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Short communication

Production of highly aligned porous alumina ceramics by extruding frozen alumina/camphene body

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Abstract

We herein propose a new technique for producing highly aligned porous ceramics by extruding a frozen ceramic/camphene body. To accomplish this, an alumina/camphene slurry with an initial alumina content of 10 vol% was first frozen unidirectionally in a 20 mm × 20 mm mold and extruded through a reduction die with a cross-section of 5 mm × 5 mm at room-temperature. This simple process enabled the formation of porous alumina ceramics with highly aligned pores as a replica of the camphene dendrites with a preferential orientation parallel to the extrusion direction. The sample showed much higher compressive strength of 280 ± 80 kPa with a porosity of 83 vol% when tested parallel to the direction of pore alignment. In addition, these materials could be used as a valuable framework for the production of ceramic/epoxy composites, particularly with a lamellar structure, which would result in a remarkable increase in mechanical properties.

Keywords: Extrusion; Porous ceramics; Mechanical properties; Al_2O_3; Biomedical applications

1. Introduction

Porous materials with aligned pores are of scientific interest and importance in a wide range of fields, because they can provide superior functions to conventional ones.[1] One of the most promising techniques for producing aligned porous materials is to freeze an aqueous ceramic slurry unidirectionally, in which highly aligned pores are produced readily by removing the ice dendrites grown preferentially along the direction of freezing.[2–4] Porous materials produced using this technique can have extremely high compressive strength owing to their aligned pores. In a similar way, camphene[5–7] and tert-butyl alcohol (TBA)[8,9] have been used successfully as an alternative to water for the production of aligned porous materials.

Fundamentally, the pore structure (e.g., the degree of pore alignment, porosity, pore size, and interconnection between the pores) achieved by unidirectionally freezing a ceramic slurry should be strongly affected by the dendritic growth of the freezing vehicle.[10] Therefore, considerable effort has been made to improve the degree of pore alignment by tailoring the growth of ice dendrites during freezing, e.g., using polymeric additives,[11–14] double-side cooling[15] and electric field[16,17] In addition, aligned porous materials with larger dimensions could be produced simply by assembling the unidirectionally frozen ceramic/camphene bodies, which is one of the most striking advantages of camphene-based freeze casting.[18]

In this study, we propose a novel way of creating highly aligned porous ceramics by extruding a frozen ceramic/camphene body at room-temperature. Unlike aqueous freeze casting, this technique makes full use of the fact that camphene dendrites grown during freeze casting can be deformed and elongated extensively during extrusion.[19] To accomplish this, an alumina/camphene slurry with an alumina content of 10 vol% was frozen unidirectionally at 3 °C in a mold with dimensions of 20 mm × 20 mm and then extruded through a reduction die with a cross-section of 5 mm × 5 mm. The extrudates were freeze dried to remove the frozen camphene, followed by sintering at 1450 °C for 3 h. The porous structure and compressive strength of the samples were evaluated to demonstrate the utility of the present method. In addition, the samples were

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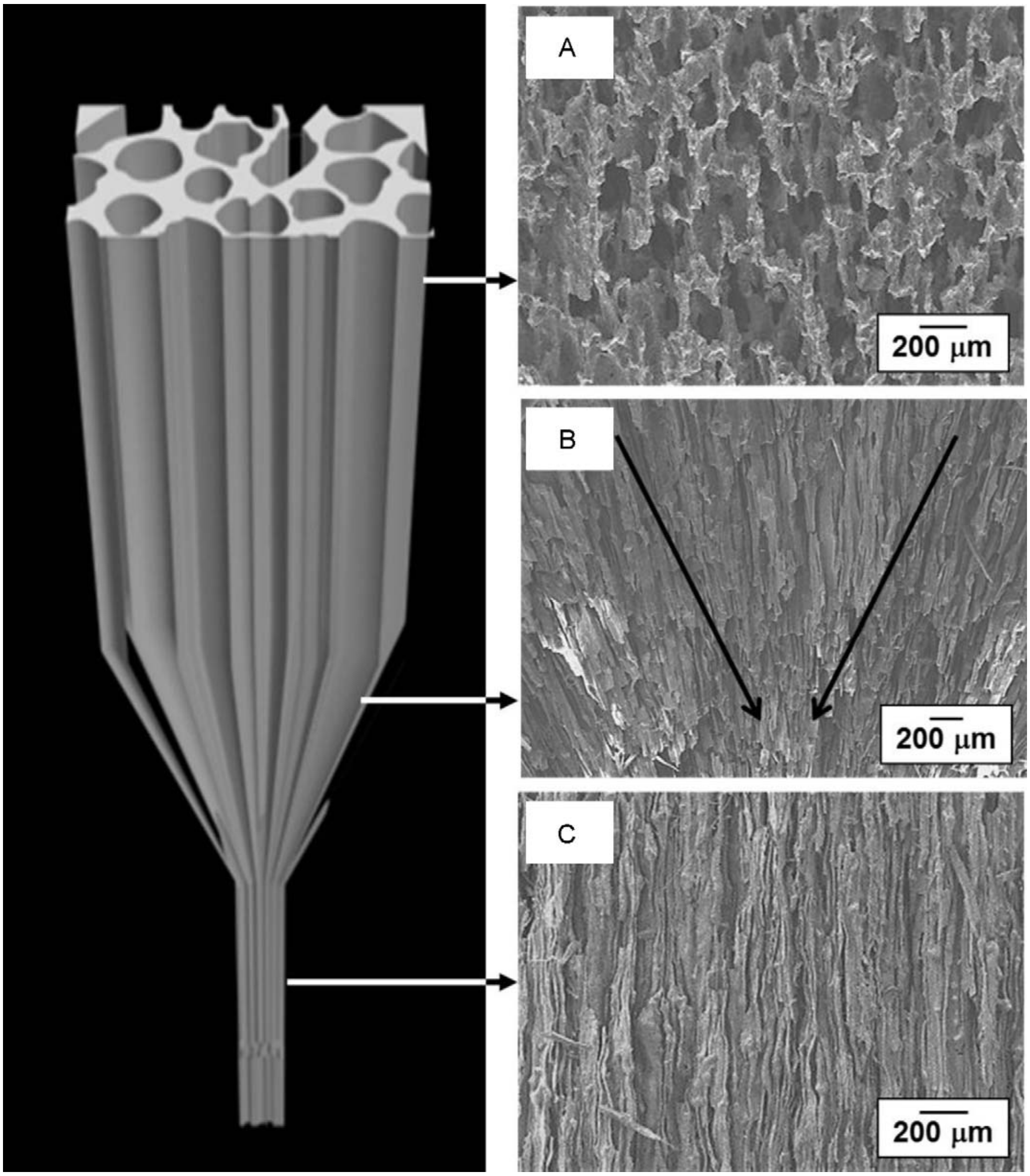

Fig. 1. SEM images showing the porous structures developed (A) before, (B) during, and (C) after extrusion.

infiltrated with epoxy to show its potential applications for the production of ceramic/epoxy composites, particularly with a lamellar structure.

2. Experimental procedure

Commercially available alumina power (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. Polystyrene (PS; $[–CH_2CH(C_6H_5)–]_n$, $M_w = 230{,}000\ \mathrm{g\,mol^{-1}}$, Sigma–Aldrich, St. Louis, MO, USA) was also used as a binder. The alumina powder was ball-milled with molten camphene with a PS content of 10 vol% and 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 10 vol%.

The prepared slurry was cast into a mold with dimensions of 20 mm × 20 mm and then frozen unidirectionally at 3 °C for 1 h, followed by heat-treatment at 33 °C for 24 h in an oven to increase the size of the camphene dendrites.[5] Subsequently, the frozen alumina/camphene body was extruded through a reduction die with a cross-section of 5 mm × 5 mm. The extruded samples were freeze dried to remove the solid camphene and then sintered at 1450 °C for 3 h to densify the alumina walls. In addition, the sintered samples were infiltrated with epoxy resin (Epoxy Mount Resin, Allied High Tech Products Inc., USA) to produce the ceramic/epoxy composites.

The pore structure (e.g., degree of pore alignment, porosity, pore size, and interconnection between the pores, and densification of 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

Table 1
The overall porosities, pore sizes and the thickness of the alumina walls of the sample before and extrusion.

Sample	Porosity (vol%)	Pore size (μm)	Wall thickness (μm)
Before extrusion	83 ± 0.62	15–300	9.1 ± 1.6
After extrusion	82 ± 0.90	30–50	2.1 ± 0.5

weight. The pore size was also calculated roughly from SEM images of the samples.

For the compressive strength test, samples with dimensions of ~4.6 mm × 4.6 mm × 10 mm were loaded at a crosshead speed of 1 mm/min using a screw driven load frame (OTU-05D, Oriental TM Corp., Korea). The samples were compressed either parallel or normal to the direction of pore alignment. 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. In addition, the fracture behavior of the ceramic/epoxy composite, ~3.9 mm × 3.5 mm × 35 mm in size, was characterized using a three-point flexure configuration at a crosshead speed of 0.5 mm/min with an outer span of 20 mm. Pure epoxy was also tested for comparison.

3. Results and discussion

We herein employed to use the extrusion of a frozen alumina/camphene body to create highly aligned pores. Fig. 1(A)–(C) shows the change in pore structure during extrusion. Before extrusion, the sample showed relatively large pores with a preferential orientation, suggesting that the camphene dendrites grew unidirectionally during freeze casting (Fig. 1(A)).[5] These camphene dendrites could be deformed and elongated extensively during extrusion (Fig. 1(B)), which allowed the formation of highly aligned pores with a remarkably reduced size (Fig. 1(C)).

The pore structure of the sample after extrusion was examined more closely by scanning electron microscopy (SEM), as shown in Fig. 2(A) and (B). A large number of extremely long alumina walls were observed in the end of the partially fractured sample (Fig. 2(A)). The creation of these lamella-like layers was more clearly visible at high magnification (Fig. 2(B)). On the other hand, pores with high aspect ratio were formed uniformly normal to the direction of extrusion (Fig. 2(C)). This indicates that highly aligned pores were formed successfully parallel to the direction of extrusion, suggesting excellent extrudability of the frozen alumina/camphene body.

Table 1 summarizes the overall porosities, pore sizes and thickness of the alumina walls of the samples before and after extrusion. Both samples showed a similar porosity of 82–83 vol%, suggesting that the initial bicontinuous structure comprised of 3-dimensional camphene and alumina networks could be preserved during extrusion. However, the pore size and thickness of the alumina walls decreased remarkably from 150–300 to 30–50 μm and 9.1 ± 1.6 to 2.1 ± 0.5 μm after extrusion, respectively. It should be noted that the alumina walls could be preserved well without fracture even after extrusion, because the camphene could act as a binder and, accordingly, hold the alumina powders during the extrusive elongation and deformation of the frozen alumina/camphene.

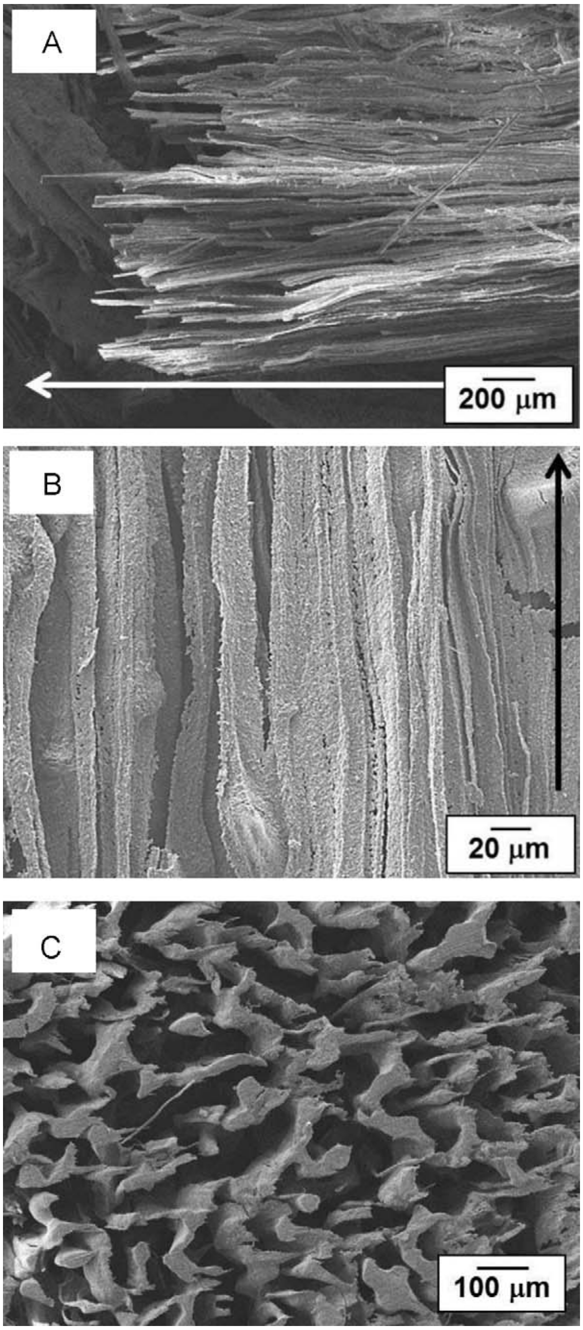

Fig. 2. SEM images of the highly aligned porous alumina showing the extremely long alumina walls (A) and highly aligned pores developed parallel (B) and normal (C) to the direction of pore alignment.

In order to examine the effect of the pore alignment on the mechanical properties of the aligned porous alumina ceramics, compressive strength tests were carried out on the samples loaded either parallel or normal to the direction of pore alignment. When the sample was compressed parallel to the direction of pore alignment, the compressive stress increased linearly with an elastic response and then decreased rapidly due to fast fracture

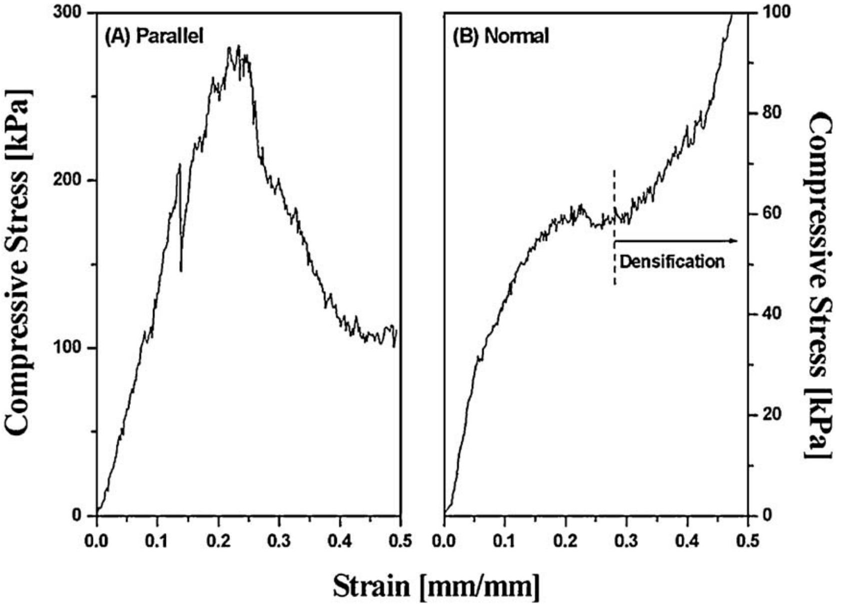

Fig. 3. Typical compressive stress versus strain responses of the samples compressed (A) parallel and (B) normal to the direction of pore alignment.

of the alumina walls, which is a typical characteristic of brittle ceramics,[20] as shown in Fig. 3(A). On the other hand, the sample exhibited considerable densification of the fractured sample immediately after reaching a peak, as shown in Fig. 3(B), as is often the case with high porosity ceramics.[20,21] The compressive strength (280 ± 80 kPa) of the sample compressed parallel to the direction of pore alignment was much higher than that (50 ± 10 kPa) of the sample compressed normal to the direction

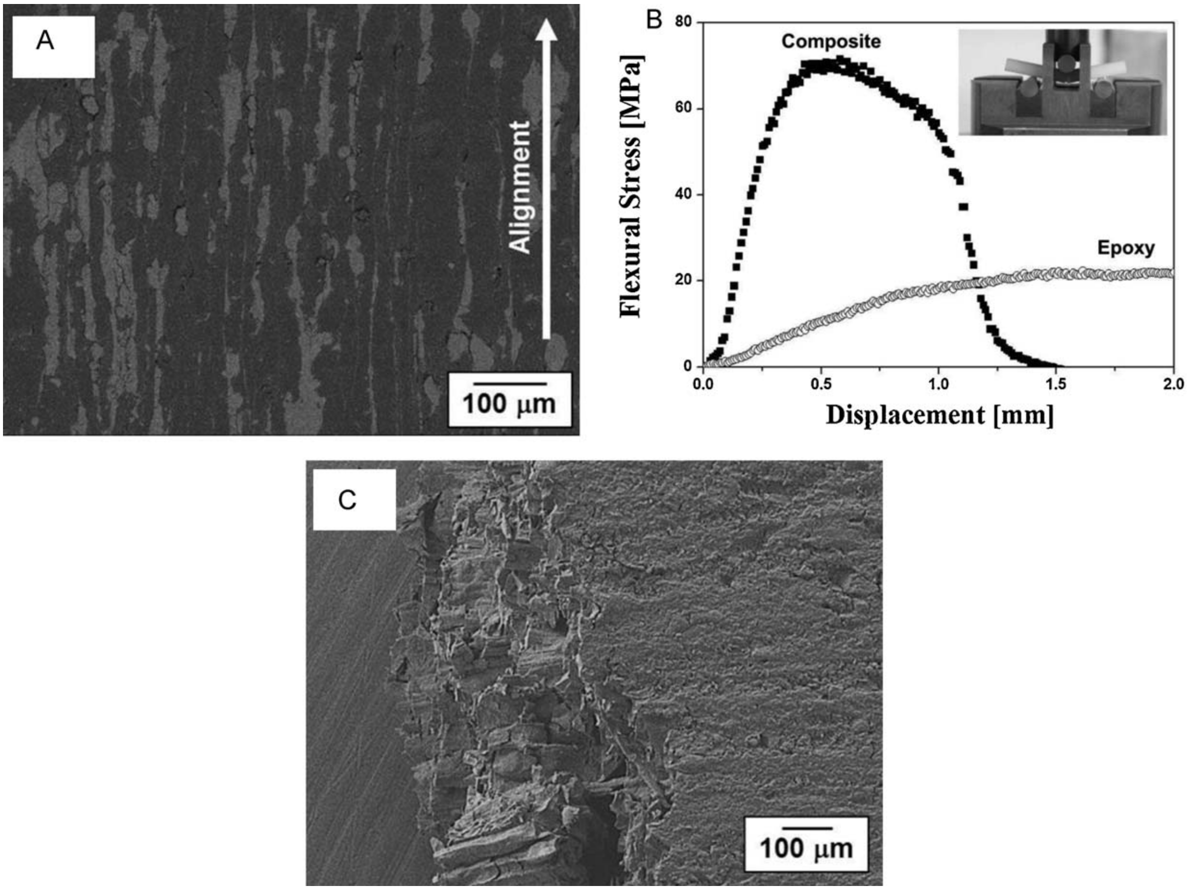

Fig. 4. (A) Typical SEM image of the composite produced by infiltrating an epoxy into the highly aligned porous alumina, (B) typical flexural stress versus displacement response of the composite and (C) SEM image of the fractured composite after 3-point bending test.

of pore alignment. This suggests that the extrusion of a frozen ceramic/camphene body can improve significantly the mechanical properties of porous materials by creating aligned pores. However, the compressive strengths obtained in this study are lower than those of the samples produced without extrusion, because of the formation of porous alumina walls, which would be caused by the extensive deformation and elongation of the frozen alumina/camphene during extrusion. On the other hand, these porous ceramic walls would find very useful applications, where a large surface area is required.

Porous materials with highly aligned pores are expected to be a valuable framework for the production of composites, which can provide exceptionally high strength and toughness, e.g., by constructing a lamellar or brick-and-mortar architecture.[22,23] To demonstrate this, the highly aligned porous alumina ceramic produced in this study was infiltrated with epoxy, as shown Fig. 4(A), where the bright and dark contrasts represent the alumina and epoxy phases, respectively, and the fracture behavior of the composite was examined roughly using a three-point flexure configuration. The stress increased linearly to a peak of ~66 MPa and decreased gradually with considerable displacement, which is a typical characteristic of ceramic-reinforced epoxy composites,[22,23] while the epoxy showed a ductile fracture, as shown in Fig. 4(B). The fractured surface exhibited a large number of the alumina walls pulled out from the composite, as shown in Fig. 4(B), which would contribute significantly to the toughening of the composite. Although more study is needed, it is reasonable to suppose that the highly aligned ceramic walls achieved in this study, particularly with good interconnections between the pores, can provide more efficient strengthening and toughening than simple laminate composites.

One of the most striking advantages of the aligned porous alumina ceramics produced in this study is the achievement of excellent interconnections between the pores, which are unobtainable by conventional extrusion techniques using deformable pore-forming agents[24] and fibers.[25] In other words, during freezing, the molten camphene grows dendritically and repels the alumina particles, which would lead to the formation of a bicontinuous structure comprised of three-dimensionally interconnected camphene dendrites and alumina particles.[26,27] This bicontinuous structure can be preserved during extrusion, whereas camphene dendrites can be deformed and elongated extensively, allowing the creation of highly aligned, interconnected pores. It should be also noted that the present technique would be applicable a range of camphene-based slurries, including ceramics and metals.

4. Conclusions

Highly aligned porous alumina ceramics were fabricated by extruding a frozen alumina/camphene body, where the camphene dendrites grown preferentially during freeze casting could be deformed and elongated extensively during extrusion. The fabricated sample showed a highly aligned porous structure with a pore size of 30–50 μm and a porosity of 82 vol%. The compressive strength of the sample was as high as 280 ± 80 kPa, when compressed parallel to the direction of pore alignment, due to the construction of the highly aligned pores. Furthermore, these materials with a lamella structure with good interconnections between the pores could be used as an effective framework for the production of ceramic/epoxy composites, which would be expected to provide improved mechanical properties by combining the unique advantages of stiff ceramic and flexible epoxy phases.

Acknowledgments

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