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Technical note

Fabrication of aligned lamellar porous alumina using directional solidification of aqueous slurries with an applied electrostatic field

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Abstract

A novel method combining directional solidification of aqueous slurries with an applied electrostatic field was used to fabricate aligned porous alumina scaffolds. A temperature gradient of 1 °C/mm induced a vertical solidification direction. The angle between the temperature gradient and the applied electrostatic field was 90°. As the electrostatic field intensity was increased from 10 to 100 kV/m, the average lamellar spacing of the porous alumina increased from 53.2 to 278.5 μm, and the angle of the lamellar pore channels changed from 7.5° to 52.6° compared to the direction of the temperature gradient. The direction of the lamellar pore channels was a vector sum of the temperature gradient and the electrostatic field intensity. The fabrication of porous alumina with an ordered, lamellar structure can be readily controlled using directional solidification combined with an applied electrostatic field.

Keywords: Shaping; Directional solidification; Porosity; Al_2O_3; Functional applications

1. Introduction

Ceramics with open pore structures are expected to find application as bone biomaterials, porous piezoelectric materials, scaffolds in solid oxide fuel cells (SOFCs) and ceramic filters because of their large surface area and excellent permeability.[1–4] Directional solidification has recently been demonstrated as a useful method for the production of porous ceramics.[5–7] Major advantages of this method are that the formation of pore structures is easily controlled and the fabricated porous ceramics have a higher porosity than those produced by other methods.[8–11] Many achievements have been made using freeze casting to fabricate porous ceramics, such as dense/porous bilayered yttria-stabilized zirconia (YSZ) ceramic composites[12] and functionally graded, continuously aligned pore structures.[13] Directional freezing is one of the most promising methods for fabricating porous ceramics. Recently, we found that using an auxiliary process during freeze casting was an effective method for controlling the pore structure of ceramics.[14,15]

In the present work, we attempt to control the direction and consistency of the pore channels in porous ceramics. Our strategy involves a novel method which combines vertical directional solidification and controlling the intensity of a horizontal electrostatic field. Both of these factors influence the formation of ice nuclei and the crystallization rate of deionized water as it freezes. The direction and size of the growing ice crystals changes with a temperature gradient and different electrostatic field intensities. Regular pore structures with consistent lamellae spacing and pore channel direction are obtained after vacuum drying and sintering. This provides a new process for controlling the pore structures formed in porous ceramics.

2. Experimental procedure

Alumina powder (GW-1, Dengfeng Smelting Materials Co., Ltd., Henan, China) with a median size (d_{50}) of 1 μm was used as a ceramic material and deionized water was used a freezing medium. Polyvinyl alcohol (PVA) (Yakuri Pure Chemicals Co., Ltd., Osaka, Japan) was used as a binder. A dispersant (SND 6800, S&D Chemical Co., Ltd., Shanghai, China) was used for stabilizing the slurry.

Alumina powder was mixed with 1 wt.% of dispersant and 0.5 wt.% binder in deionized water, and ground with a ball-mill

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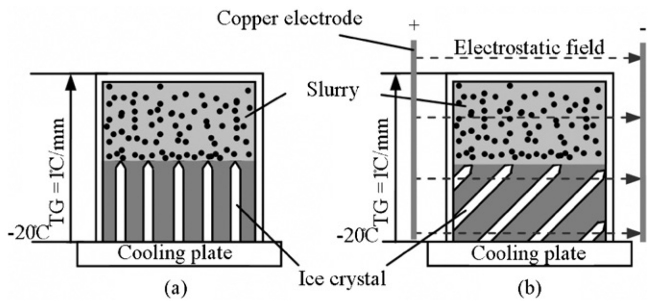

Fig. 1. Schematic diagrams of the freeze casting apparatus, showing (a) vertical ice crystal alignment after directional solidification, and (b) angled ice crystals produced by combining a temperature gradient with an applied electrostatic field. TG is the temperature gradient.

for about 12 h. The slurry contained a total of 30 vol.% solids. The prepared slurry was poured into polyethylene cylinders with a diameter of 10 mm and a height of 15 mm, then placed on a pre-cooled plate in a freeze drier (VFD2000, Boyikang Co., Ltd., Beijing, China). The samples were frozen by directional solidification for 3 h, while being maintained at a temperature gradient of 1 °C/mm, and an electrostatic field intensity of 10–100 kV/m. The angle between the temperature gradient and the electrostatic field intensity was 90°. The electrostatic field was produced by applying a high voltage generator (HVC, MS2671A, Minsheng Electronics Co., Ltd., Nanjing, China) to copper electrodes, which induced the formation of ice nuclei in the slurry. Two schematics of the experimental setups are shown in Fig. 1(a) and (b). After crystallization, the samples were dried at 0–25 °C to remove the ice and sintered at 1500 °C for 2 h.

Pore structures (e.g. the degree of alignment of the lamellar pores and the lamellar spacing) of the fabricated samples were characterized by scanning electron microscopy (SEM, 1000B, AMRAY, Cambridge, United States) and binocular stereomicroscope (SZ61, OLYMPUS, Tokyo, Japan). The lamellar spacing was determined by measuring the cross-section of the samples using the digital imaging tool; more than five specimens were tested to obtain an average value. The porosity of the sintered samples was measured using the Archimedes principle.

3. Results and discussion

An alumina scaffold with lamellae directed lengthwise was obtained, as shown in Fig. 2(a), by freeze casting the sample solution with a temperature gradient of 1 °C/mm (from −20 °C). The distribution of lamellar pore channels was random, as observed in the inset of Fig. 2(a). When a horizontal electrostatic field with an intensity of 10 kV/m as well as a temperature gradient was applied during crystallization, the resulting scaffold possessed a different morphology (Fig. 2(b)). The pores were tilted, with an average angle of 27.6° from the direction of the temperature gradient. As can be seen from the inset of Fig. 2(b), the lamellar pore channels exhibit strict orientational control.

During the freezing process, ice nuclei formed randomly in the slurry in the bottom of the mould at a low temperature (−20 °C). The water in the slurry then froze following the direction of the temperature gradient. The directional ice crystals then acted as a template to produce vertical lamellar structures in the alumina. Water is a strongly polar molecule.[16] The dipole moments of the water molecules in the slurry formed an additional electrostatic field because they were influenced by the applied electrostatic field. The water molecules tend to follow the direction of the applied electric field. Water molecules aligned by the applied electrostatic field can readily enter the crystal lattice of ice crystals and undergo phase transformation. This allowed alumina scaffolds with consistently inclined lamellar structures to be obtained. The formation of inclined pores is dependent on the induced nucleation of water molecules in the bottom of the mould being controlled simultaneously by the temperature gradient and electrostatic field intensity.

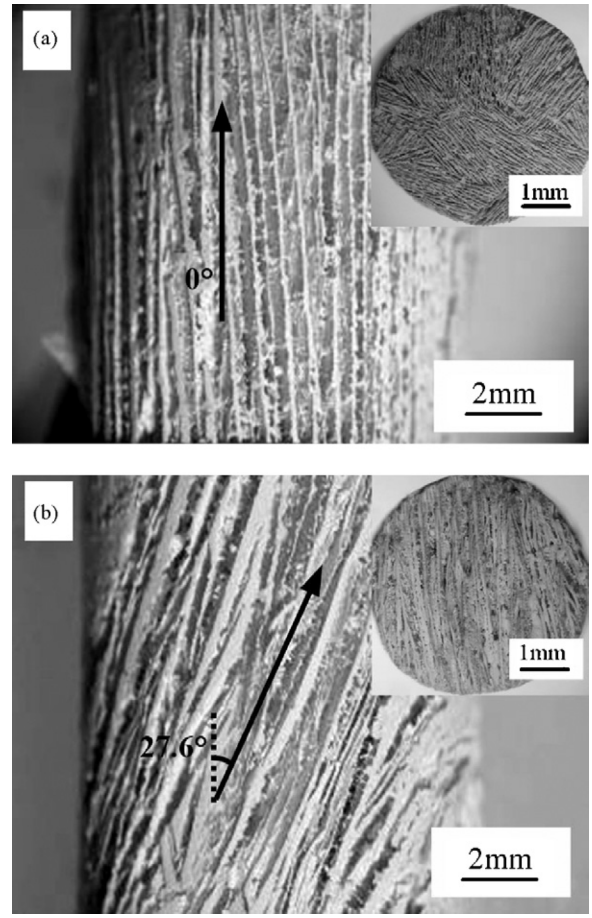

Fig. 2. Effect of electrostatic field intensity on the morphology of the alumina scaffolds produced with (a) a temperature gradient of 1 °C/mm only, and (b) a temperature gradient of 1 °C/mm and an electrostatic field intensity of 40 kV/m. The inset images show cross-sections of the scaffolds.

Table 1 lists the properties of the porous alumina scaffolds cast with 30 vol.% alumina, using directional solidification at different electrostatic field intensities. The porosity of all of the samples was about 78 vol.% regardless of the parameters used for preparation. This result indicates that the porosity is related to the initial alumina content of 30 vol.%. The average lamellar spacing in the scaffold increased from 53.2 to 278.3 μm, and the angle between the direction of the pore channel and the temperature gradient ranged from 7.5° to 278.3° as the electrostatic

Table 1
Properties of the as-synthesized porous alumina scaffolds.

No.	Electrostatic field intensity (kV/m)	Average lamellar spacing (μm)	Direction of pore channel (°)	Porosity (vol.%)
1	10	53.2	7.5	77.1
2	40	102.9	27.6	78.2
3	70	165.3	42.3	77.9
4	100	278.5	52.6	78.9

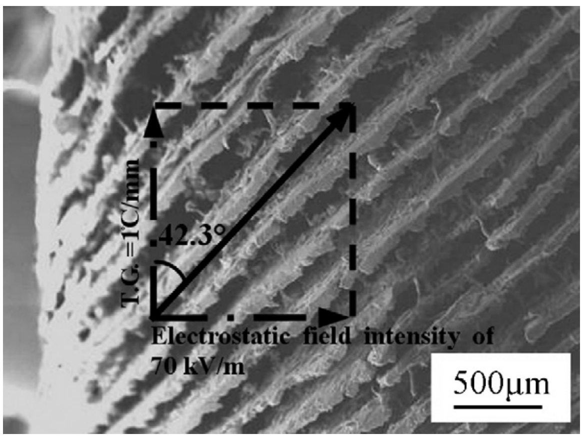

Fig. 3. Typical SEM micrograph of a sample produced using directional solidification with an electrostatic field intensity of 70 kV/m and an initial alumina content of 30 vol.%.

field intensity increased. The temperature gradient determined the lamellar spacing of the scaffold. As the growth rate of the ice crystals increased because the temperature gradient increased, the lamellar spacing decreased. In addition to controlling the direction of crystal growth, the applied electric field affected the growth of ice crystals.[17] At the same temperature gradient, a large electrostatic field intensity decreased the growth rate of ice crystals and increased the lamellar spacing.

It should be noted that the direction of growth of the ice crystals is in the range of 0–90°, because the water molecules were simultaneously subjected to a temperature gradient at an angle of 0° and a perpendicular electrostatic field intensity (i.e. at an angle 90° to that of the temperature gradient). In other words, the direction of the lamellar pore channels was a sum of the vectors of the temperature gradient and the electrostatic field intensity (see Fig. 3).

Alumina scaffolds with various average lamellar spacing and angles of pore channel were obtained by employing a combination of vertical directional solidification with an applied horizontal electrostatic field. The results illustrate that this method could feasibly be used to control the formation of pore structures in ceramics. This method is applicable to ceramic slurries in various polar solvents, and can be used to produce porous ceramics with several types of regular pore structures.

4. Conclusions

In summary, aligned lamellar porous alumina scaffolds were prepared using a combination of vertical directional solidification with an applied horizontal electrostatic field. Porous ceramics were produced from an aqueous alumina slurry subjected to these techniques as they control ice nucleation and the direction of crystal growth. The direction of the pore channels is a vector sum of the temperature gradient and electrostatic field intensity. By controlling the electrostatic field intensity, it was possible to adjust the average lamellar spacing from 53.2 to 278.5 μm, and the direction of the pore channel from 7.5° to 52.6° *versus* the direction of the temperature gradient.

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