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Multi-Material Printing of Lightweight Porous-dense Ceramic Components Showing Improved Damage Tolerance via LCM

How can multi-material 3D printing contribute to improve damage tolerance in technical ceramics? The answer lies in a selective management of porous areas within the same functional part, as the controlled lowering of density in exactly defined regions has proven to strongly influence the behaviour of crack propagation. This has been made possible by the additive manufacturing of porous-dense components on a Lithoz CeraFab Multi 2M30 printer. After alumina test samples with discrete and gradient material transitions were compared in their behaviour when exposed to thermal shock ΔT ~300 °C, a final design of alumina welding nozzles with a defined layer of porous alumina was chosen to closely examine the differences compared to the same part printed as a monolithic dense component. While adding the benefit of lightweight design, the weak and porous regions in the multi-material component improved the damage tolerance of the nozzle.

Introduction

Porous ceramics have been attracting interest for applications requiring low density, high thermal shock resistance, or solid thermal insulation property [1]. In recent years, industrial progress has sparked demand in applications such as thick barrier coating, cores for precision casting, biocompatible implants or membranes/filters. A good practical use case is improved osteointegration in bioceramic implants by increasing the contact area between bone and implant introducing open pores [2]. For such applications, varying the porosity of the components would be challenging due to the reduced strength of the parts in critical load bearing areas [3]. In order to master those strength restrictions connected to single-material porous ceramics [4], [5] the focus of attention has shifted to fabrication of multi-material porous/dense ceramic composites. Their principal effect is obvious: preserving unrestricted functionality through applying porosity while holding the structural integrity provided by the denser regions. In addition to strength issues, it would be also possible to introduce some microstructural mechanisms by applying controlled porosity in some pre-defined specific regions so that the thermomechanical properties of the components can be improved.

The LCM (Lithography-based Ceramic Manufacturing)-based CeraFab Multi 2M30 printer with the two vat-system offers two main printing approaches for combining two materials in a single component. The innovative multi-material 3D printer CeraFab Multi 2M30 (Lithoz GmbH, Vienna, Austria), launched at the Formnext 2023, can assign specific layers to a prescribed suspension, enabling the precise realisation of multilayered structures. Possibil-

Keywords
multi-material 3D printing, porous ceramics, alumina, lithography-based ceramic manufacturing (LCM), functionally-graded ceramics

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ities with multi-material printing have been discussed, for example recent works on zirconia-toughened-alumina layers, printed by CeraFab Multi 2M30 between homogeneous alumina layers, already revealed good adhesion between two materials, yielding characteristic strength of the multi-material component higher than 1 GPa [6]. Beyond a simple layer-by-layer mode, the printer is also capable of printing two different materials in the same layer with an "in-line" mode according to the designed layer images. This mode allows users to introduce discrete and gradient transitions between materials within the volume of the components. Previous thermal shock experiments have already been conducted on 3D-printed multi-material samples of alumina-zirconia (ZTA) featuring compressive residual stresses in the embedded alumina (A) regions, which serve as protective layers. The results demonstrated that thermally induced cracks on the surface of the multi-material samples could deflect and be contained within the embedded alumina layers, thereby limiting their final depth [7]. The printer's two vats working principle also allows for the combination of porous and dense regions of the same material within one part as a promising approach in ceramic multi-material applications. In this article, we will therefore focus on the latest research findings on 3D-printed multi-material porous/dense alumina using a CeraFab Multi 2M30, published in a series of studies carried out by the Chair of Structural and Functional Ceramics at Montanuniversität Leoben [8], [9] and Lithoz GmbH. In particular, the research discusses the development of multi-material lightweight ceramic components with improved thermal shock resistance. As a short summary, it will give an outlook on additional future material combinations for various application areas already being part of ongoing research projects as well as on the next steps of commercialisation as an official Lithoz product.

Multi-material printing approaches

As the LCM printer's Digital Light Processing (DLP)-based two-vat system splits blue light into single pixels by a rectangular array of movable micromirrors, the layer images are composed of many pixels. This layout allows for multi-material printing of complex shapes with various interface designs between two materials. (Fig. 1)

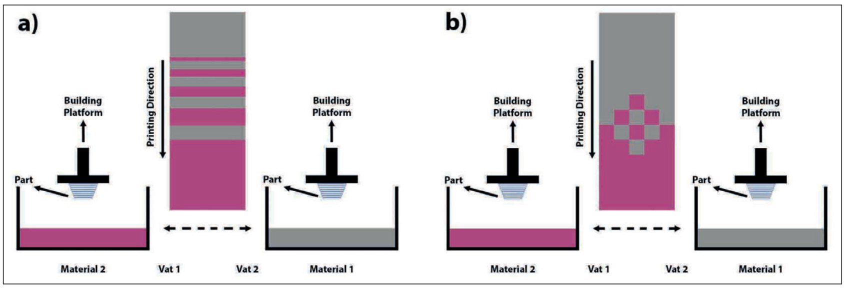

Fig. 1
Multi-material printing approaches with CeraFab Multi 2M30,
a) Layer-by-layer approach, b) Within-layer approach

Layer-by-layer approach

This basic approach assigns any layer to any of the two materials (see Fig. 1 a). Each layer is composed of one material; however, the number of layers assigned to each material can be entirely controlled. Multi-layered sandwich structures can easily be produced by using this approach.

Within-layer-approach

In this second approach, it is possible to assign any pixel in the layer image to each of the two materials (see Fig. 1 b). As a result some pixels can be printed with one material and the other selected pixels with the other material, allowing to use two materials together on the same layer. This approach is useful for the introduction of material transitions parallel and/or perpendicular to printing direction and for the realization of functionally graded designs.

How to tailor porosity into 3D-printed alumina parts

In practical applications, the inclusion of micropores within materials is highly desirable. As a result, recent efforts have focused on integrating macropores and micropores to achieve a bimodal pore distribution. Incorporating pore-forming agents (PFAs) into ceramic powder may allow the creation of porous ceramics, as these agents burn away and evaporate during the thermal post-processing [10], [11]. Utilising PFAs to introduce porosity through multi-material LCM printing provides several benefits, including the ability to tailor site-specific porosity and pore size distribution without altering the flow of the printing and thermal post-processing stages. The reference material utilised in this study was the alumina slurry LithaLox 350, as commercialized by Lithoz. In total, several slurries were prepared: LithaLox 350 pure and blends of LithaLox 350 with PFA at various contents [8]. Poly (methyl methacrylate) (PMMA) microbeads, featuring a particle size distribution with a median diameter of approximately 8 to 11 µm, were utilised as the PFA. To obtain the alumina with the desired porosity characteristics, two different ratios of PMMA particles, 20 mass-% and 30 mass-%, mixed into the alumina slurry and tested alongside the pure material without PMMA. The effect of PMMA content on the ceramic suspension's viscosity was measured using a modular compact rheometer at room temperature. To obtain an optimal printing behaviour and the desired resolution achievable with LCM technology, viscosity should preferably be at its maximum at around 20 Pa · s for a shear rate between 10 and 50 s^{-1}. According to the measurement results shown in Fig. 2, alumina material with 20 mass-% PMMA was selected to be used in preliminary studies for multi-material printing of porous/dense samples. Multi-material porous/dense test samples were printed with pure LithaLox 350 and blend of 20 mass-% PMMA to illustrate the various stages to approach the optimal formulation of alumina for multi-material printing. Following the printing process, the sample discs were cleaned by using LithaSol 20 solution and compressed air to remove any remaining slurry from their surfaces. The cleaned samples were then sintered at 1650 °C for 2 h. The entire thermal process was conducted with a heating rate of 1 °C/min. Earlier sample series are shown in Fig. 3.

Porosity Graded Ceramics

Functionally graded ceramics offer advantageous properties especially during the co-sintering of multi-material components

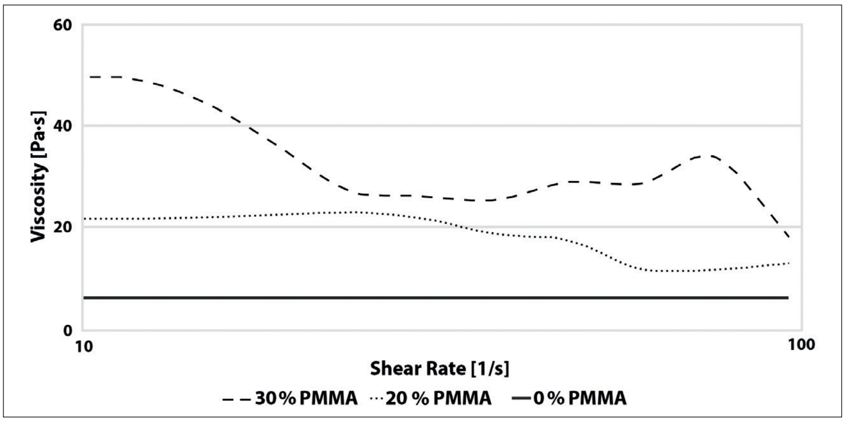

Fig. 2
Viscosity of the investigated slurries as a function of shear rate [8]

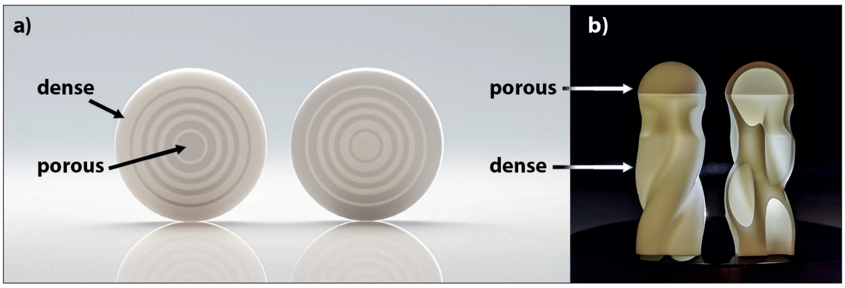

Fig. 3
Two examples of the different porous/dense multi-material designs: (a) multi-material discs with discrete porous layers in radial direction (b) Dense alumina nozzles with a porous tip

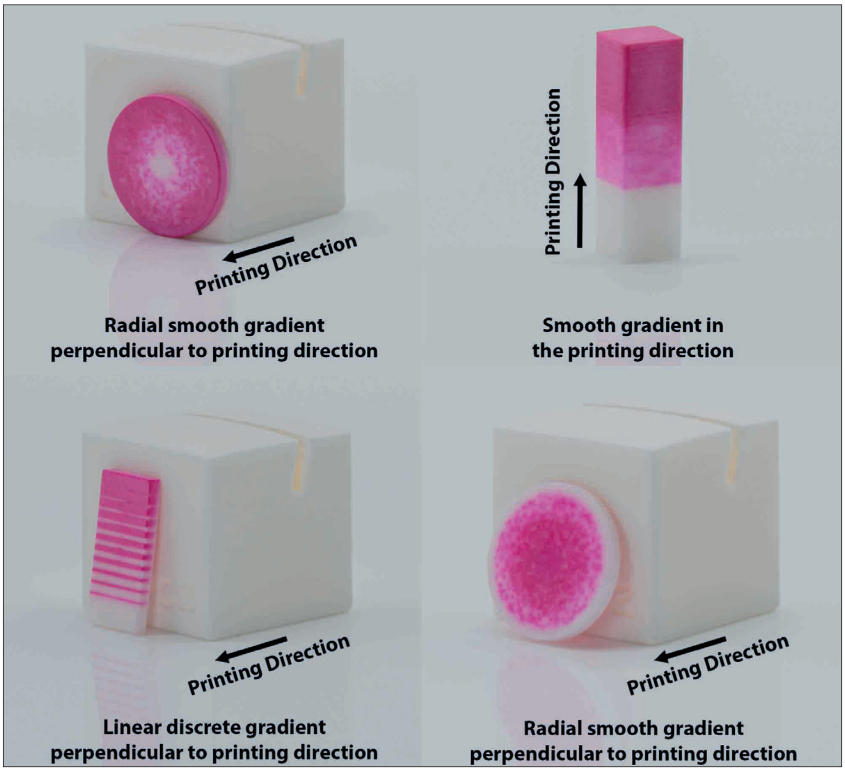

Fig 4.
Porous/dense alumina multi-material samples printed with different type and direction of gradients

composed of two materials with dissimilar sintering behaviour. Introduction of grading at the interface can improve the bonding strength between two materials and decrease the internal residual stresses occurring due to difference in shrinkage. By using conventional manufacturing techniques integrating gradient at material interfaces in different directions is challenging, especially if the component has a complex geometry.
Within-layer approach can be used for the realization of smooth and discrete material gradients in ceramic components without any need for additional manufacturing steps. Following the determination of material formulation, various examples of gradient types were developed by using porous and dense alumina slurries. For the porous alumina slurry, 20 mass-% PMMA was used. After sintering the samples, the parts were immersed in the crack infiltration dye to reveal the porosity gradient in the samples. Since the pink crack infiltration can penetrate into pores, the porous regions of the samples take the pink colour. The smooth porosity gradients alumina samples with different types of gradients in different directions are shown in Fig. 4. It has been shown that with the proposed multi-material printing approach, it is possible to introduce discrete and smooth poorosity gradients in parallel and perpendicular to printing direction.

Development of the alumina formulation: LITHALOX 1347

The multi-material printing process and the material formulations used for porous and dense alumina provided good preliminary results. A similar approach of combining porous and dense alumina was planned to be used for tailoring the thermal shock resistance of alumina. The alumina material that was used in the preliminary study had to be finetuned in terms of more suitable dynamic viscosity of the porous alumina slurries and adapted to better match the multi-material printing and co-sintering requirements when paired with porous alumina. The developed slurry resulting from these efforts was described as Litha-Lox 1347, which from this point on has been used to produce dense alumina samples/regions. This slurry was combined with 20 mass-% PMMA, respectively, to attain the desired material porosity in the specified regions.

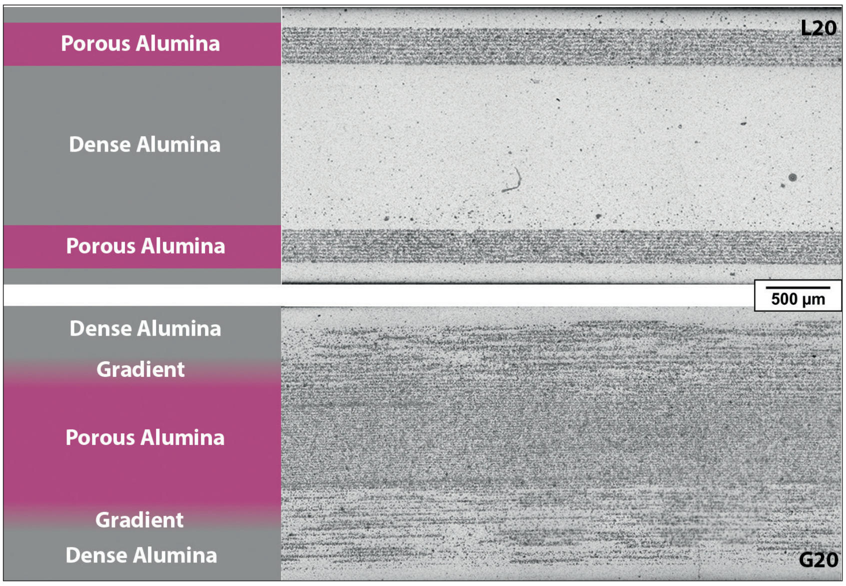

Fig. 5
The multi-material dense/porous alumina samples with discrete and gradient material transitions [9]

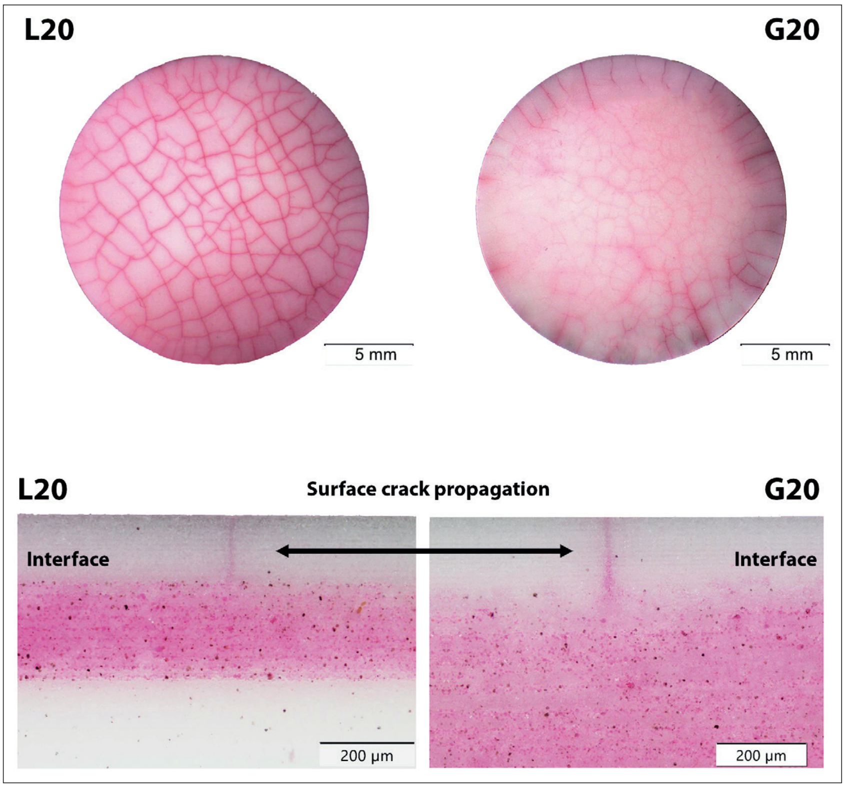

Fig. 6
The crack propagation behaviour of surface cracks as the porous/dense alumina multi-material samples experiences thermal shock [9]

Various laminate discs with discrete (L20) and gradient (G20) material transitions were designed and additively manufactured using the two-vat system on the multi-material printer. These discs incorporated porous regions between dense alumina matrix to enhance thermal shock behavior for potential lightweight applications in the future. The SEM images of the multi-material alumina components with discrete and gradient material interfaces are represented in Fig. 5.

The thermal shock test was performed by heating the samples up to the planned temperature (200 °C–400 °C) and dropping them into water with 20 °C. First, the samples were put into crack infiltration dye to observe the cracks on the surface and volume of the samples. Then a biaxial strength test was performed with the samples to determine the retained strength of the thermal shocked samples.

Fig. 6 illustrates the crack pattern in multi-material samples subjected to thermal shock testing. It shows the propagation of surface cracks after thermal shock tests into the ceramic parts. Cross-sectioning of the sample reveals how the propagating crack is retained within the porous region.

The retained strengths of the pure and dense thermal-shocked alumina and multi-material samples with discrete and gradient transitions are shown in Fig. 7. The strength values at a temperature difference of 0 °C represent the strength of the samples without thermal shock experiments. In addition, the retained strength of the components after thermal shock experiments at temperature differences of 200 °C, 300 °C and 400 °C are shown.

At a temperature difference of 400 °C, the retained strength of multi-material parts was very close to the monolithic dense alumina. It shows that the intermediate porous layers between the dense alumina matrixes maintained almost the total retained strength but offered a lightweight design by decreasing the total density of the components. Based on the observations and to demonstrate the proof of concept, ultimately a welding nozzle was printed as a single unit using dense alumina and as a multi-material with porous layers integrated between the dense outer and inner surfaces, as depicted in the figure (Fig. 8).

The thermal shock experiments were conducted at ΔT ~300 °C. The monolithic sample produced from pure and dense alumina and the multi-material sample produced by the discrete transition of porous and dense alumina interface were immersed into the crack infiltration dye in order to observe the crack propagation (Fig. 8). Cross-sections revealed longer cracks in the monolithic alumina sample, whereas the weak and porous regions in the multi-material component improved the damage tolerance of

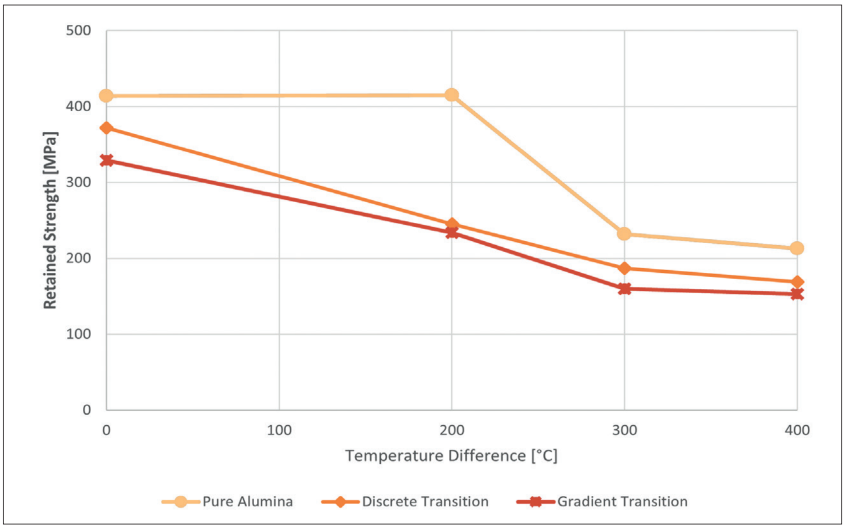

Fig. 7
Retained strength values of pure alumina, and multi-material components with discrete and gradient transitions [7]

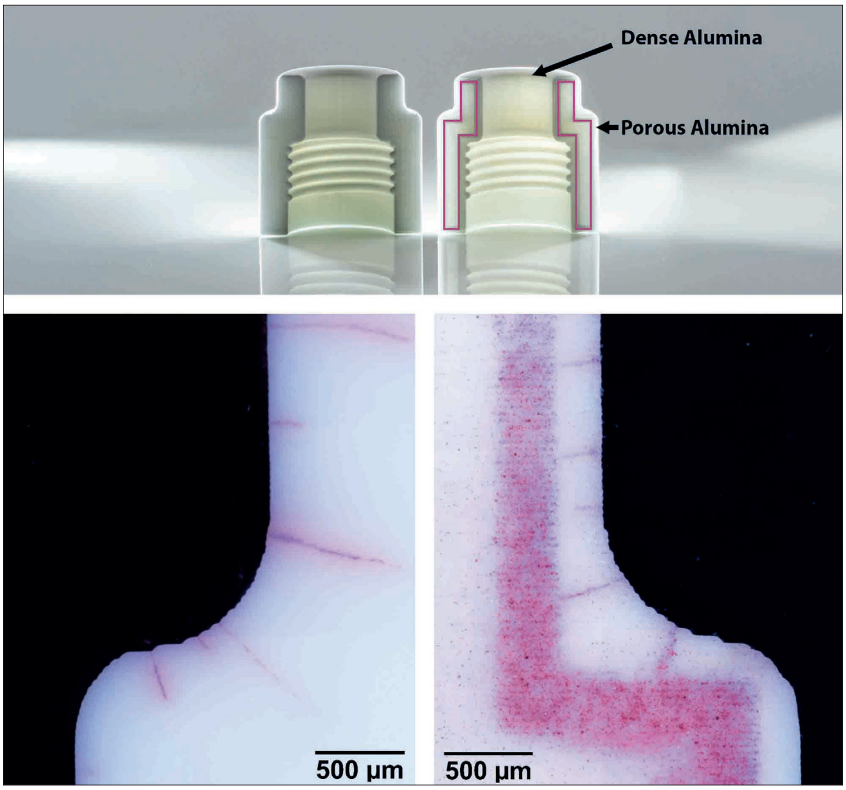

Fig. 8
Crack propagation behaviour after thermal shocking at ΔT ~300 °C in monolithic dense and porous/dense multi-material alumina welding nozzles [9]

the nozzle while offering a lightweight design.

Commercial launch and further outlook

After having consistently improved the materials in the last few years of pioneering multi-material research and development, Lithoz now takes the next important step following their commercialization strategy of ceramic multi-material printing.

At this year's Formnext, the Austrian company will reveal many more details about the future range of offered multi-material combinations. Pairings available will be based on the following possible combinations:

- porous/dense of the same ceramic material
- different ceramic materials, including colour variations
- ceramic/metal such as copper and glass ceramics.

While the range of porous/dense combinations will mainly concentrate on alumina for the time being, in the next future it is planned to follow-up with porous/dense combinations of zirconia, ATZ or even bioceramic variants. Instead, pairing two different ceramic materials, alumina and ZTA will be available as a material couple from the beginning. Another way to interpret this variant of printing two different ceramics will be colour variations, for example a pink alumina containing chromium oxide. Merging metals with ceramics in one single part, beyond the well-known copper/glass ceramic combination on sale, some co-sintered glass ceramic/silver parts (Fig. 9) on display at Formnext will show where the multi-material journey can lead.

Apart from the listed standard pairings, customers of a CeraFab Multi 2M30 can start development projects of customized multi-material combinations together with the Lithoz material engineering team. In case of varying porosity, as covered in this article, this important property can be modified and improved together with the Lithoz development team, paying special attention to the quality open porosity. In another research direction, the Lithoz team is exploring the potential of multi-modal pore size distribution as shown in Fig. 10.

Especially for bioceramic applications, introduction of multi-modal pore size distribution is very important for optimization of mechanical and biological properties, leading to improved biocompatibility, tissue integration, and overall functionality. In the above part of the article, the generation of porosity by mixing the ceramic slurry with pore forming agents was addressed.

In addition to pores due to pore forming agents, it is also possible to introduce additional porosity by partial sintering of the samples. In the following Fig. 10, a hydroxyapatite shell-core which is composed of dense outer shell and porous inner core is represented. The samples were sintered at two different temperatures. In the SEM images, it is shown that when the samples are sintered at the temperature that allows the full densification of hydroxyapatite, the pores are obtained due to the porogens. However, if the sample is partially densified, i.e., sintered at a lower temperature; smaller pores exist due to partial sintering between the pores associated with the porogens. Therefore, it is possible to generate multi-modal pore size distribution by combining partial sintering with the pore forming agents.

So far, Lithoz has already delivered their innovative multi-material machine to numerous customers from both academia and industry. First and foremost, the technology's appeal for industry lies in the potential of part consolidation. By applying smart design solutions, product components which integrate multiple conflicting or complementary properties and previously had to be produced in separate steps, could now be united into a single part and produced in just one step.

Besides the reduction of the number of single components of a product, process chains will benefit from significant savings in material and production time. Thanks to the precise LCM-based process with minimal material waste rates and multi-property components with more complex designs and intrincated architectures new efficiencies at the final assembly stages of products can be exploited.

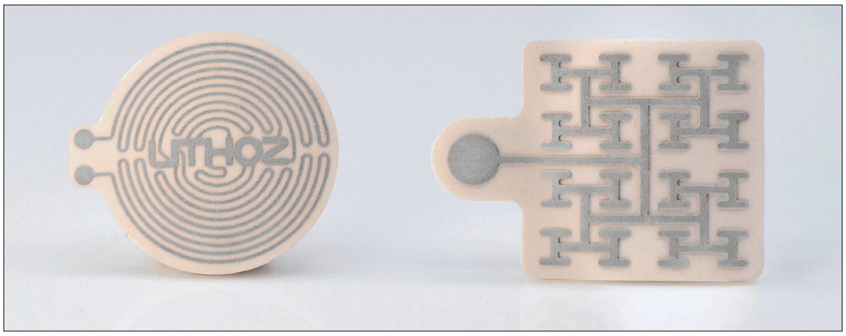

Fig. 9
Sintered glass ceramic/silver multi-material component

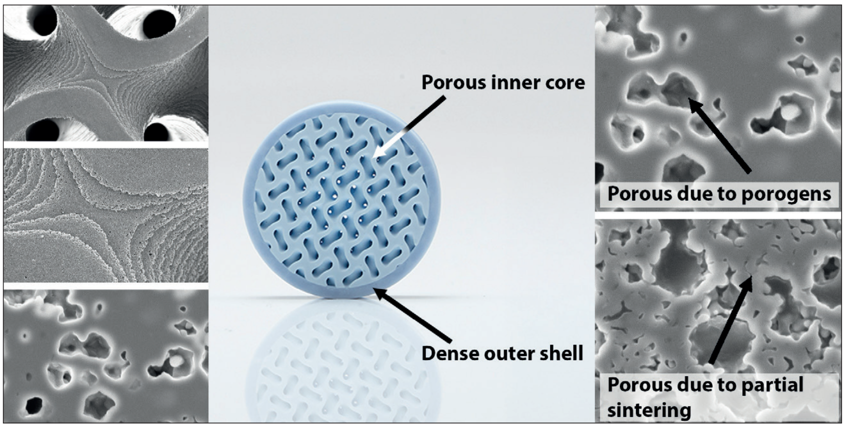

Fig. 10
Hydroxyapatite sample with multi-modal pore size distribution

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Figs. 5, 6, 7, 8 were modified/adapted from "Thermal shock resistant 3D-printed ceramic components through spatially tailored porosity", by J. Schlacher, L.B. Mateus, S. Nohut, M. Schwentenwein, R. Bermejo, 2024, Additive Manufacturing, 96, 104582. Published by Elsevier B.V.2024, with a permission under the CC BY license.

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