Ceramic additive manufacturing for industrial applications

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Introduction. Ceramic additive manufacturing (AM) consists of a diverse pool of techniques allowing mouldless fabrication of complex and near-net-shaped ceramic products through digital design. While the properties of the AM shaped ceramic materials are comparable to those manufactured using conventional powder processing methods, AM allows unprecedented freedom in design, such as mass customization of dense ceramic products, or products with designed porosity, with control over the pore size, size distribution and directionality of pores. AM techniques originally developed for polymer and metal products are now slowly becoming a viable option to mass customize or even mass produce ceramic products for selected industries, such as dental applications [1]. There are several reasons why AM techniques are specifically beneficial for ceramic manufacturing. First, ceramics (excluding glasses) are difficult to melt and cast into shape, as melting temperatures regularly exceed 2000 °C. Secondly, ceramics are brittle and intrinsically among the hardest materials know to us, making any type of subtractive manufacturing such as grinding or machining, difficult and expensive. And, thirdly, conventional ceramic manufacturing most often relies already on powder processing, i.e. shaping and consolidating ceramic powder into dense objects. Therefore, any powder-based ceramic AM method has a good selection of raw materials available, even at an industrial scale.

Keraamien 3D-tulostus (cerAM) is a collaborative "co-innovation" project between industry and academia, funded by the Finnish governmental funding agency Business Finland (Grant No 6333/31/2021). Running between 1/2022 – 9/2024, and with an overall budget of ca. 3 M€, the project is coordinated by Tamlink Oy and consists of a research project led by Tampere University, and three unique R&D projects by Planmeca Oy, Millidyne Oy and Wisematic Oy, with a holistic view towards commercialization of ceramic 3D printing. In addition, Valmet Oyj and Metso Oyj joined the project steering group as in-kind members.

cerAM project was built upon this background to facilitate technology transfer from basic and applied research towards application driven products and services, from university to company level. The holistic approach of the cerAM project combines R&D knowhow on ceramic powder processing and light curable resin development (Millidyne Oy), 3D printer development, digital design and end user products (Planmeca Oy), and automation of the 3D printing processes (Wisematic Oy). The companies joined forces with Tampere University's Ceramic

Research group who have gathered extensive knowledge on ceramic AM and powder-based ceramic processing technologies. As an example, the group was also among the first to pioneer 3D printing of advanced ceramics in Finland [1, 2], placing them in the forefront of the field also in the European/Global setting. In addition to domestic expertise, the project involved active international collaboration and research visits to the Belgian Ceramic Research Center, which helped to consolidate project goals.

Next, we will introduce case studies and key results of the cerAM research project, highlighting potential solutions to key challenges that lay on the path towards industrial applicability of ceramic AM. In addition, results are introduced from an EU-MSCA Postdoctoral Fellowship project AffordBoneS with a topic closely aligned with the cerAM project goals.

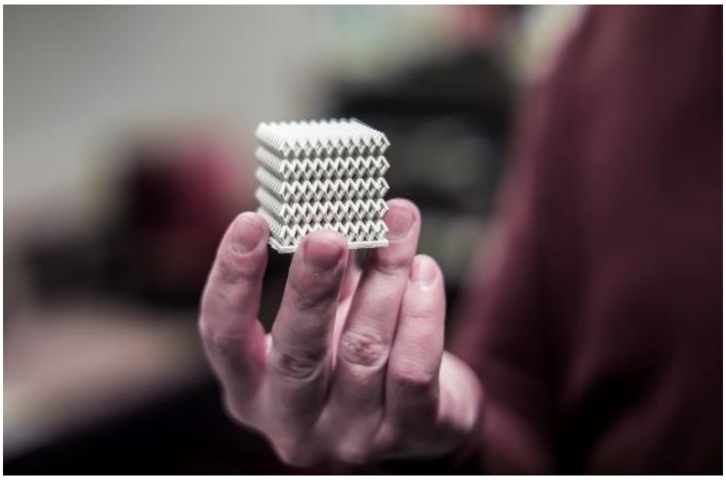

Figure 1. A 3D-printed cell structure using ceramic Vat Photo-polymerization (VPP) technique. Picture by Jonne Renvall/ Ceramic Materials research group/Tampere University.

Light curable resins for ceramic AM. Vat photopolymerization (VPP) techniques allow precise fabrication of detailed ceramic components with high dimensional accuracy and surface quality (**Figure 1**). VPP works by selectively curing layers of a photocurable ceramic resin using a light source, with a wavelength typically in the range of ultraviolet to visible light. This layer-by-layer approach allows for the creation of highly complex structures that would be challenging or impossible to achieve using conventional techniques. However, the effectiveness of VPP in the ceramic manufacturing heavily relies on the formulation of ceramic resin, particularly the light curable binder component, which plays a crucial role in the printing process and subsequent post processing [2]. Binder in the ceramic resin acts as a carrier for the ceramic particles and provides structural support during printing and part handling. Optimizing the binder composition is essential to address several challenges in VPP, including the uniformity layer deposition, minimizing shrinkage during curing, and achieving the desired mechanical properties in the final sintered parts. Our research focused on optimizing binary binder systems used in ceramic VPP. Specifically, we explored various monomers and macromers with different chemical structures and functionalities to understand how these variations affect critical properties such as viscosity, curing kinetics, shrinkage, and mechanical strength. By preparing and testing 18 different binder formulations, we were able to identify key factors that influence the performance of the printed parts. Through systematic experimentation, our findings highlight the importance of carefully selecting and optimizing binder components to enhance the overall quality and reliability of ceramic parts produced through VPP. Results indicate promising binders, notably HDDA:TMPTA$^+$ and PEG200DA:TMPTA$^+$, which demonstrated low viscosity, moderate energy for curing, moderate volume shrinkage, and good mechanical properties. For applications where higher viscosity is acceptable, the

HDDA$^+$:PETTA$^+$ formulation emerged as a strong candidate. Alternatively, for applications favoring methacrylates, PEG200DMA:PETTA$^+$ formulation presents an attractive option, offering a balanced performance profile.

Planmeca Oy. Manufacturing ceramic dental indications using additive manufacturing techniques would be a truly disruptive approach and would help bridge the gap between 3D printing and milling, which are the two manufacturing methods currently utilized in dental clinics. While additive manufacturing of polymeric materials has already proven its worth in many instances, dental milling is still considered to be the only manufacturing method for definitive ceramic restorations. The ability to cost-effectively manufacture full ceramic restorations using vat photopolymerization would be a breakthrough in the field of dental chairside manufacturing.

Aleksi Virta, Product Manager, 3D Printers

Towards more economical ceramic AM. VPP printing offers the ability to mass customize ceramic products with complex geometries and high level of detail, such as dental crowns or medical implants for bone regeneration. VPP provides an alternative solution to conventional CAD/CAM milling of ceramic green parts, with good part accuracy and low waste material generation [3]. However, the VPP printing process requires the use of a significant amount of organic binder substances to support the printed 3D shape. Before the 3D printed part is sintered into a fully dense ceramic product, these organic binder components need to be burned away in a thermal debinding step, and conventionally it must be a slow and controlled process to avoid cracking and warping of the prints during the exothermic degradation of the polymer network. The combined thermal pre-conditioning and debinding steps can take days, even up to 10 days to perform (**Figure 2**), and remains a major bottleneck in the VPP printing process [4].

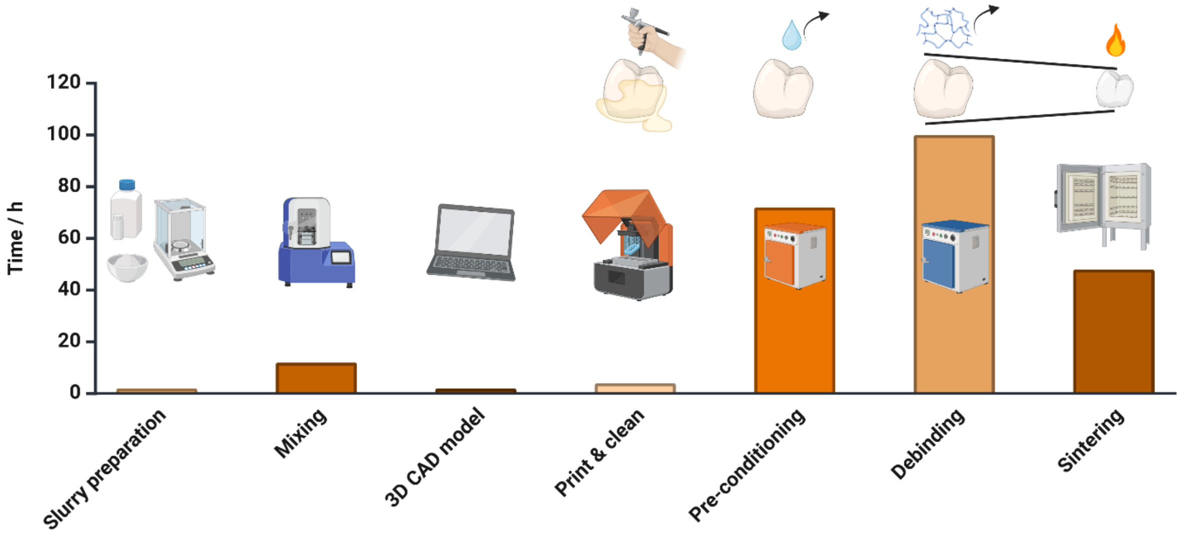

Figure 2. Processing steps of vat photopolymerization printing and the estimated average time used for each step in a 3D-printed batch of ceramic dental crowns. Created with BioRender.com.

In cerAM, this challenge was tackled by using an alternative pre-conditioning process utilizing supercritical carbon dioxide (scCO$_2$) extraction. In this method, the ceramic prints are placed in a reaction chamber, where carbon dioxide is heated and pressurized above its critical point to become a favorable solvent for certain organic compounds. Previously, the method has been successfully used for removing organics from injection molded ceramic parts [5,6], while for VPP the challenge was to find binder chemistry that works for both VPP printing and the scCO$_2$

extraction process. Our aim was to study if the $scCO_2$ extraction could be used to remove a part of the organic content of the VPP prints prior to thermal debinding, thus creating open porosity and therefore an easier route for the degradation gases to exit through during debinding. For the method to be useful, this needs to occur in a manner that preserves sufficient mechanical properties and high part density, without causing delamination between the printed layers.

The removal of 90 wt.% of the extractable organic content was successful with the use of $scCO_2$ extraction within only 2 h, once the $scCO_2$ density in the reaction chamber was high enough [7, 8]. The extraction created the desired nanosized porosity, leaving a crosslinked polymer network in the print to maintain the 3D shape of the ceramic part for further processing. Since a significant part of the organic binders were extracted with $scCO_2$, the time taken to burn away these substances was skipped during thermal debinding, already saving 30 h of the processing time. The optimized $scCO_2$ extraction did not cause delamination of the prints, and the study of the process's effect on the mechanical properties of sintered ceramic products is currently ongoing. Due to the apparent lack of alternative methods to thermal debinding, the results are highly interesting, and raise new research questions for the future regarding process optimization for different ceramic materials, with identified potential for even more savings to the processing time.

Wisematic Oy. The need for automation in ceramics printing has been clear from the start of the cerAM project. Tasks like cleaning the prints from print residue and manipulating the printed parts between different process phases still require human input. During the project, especially developing automatic cleaning methods for VPP prints was seen as a task with great potential for automation: it will shorten the time from a print to a product, reduce the need for human input, keep part quality more consistent and improve the operator safety.

Matti Suvanto, Mechanical Design Lead

Ceramic AM for improved quality of life. According to the World Health Organization (WHO), less than half of the world's population is covered by essential healthcare services and progress is needed in developing affordable solutions [9]. The AffordBoneS EU-MSCA - project (link) aims to provide personalized and affordable scaffolds for bone augmentation procedures to allow a larger population to have access to these treatments and improve their quality of the life. It is estimated that in Europe alone, 1.5 million augmentation procedures are required annually [10]. Obtaining an affordable and mass-customizable solution for maxillofacial bone augmentation procedures is essential for dental implants, for example when the patient does not have enough bone to attach the implantable screw to which the dental prosthesis can be attached. The AffordBoneS solution is to treat these patients with biomimetic scaffolds obtained by using 3D printable calcium phosphate ceramics multi-substituted with biofunctional ions (mCaP). The solution offers several advantages over the current technology, such as, removing the need for artificial growth factors, the potential cost reductions offered by the mass-customization approach and removing the need for a second scaffold removal operation.

Ion substitution represents a promising approach to improve the biological effectiveness of CaPs and composite materials currently used in bone tissue engineering applications. In AffordBoneS project, porous scaffolds mimicking the natural bone structure were additively manufactured with the ceramic VPP technique that utilizes digital light processing and photocurable ceramic resin. The impact of the selected trace elements (0, 1 and 5 mol.%

substitution) and the sintering temperature (900, 1000, 1100, 1200, and 1300 °C) was investigated in relation to the obtained crystalline phase content, microstructure, elemental distribution, thermal stability, and mechanical properties. After sintering, in addition to hydroxyapatite, β-tricalcium phosphate was detected as a result of the added trace elements in the calcium-deficient hydroxyapatite used as a starting powder. The obtained scaffolds exhibited uniform distribution of the trace elements, and they feature 3D-designed porosity predominantly ranging from 10 to 900 μm in diameter, with an average pore size of 546.25 ± 10.95 μm. The total porosity of scaffolds was 76.24 ± 1.32 vol% and an average wall thickness of 217.03 ± 8.98 μm, closely resembling the morphology of natural cancellous bone tissue. The mechanical properties of the scaffolds sintered at 1100 °C, 1200 °C, and 1300 °C were in line with those typically observed in cancellous bone. The study demonstrates the feasibility of using custom made bioactive hydroxyapatite powders together with vat photopolymerization to design the porosity and properties of the bone scaffolds on demand, based on the requirements of individual bone defects [11]. As a future direction, the obtained scaffolds with different porosities (**Figure 3**) and ion trace contents will be biologically tested in vitro using human bone marrow stem/stromal cells from both male and female donors, as we know that gender plays a significant role in bone related diseases.

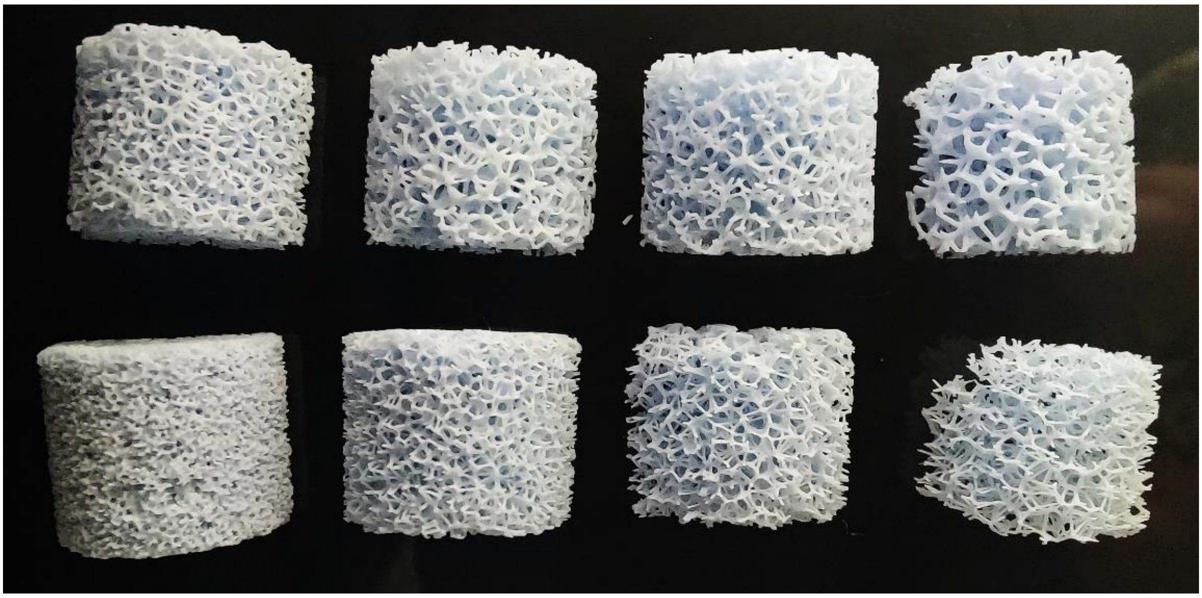

Figure 3. VPP printed and sintered ceramic scaffolds with calcium phosphate matrix. The multi-substituted scaffolds with biofunctional ions allow biomimetic and mass customizable bone implants with varying designed porosity and pore size distribution.

Additive manufacturing of Non-oxide ceramics. Silicon carbide (SiC) ceramics are an advanced group of materials used in a wide range of industries, including electronics, high-temperature processing, aerospace, abrasive applications, nuclear power, and armor protection. Due to challenging properties of SiC in solid-state sintering, the process of siliconizing, reaction bonding and reaction sintering has gained prominence as efficient and well-established technique to produce SiC ceramics. This method offers key benefits, such as fast production cycles, lower processing temperatures, and excellent adaptability to complex geometries, often requiring little to no post-machining for final shaping. In the reaction bonded SiC (RBSiC) process (**Figure 4**), molten silicon is infiltrated into a porous carbon/SiC preform consisting of primary SiC particles and carbon. This leads to the formation of additional silicon carbide (secondary SiC) in the pore spaces through a thermal reaction between the molten silicon and carbon. RBSiC has become widely adopted as an industrial ceramic material, known for its exceptional properties. However, traditional forming methods face difficulties in producing RBSiC with highly complex shapes and freedom of design, highlighting the need for new manufacturing techniques to meet the application demands.

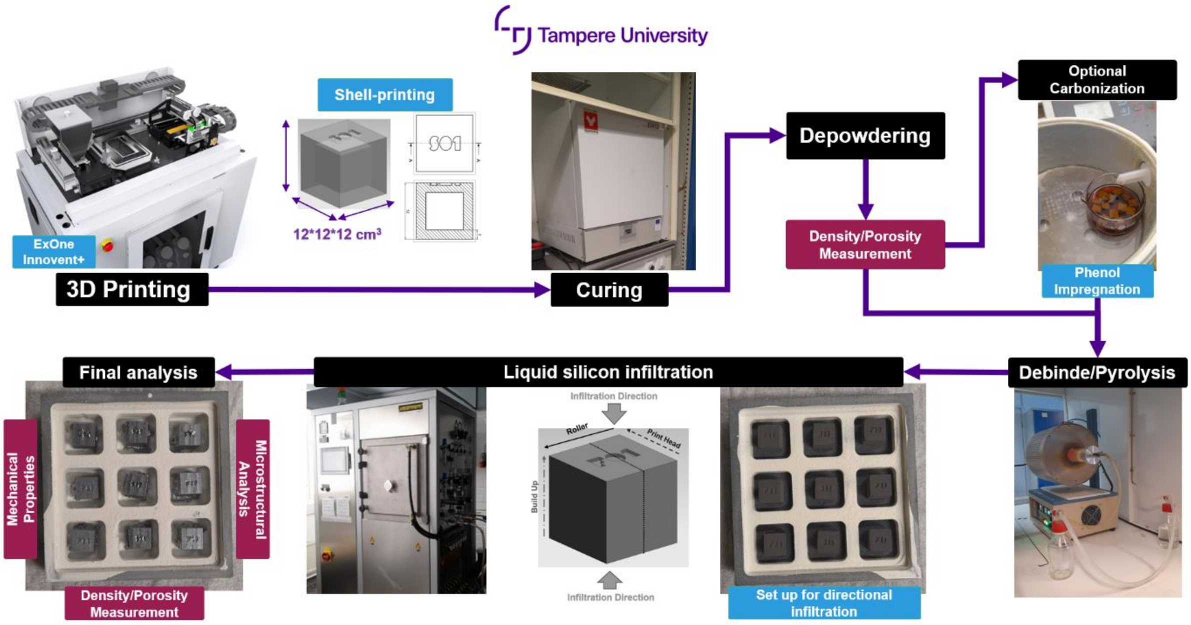

Figure 4. Diagram demonstrating the process flow in Binder Jetting of reaction bonded silicon carbide (RBSiC).

Binder Jetting (BJT), a promising additive manufacturing (AM) technology, provides design flexibility with the ability to build 3D objects layer-by-layer. In comparison to others ceramic AM methods, BJT is much less restricted in size of the printed component, with latest commercial binder jetting machines exhibiting build volumes upwards of 1 m^3. However, BJT has known challenges of creating highly porous components and having a large debinding shrinkage. The reaction sintering route has shown to be beneficial in addressing these shortcomings allowing fully dense ceramic products. The cerAM research focused on the critical factors in BJT of SiC ceramics, investigating how different parameters affect the densification, microstructure, and properties of RBSiC. Findings suggest that achieving a homogeneous microstructure and small grain size are the keys to enhance the mechanical properties of RBSiC components [12]. The research clarified important aspects of the process-structure-property relationship in Binder Jetting of Reaction Bonded SiC (BJT-RBSiC) and highlights for example that the reaction sintering is affected by layered structure of the 3D printed component.

Millidyne Oy. Binder jetting is an AM method that has several benefits, for example, large components can be printed at higher speed and with a broader selection of materials and design freedom. However, lower densities and surface finish qualities remain drawbacks to this method. Therefore, new printable materials and binders are needed to overcome these challenges. Millidyne develops ceramic powders for thermal spraying and binder jetting.

Jari Knuuttila, CTO

Summary and future outlook. Initially the cerAM project partners identified four major challenges in the way of industrial applicability of ceramic AM. Accordingly, the cerAM project has successfully: 1. Enabled the participating companies to understand where the high capital investments in light-based ceramic AM arise and identify a path towards more affordable devices. 2. Enabled the reduction of thermal post processing time in ceramic VPP up to 20%, with the potential to further decrease the time up to 50%. 3. Clarified the role of VPP binders in determining the debinding behavior, leading to better control on the final properties of the ceramic components, such as mechanical strength. 4. Successfully created premises to make the ceramic AM more user friendly and repeatable without the need of expert knowledge or prior experience, by identifying ways to automate difficult and laborious sub-processes, such as cleaning of the parts after VPP printing. In summary, the project successfully addressed all the main challenges identified, and as a result allows the continued accumulation of knowledge in ceramic AM, and transfer of technology to the Finnish industry. As an outlook to the future, there is a clear demand for more basic and applied research on the topic, however as the technology is maturing, clear market and R&D opportunities can also be identified at the company level. The challenge regarding applicability of AM remains also in the attitudes at the factory floor: by simply 3D-printing existing and mass-producible ceramic products does not create value as such and ceramic AM will not replace existing mass production methods any time soon. Instead focus should be in creating new value with the unique benefits and opportunities that the ceramic AM technology offers in creating competitive advantage. Research on ceramic AM continues at full speed at the Ceramic Materials research group of Tampere University (link) and aims to have three doctoral theses ready on the topic within the next three years. In addition, the group will host two post-doctoral researchers in the context of both VPP and BJT methods, and the group will continue to support companies interested in commercialization of ceramic AM.

References

[1] J. M. Suominen, E. J. Frankberg, P. K. Vallittu, E. Levänen, J. Vihinen, T. Vastamäki, R. Kari, L. V. J. Lassila, Three-dimensional printing of zirconia: characterization of early stage material properties, Biomaterial Investigations in Dentistry, 6:1, 23-31 (2019), https://doi.org/10.1080/26415275.2019.1640608

[2] S. Zakeri, M. Vippola, E. Levänen, A comprehensive review of the photopolymerization of ceramic resins used in stereolithography, Additive Manufacturing, Volume 35, (2020) 101177, https://doi.org/10.1016/j.addma.2020.101177

[3] C. Valenti, M. Isabella Federici, F. Masciotti, L. Marinucci, I. Xhimitiku, S. Cianetti, & S. Pagano, Mechanical properties of 3D-printed prosthetic materials compared with milled and conventional processing: A systematic review and meta-analysis of in vitro studies. Journal of Prosthetic Dentistry 132:2 (2022) 381-391. https://doi.org/10.1016/j.prosdent.2022.06.008

[4] K. Wang, M. Qiu, C. Jiao, J. Gu, D. Xie, C. Wang, X. Tang, Z. Wei & L. Shen. Study on defect-free debinding green body of ceramic formed by DLP technology. Ceramics International 46:2 (2020) 2438–2446. https://doi.org/10.1016/j.ceramint.2019.09.237

[5] T. Chartier, M. Ferrato, & J. E. Baumardat, Supercritical Debinding of Injection Molded Ceramics. J Am. Ceram. Soc 78 (1995) 1787–1792. https://doi.org/10.1111/j.1151-2916.1995.tb08890.x

[6] S. W. Kim, Debinding behaviors of injection molded ceramic bodies with nano-sized pore channels during extraction using supercritical carbon dioxide and n-heptane solvent. Journal of Supercritical Fluids 51:3 (2010) 339–344. https://doi.org/10.1016/j.supflu.2009.09.011

[7] N. Nurmi, E. J. Frankberg, M. Rinne, T. Sandblom, P. Konnunaho & E. Levänen. Enabling fast debinding of ceramic vat photopolymerization prints with supercritical carbon dioxide as a solvent. Additive Manufacturing 84 (2024) 104143. https://doi.org/10.1016/j.addma.2024.104143

[8] N. Nurmi, Debinding of Stereolithographically Printed Ceramic Parts: Supercritical Carbon Dioxide as Solvent, Master Thesis, Tampere University 2024, https://urn.fi/URN:NBN:fi:tuni-202212229727

[9] www.who.int/news/item/13-12-2017-world-bank-and-who-half-the-world-lacks-access-to-essential-health-services-100-million-still-pushed-into-extreme-poverty-because-of-health-expenses, cited on 12.9.2024

[10] A. Hoornaert and P. Layrolle, Dental Implants and Bone Grafts, Book Chapter 8 (2020) 207-215. https://doi.org/10.1016/B978-0-08-102478-2.00009-X

[11] A. Ressler, S. Zakeri, J. Dias, M. Hannula, J. Hyttinen, H. Ivanković, M.Ivanković, S. Miettinen, M. Schwentenwein, E. Levänen, E. J. Frankberg, Vat photopolymerization of biomimetic bone scaffolds based on Mg, Sr, Zn-substituted hydroxyapatite: Effect of sintering temperature, Ceramics International 50 (2024) 27403-27415. https://doi.org/10.1016/j.ceramint.2024.05.038

[12] M. I. Zakaria, Binder jetting of reaction bonded silicon carbide: Effects of printing and siliconizing modifications, Master Thesis, Tampere University 2024, https://urn.fi/URN:NBN:fi:tuni-202404254571