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Freeze casting of aqueous alumina slurries with glycerol for porous ceramics

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Abstract

Experiments have been performed to show that the mechanical properties of alumina porous ceramics may be improved by introducing glycerol into the raw slurries and then casting them under a constant cooling rate. The effects of glycerol on the freeze casting process and thereby on the microstructure and mechanical properties of porous ceramics obtained are investigated. It is shown that the addition of glycerol will increase both the slurry viscosity and sample sintered density. SEM images for microstructure of the final ceramics reveal that a good connection between ceramic lamellae has been promoted. This connection makes as-prepared porous ceramics obtain high mechanical properties. For the 30 vol.% alumina slurry with glycerol, the axial and radial compression strengths reach to, respectively, 255.1 MPa and 105.8 MPa.

Keywords: B. Microstructure-final; D. Al_2O_3; Freeze casting; Porous

1. Introduction

Porous ceramic as a technological important material posses a wide range of applications, such as separation materials [1], catalyst supports [2,3], and implantable bioceramics [4–6]. Various methods for the manufacturing of such materials have been developed in the past years. Recently, the freeze casting technique, as a novel method, causes much attention, due to its simple operation, widely controllable porosity and environmental friendliness [4–19]. In this technique, the dispersed slurry is poured into a mold and then frozen by layer by layer solidification mode [4,17–19] or unidirectional solidification mode [5–16]. During the freezing process, the particles are expelled from the moving solidification front, and pile up between the vehicle crystals until the process completed. Subsequently, sublimation of the vehicle is made to eliminate the drying stresses, avoiding shrinkage, cracks and warping of the green parts that generally existing in the normal drying. Finally, the porous materials with a lamellar or/and columnar continuous microstructure are obtained by sintering.

However, as a special unidirectional solidification, the constant cooling rate freezing method, which can achieve a homogeneous lamellae spacing and lamellae thickness by controlling a constant temperature gradient, has not arisen considerable investigation. In addition, freeze casting of aqueous slurries for porous ceramics mainly focuses on the use of slurry without antifreeze agent [6–13]. Little attention has been paid to the effect of antifreeze agent [20,21]. In this work, we introduce glycerol, as an antifreeze agent, into the slurry, to fabricate porous ceramics by a constant cooling rate process and investigate the effect of glycerol on the freeze casting process. Herein, alumina is used as model material.

2. Experimental procedure

First, distilled water, a small amount (1.2 wt.% of the alumina powder) of dispersant (Darvan 7-N, R.T. Vanderbilt Co., Norwalk, CT), binder (polyvinylalcohol, 1 wt.% of the alumina powder) and glycerol (10 wt.% of solvent) were mixed in the milling container. Then, an appropriate amount of alumina powder (99.99% α-Al_2O_3, mean particle size 0.4 μm, Dalian Luming Nanometer Material Co., Ltd., Dalian, China) was added into the mixed solutions and ball-milled for 24 h with zirconia balls and de-aired by stirring in a vacuum desiccator. Here slurries with 20 vol.% and 30 vol.% solid content were chosen for the fabrication of porous ceramics. For the purpose of comparison, the slurries containing same solid content without glycerol were also prepared.

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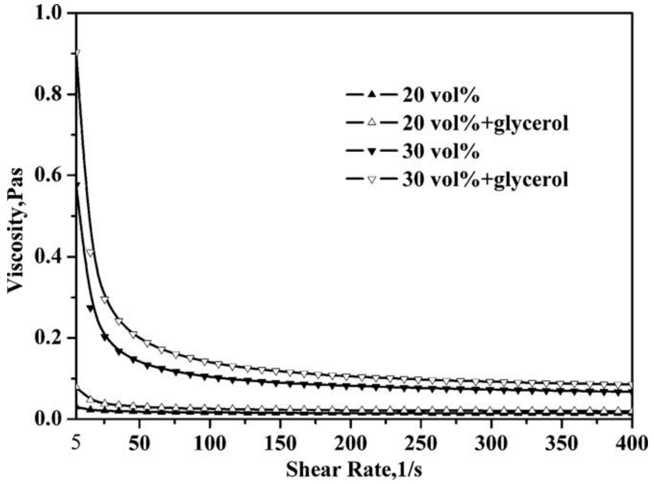

Fig. 1. Viscosity of 20 vol.% and 30 vol.% alumina slurries with and without glycerol.

The mixed slurries were poured into polyethylene molds (20 mm diameter, 15 mm long) and placed on refrigeration equipment, similar to that designed by Deville et al. [11–13]. The cooling rate is kept at 6 °C/min to induce the unidirectional solidification of the slurries from the bottom to the top. The frozen samples were then freeze-dried for 48 h to remove the solvent. All green parts were sintered in air for 2.5 h at 1550 °C with a constant rate of 5 °C/min, followed by cooling naturally in furnace to room temperature.

Table 1
Fitting results for data in Fig. 1.

Solid loading (vol.%)	Glycerol (wt.%)	η_0	η_∞	α	Correlation factor (R^2)
20	0	0.0348	0.0140	0.057	0.9912
20	10	0.1173	0.0194	0.110	0.9962
30	0	1.1303	0.0654	0.183	0.9974
30	10	1.8802	0.0804	0.200	0.9978

The viscosity of the slurries was characterized by rheometer with a concentric-cylinder geometry (Physica MCR300, Anton Paar GmbH, Graz, Austria). Zeta potential measurements were conducted with a Zetasizer 3000 (Malvern Instruments Ltd., Worcester, UK). The as-prepared products were coated with a thin layer of gold and characterized in a scanning electron microscope (FEI Quanta 200, FEI Company, Hillsboro, US). The apparent density and porosity of sintered bodies were measured using the Archimedes method. Samples of 4 mm × 4 mm × 5 mm were cut off from the sintered bodies, and were loaded at a testing machine (Instron 5569, Instron corp., Canton, US) to test the compressive strengths, with a crosshead speed of 1 mm/min. In order to obtain the average value, more than four samples of each measurement were chosen.

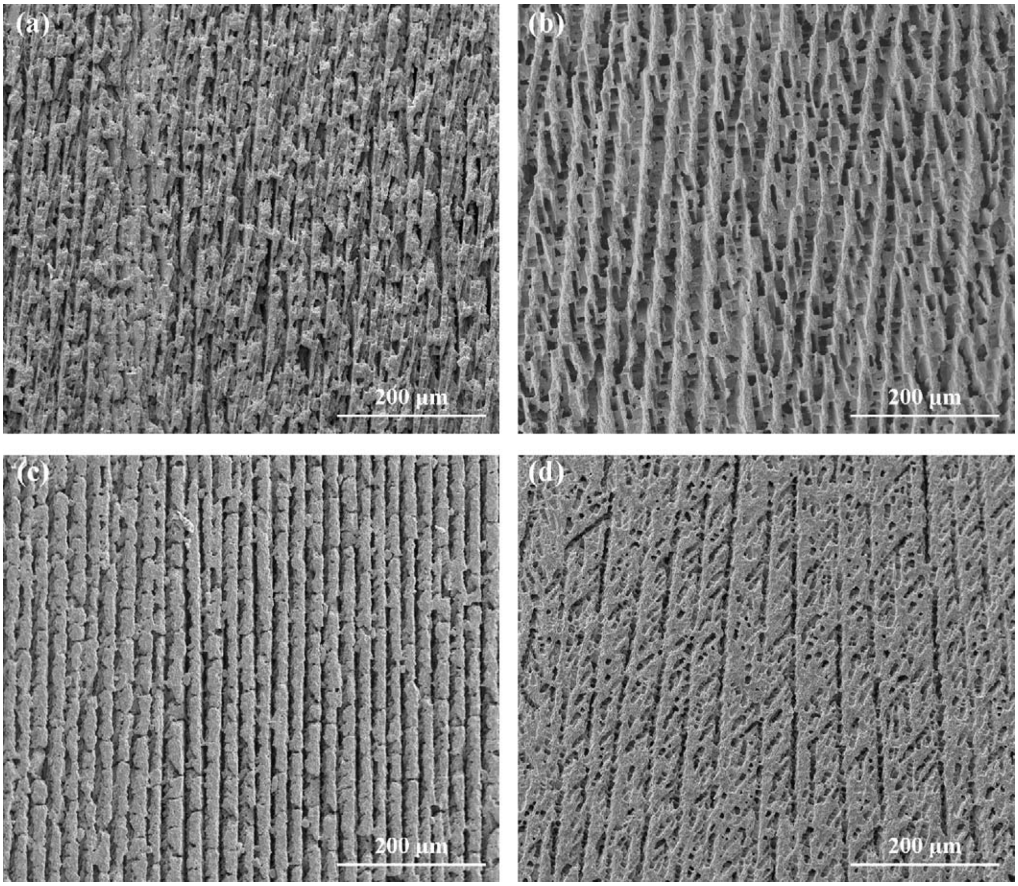

Fig. 2. Microstructure of porous alumina ceramics prepared from (a) 20 vol.% slurry without glycerol, (b) 20 vol.% slurry with glycerol, (c) 30 vol.% slurry without glycerol and (d) 30 vol.% slurry with glycerol. The direction of cross-section perpendicular to the ice front.

Table 2
Properties of sintered porous alumina ceramics.

Solid loading (vol.%)	Glycerol (wt.%)	Apparent density (g/cm^3)	Porosity (%)	Open porosity (%)	Axial compression strength (MPa)	Radial compression strength (MPa)
20	0	1.398 ± 0.018	64.9 ± 0.5	63.3 ± 1.0	96.4 ± 4.0	29.7 ± 1.7
20	10	1.431 ± 0.025	64.1 ± 0.6	63.1 ± 1.3	127.6 ± 9.3	34.1 ± 2.3
30	0	2.019 ± 0.026	49.3 ± 0.7	44.9 ± 1.4	194.2 ± 12.4	41.5 ± 3.2
30	10	2.063 ± 0.016	48.2 ± 0.4	45.9 ± 0.9	255.1 ± 14.1	105.8 ± 6.7

3. Results and discussion

Fig. 1 shows the viscosity of 20 vol.% and 30 vol.% alumina slurries with and without glycerol. It is clear that the slurries with glycerol always have a higher viscosity than those without glycerol. With the increase of shear rate, all of the slurries exhibit shear-thinning behavior.

Measurements on zeta potential show that alumina particles are negatively charged with the zeta potential about −23.0 mV and −23.9 mV for slurries with and without glycerol, respectively. This suggests that the electrostatic interaction between particles is not the main reason leading to the enhancement of viscosity. Lu et al. [22,23] supposed that the carboxyl groups can interact with the hydroxyl groups to form link structure by hydrogen bonding. Therefore, the differences of viscosity between slurries with and without glycerol perhaps come from the effect of the links. The more the links, the easier are the tanglement between the links and the greater are the viscosity values. As a result, the higher viscosities exist in the slurries with glycerol (Fig. 1).

To describe the rheological behavior of non-Newionian fluids, Cross [24] establishes a simple expression:

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + \alpha\gamma^n} \tag{1}$$

where η_0 and η_∞ are limiting viscosity at zero and infinite rate of shear, respectively. η is the slurry viscosity and vary with shear rate γ. α is a parameter with the rupture of linkages. According to the measured data in Fig. 1, the fitting variables are evaluated in Table 1. Here, n is a common exponent 10/9,

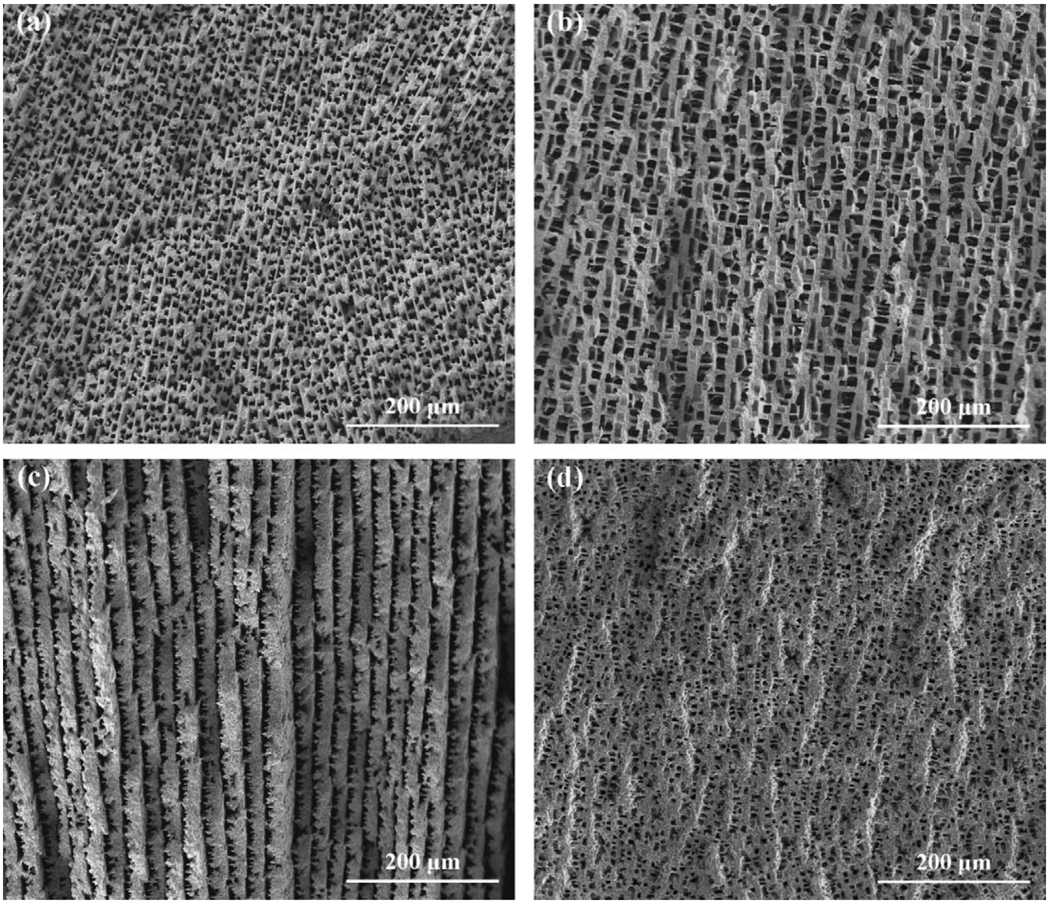

Fig. 3. SEM micrographs of porous alumina ceramics, which are prepared by using: (a) 20 vol.% slurry without glycerol, (b) 20 vol.% slurry with glycerol, (c) 30 vol.% slurry without glycerol and (d) 30 vol.% slurry with glycerol. The direction of fracture parallel to the ice front.

different from the recommended value 2/3 by Cross paper [24]. This difference is perhaps due to the influence of macromolecules links on slurry systems. In addition, basing on Cross's analysis, a high α value implies there is a large shear dependent contribution to structural breakdown [24]. In our experiments, α for the slurries containing glycerol always takes a larger value than those not (Table 1), which indirectly provides support for the existence of more links in the alumina slurry with glycerol.

The addition of glycerol changes the freezing behavior of water. For example, the volumetric expansion of water will decrease from 9% to 7.4% by volume at 10 wt.% glycerol in water [25]. Similarly, the addition of glycerol to the alumina slurries will reduce slurries expansion in the freezing process, leading to a slight increase of the sintered density of as-prepared porous ceramics (Table 2).

Measurements on the compression strength of porous ceramics show that those prepared from the slurries containing glycerol posses a higher strength (Table 2). For 20 vol.% and 30 vol.% alumina slurries with glycerol, the axial (parallel to growth direction of ice crystals) strengths are 127.6 ± 9.3 MPa and 255.1 ± 14.1 MPa, respectively. While the radial (perpendicular to growth direction of ice crystals) strength for 30 vol.% alumina slurries with glycerol also reaches as high as 105.8 ± 6.7 MPa. Therefore, the preparation of porous alumina ceramics using slurries with glycerol is beneficial to load-bearing biological application [6].

This enhancement of compression strength may be attributed to the improving on the connection between ceramic lamellae. The typical microstructures of porous ceramics prepared from the slurries containing glycerol or not are illustrated in Figs. 2 and 3. Obviously there exists a good connection between lamellar architectures in the ceramics from the slurries with glycerol (Fig. 2(b) and (d)).

In the parallel to directions of the ice front, cell-like pore structure is observed in ceramics from the 20 vol.% alumina slurries containing glycerol or not (Fig. 3(a) and (b)). The cell sizes are measured by an intercept method as 15–20 μm and 5–18 μm, respectively. It is worthy to note that the addition of glycerol obviously improves the homogeneity of cell wall (Fig. 3(a) and (b)). This may lead to the enhancement of axial and radial compression strength (Table 2). In addition, when the solid loading of the slurry containing no glycerol is increased to 30 vol.%, the cell-like structure converts into a lamellar one (Fig. 3(a) and (c)), while dendritic like features protrude on the surface of the pore walls are still maintained (Fig. 4). However, for the ceramic from slurry with glycerol, the microstructure transition does not occur. When solid loading of such slurry increases, the smaller pore exhibits in porous ceramics.

For the slurries containing same solid content, the glycerol concentration is the solely variable parameter. Thus, the difference of microstructure of sintered samples originates from the influence of glycerol on the freezing process. In that process, all of solutes are separated from and piled up around the growing pure ice crystals. The equilibrium among the diffusion rate of glycerol, ice crystal growth rate and the alumina particle ejecting rate, combined with a high heat transfer of the slurries with glycerol [25], gives rise to a different ceramic lamellae thickness and interlayer distance compared with the sample (Fig. 2) from slurry without glycerol. On the other hand, the addition of glycerol changes the hydrogen bonding of water. It is known that as the glycerol concentration increases from 0 wt.% to 10 wt.%, the average number of hydrogen bonding/water in bulk water decreased from 3.9 to 2.4 [26]. The more water molecules are bound in the first hydration shell around the polar groups of glycerol. This disrupts the complete crystallization of ice, leading to a localized amorphous structure [17]. In addition, high slurry viscosity, on some extent, also inhibits the expelling of alumina particles from the growing ice crystals. These related factors together increase the connection between lamellae and improve compression strength of porous ceramics.

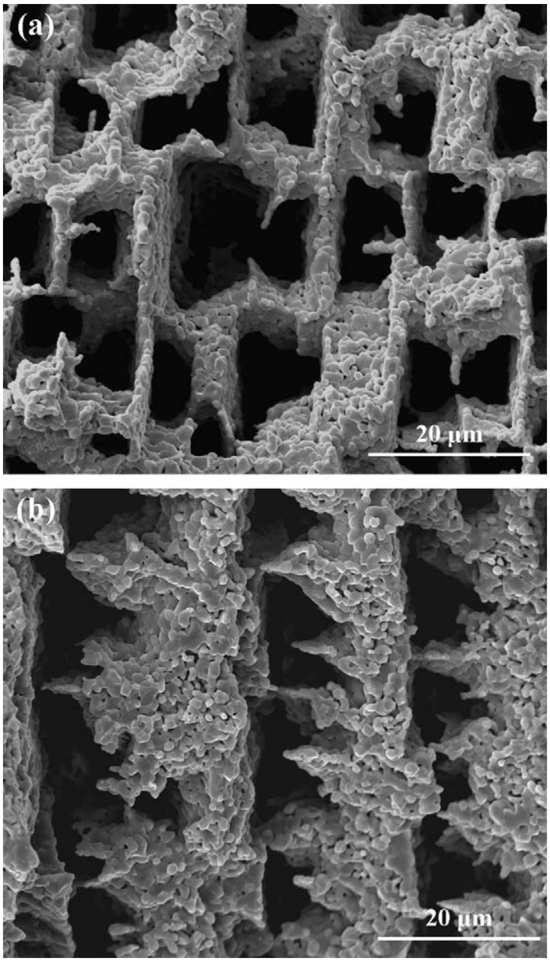

Fig. 4. SEM micrographs of dendritic like features on pore walls. Parts (a) and (b) are magnified images of Fig. 3(a) and (c), respectively.

4. Conclusions

This study demonstrated the effect of glycerol on freeze casting of aqueous alumina slurries for porous ceramics. Our experiment results indicated that the addition of glycerol into aqueous alumina slurries will increase their viscosity and decrease their volume expansion. Interaction between glycerol and other components in the slurries promotes a good connection between lamellae and thus improve the mechanical properties of porous ceramics. For the ceramics prepared from 30 vol.% alumina slurries, 31.4% and 154.9% increment for the axial and radial compression strength can be achieved.

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