Effects of Solvent Debinding on the Microstructure and Properties of 3D-Printed Alumina Ceramics

He Li, Yongsheng Liu,* Yansong Liu, Kehui Hu, Zhigang Lu, and Jingjing Liang

ABSTRACT: Solvents assist in the debinding of stereolithography-based 3D-printed alumina green bodies. The green bodies subsequently undergo thermal debinding and sintering to obtain alumina ceramics. In this study, several solvents were tested, including polyethylene glycol, oxalic acid, ammonium hydroxide, ethyl alcohol, methyl methacrylate, butyl acetate, dimethyl carbonate, methanol, ethyl acetate, and sec-butyl alcohol. The tested solvents during the debinding process showed different effects on microstructure and properties of 3D-printed alumina ceramics due to the variable aspects of their solubility toward the binders. The microstructure of the samples changed significantly after green bodies underwent solvent debinding, thermal debinding, and sintering, leading to loose spongy structures, porous aggregates, and compact structures, respectively. Shrinkage, bulk density, and open porosity changed slightly due to the debinding function of different solvents. Polyethylene glycol-impregnated samples displayed the minimum shrinkage in length direction (5.3%). Ethyl alcohol-impregnated sample showed minimum shrinkage in width (4.8%) and height (11.5%) directions. Ammonium hydroxide-impregnated samples exhibited minimum bulk density (2.8 g/cm³) and maximum open porosity (28.3%). Dimethyl carbonate-impregnated samples presented minimum flexural strength (32.6 MPa), and oxalic acid-impregnated samples revealed maximum flexural strength (63.4 MPa). In sum, the as-obtained ceramics would be used as ceramic cores for hollow blades in aircraft engines due to their high open porosity and moderate flexural strength.

1. INTRODUCTION

Additive manufacturing, also known as 3D printing, has undergone rapid development since it was first invented by Hull in 1984. Compared with traditional subtractive manufacturing, integrated objects can be fabricated layer upon layer by 3D printing, which could save raw materials. Stereolithography is a popular technique in 3D printing technology due to its high precision, low cost, and elevated production efficiency. At present, many commercial 3D printers could fabricate elaborate polymer parts with high precision at low cost. However, ceramic stereolithography-based 3D printing still at the initial development stage, and fabrication of ceramic parts with high precision and superior efficiency through the stereolithography method is still hard to achieve.

The fabrication of ceramic parts using stereolithography suffers from several drawbacks. First, the addition of inorganic powders into photosensitive resins could reduce the precision of the printed green bodies due to different refractive indexes between the inorganic powders and photosensitive resins. Second, the degree of photopolymerization could decrease because of addition of inorganic powders. Finally, during the thermal treatment process composed of debinding and sintering processes, removal of the resins could result in deformation of the ceramic parts, sometimes even leading to cracks that will deteriorate the mechanical properties of the ceramics. Though many impact factors impede the precision and integrity of the ceramic parts, stereolithography-based 3D printing technology has undergone fast development recently due to its efficiency in fabrication of ceramics parts, especially alumina ceramics with moderate refractive index, high hardness, and low toughness. As for high-temperature resistance, hardness, and strength, alumina ceramics could be used to fabricate ceramic cores for the manufacturing of hollow blades in turbine engines. On the other hand, ceramic cores require high precision and complex structures to provide an elaborate internal structure for hollow blades. Because alumina ceramic cores have complex structures, the roughness of resulting alumina ceramics is rather low and manufacturing steps are complex. Traditionally, the manufacturing of ceramic cores is performed by investment casting with a long production cycle and high cost. These drawbacks have limited the development of turbine engines. Meanwhile, alumina ceramic cores should
satisfy the requirement of high open porosity (>20%) and moderate flexural strength (>30 MPa) to maintain good stability during the hollow blade manufacturing process.

For application in aviation industry and turbine engines, the fabrication of ceramic cores through stereolithography-based 3D printing is of great importance. Wu et al. combined stereolithography with gel casting to fabricate alumina ceramic cores and adopted a freeze-drying process to prevent cracks. They suggested that future research should focus on improvement of mechanical properties, such as flexural strength. Bae et al. fabricated silica ceramic cores through stereolithography-based 3D printing. They noticed formation of cristobalite and microcracks in ceramics, leading to reduced flexural strength of the ceramics. The fabrication of ceramic cores through stereolithography-based 3D printing technology is still not well developed, and many problems require solutions. The integrated fabrication steps mainly include preparation of ceramic slurries, 3D printing of green bodies, cleaning, debinding, and sintering. Here, we particularly focused on the debinding process.

Debinding is a key step to determine the precision of the final ceramics obtained from stereolithography. During the debinding process, cured photosensitive resins are removed from the green bodies due to the volatilization of the polymers during thermal treatment, leaving pores in the original polymers as filling positions. At fast rates of resin volatilization, large pores would form. In addition, deformation, bubbles, and some cracks would appear as gas spreads from the inside of the sample to the outside. On the other hand, the solvent impregnation process could assist in the removal of unreacted photosensitive resins from green bodies to prevent formation of cracks and deformation in ceramics. The most common debinding approaches include solvent, thermal, and catalytic debinding. Solvent debinding is fast and highly efficient at low cost. During the solvent debinding process, green bodies are impregnated in low-molecular solvents, accompanied by dissolving of the binders. As the binders and low-molecular solvents diffuse from bulk to the surface of the green bodies, resins will be removed from the green bodies. Thermal debinding is suitable for green bodies with a small size. This process undergoes pyrolysis or volatilization to remove organic binders. Catalytic debinding is a fast debinding process in which the binders rapidly decompose into volatile molecules in the catalyst atmosphere. These molecules will diffuse to the surface of the samples to complete the debinding process.

Current research dealing with a debinding process for 3D-printed ceramic parts is focused on thermal debinding. Zhou et al. optimized the debinding process of 3D-printed alumina ceramics and noticed that a two-step debinding process could control the volatilization rate of binders and suppress formation of defects in alumina ceramics. Some studies focused on solvent debinding for 3D-printed ceramics due to complex composition of green bodies. Green bodies impregnated in solvents could remove some portion of binders, and combining with thermal debinding could remove all binders in the parts and reduce deformation or cracks in the ceramics. During the 3D printing process, the liquid photosensitive resins turned to solid-state resins after polymerization. Current research dealing with solvent debinding of 3D-printed ceramics is still at the early stage. The chemical formula of cured polymers is still unknown, and whether traditional solvents used in debinding processes are effective for 3D-printed green bodies still requires further investigation. Traditional solvents such as alcohols, esters, and oxalic acid have been applied in the solvent debinding process for ceramics in powder injection molding. During the solvent debinding process, binders are dissolved in solvents to achieve the removal process. Different solvents induce variable solubilities of the binders. High-concentration solvents could promote the binder’s dissolution.

In this research, 10 kinds of solvents with 100% concentration (pure solvents) were tested for effective 3D-printed green bodies. The influence of solvent debinding on the microstructure and mechanical properties of alumina ceramics was investigated. The solvents included polyethylene glycol, oxalic acid, ammonium hydroxide, ethyl alcohol, methyl methacrylate, butyl acetate, dimethyl carbonate, methanol, ethyl acetate, and sec-butyl alcohol. Alumina green bodies were fabricated through 3D printing technology followed by solvent and thermal debinding and then sintering. The physical properties, shrinkage, flexural strength, and phase composition of the as-obtained alumina ceramics were studied to investigate the influence of different solvents.

2. MATERIALS AND METHODS

2.1. Fabrication of Alumina Green Bodies. A 3D printer (AutoceraM; Beijing Ten Dimensions Technology Co., Ltd.) was used for the fabrication of alumina green bodies (50 mm × 4 mm × 3 mm). To this end, alumina powders (495 g, AW-SF; Henan Hecheng Inorganic New Material Co., Ltd.) were added to photosensitive resins (100 g, AI100-1; Beijing Ten Dimensions Technology Co., Ltd.). The mixing process was performed slowly under vigorous stirring. The obtained alumina ceramic slurries were then ball-milled for 2 h in a planet-type grinding mill at the rate of 400 rpm. Next, the slurries were defoamed in vacuum for 10 min and used for 3D printing. The exposure dose was set to 3 mW/cm², single layer exposure time was 8 s, and layer thickness was 100 μm.

2.2. Solvent Debinding Process. The green bodies were impregnated in different solvents (pure solvent) for 24 h. Polyethylene glycol, oxalic acid, ammonium hydroxide, ethyl alcohol, methyl methacrylate, butyl acetate, dimethyl carbonate, methanol, ethyl acetate, and sec-butyl alcohol (Aladdin, China) were used as solvents to yield samples denoted as A, B, C, D, E, F, G, H, I, and J, respectively.

2.3. Thermal Debinding and Sintering. The as-obtained samples were then transferred to a tube furnace (Hefei Ke Jing Materials Technology Co., Ltd., China) for thermal debinding and sintering processes. The profile of the heating curve is shown in Figure 1.

2.4. Characterization. X-ray diffraction (XRD) was performed using an X-ray diffractometer (Bruker D8 FOCUS; Bruker Corporation, Germany) using Cu Kα radiation at 2θ from 10 to 90°, with a voltage of 40 kV, a current of 30 mA, and a scan rate of 0.02°−1 per step. Scanning electron microscopy (SEM) images were recorded using Helios G4 CX (FEI Corporation) equipment.

2.5. Physical and Mechanical Properties. The bulk density and open porosity of the sintered alumina ceramics were measured by the Archimedes principle. The accuracy of the balance was 0.0001 g (Mettler Toledo, Switzerland). The flexure strength of sintered alumina ceramics was tested using an electronic universal testing machine (CMT4304; Suns, China) using three-point flexural tester at a loading speed of 0.5 mm/min and a span of 30 mm.
3. RESULTS AND DISCUSSION

3.1. Microstructure of Impregnated, Debounded, and Sintered Samples. The SEM images of the green bodies impregnated in different solvents are shown in Figure 2. Though the green bodies were impregnated in different solvents, their microstructure showed similarities. The samples displayed three parts: alumina particles, cured photosensitive resins, and pores. The green bodies were formed by photocuring of alumina ceramic slurries during the 3D printing process. Some portions of photosensitive resins remained uncured due to the limited extent of polymerization. These unreacted photosensitive resins left in the green bodies are more likely to produce cracks in the ceramics due to the violent volatilization process. The solvent impregnation process would remove unreacted photosensitive resins and help in maintaining the original shape of the ceramic parts. As shown in Figure 2a−d, alumina particles looked connected together because cured photosensitive resins served as binders. During the 3D printing process, the photosensitive resins turned to binders to complete the fabrication of green bodies. On the other hand, some portions of the binders were removed from bulk green bodies to form pores at original binder-filled positions because the green bodies were impregnated in the solvent (Figure 2h and j). Some differences among different solvent-impregnated samples were also noticed. As shown in Figure 2d and g, pores existed in the samples were more significant than those found in other solvent-impregnated samples. Also, size of the pores was larger than that of other samples, suggesting that when the green bodies were impregnated in ethyl alcohol and dimethyl carbonate, the binders were removed easily than in samples impregnated in other solvents. The pore number increased as the quantity of binders removed from the green bodies increased. As shown in Figure 2b and h, alumina particles looked well connected with almost no pores in the samples, indicating that oxalic acid and methanol could hardly remove the binders from the green bodies.

During the solvent debinding process, the binders composed of cured photosensitive resins were dissolved in the solvents and then removed from the green bodies. The microstructure of the samples demonstrated different solubility of the binders in various solvents (Figure 2). Combined with the above data, it is suggested that solubility of cured photosensitive resins in ethyl alcohol and dimethyl carbonate was greater than that in other solvents. The solubility of cured photosensitive resins in oxalic acid and methanol were low when compared with that in other solvents.

As shown in Figure 2, resins appeared to exist in every solvent-impregnated sample, indicating that the solvents could not completely remove the resins from the green bodies. This would explain why solvent-debnded samples still require thermal
debinding to remove the residue resins. The results were consistent with those reported by Zhao et al., who investigated the effect of solvent debinding in ZrO₂ ceramics in injection molding. Their data showed that binders could not be completely extracted using only solvent debinding.

The SEM images of the samples after the thermal debinding process are shown in Figure 3. After thermal debinding treatment, the microstructure of the samples changed significantly. Many pores appeared in the samples due to the removal of the binders. As shown in Figure 3b and h, the unremoved binders after the solvent debinding process were removed during the thermal debinding process (Figure 2b and h). This was due to the binders that could be decomposed at 550 °C and the resulting gas could escape from the green bodies. That is to say, the resins volatilized due to the thermal treatment process. As shown in Figure 3e and f, the particles were not connected together after thermal debinding treatment due to the relatively low debinding temperature of 550 °C, unsuitable for...
aggregation of the alumina particles. Figure 3g and i also indicated that distribution of the particles was uniform. Two types of alumina particles existed in the samples, while the small particles were surrounded by larger particles. This size difference in the alumina particles (Figure 3) was due to variation in the original size of raw materials. According to Zeng et al., the sintering driving force increased as the particle size decreased. The smaller particles could promote the sintering process of alumina ceramics. Wu et al. investigated the particle size of 3D-printed alumina ceramics and found that alumina powders are of bimodal particle size, leading to 3D ceramics with good performance. According to Chang et al., the viscosity of alumina slurries decreased as the particle size increased. The addition of some alumina particles with large size benefited the 3D printing process due to the reduced viscosity of alumina slurries. The thermal-debinned samples displayed bimodal distribution of alumina powders in raw materials, conducive to both sintering and 3D printing processes.

The SEM images of the samples after sintering are displayed in Figure 4. Compared with debinded samples (Figure 3), the microstructure of sintered alumina ceramics changed significantly. The small particles shown in Figure 3 grow larger (Figure 4). Most particles were connected together due to the growth of alumina grains under a high sintering temperature (1500 °C). As shown in Figure 4d and g, bonding of the grain boundary between alumina grains looked relatively weak due to difference in the microstructure of the samples after the solvent debinding process. More and larger pores as shown in Figure 2d and g led to a weak connection in sintered alumina ceramics (Figure 4d and g). In addition, bonding of the grain boundary between alumina grains looked relatively strong (Figure 4b and h). This was attributed to the close connection between alumina particles after the solvent debinding process (Figure 2b and h). Compared with 3D-printed Al₂O₃−ZrO₂ ceramics fabricated by Wu et al., many pores appeared as shown in Figure 4 due to lack of ZrO₂. These pores may decrease the flexural strength due to weak bonding between particles.

The microstructure of the samples after solvent debinding, thermal debinding, and sintering processes looked different. The variation at each stage could pass to the next stage and lead to changes in physical and mechanical properties. During solvent and thermal debinding processes, the binders were removed from the green bodies, creating the driving force for alumina particles to scatter. During the sintering process, the driving force promoted the aggregation of particles, leading to ceramics with high hardness, superior strength, and a stable microstructure.

3.2. Physical Properties of Sintered Alumina Ceramics.

The shrinkage of sintered alumina ceramics impregnated in different solvents is shown in Figure 5. Note that the shrinkage in different directions looked significantly different. The shrinkage in the height direction was much greater than that in length and width directions. On the other hand, the shrinkage in the length direction appeared almost equal to the shrinkage in the width direction. This phenomenon was common in 3D-printed ceramics due to layer-by-layer formation mode. Guo et al. fabricated titanium dioxide ceramics through 3D printing and found that sintered samples exhibited an anisotropic shrinkage phenomenon. In other words, shrinkage in the X (60.29%) direction was greater than that in the Y (60.21%) direction. They related the anisotropic shrinkage phenomenon mainly to the layered manufacturing process. Bourell et al. fabricated glass through 3D printing to yield ceramics with significant anisotropy. They attributed the difference to the layer-by-layer forming method and burn-off of the binders. The green bodies were formed by the pile-up of layers in the height direction, and the integrated object was built through the layer-by-layer mode. While one layer (length−width plane) was cured under certain time the photosensitive resin exposed to ultraviolet light, the object moved to certain thickness in the height direction. Thus, the connection mode and binding force in the height direction were different from those in the length−width plane. Since green bodies suffered from solvent debinding, thermal debinding, and sintering processes, the different binding forces resulted in different shrinkage of alumina ceramics.

Some differences in shrinkage of samples impregnated in different solvents were noticeable. As shown in Figure 5, the polyethylene glycol-impregnated sample showed minimum shrinkage in the length direction (5.3%). The ethyl alcohol-impregnated sample displayed a shrinkage of 5.7% in the length direction, 5.7% in the width direction, and 11.5% in the height direction. This may be attributed to the difference in the dissolving ability of each solvent. The microstructure of different solvent-impregnated samples changed slightly after the solvent debinding process, and small differences led to different shrinkage of samples after sintering. The sintering process mainly reduced the pores, promoting grain connection and the densification process. Because the sintering temperature (1500 °C) was much greater than the thermal debinding temperature, thereby, temperature is the main factor that determines the microstructure of the ceramics. As shown in Figure 5, the shrinkage in the height direction was also much greater in several samples compared with that in length and width directions. This may be linked to the weak binding force between layers in the green bodies. When green bodies were impregnated in the solvents, the binders between layers were easier to remove when compared with binders in length and width directions. The solvents showed a stronger influence in the height direction than in length and width directions, leading to great fluctuations in the height direction. From Figure 5, polyethylene glycol and ethyl alcohol were found to be good debinding solvents due to low shrinkage. The polyethylene glycol-impregnated sample displayed a shrinkage of 5.3% in the length direction, 5.7% in the width direction, and 11.6% in the height direction. The ethyl alcohol-impregnated sample resulted in a shrinkage of 5.7% in the length direction,

Figure 5. Shrinkage of sintered alumina ceramics impregnated in different solvents.
4.8% in the width direction, and 11.5% in the height direction. The ethyl alcohol-impregnated samples could remove more content of photosensitive resins than oxalic acid-impregnated samples due to its greater solubility in photosensitive resins. Therefore, the residual photosensitive resin was smaller for the ethyl alcohol-impregnated samples than that for oxalic acid-impregnated samples during the thermal treatment process. At the same time, the thermal treatment process has a significant influence on the shrinkage of the sintered samples. Therefore, the ethyl alcohol-impregnated samples exhibited a smaller shrinkage when compared with the oxalic acid-impregnated samples.

The bulk density and open porosity values of different solvent-impregnated samples are shown in Figure 6. The bulk density of different samples ranged from 2.8 to 3.0 g/cm³, and the open porosity of different samples varied from 25.8 to 28.3%. The differences in bulk density and open porosity of different solvent-impregnated samples were very small but fluctuations were observed as shown in Figure 6. Considering the application of alumina ceramics in ceramic cores, greater open porosity would benefit the removal process for the manufacturing of hollow blades. As shown in Figure 6, the ammonium hydroxide-impregnated samples resulted in greatest open porosity with a value of 28.3%. Thus, ammonium hydroxide was a better solvent for impregnation of alumina ceramics in ceramic cores, greater open porosity.

3.3. Phase Composition of Sintered Alumina Ceramics. XRD patterns of different solvent-debinding samples are shown in Figure 7. Different solvent-impregnated samples presented identical phase composition of α-Al₂O₃ without any change in phase composition. Because α-Al₂O₃ is the most stable phase among different alumina, it could resist higher temperatures when compared with other crystal alumina. This would explain why alumina was selected for the manufacturing of ceramic cores with high-temperature resistance ability. On the other hand, the solvents applied for removal of the binders mainly changed the connections between binders and alumina particles with no relationship to the alumina phase composition.

3.4. Mechanical Properties of Sintered Alumina Ceramics. The flexural strength of alumina ceramics impregnated in different solvents is shown in Figure 8. The flexural strength ranged from 32.6 to 63.4 MPa. Different solvents displayed significant influences on flexural strength of alumina ceramics. Oxalic acid-impregnated samples exhibited a maximum flexural strength of 63.4 MPa, and dimethyl carbonate-impregnated samples exhibited a minimum flexural strength of 32.6 MPa. Slight differences in the flexural strength were noticed between samples impregnated in polyethylene glycol, ammonium hydroxide, ethyl alcohol, methyl methacrylate, butyl acetate, methanol, ethyl acetate, and sec-butyl alcohol.
The microstructure of the samples changed significantly after green bodies underwent solvent debinding, thermal debinding, and sintering, leading to loose spongy structures, porous aggregates, and compact structures, respectively.

(2) Shrinkage, bulk density, and open porosity changed slightly in various solvents. Polyethylene glycol-impregnated samples showed minimum shrinkage in the length direction. Ethyl alcohol-impregnated samples displayed minimum shrinkage in width and height directions. Ammonium hydroxide-impregnated samples exhibited minimum bulk density and maximum open porosity.

(3) Dimethyl carbonate-impregnated samples displayed minimum flexural strength, and oxalic acid-impregnated samples showed maximum flexural strength. The high-temperature treatment during the sintering process formed an α-alumina phase in different samples. No phase change occurred after impregnation and sintering processes.

The influence factors of different solvents on 3D-printed alumina ceramics were examined. The diffuse driving force of binders in the solvents would be significantly influenced by concentration of the solvents and impregnation time of the green bodies. However, further research on solvent debinding is necessary in terms of concentration of the solvents and impregnation time of the green bodies.

4. CONCLUSIONS
The influence factors of debinding in different solvents on microstructures, physical properties, and mechanical properties of alumina ceramics fabricated through stereolithography-based 3D printing technology were examined. To this end, numerous solvents were tested, including polyethylene glycol, oxalic acid, ammonium hydroxide, ethyl alcohol, methyl methacrylate, butyl acetate, dimethyl carbonate, methanol, ethyl acetate, and sec-butyl alcohol. The following conclusions could be drawn:

sintering temperature (1500 °C) and the solvent debinding effect.

Compared with microstructures obtained at different stages, oxalic acid-impregnated samples showed closely connected particles after solvent impregnation (Figure 2b) with more pores after thermal debinding (Figure 3b) and strong binding between grain boundaries for sintered alumina ceramics (Figure 4b). This led to a higher flexural strength, following the maximum flexural strength of oxalic acid-impregnated samples (63.4 MPa, Figure 8). Meanwhile, dimethyl carbonate-impregnated samples displayed more pores after the solvent impregnation process (Figure 2g), loose connections between particles after thermal debinding (Figure 3g), and weak binding between grain boundaries of sintered alumina ceramics (Figure 4g). These results were consistent with the minimum flexural strength obtained with dimethyl carbonate-impregnated samples (32.6 MPa, Figure 8).

The samples without impregnation in any solvents exhibited a greater flexural strength of about 138.5 MPa. This phenomenon indicated that solvent debinding tends to lead a smaller flexural strength when compared with the samples without impregnation in any solvents. The influence factors on the flexural strength of the ceramics are complex, which may be determined by microstructures, physical properties, cracks, and other factors. Though oxalic acid presents low solubility of photosensitive resins and the corresponding samples are more likely to develop cracks, the corresponding sintered samples lead to the maximum flexural strength among these samples.

AUTHOR INFORMATION
Corresponding Author
Yongsheng Liu – Science and Technology on Thermostructural Composite Materials Laboratory and NPU-SAS Joint Research Center of Advanced Ceramics, Northwestern Polytechnical University, Xi’an, Shaanxi 710072, China; orcid.org/0000-0002-9020-7202; Phone: +86 029 88495179; Email: yongshengliu@nwpu.edu.cn; Fax: +86 029 88494620

Authors
He Li – Science and Technology on Thermostructural Composite Materials Laboratory and NPU-SAS Joint Research Center of Advanced Ceramics, Northwestern Polytechnical University, Xi’an, Shaanxi 710072, China
Yansong Liu – Science and Technology on Thermostructural Composite Materials Laboratory and NPU-SAS Joint Research Center of Advanced Ceramics, Northwestern Polytechnical University, Xi’an, Shaanxi 710072, China
Kehui Hu – Department of Mechanical Engineering and State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China
Zhigang Lu – Department of Mechanical Engineering and State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China
Jingjing Liang – Chinese Academy of Sciences, Institute of Metal Research, Shenyang 110016, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03944

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was supported by the National Key Research and Development Program of China (No. 2018YFB1106600), the
REFERENCES

(1) Hull, C. W.; inventor Apparatus for production of three-dimensional objects by stereolithography. US4575330A Patent US4. 1984.
(2) Halloran, J. W. Ceramic stereolithography: additive manufacturing for ceramics by photopolymerization. Annu. Rev. Mater. Res. 2016, 46, 19–40.
(3) Morimoto, Y.; Tan, W. H.; Takeuchi, S. Three-dimensional axisymmetric flow-focusing device using stereolithography. Biomed. Microdevices 2009, 11, 369–377.
(4) Brakora, K. F.; Halloran, J.; Sarabandi, K. Design of 3-D monolithic MMW antennas using ceramic stereolithography. IEEE Trans. Antennas Propag. 2007, 55, 790–797.
(5) Halloran, J. W.; Tomecka, V.; Gentry, S.; Das, S.; Clilino, P.; Yuan, D. Photopolymerization of powder suspensions for shaping ceramics. J. Eur. Ceram. Soc. 2011, 31, 2613–2619.
(6) Li, H.; Liu, Y.; Liu, Y.; Zeng, Q.; Hu, K.; Lu, Z.; Liang, J. Effect of burying sintering on the properties of ceramic cores via 3D printing. J. Manuf. Process. 2020, 57, 380–388.

(7) Michiel, W.; Silvia, M.; Dana, B.; Guus, B.; Egbert, O.; Willeke, F.; Toin, H. Introduction of specific 3D micromorphologies in collagen scaffolds using odd and even dicarboxylic acids. ACS Omega 2020, 5, 3908–3916.
(8) Li, H.; Liu, Y.; Liu, Y.; Zeng, Q.; Hu, K.; Lu, Z.; Liang, J. Effect of debinding temperature under an argon atmosphere on the microstructure and properties of 3D-printed alumina ceramics. Mater. Charact. 2020, 168, 110548.
(9) Li, H.; Liu, Y.; Liu, Y.; Zeng, Q.; Wang, J.; Hu, K.; Lu, Z.; Liang, J. Evolution of the microstructure and mechanical properties of stereolithography formed alumina cores sintered in vacuum. J. Eur. Ceram. Soc. 2020, 40, 4825–4836.
(10) Zukal, A.; Siklova, H.; Cejka, J. Grafting of alumina on SBA-15: effect of surface roughness. Langmuir 2008, 24, 9837–9842.
(11) Gromada, M.; Swieca, A.; Kostekci, M.; Olszy, A.; Cygan, R. Ceramic cores for turbine blades via injection moulding. J. Mater. Process. Tech. 2015, 220, 107–112.
(12) Yezaq, Q.; Albing, D.; Rui, Z. Alumina-based ceramic core composites for investment casting. Rare Metal Mat. Eng. 2007, 36, 774.
(13) Wu, H.; Li, D.; Tang, Y.; Sun, B.; Xu, D. Rapid fabrication of alumina-based ceramic cores for gas turbine blades by stereolithography and gelcasting. J. Mater. Process. Tech. 2009, 209, 5886–5891.
(14) Bae, C. J.; Kim, D.; Halloran, J. W. Mechanical and kinetic studies on the refractory fused silica of integrally cored ceramic mold fabricated by additive manufacturing. J. Eur. Ceram. Soc. 2019, 39, 618–623.
(15) Krauss, V. A.; Oliveira, A. A. M.; Klein, A. N.; Al-queshi, H. A. A model for PEG removal from alumina injection moulded parts by solvent debinding. J. Mater. Process. Tech. 2007, 182, 268–273.
(16) Liu, L.; Loh, N. H.; Tay, B. Y.; Tor, S. B.; Murakoshi, Y.; Maeda, R. Effects of thermal debinding on surface roughness in micro powder injection molding. Mater. Lett. 2007, 61, 809–812.
(17) Fu, G.; Loh, N. H.; Tor, S. B.; Tay, B.; Murakoshi, Y.; Maeda, R. Injection molding, debinding and sintering of 316L stainless steel microstructures. Appl. Phys. A: Mater. Sci. Process. 2005, 81, 495–500.
(18) Zhou, M.; Liu, W.; Wu, H.; Song, X.; Chen, Y.; Cheng, L.; He, F.; Chen, S. Preparation of a defect-free alumina cutting tool via additive manufacturing based on stereolithography—Optimization of the drying and debinding processes. Ceram. Int. 2016, 42, 11598–11602.
(19) Bordet, F.; Chartier, T.; Baumard, J. F. The use of co-solvents in supercritical debinding of ceramics. J. Eur. Ceram. Soc. 2002, 22, 1067–1072.
(20) Liu, D. F.; Huang, J. L.; Wu, B. S. Optimisation of injection moulding process for silicon nitride components. Powder metal. 1996, 39, 291–295.