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Technical note

Assembling unidirectionally frozen alumina/camphene bodies for aligned porous alumina ceramics with larger dimensions

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Abstract

This paper proposes a novel way of producing aligned porous alumina ceramics with larger dimensions by assembling unidirectionally frozen alumina/camphene bodies, particularly those containing polystyrene (PS) polymer as the binder. The compressive strength of the samples sintered at 1450 °C for 3 h increased remarkably from 2 ± 0.1 to 16 ± 2 MPa with increasing PS content from 5 to 20 vol.% due to the prevention of cracks generally caused by drying shrinkage. In addition, frozen samples with a PS content of 20 vol.% could be assembled into larger dimensions without difficulty. The height of the assembled sample produced with a lamination number of 5 could be increased to ~24 mm without a severe decrease in compressive strength (16 ± 3 MPa at a porosity of ~79 vol.%) due to the maintenance of an aligned porous structure with good interfacial bonding between the laminations.

Keywords: Suspensions; Porosity; Mechanical properties; Apatite; Biomedical applications

1. Introduction

Ice templating using an aqueous ceramic slurry has generated enormous interest on account of its ability to improve the compressive strength of porous ceramics obtained by creating aligned pores that would be formed as a replica of ice dendrites grown preferentially during freezing.[1–4] These aligned porous ceramics can be also used as a framework to produce hybrid composites with an extremely high toughness and yield strength which are even comparable to those of metallic alloys.[5,6] Considerable effort has been made to enhance the ability to control a pore structure, such as using additives,[7–10] double-side cooling[11] and electric field.[12,13] However, the pore size obtained using these techniques still need to be increased particularly for applications as a bone scaffold.

In recent years, our group has demonstrated that camphene as an alternative freezing vehicle can create very large pore >100 μm due to excessively overgrown camphene dendrites frozen at a temperature close to its solidification temperature.[14] This camphene-based freeze casting which is a variant of the ice templating can also be used to produce aligned porous ceramics with a large pore size using either two-step[15] or single-step processes.[16] However, it is practically difficult to maintain the continuous preferential growth of camphene dendrites during the entire process, which would limit the degree of aligned pores.

Therefore, this study proposes a novel, simple way of producing aligned porous alumina ceramics with larger dimensions by assembling unidirectionally frozen alumina/camphene bodies. In particular, a polystyrene (PS) polymer was added to alumina/camphene slurries as the binder to improve the green strength of the frozen bodies, which would allow the easy assembly of frozen bodies.[17,18] The effect of the addition of PS on the development of a porous structure and compressive strength of the samples was evaluated. The porous structure and compressive strength of the assembled samples with various lamination numbers (n = 1, 3, and 5) were also evaluated to demonstrate the utility of the present approach.

2. Experimental procedure

Commercially available alumina power (Kojundo Chemical Co., Ltd., Japan) with a mean particle size of 0.3 μm

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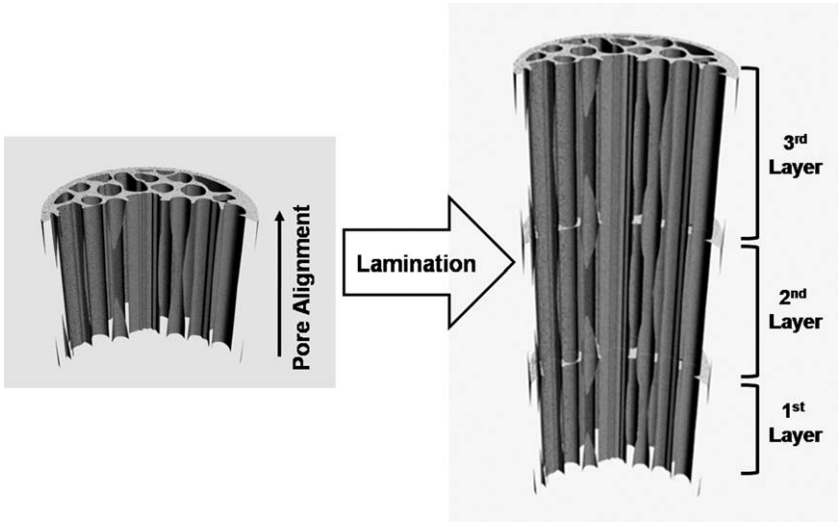

Fig. 1. A schematic showing the assembly procedure for the production of aligned porous alumina ceramics with larger dimensions.

and camphene ($C_{10}H_{16}$, Alfa Aesar/Avocado Organics, Ward Hill, MA, USA) were used as the ceramic material and freezing vehicle, respectively. Polystyrene (PS; $[–CH_2CH(C_6H_5)–]_n$, $M_w = 230{,}000\ g\ mol^{-1}$, Sigma–Aldrich, St. Louis, MO, USA) was also used as the binder. The alumina powder was ball-milled with molten camphene containing various PS contents (0, 5, 10 and 20 vol.% in relation to the alumina content) using 3 wt.% of an oligomeric polyester dispersant (Hypermer KD-4, UniQema, Everburg, Belgium) at 60 °C for 24 h. The initial alumina content in the slurry was kept at 10 vol.%. The resulting slurries were then cast into ~12.5 mm diameter polyethylene cylinders attached to a copper (Cu) plate as a cooling part and kept at 33 °C for 24 h.[16] Subsequently, the frozen samples were laminated in a polyethylene cylinder at room-temperature and pressed with finger pressure. This was followed by heat-treatment for 1 h at 33 °C that is close to the solidification of the slurry, wherein the partial re-melting of the frozen bodies could occur, which would allow the camphene dendrites at the interfaces to be merged,[14] resulting in good bonding between the laminates. A schematic of the assembly procedure for the production of aligned porous ceramics with larger dimensions is illustrated in Fig. 1. The assembled samples were freeze dried for 24 h to remove the solid camphene and sintered at 1450 °C for 3 h to densify the alumina walls.

The pore structures (e.g., pore alignment, pore shape and densification of alumina walls) of the fabricated samples were characterized by scanning electron microscopy (SEM, JSM-6360, JEOL Techniques, Tokyo, Japan). The porosity of the sample was calculated from its dimensions and weight. The pore size was also analyzed from SEM images of the samples prepared by infiltrating porous samples with an epoxy resin (Spurrs epoxy, Polysciences Inc., Warrington, PA) using the linear intercept method.[19,20] At least 50 pores were measured for each test to obtain an average and its standard deviation.

For the compressive strength test, samples with a diameter of ~ 10 mm were loaded at a crosshead speed of 5 mm/min using a screw driven load frame (Instron 5565, Instron Corp., Canton, MA, USA). The height of the samples produced with a lami-

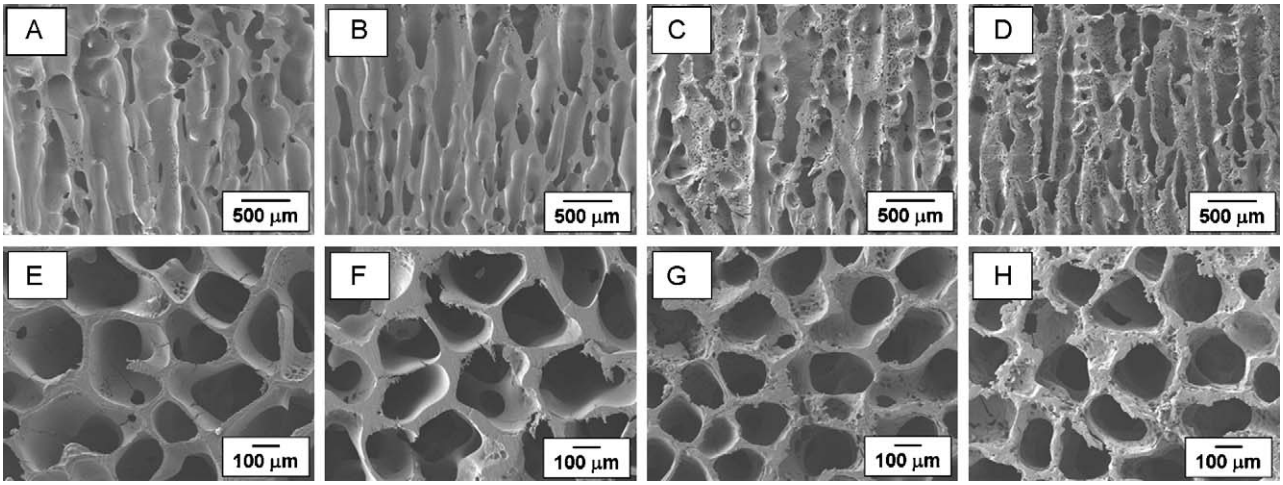

Fig. 2. SEM images of the porous alumina ceramics with aligned pores produced at various PS contents of 0 vol.% (A and E), 5 vol.% (B and F), 10 vol.% (C and G) and 20 vol.% (D and H). The upper and bottom images show the pores formed parallel and normal to the direction of freezing, respectively.

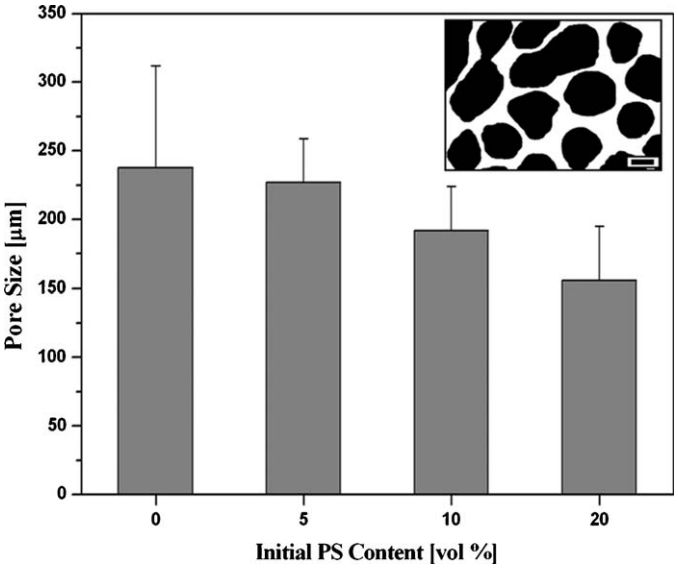

Fig. 3. Measured pore size of the samples as a function of the initial PS content. The inset shows a typical digitally colored image of the epoxy-filled sample produced at a PS content of 20 vol.% (scale = 100 μm).

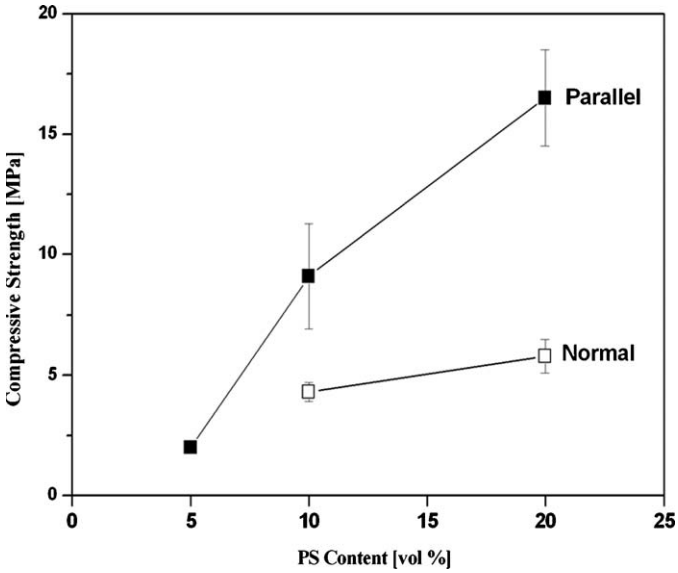

Fig. 4. Compressed strength of the samples as a function of the PS content tested either parallel or normal to the direction of pore alignment.

nation number of 1, 3, and 5 was ~5, 15, 24 mm, respectively. The stress and strain responses of the samples were monitored during the compressive strength tests. Six samples were tested to obtain an average value and its standard deviation.

3. Results and discussion

Aligned porous alumina ceramics with larger dimensions were fabricated by assembling unidirectionally frozen alumina/camphene bodies. The effect of the PS binder on the development of the porous structure and microstructure of the alumina walls was first examined, as shown in Fig. 2(A)–(F). Regardless of the PS content, all the fabricated samples showed an aligned porous structure formed as a replica of preferentially grown camphene dendrites,[15,16] as shown in Fig. 2(A)–(D). However, the sample prepared without the addition of a PS binder showed a number of cracks caused during freeze drying because of its relatively low green strength. The formation of cracks was suppressed efficiently by increasing the PS content to 10 vol.% (Fig. 2(B)). However, at a higher PS content, a number of small pores appeared on the surface of the alumina walls, presumably due to the removal of the PS polymer (Fig. 2(C) and (D)).[17,18] More specifically, the PS polymer dissolved completely in the molten camphene would experience thermally induced phase separation (TIPS) during freezing, which would promote favorable formation of side-arms of camphene dendrites, resulting in the formation of pores when high PS contents are used.

The pore size of the samples produced at various PS contents was calculated from the SEM images of the epoxy-filled samples. The inset in Fig. 3 shows a typical digitally colored image of the sample prepared with a PS content of 20 vol.%. The pore size measured roughly using the linear intercept method decreased from 237 ± 74 to 155 ± 39 μm with increasing PS content from 0 to 20 vol.%, as shown in Fig. 3. This was attributed mainly to decrease in the degree of supercooling caused by the PS polymer in the slurry.[8,18] However, it should be noted that the smallest pore size obtained in the sample produced with a PS content of 20 vol.% was >100 μm, which would be highly beneficial to bone ingrowth when used as a bone scaffold.[21] The porosity of the samples produced with a PS content of 0, 5, 10, and 20 vol.%, which was measured by considering their dimensions and weight, was 83, 83, 80, and 79 vol.%, respectively.

The compressive strength of the porous alumina ceramics with aligned pores produced at various PS contents (5, 10, and 20 vol.%) was measured, as shown in Fig. 4. The samples were compressed either parallel or normal to the direction of pore alignment. The compressive strength increased remarkably from 2.0 ± 0.1 MPa to 16.5 ± 2.0 MPa with increasing PS content from 5 to 20 vol.%, which was attributed to the prevention of cracks that are generally caused by drying shrinkage.[18] In addition, the samples showed much higher compressive strength when tested parallel to rather than normal to the direction of pore alignment, indicating the significance of the aligned pores.

On the basis of these results, aligned porous alumina ceramics with larger dimensions were produced by assembling unidirectionally frozen bodies with a PS content of 20 vol.%. Fig. 5 shows an optical photograph of the samples produced with various lamination numbers (n = 1, 3, and 5). The height of the sample produced with a lamination number of 5 could be increased to 24 mm without any noticeable interfacial delamination. In addition, an aligned porous structure was well preserved with good interfacial bonding between the laminations, as shown in Fig. 5(B).

The compressive strength of the samples produced with various lamination numbers (n = 1, 3, and 5) was measured. All the fabricated samples exhibited a brittle fracture behavior. Fig. 6 shows the typical compressive stress versus displacement of the sample produced with a lamination number of 5, in which the stress increased linearly and then decreased rapidly due to

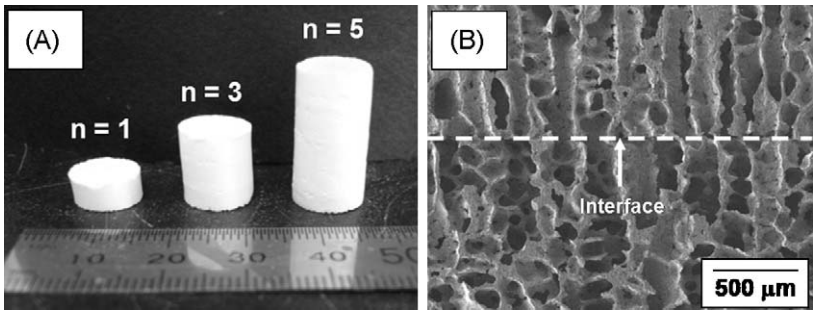

Fig. 5. (A) Optical photograph of the samples produced by assembling frozen bodies with various lamination numbers ($n = 1$, 3, and 5) and (B) SEM image showing good interfacial bonding between the laminations.

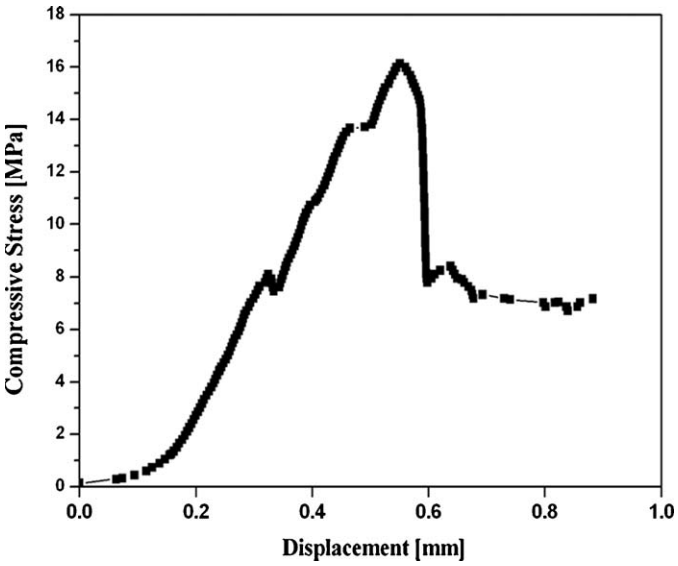

Fig. 6. Typical compressive stress versus displacement response of the sample produced with a lamination number of 5.

Table 1
Compressive strengths of the samples produced by assembling unidirectionally frozen bodies with various lamination numbers ($n = 1$, 3 and 5).

Lamination number [#]	1	3	5
Compressive strength [MPa]	16 ± 2	16 ± 4	16 ± 3

the fast fracture of the sample.[22] The compressive strength of the samples produced with a lamination number of 1, 3, and 5 was 16 ± 2, 16 ± 4, and 16 ± 3, respectively, as summarized in Table 1. This suggests that aligned porous ceramics with larger dimensions could be produced simply by assembling unidirectionally frozen ceramic/camphene bodies without sacrificing their high compressive strength owing to the preservation of the aligned pore structure.

4. Conclusions

Aligned porous alumina ceramics with larger dimensions were produced by assembling unidirectionally frozen alumina/camphene bodies at room-temperature, followed by freeze drying and sintering at 1450 °C for 3 h. In particular, the PS polymer was used as a binder to improve the strength of the frozen bodies, which resulted in a remarkable increase in compressive strength without deteriorating the construction of aligned pores. The assembled sample produced with a lamination number of 5 maintained a reasonably high compressive strength of 16 ± 3 at a porosity of ~79 vol.%, whereas its height could be increased to 24 mm by preserving the aligned pores and good interfacial bonding between the laminates.

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