. Both materials are debindered and sintered under the same conditions. Due to the presence of the 316L stainless steel, thermal processing takes place under a reducing atmosphere. This atmosphere removes the lattice oxygen from the zirconium oxide and turns it black. The mechanical properties remain unchanged. For this reason, the discolouration is uncritical.

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Conclusion

Additive Manufacturing technologies increase the degrees of freedom concerning the design of ceramic components significantly and will open the door to manifold new applications for ceramic components. But the development of technologies and materials, which allow AM of FGM, will increase the degrees of freedom further concerning the material properties. Ceramic-based components can be realised, which combine complex design with variable material properties inside which will allow the functionalization and miniaturisation of the components.

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