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Short communication

Freeze gelcasting of aqueous alumina suspensions for porous ceramics

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Abstract

A novel route combining the conventional freeze casting and gel casting was proposed for the fabrication of aligned pore structures. In comparison with the conventional freeze casting, the utilization of a water-soluble Hydantoin epoxy resin in the freeze casting promoted the gelation process and led to a higher compressive strength of the green body. After sintering, the freeze gelcast samples exhibited a twice higher compressive strength and 15.6% higher porosity at the same time than those of conventional freeze cast sample. The improvements were attributed to the combination of gelation of Hydantoin epoxy resin and the aligned ice growth, which led to the coexistence of aligned cylindrical and lamellar pore structures.

Keywords: A. Suspensions; B. Porosity; C. Mechanical properties; D. Al_2O_3; Freeze gelcasting

1. Introduction

Porous ceramics have found a wide range of applications owing to their distinct advantages such as large specific surface area, high melting point and wear resistance. The properties of porous ceramics can be tailored readily for each specific application by controlling the composition and microstructures, which in turn were highly influenced by the processing route. Recently porous ceramics with aligned pore structures have been realized successfully by a freeze casting process [1,2], which takes advantage of the principle of unidirectional solidification of a liquid vehicle such as water, also known as ice-templating. After the sublimation of the solidified vehicle, the aligned pores are obtained from the replication of the ice crystals and become attractive in applications of catalysts supports [3], filters [4], absorbent [5] and bone substitute [6], etc.

Gel-casting is a well-known forming technique for fabricating ceramic parts by means of in situ polymerization through which a macromolecular network is created to hold the ceramic particles together [7]. It exhibits advantages such as the microstructural homogeneity, the ability to form complex-shaped ceramic parts and high-strength green bodies. In order to combine the advantages of the two methods, a freeze–gelcasting process was developed recently. Yang et al. prepared aligned porous hydroxyapatite [8,9] and coal fly ash [10], and Chen et al. fabricated the porous alumina [11] with unidirectional ordered and gradient structures. However, all reports utilized the tert-butyl alcohol (TBA)-based suspension with the acrylamide (AM) as the monomer. Tert-butyl alcohol (TBA) is a toxic and carcinogenic substance [12,13], and is an emerging environmental contaminant [14]. Acrylamide (AM) is recognized as neurotoxic [15] and its polymerization is easily inhibited by atmospheric oxygen [16].

To further investigate the combination of freeze/gelcasting process, a Hydantoin epoxy resin was employed as the monomer in water-based alumina suspension. The influences of solids loading and the contents of Hydantoin epoxy resin on the pore morphology, porosity and compressive strength were investigated. The pore structure and corresponding properties by conventional freeze casting without the gelation process were also reported for the comparison purpose.

2. Experimental procedure

Commercial alumina powder (AES-11, Sumitomo Chemical Co. Ltd., Tokyo, Japan) with an average particle size of 0.5 μm and a purity of 99.8%, deionized water and ammonium polyacrylate (HydroDisper A160, Shenzhen Highrun Chemical

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Industry Co. Ltd., PR China) were used as the starting materials, freezing vehicle and the dispersant, respectively. Polyvinyl alcohol (PVA, 420, Kuraray Co. Ltd., Japan) was used as the binder in conventional freeze-casting. Hydantoin epoxy resin (MHR070, Wuxi Meihua Chemicals Co. Ltd., PR China) and 3,3′-diaminodipropylamine (DPTA, >98%, Tokyo Chemical Industry Co. Ltd., Tokyo, Japan) were used as the water-soluble epoxy resin and the hardener, respectively. Alumina suspensions of a range of solids loading and polymer contents were ball-milled for 24 h in zirconia media and de-aired by stirring in a vacuum desiccator, until complete removal of air bubbles. 6 wt.% aqueous solutions of Hydantoin epoxy resin and PVA were also prepared separately without the addition of alumina powders. Freezing of the suspension and aqueous solution were carried out by pouring them into a transparent aligned cylindrical polydimethylsiloxane (PDMS) mould (10 mm diameter × 15 mm high), which was then transported to a copper cold finger placed in a liquid nitrogen container. Frozen samples were then demoulded and then placed in the vacuum chamber (<10 Pa) of a freeze-drier (FD-1A-50, Beijing Boyikang Medical Equipment Co., China) for 36 h to allow the ice sublimate. The dried ceramic samples with the addition of aqueous gelation were heated at 100 °C for 10 min in an oven for the rapid polymerization of Hydantoin epoxy resin with the hardener. Both types of the dried samples were heated at 600 °C for 3 h in order to burn out the organic additives and sintered at 1550 °C for 3 h. The apparent porosity was derived from the density data. The microstructures of the samples were analyzed by environmental scanning electron microscopy (ESEM, Quantan 200, JEOL, Tokyo, Japan). The compressive strength of the porous ceramics with a diameter of ∼10 mm and a height of ∼15 mm were tested with a crosshead speed of 0.2 mm/min using Electronic Universal Testing Machine (KD11-2, Shenzhen KEJALI Technology Co. Ltd., China).

3. Results and discussion

Fig. 1(A)–(D) shows SEM micrographs of sintered porous Al_2O_3 ceramics obtained from 10–30 vol.% suspensions with the addition of 8 wt.% Hydantoin epoxy resin. Dense ceramic walls without apparent cracks and pore defects were obtained. All samples exhibited aligned pores in the surface parallel to the macroscopic ice growth direction and the coexistence of aligned cylindrical and lamellar pore morphology and aligned perpendicularly. With the increase of the solids loading, the pore morphology changed from lamellar to cylindrical, and the pore thickness and pore width became thinner and smaller respectively. The aligned cylindrical pores obtained from 20 vol.% solids loading suspension uniformly distributed on the surface parallel to the temperature gradient, showing the cylindrical pore architectures with a pore width of 6–8 μm, as shown in Fig. 1(E) in a higher magnification. These interconnected pores prepared by the modified freeze gelcasting exhibited distinctive characteristic and differed much to previous reports using TBA/AM gel system by both Yang and coworkers [8–10] and Chen et al. [11] where only the unidirectional pore channels can be observed parallel to the macroscopic TBA solvent growth direction. In the contrast, Fig. 1(F) shows a SEM micrograph of sintered porous Al_2O_3 ceramic obtained from 20 vol.% solids loading suspensions with the addition of 1 wt.% PVA binder. However, for samples with the addition of PVA binder, only the lamellar architecture can be observed with the lamellar pore width and lamellar thickness of 7–12 μm and 3–10 μm, respectively, as shown in Fig. 1(F). Dendritic and branch-like characteristics were barely observed in the surface of freeze gelcast samples, but became the main feature in the conventional freeze cast sample with the addition of PVA binder.

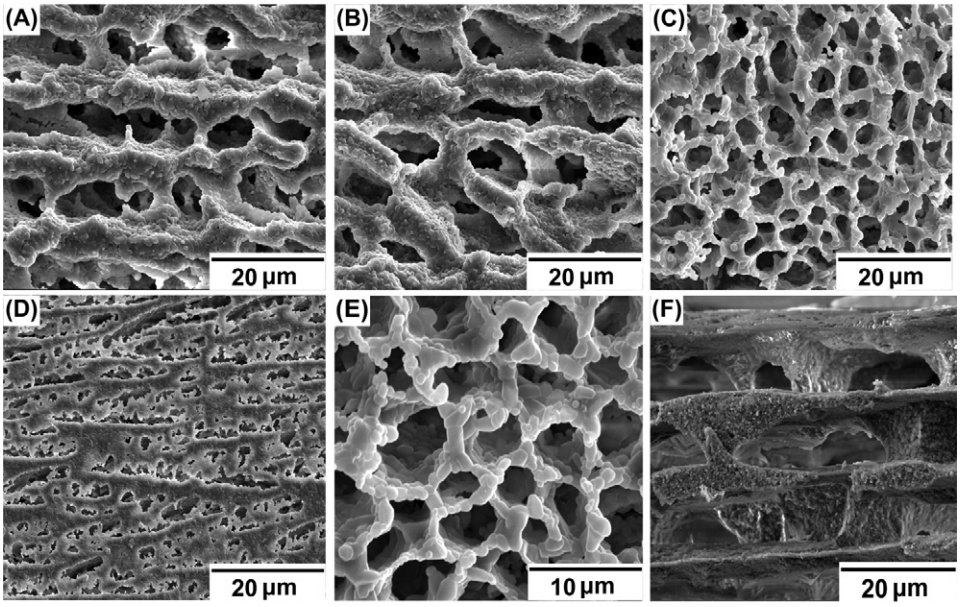

Fig. 1. SEM micrographs of sintered alumina porous ceramics prepared using 8 wt.% Hydantoin epoxy resin with a range of initial solids loadings: (A) 10 vol.%, (B) 15 vol.%, (C) 20 vol.%, (D) 30 vol.%, and (E) 20 vol.% at high magnification. (F) Prepared using 1 wt.% PVA binder with 20 vol.% solids loading. The freezing direction was parallel to the macroscopic ice growth direction.

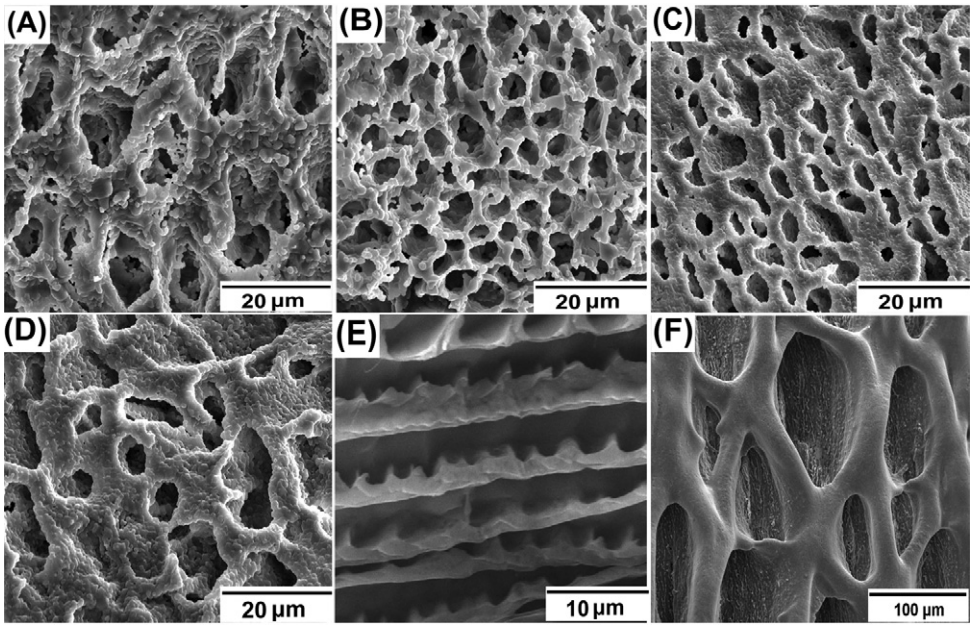

Fig. 2. SEM micrographs of porous alumina prepared using 20 vol.% solids loading with different. Hydantoin epoxy resin addition: (A) 4 wt.%, (B) 8 wt.%, (C) 10 wt.%, and (D) 12 wt.%. SEM micrographs of (E) porous PVA binder, (F) porous Hydantoin epoxy resin. The freezing direction was parallel to the page.

Fig. 2(A)–(D) shows SEM micrographs on the surface of sintered porous Al_2O_3 ceramics prepared from 20 vol.% solids loading suspensions with different contents of Hydantoin epoxy resin. Dense ceramic walls without apparent cracks or pore defects and interconnected pore morphologies were observed for all contents of Hydantoin epoxy resin. The addition of Hydantoin epoxy resin can modify not only the pore size but also the pore morphology. 8 wt.% sample exhibited a uniformly distributed pore structures and 12 wt.% sample showed the lowest pore interconnectivity. Fig. 2(E) and (F) shows SEM micrographs of porous PVA and Hydantoin epoxy resin prepared by the conventional freezing casting method, respectively. Aligned pore structures with a fish-bone structure [17] can be observed in freeze cast porous PVA, while macroporous structures with a cylindrical morphology was observed in porous Hydantoin epoxy resin. Comparing Fig. 2(F) with Fig. 2(A)–(D), it can be concluded that the water-soluble Hydantoin epoxy resin can be solidified with the water, acting as secondary template to form the cylindrical pores during the phase separation and finally the rearrangement of the alumina particles in the freezing process.

Fig. 3 shows the effects of solids loading with the addition of 8 wt.% Hydantoin epoxy resin on the compressive strength and porosity of porous Al_2O_3 ceramics in both green and sintered states. The freeze gelcast samples exhibited significant improvement in the compressive strength and obvious increase in the porosity comparing to conventional freeze cast samples. It can be concluded that the addition of Hydantoin epoxy resin resulted in the formation of cross-linked network during the gelation process, which contributed to the large increase of the compressive strength of the green body, i.e. 26.49 MPa versus 4.63 MPa for samples obtained from the suspensions of 20 vol.% solids loading. After sintering at 1550 °C, the compressive strengths were all further improved comparing to the green body,

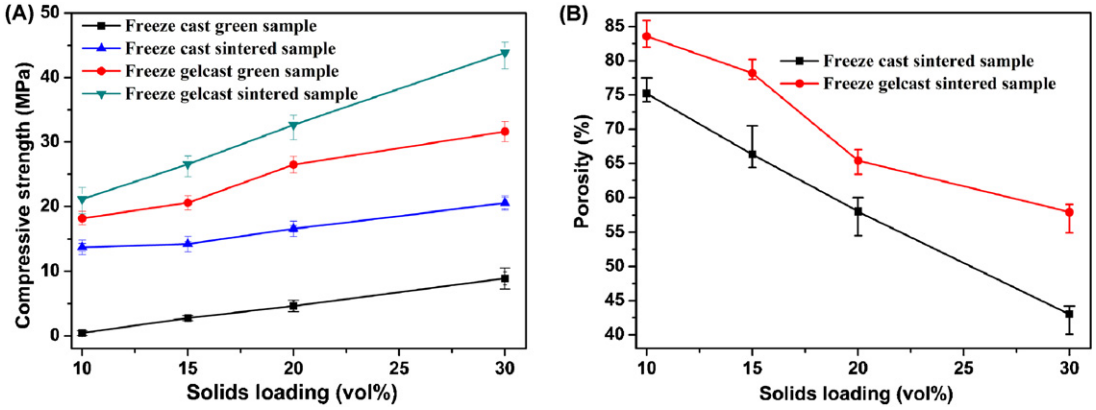

Fig. 3. (A) Compressive strengths of freeze cast and freeze gelcast samples in both green and sintered states versus solids loading of the initial suspensions. (B) Porosities of the sintered ceramics prepared by freeze casting and freeze gelcasting versus solids loading of the initial suspensions. The compressive tests were carried out parallel to the solidification direction.

and the compressive strengths of freeze gelcast samples were almost twice of that of conventional freeze cast samples. Meanwhile, it is interesting to notice that higher porosities were obtained in freeze gelcast samples with an increase of around 15.6%. The interconnected pores and the coexistence of perpendicularly aligned cylindrical and lamellar pore structures, as shown in Fig. 1(A)–(D), contributed to the improvement of the mechanical strength and the increase of the porosity of freeze gelcast sintered samples at the same time. The combination of gelation of Hydantoin epoxy resin and the aligned ice growth in this innovative freeze gelcasting resulted in this specific porous structure and the improvements in both green and sintered states, leading to easier handling, better processability and wider applications for such type of porous material.

4. Conclusions

The paper presented a novel method for fabricating aligned pore microstructures by combining freeze casting and gel casting. The incorporation of Hydantoin epoxy resin had a strong influence on the pore morphology, pore size, porosity and mechanical properties. Higher compressive strengths of the freeze gelcast green bodies were achieved due to the formation of cross-linked network during the gelation process. The coexistence of aligned cylindrical and lamellar pore structures contributed to higher compressive strength and porosity at the same time of the freeze gelcast sintered samples than those of conventional freeze cast samples.

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References

[1] K.C. Zhou, Y. Zhang, D. Zhang, X.Y. Zhang, Z.Y. Li, G. Liu, T.W. Button, Porous hydroxyapatite ceramics fabricated by an ice-templating method, Scripta Materialia 64 (2011) 426–429.

[2] S. Deville, E. Saiz, R.K. Nalla, A.P. Tomsia, Freezing as a path to build complex composites, Science 311 (2006) 515–518.

[3] P.H.C. Keller N, S. Roy, M.J. Ledoux, C. Estournes, J. Guille, Influence of the preparation conditions on the synthesis of high surface area SiC for use as a heterogeneous catalyst support, Journal of Material Science 34 (1999) 3189–3202.

[4] P.H. Pastila, V. Helanti, A.-P. Nikkilä, T.A. Mäntylä, Effect of crystallization on creep of clay bonded SiC filters, Ceramic Engineering and Science Proceedings 19 (1998) 37–44.

[5] A. Tampieri, S. Sprio, A. Ruffini, G. Celotti, I.G. Lesci, N. Roveri, From wood to bone: multi-step process to convert wood hierarchical structures into biomimetic hydroxyapatite scaffolds for bone tissue engineering, Journal of Materials Chemistry 19 (2009) 4973–4980.

[6] S. Deville, E. Saiz, A.P. Tomsia, Freeze casting of hydroxyapatite scaffolds for bone tissue engineering, Biomaterials 27 (2006) 5480–5489.

[7] X. Xin, J.M.F. Ferreira, Temperature-induced gelation of concentrated sialon suspensions, Journal of the American Ceramic Society 88 (2005) 593–598.

[8] J.H. Kim, J.H. Lee, T.Y. Yang, S.Y. Yoon, B.K. Kim, H.C. Park, TBA-based freeze/gel casting of porous hydroxyapatite scaffolds, Ceramics International 37 (2011) 2317–2322.

[9] T.Y. Yang, J.M. Lee, S.Y. Yoon, H.C. Park, Hydroxyapatite scaffolds processed using a TBA-based freeze–gelcasting/polymer sponge technique, Journal of Materials Science Materials in Medicine 21 (2010) 1495–1502.

[10] J.H. Lee, W.Y. Kim, T.Y. Yang, S.Y. Yoon, B.K. Kim, H.C. Park, Fabrication of porous ceramic composites with improved compressive strength from coal fly ash, Advances in Applied Ceramics 110 (2011) 244–250.

[11] R.F. Chen, C.A. Wang, Y. Huang, L.G. Ma, W.Y. Lin, Ceramics with special porous structures fabricated by freeze–gel casting: using tert-butyl alcohol as a template, Journal of the American Ceramic Society 90 (2007) 3478–3484.

[12] A.E.H.K.R.J.D. Cirvello, D.R. Farnell, C. Lindamood, Toxicity and carcinogenicity of t-butyl alcohol in rats and mice following chronic exposure in drinking water, Toxicology and Industrial Health 11 (1995) 151–166.

[13] T.C. Schmidt, M. Schirmer, H. Weiß, S.B. Haderlein, Microbial degradation of methyl tert-butyl ether and tert-butyl alcohol in the subsurface, Journal of the Contaminant Hydrology 70 (2004) 173–203.

[14] A. Sgambato, I. Iavicoli, B. de Paola, G. Bianchino, A. Boninsegna, A. Bergamaschi, A. Pietroiusti, A. Cittadini, Differential toxic effects of methyl tertiary butyl ether and tert-butanol on rat fibroblasts in vitro, Toxicology and Industrial Health 25 (2009) 141–151.

[15] M.A. Janney, O.O. Omatete, C.A. Walls, S.D. Nunn, R.J. Ogle, G. Westmoreland, Development of low-toxicity gelcasting systems, Journal of the American Ceramic Society 81 (1998) 581–591.

[16] A.C. Young, O.O. Omatete, M.A. Janney, P.A. Menchhofer, Gelcasting of alumina, Journal of the American Ceramic Society 74 (1991) 612–618.

[17] H.F. Zhang, A.I. Cooper, Aligned porous structures by directional freezing, Advanced Materials 19 (2007) 1529–1533.