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Porous alumina ceramics with highly aligned pores by heat-treating extruded alumina/camphene body at temperature near its solidification point

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Abstract

This study reports a novel way of increasing the pore size of highly aligned porous alumina ceramics by heat-treating an extruded alumina/camphene body at a temperature near its solidification point. The pore size obtained increased remarkably from 51 ± 8 to 125 ± 27 μm with increasing heat-treatment time from 1 to 24 h, due to the continuative overgrowth of the camphene dendrites during heat-treatment, while a highly aligned porous structure was preserved. In addition, interestingly, this heat-treatment enabled alumina walls to be densified quite well, whereas porous walls were observed in the sample produced without heat-treatment, which led to a considerable increase in compressive strength. The sample produced with a heat-treatment time of 12 h showed a high compressive strength of 11.6 ± 1.2 MPa at a porosity of approximately 84 vol%, which was much higher than that (0.28 ± 0.1 MPa) of the sample produced without heat-treatment.

Keywords: A. Extrusion; C. Mechanical properties; D. Al_2O_3; E. Biomedical applications; Porous ceramics

1. Introduction

Recently, there has been considerable interest in the application of unidirectional freeze casting for the production of porous materials, particularly with aligned pores with extremely high compressive strengths.[1–3] Fundamentally, this technique makes full use of the unidirectional growth of freezing vehicles, such as water,[1–3] camphene,[4–6] and tert-butyl alcohol (TBA).[7,8] In other words, ice (or camphene and TBA) dendrites grow preferentially along the direction of freezing, which can create aligned pores after removing the dendrites.

One of the most important and active researches areas in unidirectional freeze casting is to examine new ways of enhancing the degree of pore alignment to improve the functions of porous materials.[9] Thus far, considerable effort has been focused on promoting the preferential growth of ice dendrites during freezing, for example, using polymeric additives,[10–13] double-side cooling[14] and electric field.[15,16] However, in the case of camphene as a freezing vehicle, the size of aligned porous materials can be increased remarkably simply by assembling unidirectionally frozen ceramic/camphene bodies, which is one of the most striking features of camphene-based freeze casting.[17] Furthermore, this technique allows frozen ceramic/camphene body to be extruded successfully even at room-temperature, which would extensively elongate the camphene dendrites, enabling the formation of highly aligned pores.[18] These aligned porous materials can serve as a valuable framework for the production of ceramic/polymer composites with a lamellar structure. However, the pore size obtained using this approach needs to be higher to increase the applications of porous materials, for example, as bone scaffolds with a pore size ≥ 100 μm.

Therefore, this study proposes a new, simple way of increasing the pore size of highly aligned porous alumina ceramics by heat-treating extruded alumina/camphene bodies at 33 °C, which is close to the solidification temperature of an alumina/camphene slurry, as illustrated in Fig. 1. This heat-treatment allows camphene dendrites in the extruded body to overgrow continuously, while preserving their preferential orientation, which is achieved originally by extrusion.[4] To accomplish this, an alumina/camphene slurry was frozen unidirectionally in a 20 × 20 mm mold and then extruded through a reduction die with a cross-section of 5 × 5 mm. The extruded

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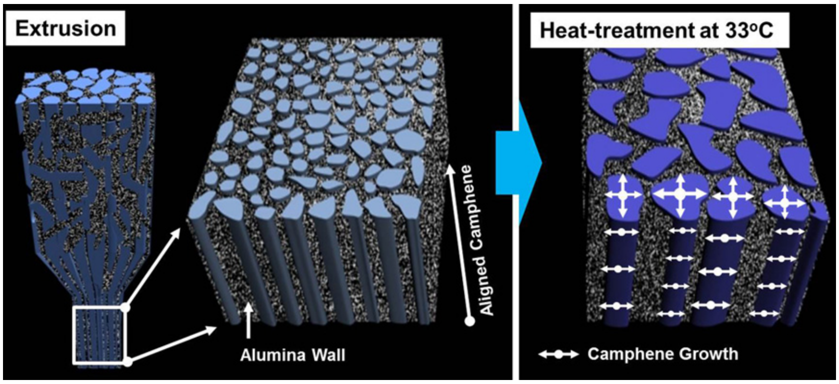

Fig. 1. Schematic diagrams showing the experimental procedure for increasing the pore size of highly aligned porous alumina ceramics by heat-treating an extruded alumina/camphene body at 33 °C.

alumina/camphene bodies were heat-treated at 33 °C for various times, ranging from 1 to 24 h. The green samples were freeze dried to remove the frozen camphene and then sintered at 1450 °C for 3 h to densify the alumina walls. The porous structure, such as porosity, pore size, degree of pore alignment, and densification of the alumina walls, of the fabricated samples was characterized by field emission scanning electron microscopy (SEM). The compressive strengths of the samples produced with heat-treatment for various times (1, 6, 12 and 24 h) were measured.

2. Experimental procedure

Commercially available alumina powder (Kojundo Chemical Co., Ltd, Japan) with a mean particle size of 0.3 μm and camphene ($C_{10}H_{16}$, Alfa Aesar/Avocado Organics, Ward Hill, MA, USA) were used as the ceramic and freezing vehicle, respectively. An alumina/camphene slurry was prepared by mixing the alumina powder and molten camphene containing 10 vol% of the polystyrene binder (PS; $[–CH_2CH(C_6H_5)–]_n$, $M_w = 230{,}000\ \mathrm{g\ mol^{-1}}$, Sigma–Aldrich, St. Louis, MO, USA) and 3 wt% of the oligomeric polyester dispersant (Hypermer KD-4, UniQema, Everburg, Belgium) by ball-milling at 60 °C for 24 h.

The prepared slurry was frozen unidirectionally in a 20 × 20 mm mold at 3 °C for 1 h and extruded through a reduction die with a 5 × 5 mm cross-section using a screw-driven load frame (OTU-05D, Oriental TM Corp., Korea).[18] The load required for extrusion was monitored as a function of time and distance, in order to evaluate the extrudability of a frozen alumina/camphene body. For comparison, a pure camphene was also tested.

The extruded alumina/camphene bodies were heat-treated at 33 °C for various times (1, 6, 12, and 24 h) in an oven to allow continuous overgrowth of the camphene dendrites. In addition, the sample with larger dimensions was produced by assembling the green extrudates at room-temperature, followed by heat-treatment at 33 °C for 12 h. Subsequently, the green samples were freeze dried to remove the solid camphene and then sintered at 1450 °C for 3 h to densify the alumina walls.

The pore structure (e.g. porosity, pore size, degree of pore alignment, interconnections between the pores, and densification of the alumina walls) of the fabricated samples was characterized by field emission scanning electron microscopy (FE-SEM, JSM-6701F, JEOL Techniques, Tokyo, Japan). The porosity of the sample was calculated from its dimensions and weight. The pore size was also measured from SEM images of the epoxy-filled samples that had been prepared by infiltrating an epoxy resin (Epoxy Mount Resin, Allied High Tech Products Inc., USA) into the porous alumina ceramics.

The mechanical properties of the samples produced with various times were evaluated by the compressive strength test. The sintered samples were cut into pieces ∼11 mm in length by a dental handpiece and then their top, bottom, and faces were gently ground using SiC abrasive papers to produce rectangular specimens. The samples with dimensions of ∼4 × 4 × 10 mm were loaded parallel to the direction of pore alignment at a crosshead speed of 1 mm/min using a screw driven load frame (OTU-05D, Oriental TM Corp., Korea). The samples produced with the heat-treatment for various times (1, 6, 12 and 24 h) were tested. The stress and strain responses of the samples were monitored during the compressive strength tests. Six samples were tested to obtain the mean value and standard deviation.

3. Results and discussion

In order to evaluate the extrudability of a frozen alumina/camphene body, the load applied was monitored during extrusion through a reduction die with a 5 × 5 mm cross-section, as shown in Fig. 2. The load increased gradually with increasing time and reached a constant value of ∼1750 N, which represents the maximum load required for the extrusion of the frozen alumina/camphene body. The extruded alumina/camphene body showed excellent shape tolerance without any defects, such as cracks and tearing, as shown in inset in Fig. 2. This suggests that the frozen alumina/camphene can be extruded without difficulty under normal conditions for extrusion, which would be attributed to the use of camphene as an extrudable binder, and the low alumina content of 15 vol% used in the frozen alumina/camphene body.[18] The load for extrusion of a

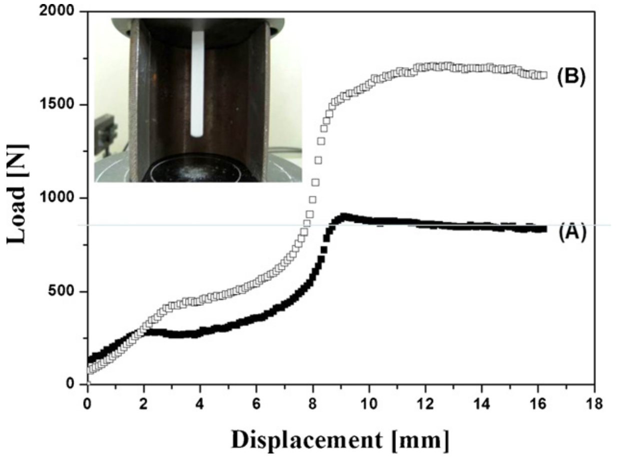

Fig. 2. The load required for the extrusion of the frozen alumina/camphene body and the pure camphene. The inset shows the extruding alumina/camphene body through the reduction die.

pure camphene was ~800 N. It should be noted that the load required for extrusion should be affected not only by the content of ceramic powders but also by the processing parameters for extrusion, such as extrusion speed and reduction ratio.

A highly aligned porous alumina ceramic could be produced successfully by extruding a frozen alumina/camphene body at room-temperature, where aligned pores were formed as a replica of the camphene dendrites that had been elongated extensively by extrusion,[18] as shown in Fig. 3(A). However, the alumina walls were porous even after sintering at 1450 °C for 3 h (Fig. 3(C)). On the other hand, when the extruded alumina/camphene body was heat-treated at 33 °C for 1 h, the pores became larger notably due to the overgrowth of camphene dendrites during heat-treatment[4] while preserving the highly aligned porous structure, as shown in Fig. 3(B). In addition, interestingly, the alumina walls were densified quite well (Fig. 3(D)).

Although this phenomenon is uncommon in freeze casting, it is reasonable to suppose that the highly packed alumina powder walls formed initially by freeze casting[19,20] would be partially destroyed by extensive deformation during extrusion. However, these loosely packed alumina powders can be redistributed by the continuous overgrowth of camphene dendrites during heat-treatment. This will result in the formation of highly concentrated alumina powder walls, enabling excellent densification of the alumina walls after sintering at 1450 °C for 3 h. In addition, it should be noted that porous materials produced using this approach can have excellent interconnections between the pores, which are unobtainable using conventional extrusion techniques.[21,22]

The effect of the heat-treatment time on pore alignment was examined by SEM. Fig. 4(A)–(F) shows the typical SEM images of the samples produced with various heat-treatment times (6, 12 and 24 h). Regardless of the heat-treatment time, all the fabricated samples had a highly aligned porous structure (Fig. 4(A)–(C)). This suggests that camphene dendrites can overgrow continuously, mainly along the direction normal to their original orientation.[4] However, the degree of pore alignment decreased slightly with increasing heat-treatment time. All the fabricated samples showed the excellent densification of alumina walls, as shown in Fig. 4(D)–(F).

Fig. 5(A)–(D) shows the typical SEM images of the samples produced with various heat-treatment times (1, 6, 12 and 24 h), representing the porous structure developed normal to the freezing direction. Honeycomb-like pores were formed uniformly for all the fabricated samples. However, the pores became notably larger with increasing heat-treatment time. These results suggest that the pore size can be increased remarkably without

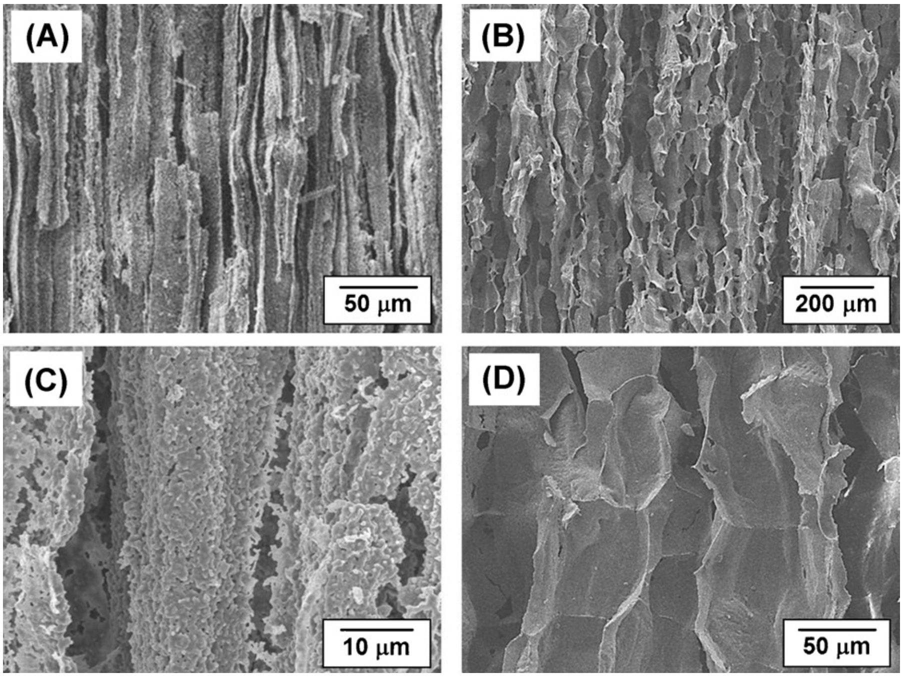

Fig. 3. SEM images showing the porous structures of the samples produced without (A, C) and with (B, D) heat-treatment at 33 °C for 1 h.

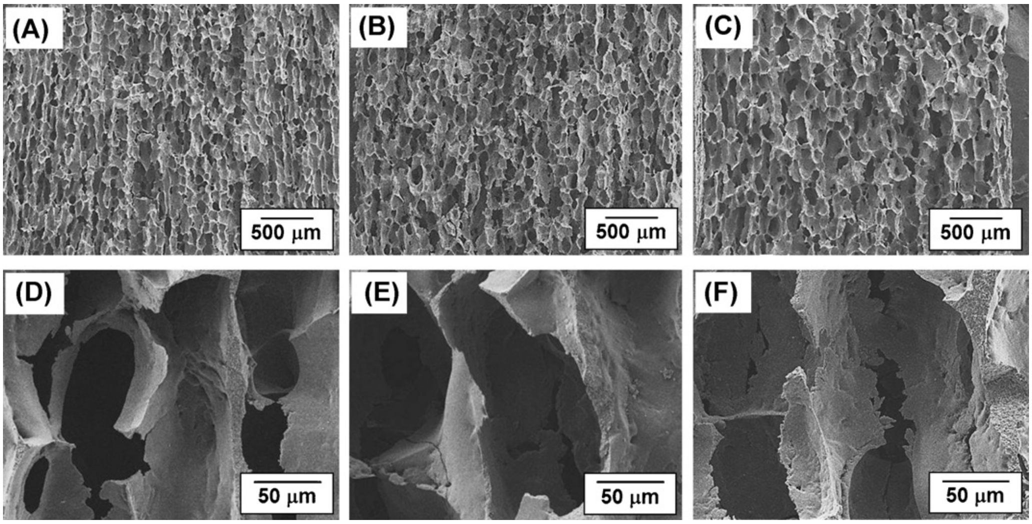

Fig. 4. SEM images of the porous structures of the samples produced with heat-treatment at 33 °C for various times of 6 h (A, D), 12 h (B, E), and 24 h (C, F). Fig. 4(A)–(C) and (D)–(F) represents the porous structures developed parallel to the direction of pore alignment and the densifications of the alumina walls, respectively.

disturbing the aligned porous structure by heat-treating extruded ceramic/camphene bodies at a particular temperature (for example, 33 °C in this study), which is close to the solidification point of a ceramic/camphene slurry.

The pore size of the samples produced with various heat-treatment times was measured from SEM images of the epoxy-filled samples. The inset in Fig. 6 shows a typical digitally colored image of the sample produced with a heat-treatment time of 12 h, where the dark and bright contrasts represent the epoxy and alumina phases, respectively. The pore size increased remarkably from 51 ± 8 to 125 ± 26 μm, with increasing heat-treatment time from 1 to 24 h, as shown in Fig. 6. These large pores would be expected to provide a favorable environment for bone ingrowth when used as a bone scaffold. A longer heat-treatment time would increase the pore size further, but would inevitably deteriorate the degree of pore alignment. On the other hand, the porosity of the samples changed negligibly (82–83 vol%) with increasing heat-treatment time, suggesting that there was no considerable phase separation between the camphene and alumina powder networks.

Fig. 7 shows the effect of the heat-treatment time on the compressive strength of the samples. The samples were compressed parallel to the direction of pore alignment, as shown in inset in Fig. 7. Basically, all the fabricated samples showed typical

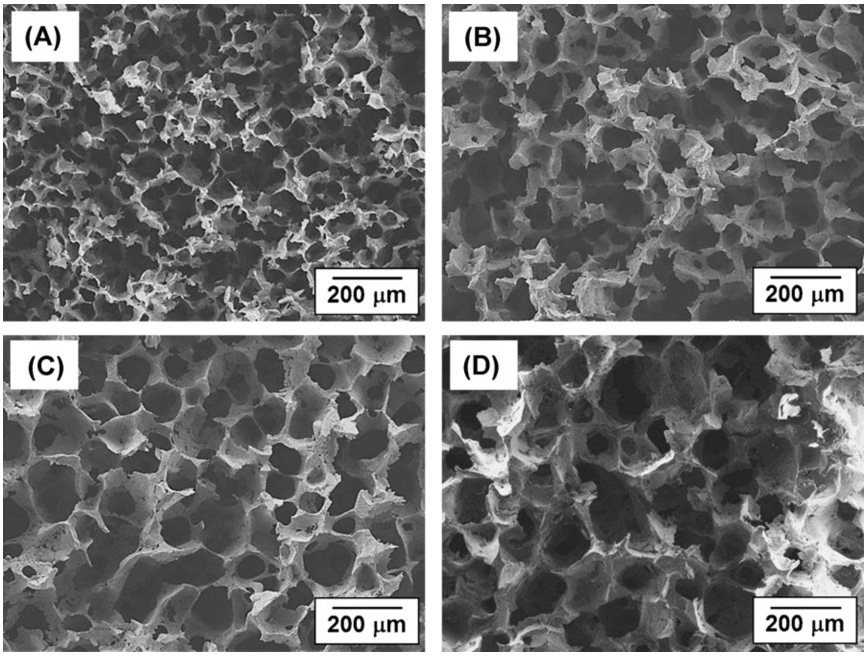

Fig. 5. SEM images of the porous structures of the samples produced with heat-treatment at 33 °C for various times of (A) 1 h, (B) 6 h, (C) 12 h, and (D) 24 h, showing the porous structures developed normal to the direction of pore alignment.

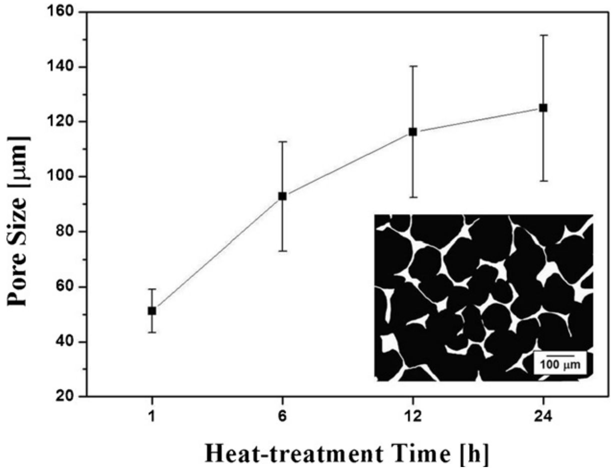

Fig. 6. Pore size of the samples as a function of the heat-treatment time at 33 °C. The inset shows a digitally colored image of the sample produced with a heat-treatment time of 12 h.

brittle fracture of porous ceramics, namely, the compressive stress increased linearly with an elastic response and then decreased rapidly due to fast fracture of the alumina walls.[23] The compressive strength increased from 6.4 ± 1.5 to 11.6 ± 1.2 MPa with increasing heat-treatment time from 1 to 12 h, which was attributed to an increase in the densification of the alumina walls. However, a longer heat-treatment time of 24 h led to a slight decrease in compressive strength because of a decrease in the degree of pore alignment. These values were much higher than that (0.28 ± 0.1 MPa) of the sample having porous alumina walls produced without the heat-treatment. It should be noted that the compressive strength of the porous samples with aligned pores compressed parallel to the direction of pore alignment would be much higher than that of the sample compressed normal to the direction of pore alignment.[18]

One of the most striking advantages of camphene-based freeze casting is the ability to achieve larger dimensions simply by assembling the frozen ceramic/camphene bodies.[17] To demonstrate this, the extruded alumina/camphene bodies were assembled at room-temperature, followed by heat-treatment at 33 °C for 12 h, as shown in Fig. 8(A). The inset in Fig. 8(B) shows an optical image of the samples (E: extrudate, A: assembled sample). The sample showed good interfacial bonding between the assemblies, as indicated by the arrows, while preserving the preferential orientation of pores, as shown in Fig. 8(B). It should be noted that the present method can be applicable to a range of materials, when a heat-treatment temperature that is close to the solidification of the slurry can be determined properly.

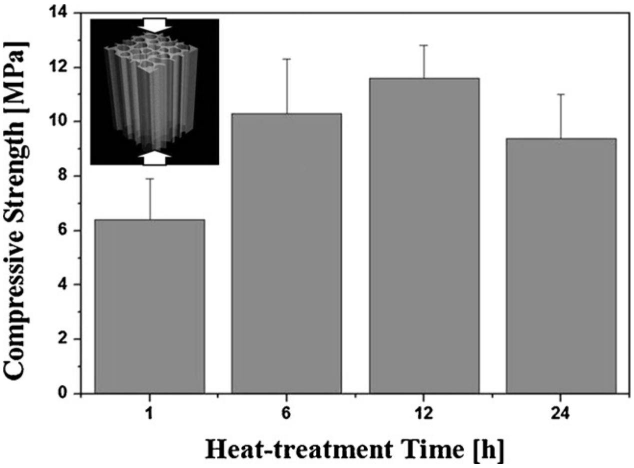

Fig. 7. Compressive strengths of the porous alumina ceramics as a function of the heat-treatment time at 33 °C. The inset shows a schematic of the direction of compression on the sample.

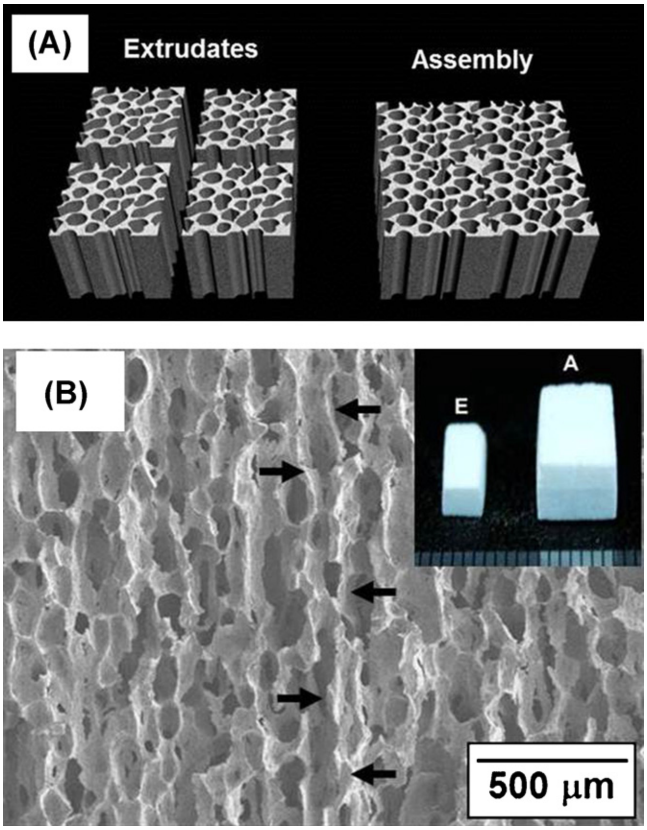

Fig. 8. (A) Schematic diagram showing the assembly procedure for producing the sample with larger dimensions and (B) typical SEM image of the assembled sample showing good bonding between the assemblies, as indicated by the arrows. The inset in Fig. 8(B) shows an optical image of the samples (E: extrudate and A: assembled sample) (scale = 1 mm).

4. Conclusions

The pore size of highly aligned porous alumina ceramics increased remarkably from 51 ± 8 to 125 ± 27 μm with increasing heat-treatment time from 1 to 24 h at a particular temperature of 33 °C, where camphene dendrites could overgrow continuatively, while preserving their highly aligned porous structure. Furthermore, all the fabricated samples showed that alumina walls were densified quite well, which is unlike the sample having porous alumina walls produced without heat-treatment. This led to a considerable increase in compressive strength; 0.28 ± 0.1 MPa and 11.6 ± 1.2 MPa for the samples produced without and with the heat-treatment for 12 h, respectively. In addition, the samples could be assembled successfully into larger dimensions with good interfacial bonding between the assemblies.

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References

1. Deville S, Saiz E, Tomsia A. Freeze casting of hydroxyapatite scaffolds for bone tissue engineering. *Biomaterials* 2006;**27**:5480–9.
2. Deville S, Saiz E, Tomsia AP. Ice-templated porous alumina structures. *Acta Mater* 2007;**55**:1965–74.
3. Liu G, Zhang D, Meggs C, Button TW. Porous Al_2O_3–ZrO_2 composites fabricated by an ice template method. *Scripta Mater* 2010;**62**:466–8.
4. Yoon BH, Choi WY, Kim HE, Kim JH, Koh YH. Aligned porous alumina ceramics with high compressive strengths for bone tissue engineering. *Scripta Mater* 2008;**58**:537–40.
5. Soon YM, Shin KH, Koh YH, Lee JH, Kim HE. Compressive strength and processing of camphene-based freeze cast calcium phosphate scaffolds with aligned pores. *Mater Lett* 2009;**63**:1548–50.
6. Soon YM, Shin KH, Koh YH, Lee JH, Cohi WY, Kim HE. Fabrication and compressive strength of porous hydroxyapatite scaffolds with a functionally graded core/shell structure. *J Eur Ceram Soc* 2011;**31**:13–8.
7. Chen R, Wang CA, Huang Y, Ma L, Linz W. Ceramics with special porous structures fabricated by freeze-gelcasting: using tert-butyl alcohol as a template. *J Am Ceram Soc* 2007;**90**:3478–84.
8. Hu L, Wang CA, Huang Y, Sun C, Lub S, Hub Z. Control of pore channel size during freeze casting of porous YSZ ceramics with unidirectionally aligned channels using different freezing temperatures. *J Eur Ceram Soc* 2010;**30**:3389–96.
9. Deville S. Freeze-casting of porous ceramics: a review of current achievements and issues. *Adv Eng Mater* 2008;**10**:155–69.
10. Fu Q, Rahaman MN, Dogan F, Bal BS. Freeze casting of porous hydroxyapatite scaffolds-i. processing and general microstructure. *J Biomed Mater Res B* 2008;**86**:125–35.
11. Pekor CM, Kisa P, Nettleship I. Effect of polyethylene glycol on the microstructure of freeze-cast alumina. *J Am Ceram Soc* 2008;**91**: 3185–90.
12. Munch E, Saiz E, Tomsia AP, Deville S. Architectural control of freeze-cast ceramics through additives and templating. *J Am Ceram Soc* 2009;**92**:1534–9.
13. Zuo KH, Zeng YP, Jiang DL. Effect of cooling rate and polyvinyl alcohol on the morphology of porous hydroxyapatite ceramics. *Mater Des* 2010;**31**:3090–4.
14. 14.Waschkies T, Oberacker R, Hoffmann MJ. Control of lamellae spacing during freeze casting of ceramics using double-side cooling as a novel processing route source. *J Am Ceram Soc* 2009;**92**:S79–84.
15. Zhang YM, Hu LY, Han JC. Preparation of a dense/porous bi-layered ceramic by applying an electric field during freeze casting. *J Am Ceram Soc* 2009;**92**:1874–6.
16. Tang YF, Zhao K, Wei JQ, Qin YS. Fabrication of aligned lamellar porous alumina using directional solidification of aqueous slurries with an applied electrostatic field. *J Eur Ceram Soc* 2010;**30**:1963–5.
17. Soon YM, Shin KH, Koh YH, Choi WY, Kim HE. Assembling unidirectionally frozen alumina/camphene bodies for aligned porous alumina ceramics with larger dimensions. *J Eur Ceram Soc* 2011;**31**:415–9.
18. Moon YW, Shin KH, Koh YH, Choi WY, Kim HE. Production of highly aligned porous alumina ceramics by extruding frozen alumina/camphene body. *J Eur Ceram Soc* 2011;**31**:1945–50.
19. Araki K, Halloran JW. Porous ceramic bodies with interconnected pore channels by a novel freeze casting technique. *J Am Ceram Soc* 2005;**88**:1108–14.
20. Koh YH, Song JH, Lee EJ, Kim HE. Freezing dilute ceramic/camphene slurry for ultra-high porosity ceramics with completely interconnected pore networks. *J Am Ceram Soc* 2006;**89**:3089–93.
21. Isobe T, Kameshima Y, Nakajima A, Okada K. Preparation and properties of porous alumina ceramics with uni-directionally oriented pores by extrusion method using a plastic substance as a pore former. *J Eur Ceram Soc* 2007;**27**:61–6.
22. Okada K, Shimizu M, Isobe T, Kameshima Y, Sakai M, Nakajima A, et al. Characteristics of microbubbles generated by porous mullite ceramics prepared by an extrusion method using organic fibers as the pore former. *J Eur Ceram Soc* 2010;**30**:1245–51.
23. Gibson LJ, Ashby MF. *Cellular solids, structure and properties*. 2nd ed. UK: Cambridge University Press; 1999.