# CerAMfacturing of $Si_3N_4$ Components

**Silicon nitride ($Si_3N_4$) is a high performance ceramic material. The entirety of its outstanding properties such as strength, toughness and hardness, even at very high temperatures makes it superior compared to most of technical ceramics due to its covalent bonding type [1].**

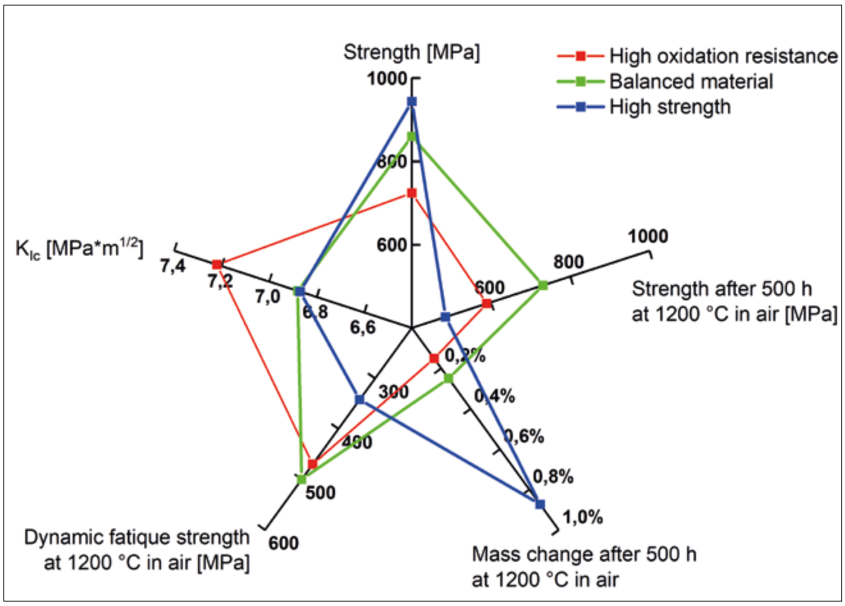

*Fig. 1*
*Relevant properties of three different $Si_3N_4$ compositions for gas turbine applications*

## Introduction

To sufficiently densify $Si_3N_4$ after sintering, specific oxides can be added to determine the resulting mechanical, chemical and tribological properties of the material. Due to a specific adjustment of the composition and the heat treatment certain properties can be emphasized and allow the use in different fields of application also under demanding conditions. Fig. 1 shows an example for the possible adjustment of properties of three $Si_3N_4$-materials with different amounts of yttria and alumina.

In the last decades of the 20th century, $Si_3N_4$ was extensively developed for high-temperature applications. In 2016 a gas turbine rotor was developed within an internal Fraunhofer project "Turbokeramik" by six Fraunhofer Institute, manufactured at the Fraunhofer Institute for Ceramic Technologies and Systems (IKTS) by various shaping methods and tested at a speed of 96 000 min$^{-1}$ and about 900 °C (Fig. 2).

***Keywords***
*ceramics, additive manufacturing,*
*silicon nitride, CerAMfacturing,*
*CerAM MMJ, CerAM VPP, CerAM FFF*

Now in the 21st century, other applications such as in the medical sector are coming into focus. In addition to its outstanding mechanical properties, $Si_3N_4$ also has very particular surface characteristics [2]. When immersed in an aqueous environments the slow elution of silicon and nitrogen from its surface promotes the healing of soft and bony tissue, but also inhibits bacterial proliferation and kills viruses [3]. These benefits enable $Si_3N_4$ to be used in a wide array of different disciplines inside and outside of the human body including orthopedics, dentistry, virology, agronomy and environmental remediation [2].

Furthermore $Si_3N_4$ offers even more features that can be used to address more special applications. By adding molybdenum disilicide ($MoSi_2$) or titanium nitride (TiN), composites can be realized that combine the already mentioned high oxidation resistance with good electrical conductivity. A composite material of $Si_3N_4$, $MoSi_2$ and silicon carbide (SiC) has been established that has electrical conductivities of up to $10^4$ Ohm$^{-1}$ · cm$^{-1}$. These $Si_3N_4$–$MoSi_2$–SiC composites are ideal for heater applications [4].

The electrical conductivity is based on the formation of a three-dimensional network of conductive grains with a percolation threshold, above which the composite becomes electrically conductive. Below the threshold the composite remains electrically insulating. On the one hand, this behavior offers the possibility to selectively adjust the electrical behavior of the components and, on the other hand, to combine the electrically conductive and insulating sections in one component to protect against corrosion for instance. The latter was realized e.g. in ceramic glow plugs. The ceramic composite allowed higher heating rates and temperatures than conventional glow plugs made of metal. The defect-free processing of these two-phase components could be demonstrated not only for pressed but also for injection-molded components [4] (Fig. 3).

*Uwe Scheithauer, Johannes Abel,*
*Eric Schwarzer, Steven Weingarten,*
*Willy Kunz, Tassilo Moritz,*
*Hagen Klemm*

*Fraunhofer Institute for Ceramic*
*Technologies and Systems – IKTS*
*01277 Dresden, Germany*

*E-mail:*
*Uwe.Scheithauer@ikts.fraunhofer.de*

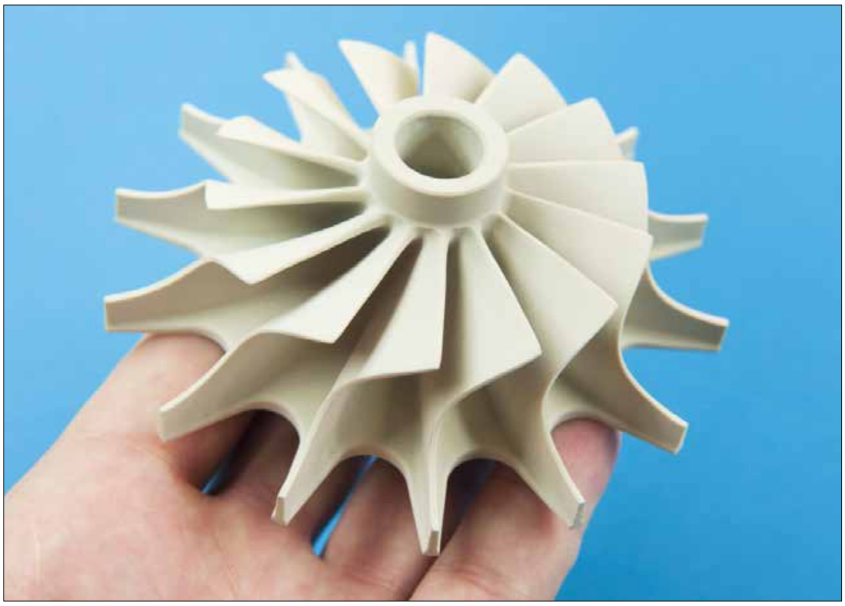

*Fig. 2*
*$Si_3N_4$ rotor for gas turbines manufactured by ceramic high-pressure injection molding (105 mm diameter)*

*Fig. 3*
*Combined electrically insulating and conductive $Si_3N_4$–$MoSi_2$–SiC component (approx. 40 mm in height) manufactured by low-pressure injection molding [4]*

A major market entry barrier is the high manufacturing effort and the resulting high costs for geometrically complex components. The green bodies manufactured during the conventional shaping process have only simple geometries and must then be extensively machined in the green or sintered state. Alternatively, geometrically complex shaping tools are required. But the production of these is very time-consuming and costly. This pays off for high production volumes only.

Nevertheless, the worldwide trend is increasingly towards functionalization, miniaturization and individualization of components, which requires an increase in geometric complexity.

These needs are met by Additive Manufacturing (AM) technologies. Due to the layered structure of the components, highly complex geometries up to undercuts can be realized and the use of forming tools can be avoided. In the meantime, work has been going on for almost 40 years on this class of shaping technologies, which combines a variety of different processes with very specific characteristics and possibilities.

However, while in the plastics sector the technologies are already state of the art and components can be produced virtually at the push of a button, and in the case of metals a large number of components are already manufactured additively, development in the field of ceramics is lagging significantly behind. The main reasons for this are the complex process chain for ceramic materials and the fact that AM technologies only cover the shaping, while subsequent debinding and sintering of the components are still necessary. Consequently, AM of defect-free and dense components requires not only the appropriate infrastructure but also extensive know-how of processes and materials. Nevertheless, almost all known AM technologies have been tested on ceramic materials and successfully adapted for some of them [5–7].

At the Fraunhofer IKTS, the authors are working with various AM technologies to manufacture ceramic components additively. Since the names of the AM technologies for ceramic components do not differ from those for polymer and metallic components, the authors have coined the term CerAMfacturing and added the short form CerAM to terms such as VPP or FFF [8].

One of the main goals is to increase the material portfolio for the various CerAM technologies. In doing so, the authors benefit from decades of experience in material development and processing as well as the extensive infrastructure for all process steps at the IKTS. In the field of $Si_3N_4$, the authors are currently working on three different AM technologies, which are presented in more detail below.

### CerAM VPP (Vat Photo Polymerization)

Vat Photo Polymerization is a well-known technology for AM of polymers and a large number of suppliers for AM devices and polymeric materials (mainly acrylates) are existing. The CerAM VPP technology (which is also known as Lithography-based Ceramic Manufacturing – LCM [9]) is based on the selective initiation of photo polymerisation in a highly particle-filled suspension (typical particle sizes: between 0,05–2 µm; typical ceramic content: 35–50 vol.-%) by irradiation with blue light (wavelength: 450–465 nm). Different process strategies are known, which can be differentiated with regard to the build-up principle (bottom-up or top-down) [10], the suspension application (rotating vat, moved tape or doctor blade) and the exposure method (laser or Digital Micromirror Device – DMD). Suspensions based on alumina, zirconia, and other oxide and nonoxide ceramics (e.g. for implants and bone-replacement – tricalcium phosphate, for electronics – silicon-nitride) are commercially available and are used for different applications such as micro components [11], electronics [12], and in medicine [13, 14]. Compared to other AM

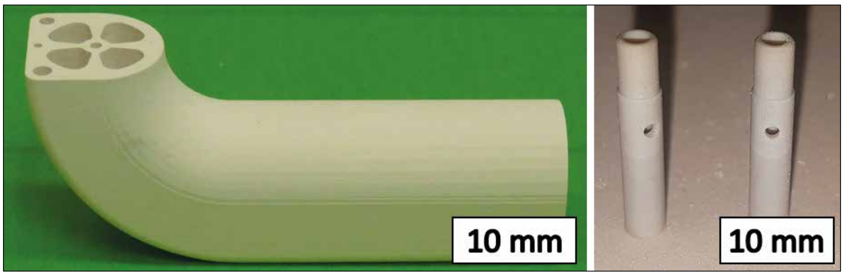

*Fig. 4*
*$Si_3N_4$-components manufactured with CerAM VPP: left: white body of test structure; right: sintered test structure (II)*

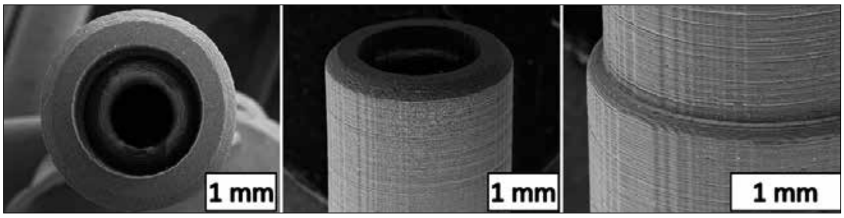

*Fig. 5*
*SEM-images of the surface of a sintered $Si_3N_4$-component (test structure (II)) manufactured with CerAM VPP*

technologies, CerAM VPP is currently the benchmark in terms of minimum feature size, manufacturing tolerances and surface quality.

Fraunhofer IKTS uses three different devices from Lithoz/AT, which works with a bottom-up CerAM VPP approach. A suspension layer is applied by the rotation of a vat in combination with a static wiper blade. The bottom of the vat is transparent so the light source can illuminate the suspension from below. The projected image is generated via a DMD (digital micromirror device, a microoptoelectromechanical system, e.g. used in beamers), e.g. with a resolution of 1920 pixel x 1080 pixel.

Using a dedicated optical system, the resolution in the X–Y plane can be adjusted to 40 µm and a minimum wall thickness as low as 80 µm can be achieved in the sintered components. The manufacturing tolerances are in the range of <40 µm and the sintered surfaces have a $R_a$-value between 0,4–1 µm (alumina).

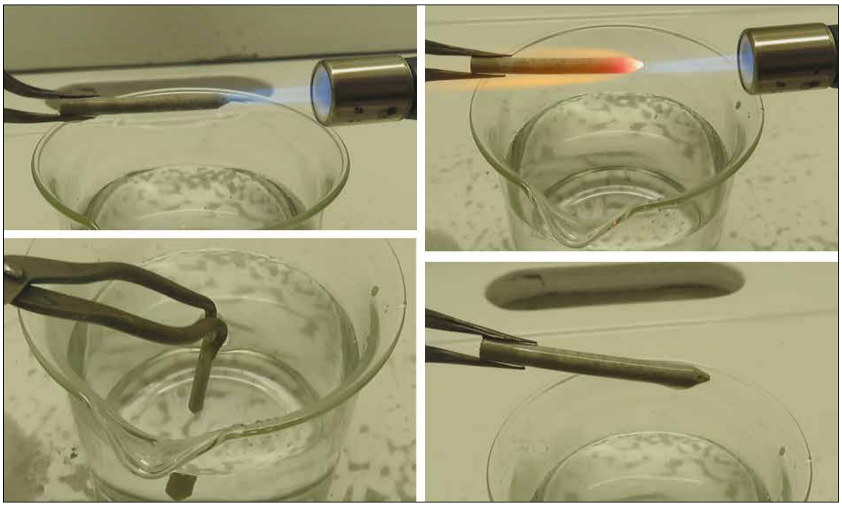

*Fig. 6*
*Thermal shock testing for the CerAM VPP test structure (III); top: heating process; bottom: immersion in water (left) and result (right)*

CerAMfacturing of multi-material components based on the CerAM VPP technology is very challenging and currently still in the development stage. Lithoz is working on a laboratory device with two separated vats, which will be available soon for multi material components, and the first multi-material test structures look very promising. At IKTS, the authors are focusing their work in the field of CerAM VPP on the development of single-material components.

Two main fields of application are addressed. Firstly, applications in the high temperature range and secondly, medical applications. Based on two different mixtures of $Si_3N_4$ and sinter-additives, the suspension development and the determination of suspension-specific process parameters for AM as well as thermal processing were carried out.

With the powder mixture for high-temperature applications, a solids content of 38 % by volume could be achieved. In order to solidify layers with a thickness of 25 µm and to bond them to the layer before, an energy input of 700–800 $mJ/cm^3$ was required.

Different test structures were designed, shaped and thermally processed. Fig. 4 shows test structure (I) as white body (I.) and a simplified test structure (II) for high-temperature applications in gas turbines specified by Vectoflow/DE in the sintered state.

The test structures showed no visible defects and were characterized by SEM regarding to the generated surfaces (Fig. 5). Although the individual layers of the components became visible, which are a result of the shaping process. Overall, the test structures showed very good surface properties and geometric accuracy.

In order to investigate the behavior of the components during thermal shock, a simple test was carried out with another test structure (III). Using a Bunsen burner, the tip of the test structure with a length of 50 mm was heated up to approx. 1000 °C and then immediately immersed in water at room temperature (Fig. 6). Even after this test, no cracks or spallation occurred (Fig. 6, bottom right).

## CerAM FFF (Fused Filament Fabrication)

FFF is a direct AM method (selective deposition of the material) [6] established in thermoplastics AM using e.g. polylactide

(PLA), Acrylonitrile Bbutadiene Styrene (ABS) or polycarbonate (PC) filaments that are molten in a heatable nozzle and are formed in a soft state of the material. This method is adapted for CerAMfacturing by using the same thermoplastic filaments but filling them with ceramic particles prior for AM deposition. Typical particle sizes in use are between 0,1–5 µm, at a solid loading of 45–60 vol.-%. Materials for which the CerAM FFF technique has been demonstrated are alumina [15], zirconia [16, 17], fiber reinforced SiC, liquid phase sintered silicon carbide (LPSSiC), different steels [16, 17], and even hard metals [18].

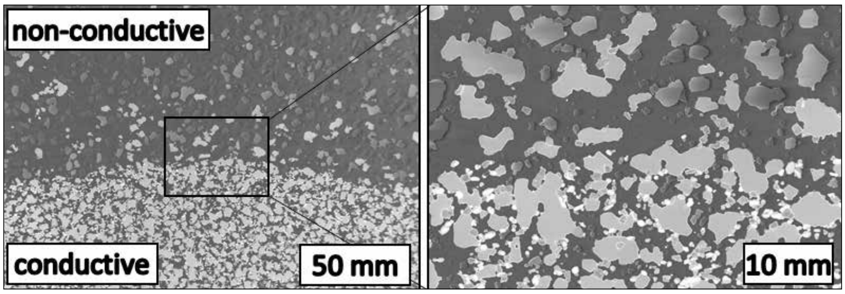

*Fig. 7*
*SEM-images of cross-section at the interface between the electrically non-conductive (top) and conductive phase (bottom) in a sintered CerAM FFF component); bright phases indicate percolation of the conductive phases*

Comparatively cheap devices are commercially available for FFF processing providing large building platforms (size up to 1 m³) at fast processing velocities (typically up to 60 mm/s). We use a FFF device, which was developed by Hage3D/AT within the H2020 project CerAMfacturing (GA no. 678503) and adapted this to CerAM FFF with a special belt drive for secure conveying of the particle-filled filaments and with two printheads to provide simultaneous deposition of two materials [17].

The authors current developments, which are described here, are dealing with different mixtures of the material system $Si_3N_4$–$MoSi_2$–SiC, in which, depending on the proportion of the conductive phases ($MoSi_2$/SiC), an electrically conductive material or an electrically insulating material is present. The aim is to combine both, conductive and non-conductive materials, via multi-material AM. Manufacturing of complex resistance heating elements, whose electrically conductive core is surrounded by a non-conductive shell for corrosion protection or electrical insulated fixation, will become possible. The CerAM

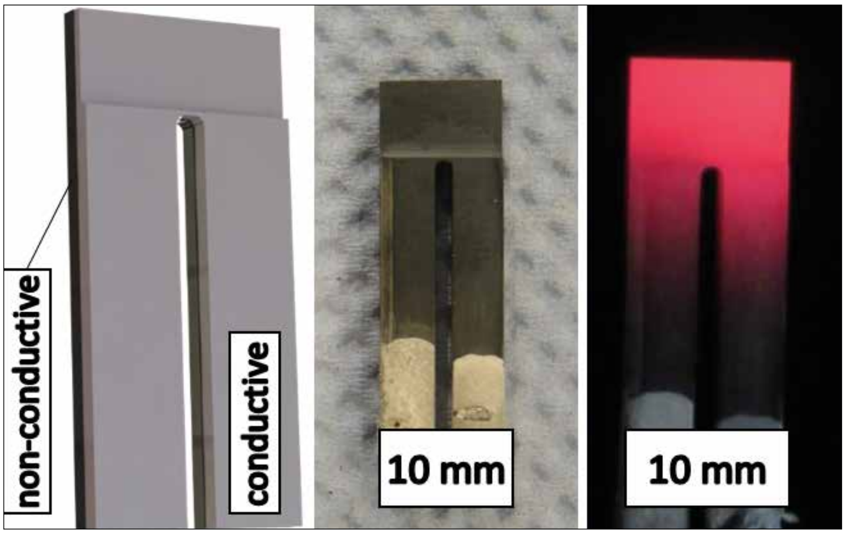

*Fig. 8*
*Heater as multi-material CerAM FFF-test structure; left: scheme; in the middle: sintered component; right: heating experiment with 40 W electrical power*

FFF process offers good possibilities for the manufacturing of such components due to its economic efficiency, fast processing and very good availability. Dense microstructures can be attained having the same properties like conventionally manufactured samples. The microstructure of the a multi component heater in the area of the material transition is shown in Fig. 7. To demonstrate the functionality of the material system and the CerAM FFF technology a two-component heater was shaped and processed. Fig. 8 shows a schemata of the heater structure, an image of the sintered component with added electrodes as well as the glowing heater, which was electrically heated. By applying an electrical power of 40 W, 700 °C were reached in a few seconds even with this non-optimized test geometry.

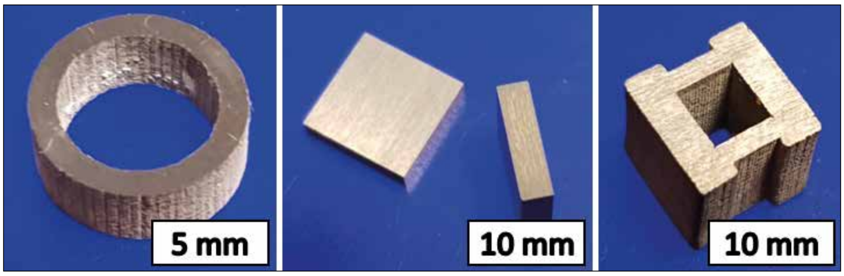

*Fig. 9*
*Single-material $Si_3N_4$-components manufactured with CerAM MMJ*

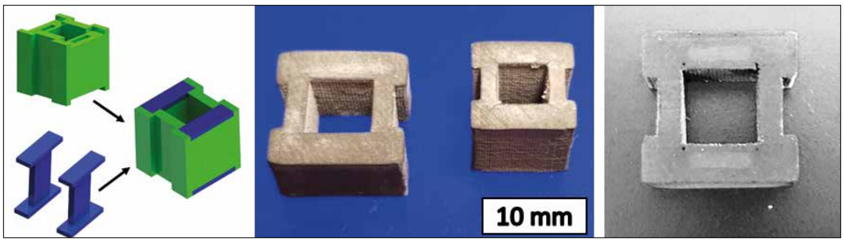

*Fig. 10*
*Multi-material $Si_3N_4$–$MoSi_2$–SiC components manufactured with CerAM MMJ; left: scheme; in the middle: sintered test structures; right: false color image with better phase contrast*

**CerAM MMJ (Multi-Material Jetting)**

CerAM MMJ, also known as CerAM T3DP (Thermoplastic 3D-Printing) is based on the selective deposition of molten particle-filled thermoplastic feedstock as single droplets [19]. This CerAM technology was developed at IKTS especially for the AM of Multi-Material (MM) and Multi-Functional (MF) components. To generate the droplets, commercially available micro-dispensing units (VERMES/DE) are used, which work on the drop-on-demand principle. Particle-filled polymers (at high loading this corresponds to ceramic feedstocks) can be processed with this AM technology. For ceramics, metals, glass and other materials the thermoplastic binder systems enable the processing of almost all materials (typical particle sizes: between 0,1 and 2 µm), even hard metals [20]. For this purpose, the shaped green bodies must then be debinded and sintered. While the resolution of CerAM MMJ (typical droplet diameter: 200–500 µm) is significantly lower than that of CerAM VPP the achievable productivity is much higher and because of the selective deposition of the materials it is much more suitable for the parallel processing of two and more materials.

Since CerAM MMJ is a proprietary development of IKTS, no comparable equipment is commercially available. IKTS has a laboratory system that operates with up to four dosing systems in parallel (max. building size: 200 mm x 200 mm x 180 mm). In addition, another CerAM MMJ device is currently under construction and verification and will exhibit significantly improved reproducibility for droplet deposition. CerAMfacturing and defect-free co-sintering of MM and MF components based on CerAM MMJ have been successfully demonstrated for black-and-white zirconia [21], dense and porous zirconia [22], dense and porous alumina [23], and functionalized glasses (luminescent, electrically conductive) [24].

For the processing of the different compositions, different suspensions were developed and process parameters (drop dosing and thermal processing) were determined. The solids content in the suspensions was 45 vol.-%. Debinding was carried out in a powder bed and under nitrogen atmosphere up to 450 °C. Fig. 9 shows different single-material CerAM MMJ test structures. In Fig. 10 sintered multi-material CerAM MMJ components are presented, which combine the electrical conductive and the insulating $Si_3N_4$-$MoSi_2$-SiC phases.

## Summary

$Si_3N_4$ is used in a wide range of applications, such as a material for ball bearings, mechanical seals in chemical plant construction, blades for gas turbines, spark plugs or probes for measuring pressure at extremely high temperatures. By combining the geometric degrees of freedom of AM with the outstanding properties of $Si_3N_4$, many more application areas can be addressed in the future. For the three different CerAM technologies CerAM VPP, CerAM FFF and CerAM MMJ, the authors were able to develop the required feedstocks and suspensions with adapted process parameters, so that the additive manufacturing and sintering of $Si_3N_4$ is possible. The Fraunhofer IKTS thus not only has many years of experience in thermal processing and the associated infrastructure in a wide range, but also the most modern shaping technologies. Also together with the extensive range of conventional shaping technologies available at Fraunhofer IKTS, this is the basis for the authors to turn customer wishes and ideas into reality.

## Acknowledgements

Some of the work presented in this publication was developed in the Agent-3D:MultiBeAM project, which was financially supported by the BMBF (Project Management PT Jülich, 03ZZ0209B). Furthermore, the authors would like to thank the Vectoflow team around Katharina Greitz for providing its expertise in the field of aerodynamic measurement in engines and the requirements for the components under extreme conditions.

## Reference

[1] Klemm, H.: Silicon Nitride for High-Temperature Applications. J. Amer. Ceram. Soc. **93** (2010) [6] 1501–1522

[2] Pezzotti, G.: Silicon Nitride: A Bioceramic with a Gift. ACS Applied Materials & Interfaces **11** (2019) 30, 26619–26636, DOI: 10.1021/acsami.9b07997

[3] Pezzotti, G.; et al.: In vitro antibacterial activity of oxide and nonoxide bioceramics for arthroplastic devices: I. In situ time-lapse Raman spectroscopy. Analyst, 2018, 143, 3708, DOI: 10.1039/c8an00233a

[4] Zschippang, E.; et al.: Charakterisierung und Verarbeitung von $Si_3N_4$-SiC-$MoSi_2$-Kompositen für Heizleiteranwendungen, Keram. Zeitschrift (2013) [5]

[5] Travitzky, N.; et al.: Additive Manufacturing of ceramic-based materials. Adv. Engin. Mater. **16** (2014), 729–754, DOI:10.1002/adem.201400097

[6] Zocca, A.; et al.: Additive manufacturing of ceramics: Issues, potentialities, and opportunities. JACerS, 98 (2015) [7] 1983–2001, DOI: 10.1111/jace.13700

[7] Chen, Z.; et al.: 3D printing of ceramics: A review, JECerS, 2018, https://doi.org/10.1016/j.jeurceramsoc.2018.11.013

[8] Scheithauer, U.; et al.: Additive Manufacturing of Ceramic-Based Functionally Graded Materials, CERAMIC APPLICATIONS **6** (2018) [2] 30–36

[9] Homa, J.: Rapid Prototyping of high-performance ceramics opens new opportunities for the CIM industry. Powder Injection Moulding Int. **6** (2012) [3] 65–68

[10] Santoliquido, O.; et al.: AM of ceramic components by Digital Light Processing: A comparison between the “bottom-up” and the “top-down” approaches, JECerS, 10.1016/j.jeurceramsoc.2019.01.044

[11] Zanchetta, E.; et al.: Stereolithography of SiOC ceramic microcomponents, Adv. Materials **28** (2016) [2] 370–376

[12] Sattler, S. W.; et al.: Emerging technologies and concepts for 5G applications. International Symposium on VLSI Technology, Systems and Application (VLSI-TSA), 2018, p. 1–6, IEEE

[13] Lantada, A.D.; et al.: Tissue engineering scaffolds for bone repair: general aspects, In Microsystems for Enhanced Control of Cell Behavior, p. 269–285, 2016, Springer, Cham

[14] Weber, F.E.: Reconsidering Osteoconduction in the Era of Additive Manufacturing. Tissue Engineering Part B: ReviewsVol. 25 (2019) [5]: DOI: 10.1089/ten.TEB.2019.0047

[15] Agarwala, M.K.; et al.: Filament Feed Materials for Fused Deposition Processing of Ceramics and Metals in Solid Freeform Fabrication Proceedings, Vol. 7, 1996, in: Marcus, H.L.; Beaman, J.J.; Barlow; J.W.; Bourell, D.L.; Crawford, R.H. (Eds.), University of Texas at Austin, 1996, Austin, USA

[16] Gonzalez-Gutierrez, J.; et al.: Additive Manufacturing of Metallic and Ceramic Components by the Material Extrusion of Highly-Filled Polymers: A Review and Future Perspectives. Materials **11** (2018) 840–875, 10.3390/ma11050840

[17] Abel, J.; et al.: Fused Filament Fabrication (FFF) of Metal-Ceramic Components, Journal of visualized experiments: JoVE, 2019, Issue 143, e57693, 10.3791/57693

[18] Berger, C.; et al.: Properties of Additive Manufactured Hardmetal Components produced by Fused Filament Fabrication (FFF). Proceedings of European Powder Metallurgy, Bilbao, 2018, Spain

[19] Scheithauer, U.; et al.: Thermoplastic 3D Printing – An Additive Manufacturing Method for Producing Dense Ceramics. Int. J. Appl. Ceram. Technol. **12** (2015) [1] 26–31, 10.1111/ijac.12306

[20] Scheithauer, U.; et al.: Droplet-based additive manufacturing of hard metal components by thermoplastic 3D printing (T3DP). J. Ceram. Sci. Technol. **8** (2017) 155–160, 10.4416/JCST2016-00104.

[21] Weingarten, S.; et al.: Multi-material Ceramic-Based Components – Additive Manufacturing of Black- and White-Zirconia Components by Thermoplastic 3D-Printing (CerAM - T3DP), JoVE (2019) [143] 10.3791/57538.

[22] Scheithauer, U.; et al.: Ceramic-Based 4D Components: Additive Manufacturing (AM) of Ceramic-Based Functionally Graded Materials (FGM) by Thermoplastic 3D Printing (T3DP). Materials, 10.3390/ma10121368

[23] Scheithauer, U.; et al.: Alternative Process Routes to Manufacture Porous Ceramics – Opportunities and Challenges. Materials (2019) [12] 663, 10.3390/ma12040663

[24] Moritz, T.; et al.: Ceramic Additive Manufacturing Methods Applied to Sintered Glass Components with Novel Properties. Ceramics in Modern Technologies, 2019