

Gel-casting for manufacturing porous alumina ceramics with complex shapes for transpiration cooling

Y. Belrhiti^a, P. Kerth^b, M. McGilvray^b and L. Vandeperre^a

^aDepartment of Materials, Imperial College London, London, UK; ^bOxford Thermofluids Institute, University of Oxford, Oxford, UK

ARTICLE HISTORY Received 6 December 2022; Accepted 26 September 2023

Introduction

Various porous materials have been used for transpiration cooling experiments including ultra-high-temperature-ceramic (UHTCs) such as ZrB₂ [1]. Thanks to their low thermal conductivity, high emissivity and ability to be formed into complex shapes, Al₂O₃ porous ceramics are good candidates for short-duration hypersonic wind tunnel testing [2] to mimic the porous structure of ZrB₂ used for transpiration cooling in hypersonic flights at high temperatures [3]. Transpiration cooling technology is based on the introduction of a cool layer of gas between the component and the hot freestream flow to reduce the heat flux to the material in a hostile environment [4–9]. Different techniques can be used to obtain ceramic materials of complex shapes such as 3D printing which enables the creation of complex shapes layer by layer making it highly customisable, however, material choices might be limited in addition to the slip-casting process which involves pouring a ceramic slurry into a mould, making it suitable for complex shapes. It is more adapted for high-density ceramics and achieving uniform material distribution can be challenging. The process selected to prepare these porous samples is gel-casting which has rapidly evolved from a laboratory [10] invention to industrial applications in different sectors. Its great advantages [11] are that very complex shapes at different scales can be made with relative ease with high green strength, low organic content, easy binder removal performed during sintering and highly homogeneous material properties. Previously in gel-casting formulations, gelation was obtained through polymerisation of acrylamide monomers, which are classified as neuro-toxic, then, replaced by a non-toxic gel former such as gelatine [12].

This paper is dedicated to describing the different steps adopted and the challenges faced to prepare complex shapes of porous Al₂O₃ ceramics using gel-casting. The gel-cast parts are consisting of water

deionised, powder, dispersant, anti-foaming agent, urea and gelation initiator and are obtained from a slurry that is cast, gelled, dried then sintered. The process has been optimised to satisfy the required specifications without damage or defect.

Among these challenges, drying uniformly at the same rate remains one of the most critical. Indeed, porous materials with low loading powder and complex shapes are particularly difficult to properly dry without introducing internal stresses. Decreasing solid loading in the porous structure of the gel-cast part induces a higher water potential in addition to this, the low solid particle packing is equivalent to the low resistance of internal moisture diffusing to the surface of the gel-cast part. Besides, the shape complexity presents a non-uniform and differential drying, and so, mechanical stress apparition is caused by non-uniform shrinkage in the edges separating different parts with nonuniform thicknesses. Different solutions are proposed to obtain a sintered sample without damage [13–15].

Experimental

Gel-casting approach can be summarised in three states represented in Figure 1:

- *A fluid state* (a) in which the suspension of ceramic powder is liquid, particles made to repel each other via surface charge or dispersant.
- *A wet weak solid* (b) in which the suspension of ceramic powder is gelled. The gelation of liquid freezes the entire system, and the fluid becomes solid.
- *A dry rigid solid* (c) in which ceramic particles are in contact. Drying removes the water and shrinks the body.

Figure 2 details the different steps of the process: Solution preparation

CONTACT Y. Belrhiti  younes.belrhiti@gmail.com  Department of Materials, Imperial College London, London, SW7 2A, UK

© 2023 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group
 This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. The terms on which this article has been published allow the posting of the Accepted Manuscript in a repository by the author(s) or with their consent.

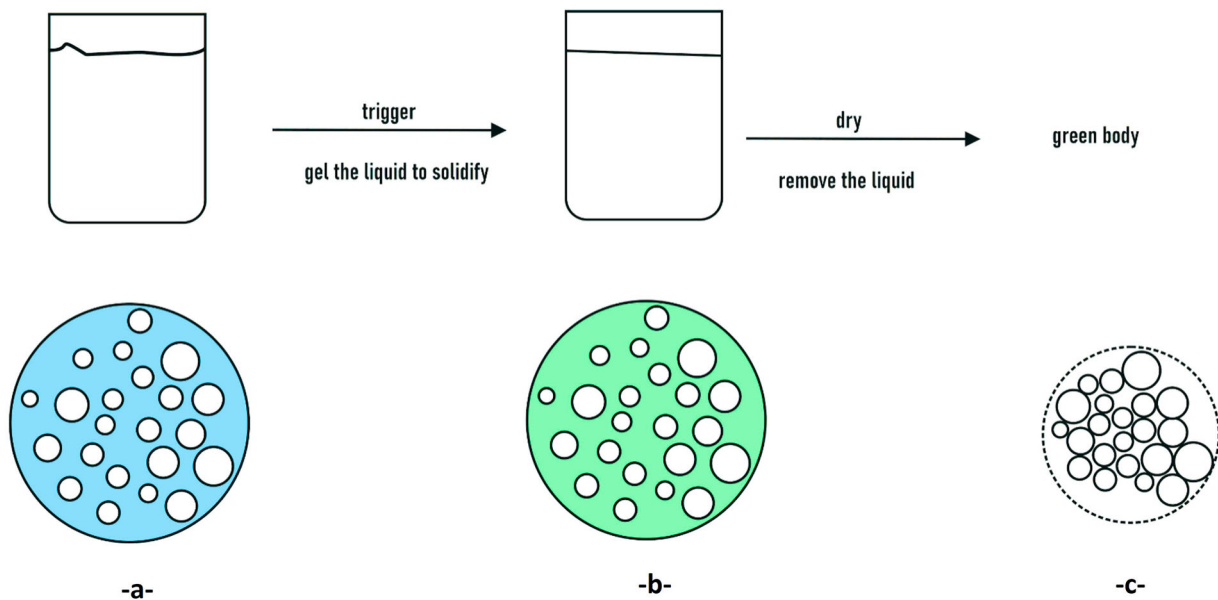


Figure 1. Gel-casting principle.

1. Gelatine (3wt-%) from bovine skin (type B, powder) is dissolved with 15% wt of Urea (Sigma Altech) which is a waste product that the liver makes when it degrades proteins both from the diet and from tissue protein turnover. Gelatine has been used as a binder which has clear advantages over monomers in terms of toxicity [12]. Gelatine will remain in solution as individual long chains and the suspension will remain fluid as the addition of Urea avoids heating gelatine so it can be used at room temperature.
2. Dispersant (Dolapix CE 64) is added (2 ml/100 g of powder) with an anti-foaming agent (Octanol)

and 45%vol alumina powder (Almatis, $d_{0.5} = 6.45\mu\text{m}$). The solution is homogenised by ball milling with alumina media for 24 h using normal rotation.

Gel-casting initiation

3. Urease (*Canavalia ensiformis*) is added which is an enzyme that catalyses urea hydrolysis (5U/mmol of urea). Urease initiates the gelation process and is an enzyme that catalyses urea hydrolysis, forming

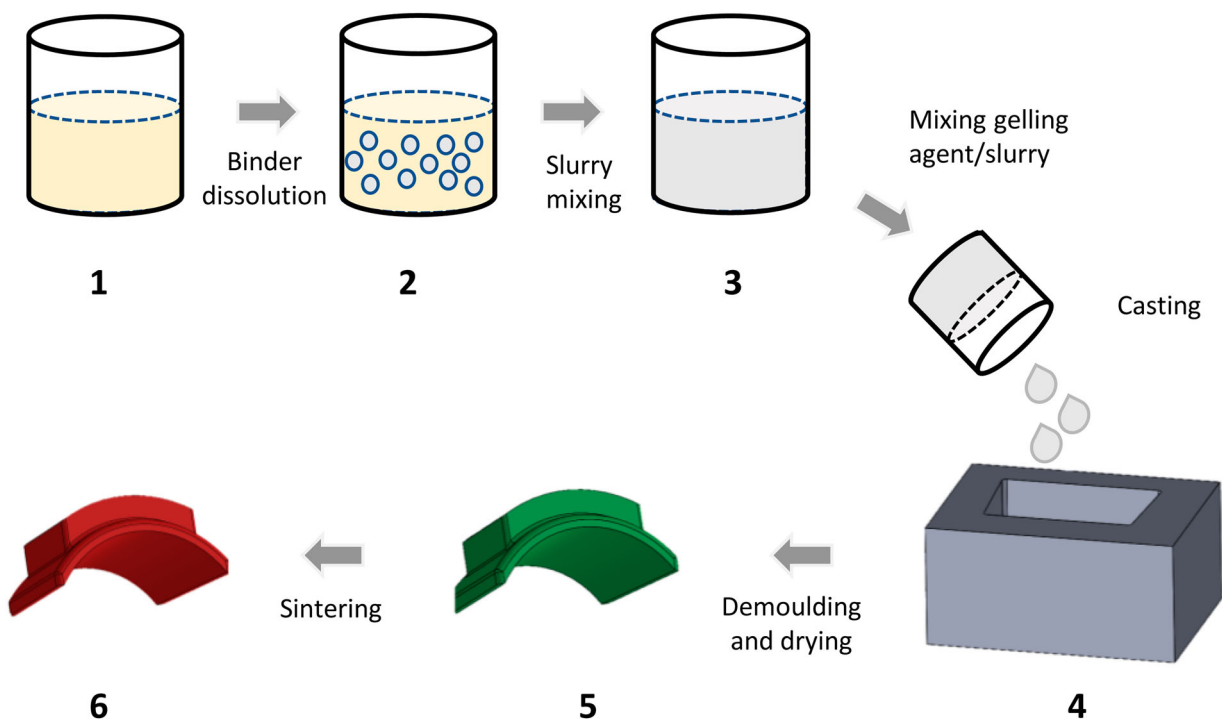
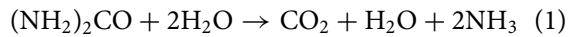


Figure 2. Different steps of the gel-casting process.

carbon dioxide and ammonia as described in the Equation (1):



The solution is mixed slowly for 1 h using ball milling before casting

Casting

- The slurry is cast in the mould. The mould was prepared using DLP (Digital Light Printing) and CNC machining. A spray WD40 was used for an easy demould before casting. Casting is coupled with vibration to avoid the presence of air trapped inside the slurry. The sample is kept for the gelation step for 24–48 h inside the mould depending on sample geometry.

Drying and sintering

- The sample is demoulded and dried.
- The green body is sintered with slow heating (3°C/min) with 1 h dwell time at 350°C for the elimination and the burnout of the binders and 3 h dwell time at 1500°C.

Results

Case of study 1: Al_2O_3 cones with different nose tip diameter

Two conical porous Al_2O_3 ceramics are elaborated using the process of gel-casting. Both shapes contain a central conical hole with a base diameter of 5 mm:

- 1 mm nose tip: cone length is 65 mm and the hole length is 64.5 mm.
- 3 mm nose tip: cone length is 51 mm and the hole length is 48.5 mm.

The mould (Figure 3(a)) is conceived using DLP. To generate the internal hole, needles are designed, printed using DLP and introduced into the gel after casting, then removed before sintering. The sample is partially dried in the mould after removing the needle (Figure 3(b)) in the air. After demoulding, it was noticed that while free drying in the air or the dryer (80°C), cracks are initiated and propagated inducing sample damage. This can be justified by the low content of ceramic powder and the different thicknesses of the geometry which induces a nonuniform and differential drying generating structural and residual stresses.

This issue was resolved using the following solutions:

- Drying using liquid desiccant* [14]: The sample is brought into contact with an appropriate liquid desiccant by immersion (PEG6000). The reason for the effect of the liquid desiccant on a gel-cast part is the osmotic difference between the liquid desiccant and the gelled sample. Drying in the PEG6000 is suitable for the gel-cast part to avoid cracking. Samples lose more weight with the increase in the PEG molecular weight which tends to form hydrogen bonds with H_2O and so promotes the penetration of the moisture of the green body into the PEG solution. The sample was dried for 3 h in a PEG6000 solution (60% wt. of DI water mixed with 40% wt. of PEG6000).
- Drying in the mould with specific heating*: The sample is kept in the mould in a preheated oven

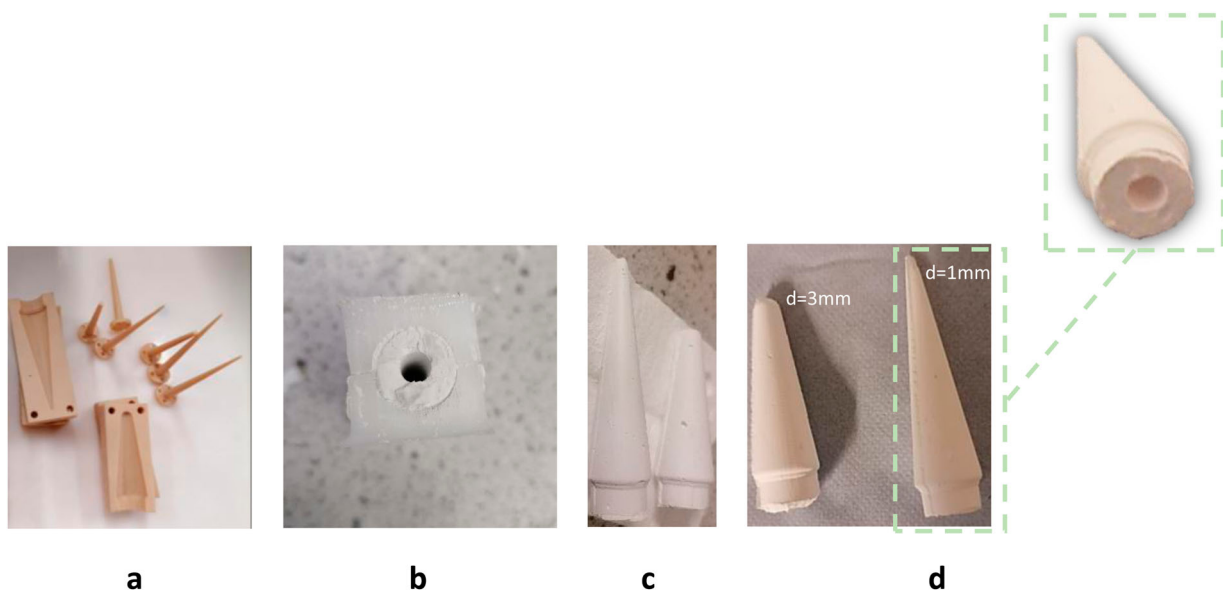


Figure 3. Al_2O_3 cones elaboration.

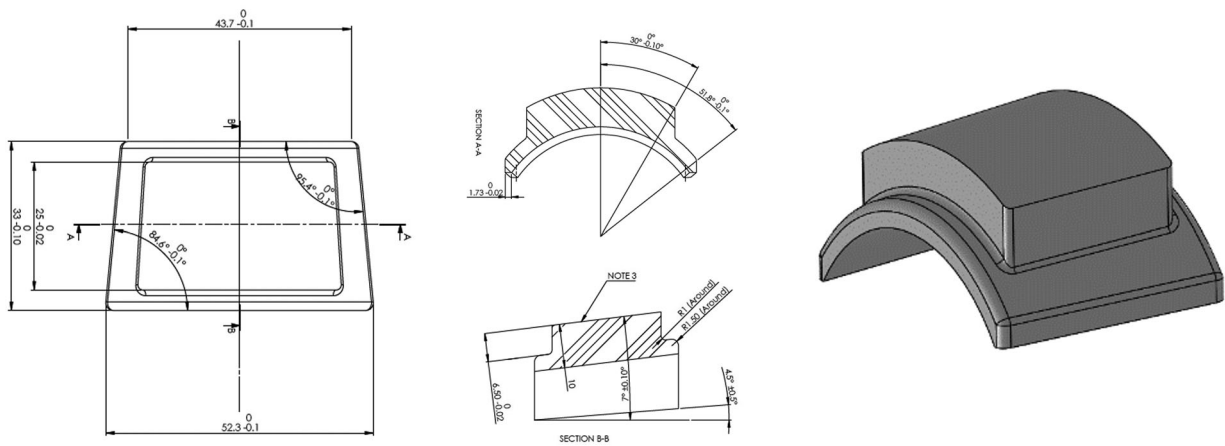


Figure 4. Frustum insert geometry.

at 60°C for 30mn [16], then, demoulded (Figure 3 (c)). It allows the acquisition of additional mechanical properties.

The samples are then sintered. The density evaluated of obtained samples in this study is 2.58 (± 0.01) g/cm³ and the open porosity estimated is 25 (± 1) %.

The final shapes are represented in (Figure 3(d)). It was noticed that during sintering, a shrinkage of 1% was noticed. For this reason, a scale factor of 1.01 was applied to catch up with the noticed difference.

Case of study 2: Al₂O₃ Frustum insert

A curved shape with two different thicknesses to be inserted into an experimental cavity dedicated to

transpiration cooling testing is elaborated using gel-casting (Figure 4).

The same process presented previously is used. Among the challenges faced with this shape, in addition to shrinkage catch-up, is to obtain a complete sample without damage with a smooth external surface without inclusions or bubbles. To do so, it was necessary to limit vibration during casting.

After demoulding the sample, it was noticed a shape deformation (an increase of the angle of curvature) owing to the weak wet body which doesn't have enough mechanical properties to keep a fixed shape in addition to crack initiation in the edges between the different parts with different thicknesses.

For this reason, it is necessary to improve the demoulding and drying steps. Considering the complexity of this shape, drying inside the mould was preferred to avoid shape deformation while demoulding or drying:

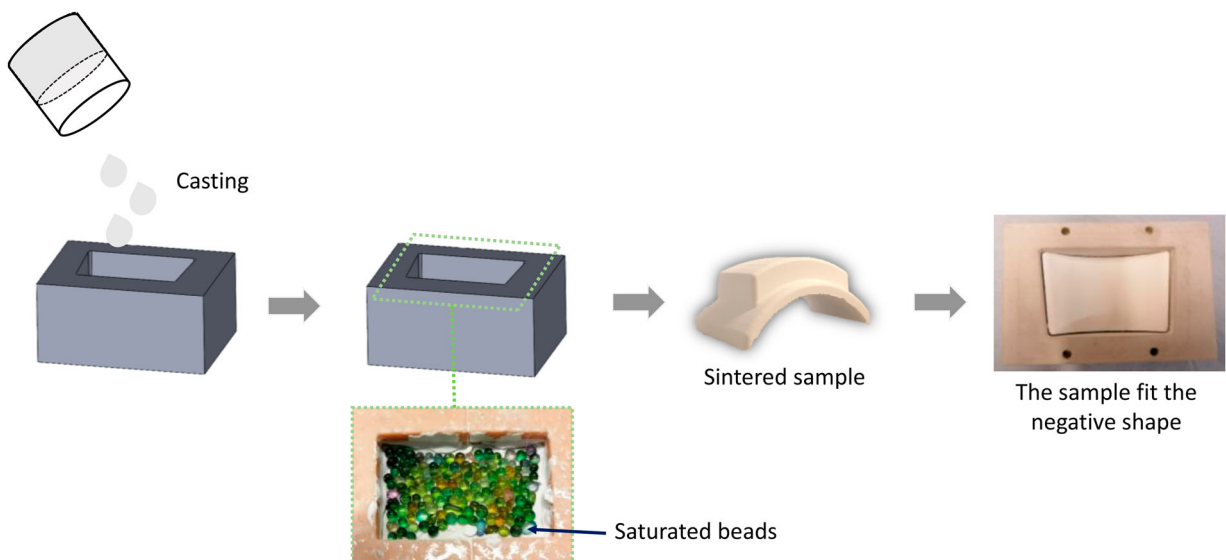


Figure 5. Drying and demoulding steps for the frustum insert.

- *Drying in the mould with specific heating* [16]: The sample is dried inside the mould in a preheated oven at 60°C for 30 mn, then, demoulded.
- *Drying using solid desiccant*: Envirogel beads (Brownell limited) were used on the upper surface in contact with the alumina slurry. They indicate an orange/yellow colour when active and change to green when they become saturated. A layer of beads (4 grammes) was deposited on the upper surface of the gelled alumina. The beads absorb slowly the water in a uniform vertical direction. The first to become dry is then the zone in contact with the beads. After 3 h, the beads become saturated (green as represented in Figure 4) and their weight increases by 1.5 grammes. This solution was repeated (2–3 times) until the beads' colour remains orange which corresponds to a dry state of the sample. After this, the dry rigid solid sample is demoulded and sintered and introduced into the negative shape (Figures 4 and 5).

Conclusion

Gel-casting process has been selected to manufacture porous Al₂O₃ ceramics for transpiration cooling application at high temperatures. Different geometries were elaborated, some of them were realised with relative ease in comparison to others. The steps of the process were detailed. The main challenges faced concerned the drying and the demoulding step considering the porous structure which increases water potential, the low solid particle packing which decreases the resistance of internal moisture diffusing to the surface and the complex geometry which is behind a non-uniform and differential drying. The adopted solutions to control the drying environment and avoid residual stresses during free-drying were described within the case study presented (cones and frustum insert).

This study validates the use of gel-casting to elaborate porous Al₂O₃ samples dedicated to transpiration cooling application. As this technique is not limited to a specific ceramic powder, it can be extended to manufacture and elaborate porous materials for transpiration cooling using different powders to elaborate porous ultra-high temperature ceramics UHTCs with homogenous materials properties.

Acknowledgements

The authors would like to thank Imperial Hackspace staff for their help and advices concerning moulds preparation. Lastly, the authors would like to extend their gratitude toward the reviewers who improved the quality of this paper.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

The funding for this research by the EPSRC grant 'Transpiration Cooling Systems for Jet Engine Turbines and Hypersonic Flight' is gratefully acknowledged.

ORCID

Y. Belrhiti  <http://orcid.org/0000-0003-4305-1310>

References

- [1] Vandeperre L. Challenges and opportunities with ultra-high temperature ceramics. Beyond Nickel-Based Superalloys II. 2016.
- [2] Naved I, Hermann T, McGilvray M, et al. Heat transfer measurements of a transpiration-cooled stagnation point in transient hypersonic flow. *J Thermophys Heat Transfer*. 2022;37:1–13.
- [3] Hermann T, McGilvray M, Naved I. Performance of transpiration cooled heat shields for re-entry vehicles. *AIAA J*. 2019;58(2).
- [4] Ewenz Rocher M, McGilvray M, Hermann TA, et al. Testing a transpiration cooled zirconium-di-boride sample in the plasma tunnel at IRS. *AIAA Scitech 2019 Forum*. 2019: 1552.
- [5] Ifti HS, Hermann T, McGilvray M, et al. Flow characterization of porous ultra-high-temperature ceramics for transpiration cooling. *AIAA J*. 2022;60(5):3286–3297. doi:10.2514/1.J061009
- [6] Ifti HS, Hermann T, Ewenz Rocher M, et al. Laminar transpiration cooling experiments in hypersonic flow. *Exp Fluids*. 2022;63(6):102, doi:10.1007/s00348-022-03446-1
- [7] Naved I, Hermann T, Hambidge C. Quantifying the surface heat transfer on transpiration cooled porous materials in laminar and turbulent hypersonic boundary layers'. 2022.
- [8] Hedgecock R, Vandeperre L. Porous UHTCs for transpiration cooling of hypersonic flight. *Ultra-High Temp Ceram: Mater Extrem Env Appl V.*, ECI Symposium Series. Jun. 2022.
- [9] McGilvray M, Hermann T, Ifti HS, et al. Ultra-high temperature ceramics for transpiration cooling applications in hypersonic vehicles. *Ultra-High Temp Ceram: Mater Extrem Env Appl V*. Jun. 2022.
- [10] Omatete OO, Janney M, Strehlow R. Gelcasting: a new ceramic forming process. *Undefined*, 1991.
- [11] Montanaro L, Coppola B, Palmero P, et al. A review on aqueous gelcasting: a versatile and low-toxic technique to shape ceramics. *Ceram Int*. 2019;45(7) Part B:9653–9673. doi:10.1016/j.ceramint.2018.12.079
- [12] Vandeperre LJ, De Wilde AM, Luyten J. Gelatin gel-casting of ceramic components. *J Mater Proce Technol*. 2003;135(2):312–316. doi:10.1016/S0924-0136(02)00862-2
- [13] Janney M, Walls CA, Kupp DM, et al. Gelcasting SiAlON radomes. *Am Ceram Soc Bull*. Jul. 2004;83.

- [14] Liu W, Yang J-L, Dong Y-G, et al. Drying behaviour of gelcast green alumina parts utilizing PEG solution. *Trans Indian Ceram Soc.* 2010;69(4):241–244. doi:10.1080/0371750X.2010.11090842
- [15] Hammel EC, Pettaway K, Ichite T, et al. Towards optimization of the osmotic drying process of alumina-gelatin objects: regression analysis and verification. *Ceram Int.* 2019;45(5):5223–5230. doi:10.1016/j.ceramint.2018.11.218
- [16] Dhara S, Kamboj RK, Pradhan M, et al. Shape forming of ceramics via gelcasting of aqueous particulate slurries. *Bull Mater Sci.* 2002;25(6):565–568. doi:10.1007/BF02710552