Journal of Additive Manufacturing Technologies
DOI: 10.18416/JAMTECH.2212678

Infinite Science | Publishing

Functionally graded ceramics by lithography-based ceramic manufacturing (LCM)

S. Nohut[1,2*], S. Geier[1], I. Kraleva[3], M. Schwentenwein[1] and R. Bermejo[3]

[1] Lithoz GmbH, Mollardgasse 85a/2/64-69, A-1060, Vienna, Austria
[2] Department of Mechanical Engineering, Piri Reis University, 34940, Istanbul, Turkey
[3] Department of Materials Science, Montanuniversitaet Leoben, Franz Josef Strasse 18, A-8700, Leoben, Austria
[*] Corresponding author, email: snohut@lithoz.com

Abstract

With the development of new industries and technological processes, the use of pure materials in sophisticated applications is declining due to the demand of conflicting property requirements in a single component. The interest on functionally graded ceramics (FGCs) that can be used under severe service conditions with high reliability has increased in parallel to the higher demand on complex advanced ceramics in various applications. Conventional methods are not totally capable of cost-effective fabrication of near-net shape FGCs with flexible and complex gradient designs. Lithography-based ceramic manufacturing (LCM) is an additive manufacturing (AM) method that works according to the principle of selective curing of photosensitive formulations utilizing the digital light processing (DLP) approach. The recently developed LCM multi-material printer allows fabrication of ceramic-ceramic and metal-ceramic combinations with high dimensional precision. Printing methodologies were developed to manufacture FGCs which show both discrete and continuous porosity gradient in parallel and perpendicular to the deposition direction. FGC combinations were produced by developing suitable suspensions, optimizing the debinding and sintering processes according to the single material thermo-elastic properties, design, and optimization of printing processes. The main challenges and future possibilities in realization of FGCs by LCM will be presented.

Keywords: Functionally graded ceramics; Additive manufacturing, Stereolithography, Multi-materials.

1. Introduction

Functionally graded ceramics (FGCs), a kind of functionally graded materials (FGMs) including at least one ceramic material, provide gradual variation of porosity, microstructure and/or composition over the volume [1, 2]. The demand of recent applications on more complex technical and functional ceramics increased the interest on FGCs [3]. A gradient in material/material properties may offer improved site-specific functionality and conflicting properties in single ceramic-based components without any interface delamination [4]. Gok and Goller has shown that the thermal cycling of $Gd_2Zr_2O_7$/CYSZ thermal barrier coatings was improved by using functionally graded design where the graded distribution decreased the thermal stresses and provided good adhesion between the layers [5]. FGCs with improved local properties and minimized stress shielding effect and delamination are of high interest, especially in biomedical and dental applications [6, 7]. Hydroxyapatite (HA)/bioactive glass functionally graded ceramics produced with two different compositional gradient design showed tailored microstructure, compactness, hardness, elastic modulus, and control of vitro bioactivity [8].

Porosity graded HA and beta-tricalcium phosphate (β-TCP) have become strong alternatives for bone substitutes mimicking the core-shell structure [9, 10]. Alumina-zirconia multi-material samples including direct and gradient material transitions have been produced by the direct additive manufacturing method based on laser directed energy deposition [11]. As opposed to samples produced with direct material transition, the one that have gradient transition zone showed an improved interfacial bonding, no microcracking as well as variation of hardness and fracture toughness.

Although FGCs offer very advantageous properties, there are still some gaps that must be investigated for integration of them into technical applications. From materials science and product development point of view, novel processing concepts should be developed, and/or current methods should be adapted to make them suitable for mass production and mass customization of complex shaped FGC components in a cost-effective manner. The post-machining processes applied to FGCs produced by conventional methods is labor-intensive since production of near net shapes is not possible [12]. At this point, technological developments in AM methods have gained more importance for the widespread use of FGCs [13, 14].

Lithography-based ceramic manufacturing (LCM) is an indirect AM method which works according to the principle of digital light processing, where a photosensitive suspension is selectively cured at desired areas by exposing blue light with a wavelength of 460 nm [15]. The printing process is followed by debinding (i.e., the organic part of the green body is burned out) and sintering thermal post-processes. LCM method enables manufacturing of very complex and net-shaped structures from commercially available ceramic powders with a high resolution [16, 17]. The LCM technology can work with different kinds of materials (polymers, ceramics, and metals), what makes it a good candidate for combining them to obtain designs with superior properties. Furthermore, it is nowadays possible to use LCM method with almost all kinds of commercially available ceramic powders [18-20].

Recently developed multi-material CeraFab Multi 2M30 LCM printer enables us to realize multi-material design including heterogenous or gradient transition in materials and/or material properties with the two-vat system and corresponding printing approaches [21]. In a recent work, multilayered discs composed of zirconia-toughened-alumina layers between homogeneous alumina outer layers were printed. Tailoring of the different layers yielded a biaxial strength of 1 GPa compared to 650MPa on reference single alumina, owed to the presence of in-plane residual compressive stresses in the outer alumina layers, generated during cooling form the sintering step [22].

In our previous article [21], we introduced porosity graded ceramics with a gradient in parallel to deposition direction. In this article, the gradient in perpendicular to deposition direction will be discussed for the first time. As a result, this article presents the effectiveness of multi-material printing approaches for fabrication of FGC components that contain porosity gradient profile in various orientations (i.e., parallel and perpendicular to deposition) and discusses the main challenges and future possibilities of fabrication of customized and application specific FGCs.

2. Materials and methods

The material employed in this work is, alumina slurry LithaLox 350 (including submicron α-Al2O3 powder content of 49%vol.) provided by Lithoz GmbH. For the generation of porosity, the pure alumina slurry was mixed with polymethyl methacrylate (PMMA) microbeads (particle size distribution of $d_{50} = 8\sim11\ \mu$m) as pore forming agent (PFA) with a mass content of 20%. The mixed slurry was stirred with a speed mixer at 1600 rpm for 2 min and 1750 rpm for 1 min. The multi-material 3D printer CeraFab Multi 2M30 (Lithoz GmbH, Vienna, Austria) was used for the manufacturing of samples (see Fig. 1). The printer is composed of two vats that can move horizontally for the change of material, a building platform that moves vertically, and an integrated cleaning station. The projector optics in this printer offers a lateral resolution of 35 μm/pixel with a building area of 2194 × 1234 pixels. The integrated in-line cleaning station can be activated after every vat change to avoid cross contamination by removing of the excess slurry.

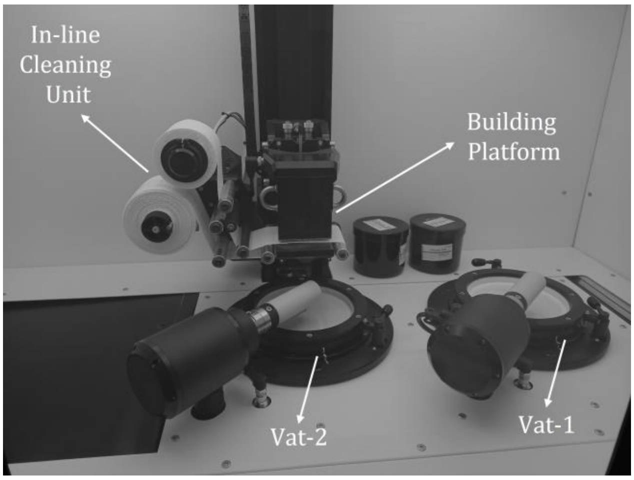

Fig 1. CeraFab Multi 2M30 printer.

The multi-material 3D printer offers two different processing approaches by which fabrication of FGCs can be realized: (i) "layer-by-layer" or (ii) "within-layer" [21]. In the "layer-by-layer" approach, one material is used for each layer and any individual layer can be assigned to respective material [22]. By using this approach, the change of material in the deposition direction is possible. Therefore, this approach can successfully be used for fabrication of multi-layered and sandwich structures [22]. In Fig 2(a), a multi-layered sample composed of dense and porous alumina regions, showing a discrete heterogenous transition is shown. The first half of the layers (dark color) were assigned to dense alumina and the rest (light color) to porous alumina. In the "within-layer", the two materials are intended to be used in the same layer. In this case, specific pixels are cured by the respective material according to the layer picture of the component design. In Fig. 2 (b), the layer pictures for each vat and some sintered porous/dense alumina samples are shown.

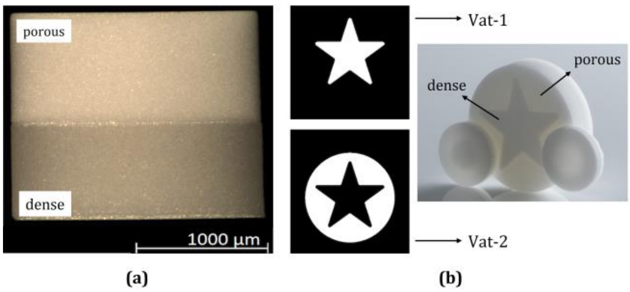

Fig 2. Combination of porous dense alumina using a) "layer-by-layer" and b) "within-layer" approaches.

In Vat-1, the inner side of the sample (shown with white color) is printed with dense alumina. Then the vats move horizontally, and the platform moves to the same height, with the outer part being cured in Vat-2 with the porous alumina slurry. In layer-by-layer approach, the platform moves by an amount of layer thickness after every curing step at Vat-1 or Vat-2. However, in the within-layer approach, the platform moves by an amount of layer thickness after executing the printing process both in Vat-1 and Vat-2. In this case, two pictures are required each for Vat 1 and Vat 2 respectively to print one layer. All samples were manufactured with 25 µm layer thickness by exposing to 150 mJ/cm² with a power of 50 mW/cm². After the printing, the excess slurry on the green parts was cleaned by using the solution LithaSol20 (Lithoz GmbH, Austria) and compressed air. The green bodies were then sintered at 1650 °C for 2 hours. The optical microscope (LiMi BX50, Olympus) and scanning electron microscope (JEOL JCM-6000Plus, NeoscopeTM, JEOL Ltd., Tokyo, Japan) were used for getting microstructural images of the samples. The samples were prepared by polishing to 1 μm surface finish by using a Struers RotoForce4.

3. Results and discussion

In 3D printing of FGCs, two important issues that determine the gradient architecture are the type of gradient (i.e., continuous, or discrete) and the direction of gradient (i.e., parallel, or perpendicular to the deposition direction) (see Fig. 3). In the continuous transition, no clear separation zones can be observed at the material transition interfaces. This offers reduction of internal residual stresses which are generated due to the difference in thermal expansion coefficients. In the discrete transition, a discontinuous stepwise gradient is obtained: this is advantageous in cases where the exact definition of a material or material property at a specific position is of interest [23].

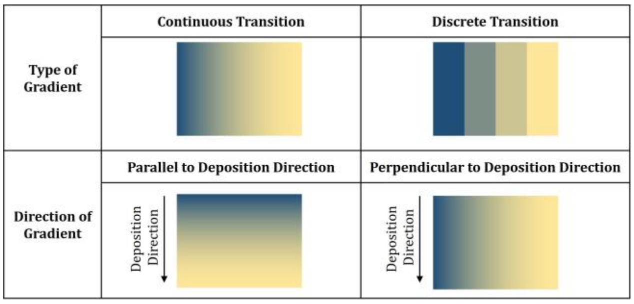

Fig 3. Type and direction of gradient.

Since additive manufacturing is a layer-wise printing process, introducing gradient not only in parallel but also perpendicular to deposition direction is an important issue in realization on complex three-dimensional gradient architectures. This also offers flexibility to the users in terms of realization of more complex designs and functionality and optimized placement of the ceramic components on the building platform. In the following, results on both types of gradients in different directions will be presented by using dense/porous alumina combinations.

3.1. Discrete Transition

Dense/porous alumina samples with discrete gradient in deposition direction were printed by layer-by-layer approach. In Fig. 4, the scanning electron microscope (SEM) image of the porosity graded alumina sample is represented. The gradient was achieved by increasing the ratio of the layer number of one material to another after every repeating 20 printing layers. The upper and lower parts of the sample are dense and porous, respectively. No defects were observed inside the layers or at the interfaces.

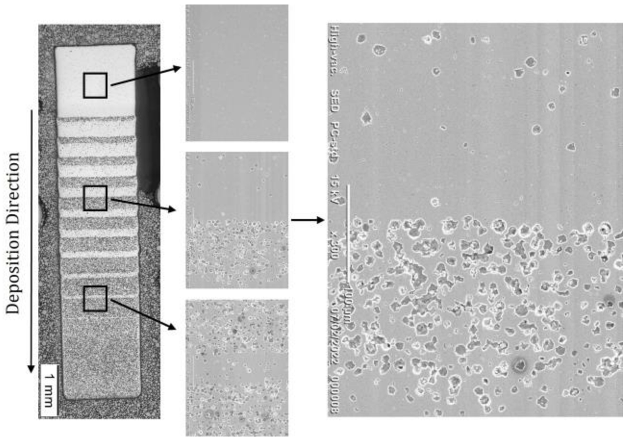

Fig 4. Porosity graded alumina with discrete transition in deposition direction.

The within-layer can be used to produce discrete gradient perpendicular to deposition (i.e., on the horizontal plane) direction by preparing suitable layer pictures. In Fig. 5, SEM image of a porosity graded alumina shows gradient on the printing plane with discrete transitions.

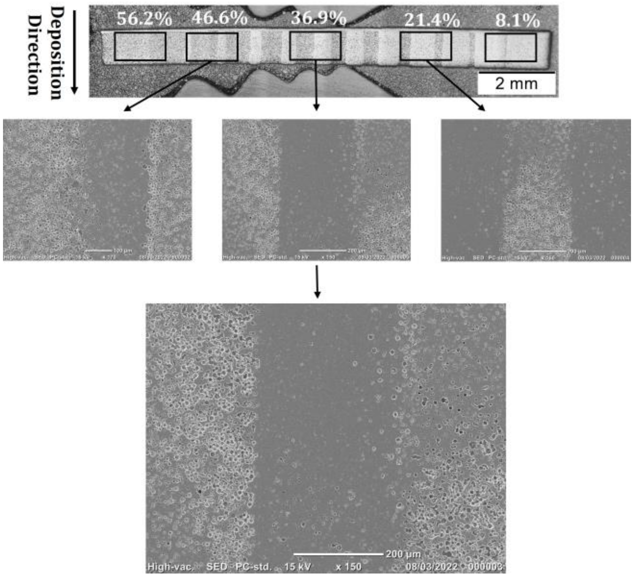

Fig 5. Porosity-graded alumina with discrete transition perpendicular to deposition direction.

The pure LithaLox 350 and mixture with PMMA were used for the printing. The average total porosity found by using the pore surface areas calculated from 2D images taken by SEM changes from 8.1% to 56.2% from one side to another. In this type of gradient with discrete transition, the sintering behavior of the materials used together should be similar to each other in order to avoid micro defects which might originate at the interfaces. Furthermore, the slurries should be adapted so that the adhesion during the printing process at the transition layers are strong enough.

3.2. Continuous Transition

Continuous transition of material in the gradient region provides position-based smooth changes in the volume. Since the smooth change includes small amount of increase or decrease in content of one material relative to another, the delamination problems arising at the interface layers of multi-layered structures due to high difference in thermal expansion coefficients can be avoided. In Fig. 6, the porosity graded alumina with a smooth gradient zone is shown.

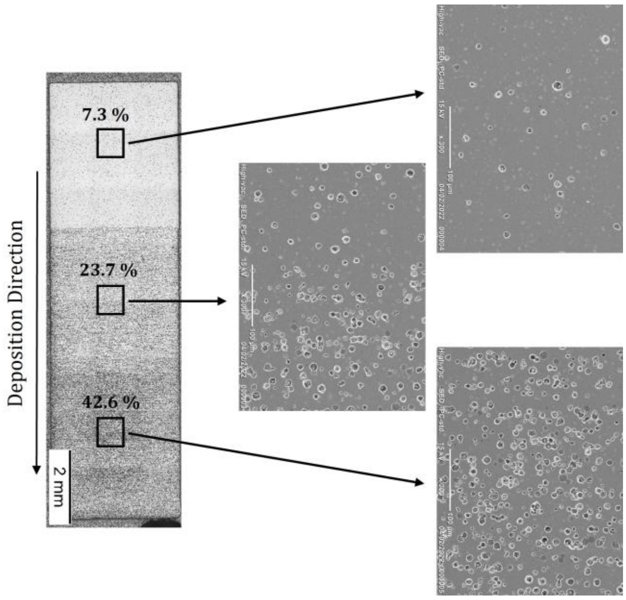

Fig 6. Porosity graded alumina with smooth transition in parallel to deposition.

The gradient in composition was accomplished by increasing the pixel-based content of one material to another on the layer pictures in the deposition direction by using within-layer approach. The sample is composed of a low porous part (i.e., upper part of the sample), high porous part (i.e., lower part of the sample) and a porosity graded region between them. Firstly, the low porous part was printed. Then, in the gradient region, after printing each layer, a new layer picture that includes a higher content of porous alumina was used until the end of this zone. For the low porous and high porous parts, a single vat was used. However, the gradient region was printed using the within-layer approach. In Fig. 7, some designs that were used for the fabrication of this sample are shown. The black pixels were distributed randomly in the whole surface by using image processing. They represent the porous alumina, with its ratio increasing continuously. A smooth gradient in the porosity was observed in all samples: no cracking was observed. It is worth mentioning that single pores wee only observed up to a porosity of 15%: after this value, connection between the pores and open pores appeared in the microstructure. A smooth material transition in the direction perpendicular to the deposition direction could also be achieved by using the within-layer approach, as shown in Fig. 8.

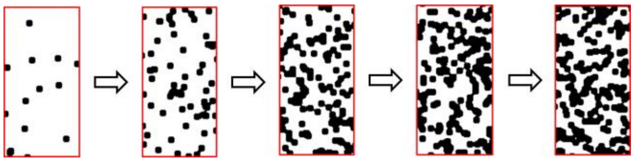

Fig 7. Layer pictures used for enabling smooth gradient in deposition direction.

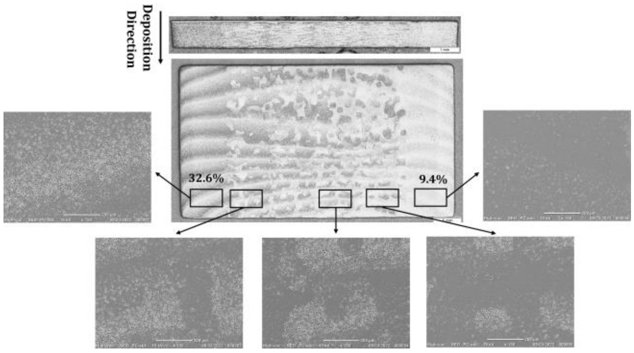

Fig 8. Porosity-graded alumina with smooth transition perpendicular to deposition direction.

The gradient in porosity from 32.6% to 9.4% was achieved by increasing the pixel-based content of one material to another on the printing plane. A layer picture example used to produce this sample is shown in Fig. 9. These pictures are complementary so that in Vat 1 and Vat 2, the black pixels of the corresponding pictures are cured.

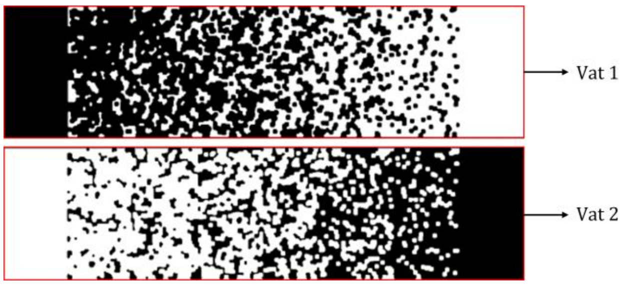

Fig 9. Layer picture used for porosity graded alumina with smooth transition.

4. Conclusions

In this article, two main approaches, namely layer-by-layer and within-layer, were investigated to manufacture functionally graded ceramics by LCM with discrete and smooth material transitions parallel and perpendicular to deposition direction. The layer-by-layer approach enables discrete material transitions only in the deposition direction. However, by using within-layer approach, discrete and continuous material transitions in both directions can be realized. Combination of both approaches will offer more complex gradient designs. In multi-material ceramic components, mostly the internal defects and/or cracks occur at the interfaces between the materials due to dissimilar thermal properties. In this study, no defects were observed at the transition regions between dense and porous alumina. Therefore, the production of crackfree functionally graded ceramics will allow combination of different types of material, especially ceramic-ceramic and metal-ceramic, and will increase the widespread use of FGCs by adding more functionality and site-specific properties. In the future, various combinations including metals will be investigated with more complex gradient architectures. Furthermore, the data-driven methods will play an important role in transferring knowledge on single-material process parameters to multi-material printing.

Acknowledgments
This work is part of the Marie Skłodowska-Curie Individual Fellowship (H2020-MSCA-IF-2020) project entitled "GraCerLit–Development of Functionally Graded Ceramics by Lithography-based Ceramic Manufacturing (LCM)". This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 101020104. Funding for this research was also provided by the European Research Council (ERC) excellent science grant "CERATEXT" through Horizon 2020 program under contract 817615.

Author's statement
Conflict of interest: The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: M. Schwentenwein and Sebastian Geier are employees of Lithoz GmbH, manufacturer and supplier of the used CeraFab 3D printer. Informed consent: Informed consent has been obtained from all individuals included in this study. Ethical approval: n/a.

References
1. Naebe, M. and K. Shirvanimoghaddam, *Functionally Graded materials: A review of fabrication and properties*. Applied Materials Today, 2016. **5**: 223–245.
2. Yang, L., H. Miyanaji, D. Janaki Ram, A. Zandinejad and S. Zhang, *Functionally graded ceramic based materials using additive manufacturing: review and progress.* Additive Manufacturing and Strategic Technologies in Advanced Ceramics, 2016. **258**: 43–55.
3. Petit, C., L. Montanaro and P. Palmero, *Functionally graded ceramics for biomedical application: Concept, manufacturing, and properties*. International Journal of Applied Ceramic Technology, 2018. **15**: 820–840.
4. Nohut, S. and M. Schwentenwein, *Vat Photopolymerization Additive Manufacturing of Functionally Graded Materials: A Review.* Journal of Manufacturing and Materials Processing, 2022. **6**: 17.
5. Gok, M. G. and G. Goller, *Production and characterisation of GZ/CYSZ alternative thermal barrier coatings with multilayered and functionally graded designs*. Journal of the European Ceramic Society, 2016. **36**: 1755–1764.
6. Sola, A., D. Bellucci and V. Cannillo, *Functionally graded materials for orthopedic applications – an update on design and manufacturing*. Biotechnology Advances, 2016. **34**: 504–531.
7. Madfa, A. A. and X. G. Yue, Dental prostheses mimic the natural enamel behavior under functional loading: A review article. Japanese Dental Science Review, 2016. **52**: 2–13.
8. Luginina, M., D. Angioni, S. Montinaro, R. Orrù, G. Cao, R. Sergi, D. Bellucci and V. Cannillo, *Hydroxyapatite/bioactive glass functionally graded materials (FGM) for bone tissue engineering*. Journal of the European Ceramic Society, 2020. **40**: 4623–4634.
9. Zhou, C., et al., *Mechanical and biological properties of the micro-/nano-grain functionally graded hydroxyapatite bioceramics for bone tissue engineering*. Journal of the Mechanical Behavior of Biomedical Materials, 2015. **48**: 1-11.
10. Lindner M., et al., *Calcium phosphate scaffolds mimicking the gradient architecture of native long bones*. Journal of Biomedical Materials Research Part A, 2014. **102**: 3677-3684.
11. Wu, D., J. Shi, F. Niu, G. Ma, C. Zhou, B. Zhang, *Direct additive manufacturing of melt growth Al_2O_3-ZrO_2 functionally graded ceramics by laser directed energy deposition*. Journal of the European Ceramic Society, 2022. **42**: 2957–2973.
12. Ewais, A. M. M., D. H. A. Besisa, Z. I. Zaki and A. H. T. Kandil, *Tailoring of functionally graded zirconia–mullite/alumina ceramics*. Journal of the European Ceramic Society, 2012. **32**: 1561-1573
13. Travitzky, N., et al., *Additive manufacturing of ceramic-based materials*. Advanced Engineering Materials. 2014. **16**: 729 - 754.
14. Li, W., et al., *Extrusion-based additive manufacturing of functionally graded ceramics*. Journal of the European Ceramic Society, 2021. **41**: 2049–2057.
15. Altun, A.A., F. Ertl, M. Marechal, A. Makaya, A. Sgambati and M. Schwentenwein, *M. Additive manufacturing of lunar regolith structures*. Open Ceramics, 2021. **5**: 100058.
16. Huang, X., H. Dai, Y. Hu, P. Zhuang, Z. Shi and Y. Ma, *Development of a high solid loading β-TCP suspension with a low refractive index contrast for DLP-based ceramic stereolithography*. Journal of the European Ceramic Society, 2021. **41**: 3743–3754.
17. Borlaf, M., L. Conti and T. Graule, *Influence of tensile edge design and printing parameters on the flexural strength of ZrO2 and ATZ bars prepared by UV-LCM-DLP*. Open Ceramics, 2021. **5**: 100066.
18. Rauchenecker, J., J. Rabitsch, M. Schwentenwein and T. Konegger, *Additive manufacturing of aluminum nitride ceramics with high thermal conductivity via digital light processing*. Open Ceramics, 2022. **9**: 100215
19. Hofer, A. K., I. Kraleva and R. Bermejo, *Additive manufacturing of highly textured alumina ceramics.* Open Ceramics, 2021. **5**: 100085.
20. Baumgartner, S., R. Gmeiner, J. A. Schönherr and J. Stampfl, *Stereolithography-based additive manufacturing of lithium disilicate glass ceramic for dental applications*. Materials Science & Engineering C, 2020. **116**: 111180.
21. Nohut, S., S. Geier, I. Kraleva, M. Schwentenwein and R. Bermejo, *Lithography-based additive manufacturing of porosity graded alumina*. Additive Manufacturing Letters, 2022. 3: 100060.
22. Schlacher, J., A. K. Hofer, S. Geier, I. Kraleva, R. Papsik, M. Schwentenwein, R. Bermejo, Additive manufacturing of high-strength alumina through a multi-material approach. Open Ceramics, 2021. 5: 100082.
23. Pandey, P. M., S. Rathee, M. Srivastava and P. K. Jain, Functionally Graded Materials (FGMs). CRC Press, 2021. ISBN: 9781003097976.