Material- and Process Hybridization for Multifunctional Ceramic and Glass Components

The demand for multifunctionality and the combination of materials and structures with different properties plays an increasing role for a variety of applications like surgical components, automotive parts or intelligent tools. Material hybrids allow distinctive property combinations like electrical conductivity/insulation, magnetism/non-magnetism, ductility/hardness or visual appearance with differing colours. In addition, as known from MEMS (Micro Electro-Mechanical Systems), hybrid components can be equipped with sensor or actor functions.

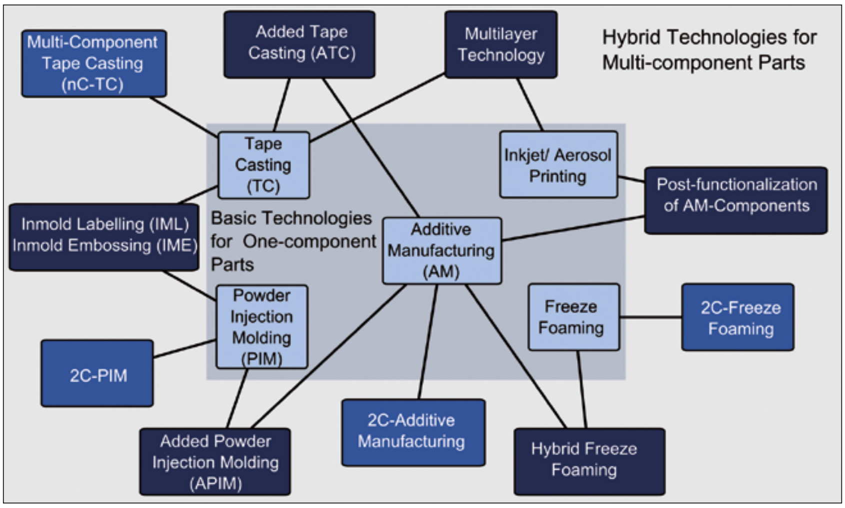

Fig. 1
Hybrid technologies as combinations of established shaping methods

Introduction

The combinations of materials are achievable by either mixing/pairing different materials within one process and/or by combining entirely different technological approaches providing distinctive structural features. However, combining different materials and processes requires the adjustment of the material properties and a tuning and hybridization of co-processing and process technology.

This contribution gives an overview about the main challenges, opportunities and recent developments of material and process hybridization of conventional shaping technologies with special focus on the potential arising from Additive Manufacturing techniques.

Keywords
hybrid technology, multifunctional ceramic and glass

Hybrid technologies

Fig. 1 illustrates the basic technological shaping approaches for instance Powder Injection Moulding (PIM), Tape Casting (TC), Additive Manufacturing (AM) or inkjet/aerosol printing and the chosen process combinations – hybrid technologies – relevant for achieving multi-component parts and materials presented in this contribution.

Hybridization of different materials and structures usually takes place starting from the green state followed by co-processing (e.g. green-in-green manufacturing of tapes, nC-tape casting) or from the sintered state followed by post-processing (e.g. post-functionalization of AM-components). In some cases, only a co-manufacturing of pre-sintered material and green state material succeeded (e.g. hybrid Freeze Foaming).

Manufactured parts can be furthermore classified according to the interface and

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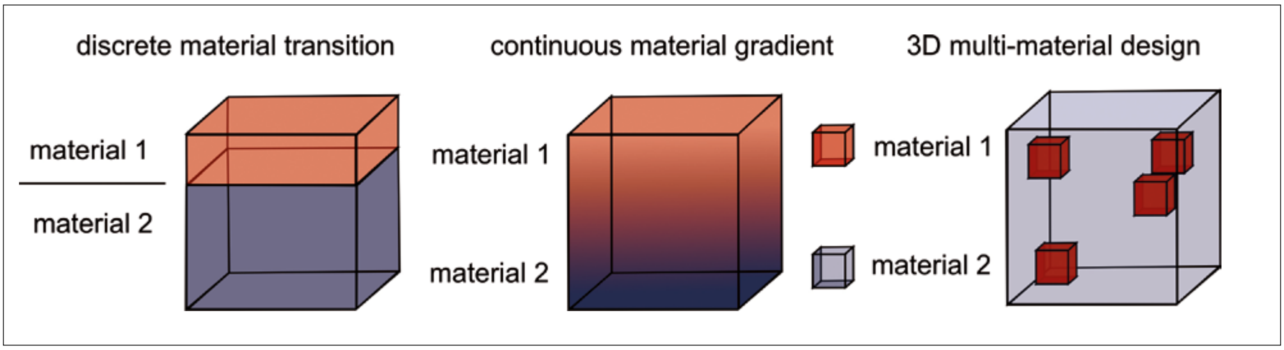


Fig. 2
Classification of material hybrids (from [1])

distribution of the second phase [1]. By combining two components with a homogeneous volume, a defined interface with discrete material transition is created which is characterized by a sharp change of properties (manufacturable by 2C-PIM, inmould labelling, nC-tape casting, 2C-AM, post-functionalization of AM products, hybrid Freeze Foaming).

A continuous material gradient is provided by a graded change of the composition (nC-tape casting, 2C-AM, inmould labelling).

For true 3D-multi-material designs, the phases intersect and form substructures within a matrix material (2C-AM, multilayer technology).

Requirements for material hybridization

The co-processing of two materials from the green state to the sintered state involves a number of challenges and demands to be met. Choosing a suitable material couple is one key issue for a successful co-sintering process because chemical and physical properties cannot easily (or only very limited) be changed by process adjustments.

The following material properties need attention:

- coefficient of thermal expansion (CTE):
  Differences in CTE lead to stresses in the interface during thermal treatment, especially during cooling if thermal contraction deviates too much.
- chemical compatibility:
  During co-sintering chemical reactions in the interface between the different materials may cause the formation of instable or brittle phases which may limit the long-term stability of the interface.
- sintering conditions:
  Both materials should sinter within the same temperature range and atmosphere without melting or decomposition of one partner but still reach desired densities.

In addition to the above-mentioned material properties subjected to chemical/physical properties, the process technologies each have their individual requirements, which include:

- good processing of slurries, pastes or feedstocks:
  The properties of the slurries, pastes and feedstocks depend on the solid loading, which influences greatly the viscosity. The viscosity in turn effects flow or foaming behaviour as well as mold filling behaviour and therefore defect formation.
- compatibility of binders:
  Chemically incompatible binders can lead to delamination between the components. Both involved binder systems have to fit co-debinding conditions (e.g. extraction debinding).
- sufficient green strength:
  When the second component is added, the first component has to withstand mechanical and thermal stresses without deformation or delamination.
- similar solid loading for same total shrinkage:
  The final shrinkage of the involved materials must be in the same order to keep the stress gradients at a low level. A mismatch of constrained deformation (caused by sintering stresses) leads to warpage or even defect formation. This

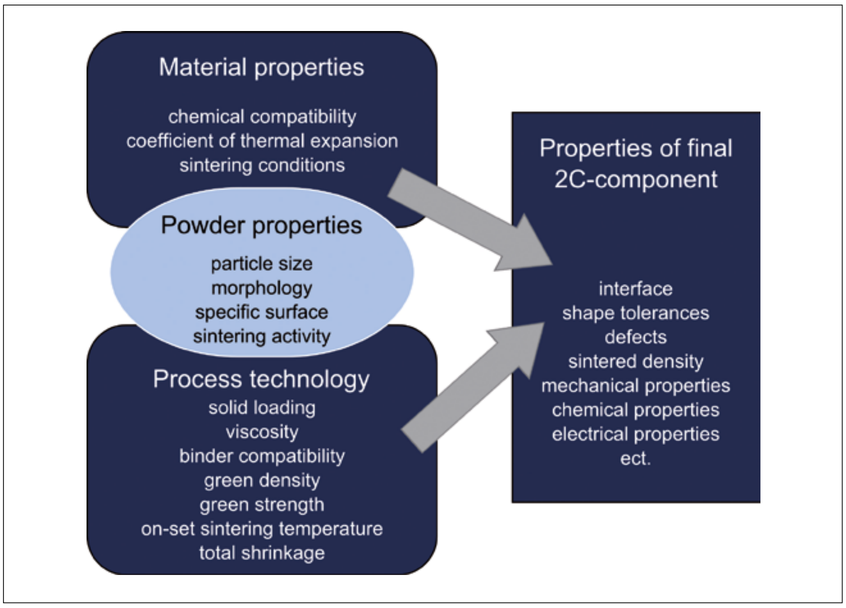


Fig. 3
Material and process related requirements for manufacturing multi-component parts

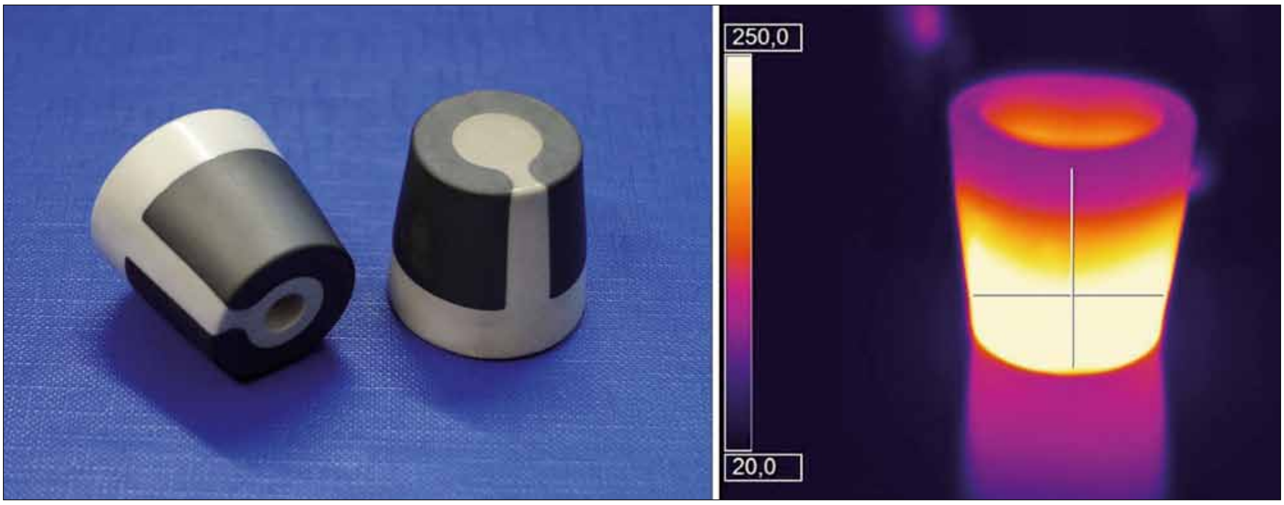


Fig. 4
Glass-carbon-composite nozzle and crucible manufactured by 2C-PIM and IR-image during heating (Source: Fraunhofer IKTS)

can be adjusted by the solid loading, which effects the particle packing density in the green body.

- close on-set sintering temperature: sintering should start at a similar temperature in order to prevent cracking of the fragile debinded body caused by a stress gradient.

Both fields, material and process related requirements, do not always go together since some points demand opposed actions. Therefore, selecting the raw powders plays a crucial role. First and foremost, sintering activity is influenced by particle size and specific surface. The smaller the particles the higher the driving force for sintering and the lower the on-set sintering temperature. In case of metal powders, the sintering activity can be influenced by a special comminution and high-energy milling treatment, which increases dislocation density [2, 3]. In order to adapt total shrinkage, the packing density has to be adjusted which depends on particle size but also on the powder morphology (spherical, platelets). Processing the powder according to its "natural" packing density at an optimal solid loading gives the best shaping results. Using too high or low solid loadings may cause insufficient flow behaviour, warpage during debinding or high residual porosity. Therefore, solid loading has to be treated with care for both partners. It is advantageous to invest high efforts into modifying the raw powders (e.g. by bimodal powder mixtures or alloyed powders) for tailoring the pairing.

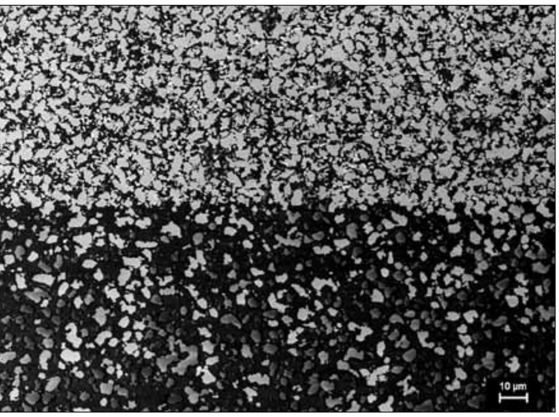


Fig. 5
Interface of sintered 2C-part consisting of two Si_3N_4–$MoSi_2$-compounds (IML) (Source: Fraunhofer IKTS)

Combination of conventional shaping techniques

Several hybrid technologies of established ceramic shaping techniques have been developed in the last years which were already transferred to serial production or which are on the edge to industrial application. In two-component powder injection moulding (2C-PIM) two feedstocks are used which are adjusted in shrinkage behaviour in order to form a two-component part with integrated functions. One example developed in an IGF-project (2K-Sinterglas 17755 BR) is the combination of two types of glasses [4]. An electrically insulating and an electrically conductive glass-composite have been joined by co-sintering to create a heated nozzle or crucible. The electrical conductivity of the glass has been adjusted by adding a certain amount of graphite to the glass matrix for attaining a percolation chain of the graphite platelets as conductive paths. Within 120 s, a temperature of 250 °C was achieved (Fig. 4).

Another application combining an insulating and conductive Si_3N_4–$MoSi_2$-compound is under development within the publically funded ZIM-project LabEmboss (KF2087364AG4). It is applied for making novel sensors for steel melts. In this case, one component is provided as green tape produced by conventional tape casting and the other as shrinkage adapted PIM-feedstock. In the so-called inmould-labelling (IML) the green tape is inserted into an injection moulding tool. Subsequently, the thermoplastic feedstock is injected onto the tape. For avoiding any damage of the tapes, a suited binder system of the tapes has to be chosen. It should provide a sufficient flexibility and sufficient mechanical resistance against the flowing feedstock and has to be chemically adapted to adhere with the feedstock binder and allow defect-free interfaces (Fig. 5).

Pressure sensors with integrated housing were developed in the IGF-project KombiPIM (17921 BR). For both partners the same material (LTCC) was used. The tape was produced in known multilayer technology by joining several LTCC-tapes, which are equipped with functional sensor structures (membrane, Wheatstone bridge

Fig. 6
Pressure sensors with integrated housing produced by IML (Source: Fraunhofer IKTS)

Fig. 7
Combination of black and white zirconia manufactured by 2C-PIM and IML/IME (Source: Fraunhofer IKTS)

and temperature sensor). Conventionally, this technology is limited to 2D or 2,5D and does not allow real 3D structures. Cost and time consuming efforts have to be taken to join a housing in post-processing. IML allows to integrate this joining step into the shaping process before co-sintering by inserting the green multilayer component into the injection moulding tool (Fig. 6) [5].

For decorative applications, black and white zirconia was combined by 2C-PIM and by IML (ZIM-project CombiColor KF-2087326AG1). A black zirconia tape was developed which was used to decorate an injection moulded base body.

In this way the amount of black zirconia and hence the amount of colouring pigments can be reduced to a minimum which prevents the white component from becoming brownish during heat treatment. For attaining the decorative structures (e.g. letters or numbers) the special process in-mould-embossing was applied (Fig. 7). For that purpose, the injection-moulding tool is provided with an internal microstructure, which embosses the inserted tape during the injection step of the feedstock by the applied injection pressure. Furthermore, the tool can be made compressible after the injection step. This allows for a further improvement of the tolerances of the structures [6].

Carbon-free refractories were developed within the Priority Program SPP 1418 “FIRE” (Part I and II) which was financially supported by the German Research Foundation – DFG under the reference number MI 509/10-1 and -2. Multilayers with graded microstructure can improve the thermal shock behaviour by decreasing the residual mechanical stresses. Fig. 8 shows FESEM cross section images of such tailored materials [7]. MgO–ZrO$_2$–multilayer structures with alternating layers of dense and porous tapes were manufactured by multilayer technique.

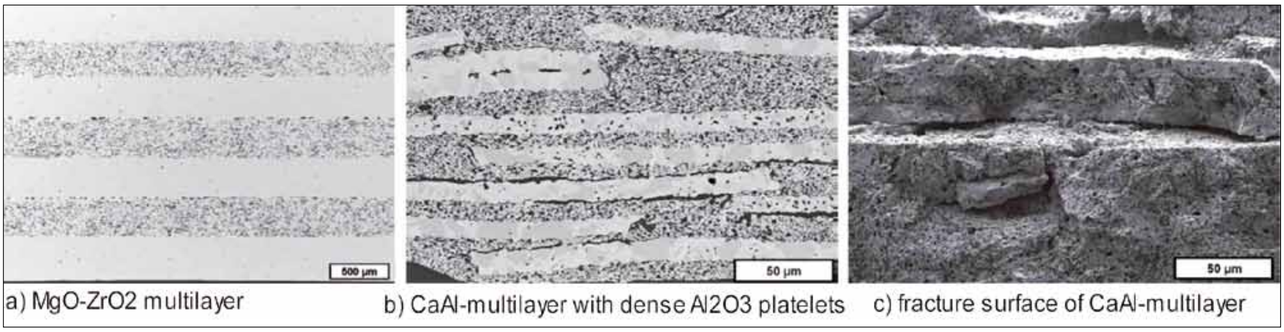
A calcium aluminate composite was developed with integrated dense alumina platelets, which were oriented in situ during tape casting by the casting direction. The resulting discrete property change from layer to layer allows for crack-deflection and energy dissipation during breaking as the cracked surface illustrates.

Combination of AM techniques

So far, most AM technologies used for ceramic components are only suited for single material applications because of the so called “indirect” work principle. The used material is deposited onto the whole area of each layer and the solidification occurs selectively.

For instance, in powder-bed based technologies the single material powder-bed cannot be simply changed. It is the same for lithography-based AM where a change of the light curable ceramic suspensions would cause an impurification of the following suspension having a different composition. Nevertheless, there are first publications regarding multi-material approaches in AM.

Kollenberg [8] describes multi-material 3D-printing by using particle-filled inks for



a) MgO-ZrO2 multilayer
b) CaAl-multilayer with dense Al2O3 platelets
c) fracture surface of CaAl-multilayer

Fig. 8
Multilayer structures produced by nC-tape casting [7] (Source: Fraunhofer IKTS)

Fig. 9
Thermoplastic 3D-printing equipment with 4 printing units (Source: Fraunhofer IKTS)

dense microstructure, locally reinforced microstructures, and combination of different properties or colours.

“Direct” working AM technologies deposit the material only in those areas where it is needed. This offers the possibility to deposit different materials side by side to realize material transition, 3D-material design or material and property gradients in all three dimensions. One direct working AM technology, the so-called Thermoplastic 3D-Printing (T3DP), is under development at Fraunhofer IKTS within the BMBF Agent-3D project MultiBeAm (03ZZ0209B). The components are built up by means of drop-wise deposition of melted low viscous thermoplastic suspensions, which are applied by special dispensing units. The droplets solidify by cooling which makes this method material-independent. The thermoplastic binder can be loaded with metal, ceramic or glass powders. By using two or more dispensing units a multi material AM process can be realized since different materials may be combined within one layer as well as in different layers (Fig. 9–10).

Another promising approach for multi functionalization of AM components is the combination of established AM techniques for ceramics with the above-mentioned methods known from multilayer technology, like ink-jet printing, aerosol jetting or dispense jetting. Currently, the ceramic 3D parts made by the AM techniques are provided in the sintered state and can be functionalised by using special inks or pastes. As an example, an alumina pipe-like component has been made by Lithography-based Ceramic Manufacturing (LCM, [9, 10]) with a complex outer shape to realize a very thin wall thickness of 300 µm in a selected area. Furthermore, the component is provided with fluidic ports in one manufacturing step – an important advantage of AM processes. In a subsequent processing step different heating, sensor, and conductive structures have been applied to the sintered component to provide multifunctional properties for realizing a flow sensor. Furthermore, a complex static mixer with heating properties for advanced heat transfer was manufactured using LCM and aerosol jetting with RuO-glass ink (Fig. 11).

Combination of AM techniques with conventional shaping methods

A third way for hybridization is provided by combining AM methods with conventional shaping routes. As first example of its kind, a particular foaming technique is combined with AM to manufacture complex-shaped components for a possible use as personalized bone replacement material [11, 12] (BMBF project BONEFOAM 01DS13010, 01DS15004). In a first manufacturing process, an outer and complex-shaped shell structure is made by LCM.

This shell is then filled with a so-called Freeze Foam providing the porous inside. A Freeze Foam is attained by inflating an aqueous suspension under a certain vacuum pressure until the evolving foam scaffold suddenly freezes and thus, stabilizes. A further pressure reduction leads to sublimation of the frozen water and a dry porous green part [13, 14]. The porous structure shows a special pore morphology (e.g., microporous pore walls and struts) which cannot be easily attained by AM techniques, among others because this would involve huge CAD data volumes to be generated and handled (Fig. 12).

In order to avoid that the hybrid structures are destroyed due to a too low or a too high shrinkage of the porous foam structure in comparison to the surrounding denser LCM shell, the shrinkage of both parts must be adjusted precisely. To further avoid high stresses acting on the shell structure, for some materials the LCM component needs pre-sintering to provide a sufficient initial strength. Beside bone replacement components, the combination of porous and dense materials/structures can become relevant for storage components, catalyst supports, micro-reactors or lightweight structural components etc.

Recently, developments of other combinations of conventional shaping techniques with AM routes have started. In the EC funded project CerAMfacturing (678503) the consortia develops customized products for consumer and medical applications by Added Tape Casting and started combining tapes with AM methods like LCM, T3DP and Fused Filament Fabrica-

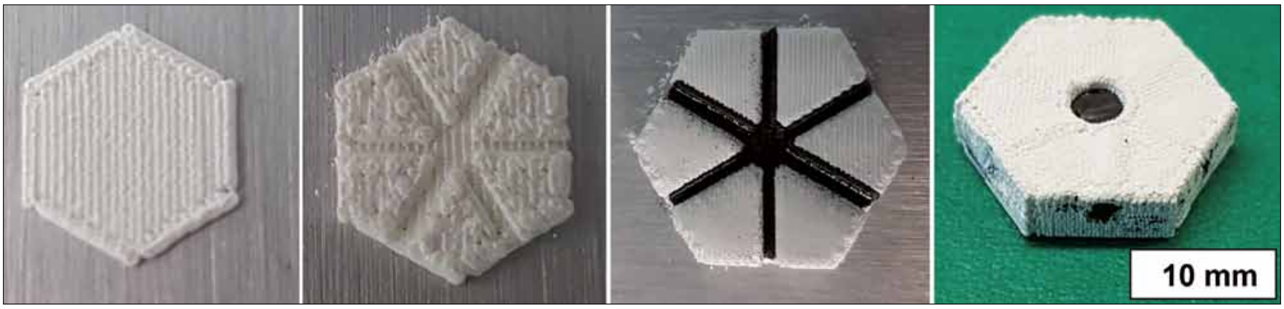


Fig. 10
AM of multi-material-component by T3DP (f. l. t. r.): deposition of material A as full layer – deposition of material A in selected areas – deposition of material B – deposition of material A as top layer (Source: Fraunhofer IKTS)

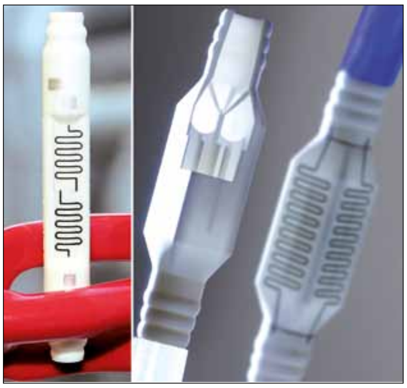


Fig. 11
Flow sensor (l.) and ceramic heater (r.) made by combination of LCM and aerosol printing (Source: Fraunhofer IKTS)

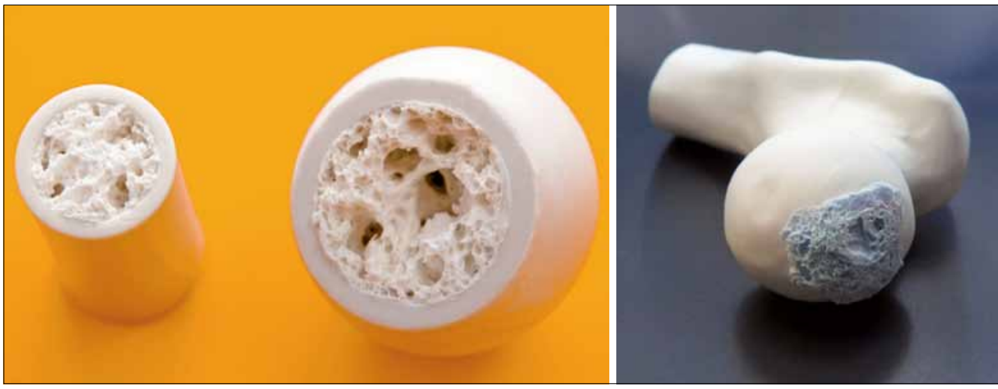


Fig. 12
Images of a ceramic hybrid freeze foam made by combination of LCM (outer dense structure) and Freeze Foaming process (porous inner structure) (Source: Fraunhofer IKTS)

tion (FFF). Furthermore, Powder Injection Moulding (PIM) shall be combined with the above-mentioned methods for enabling an individualization of large-series parts by Added PIM.

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Conclusion

Hybridization of materials and shaping routes offers innovative and promising property combinations for novel multifunctional components. Already, the combination of conventional shaping routes (e.g. Multilayer Technology, 2C-PIM etc.) is promising and challenging. However, combining AM methods among each other or with conventional shaping technologies (additionally e.g. hybrid Freeze Foaming, APIM) provides the opportunity for individualization and personalization of components and allows for completely new functionalities. Hybrid technologies will have an outstanding importance in the future. Nevertheless, the rules for material combinations by co-processing and co-sintering will persist for all chosen combinations and are the foundation for all successfully manufactured parts.

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