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Short communication

# The controllable microstructure of porous $Al_2O_3$ ceramics prepared via a novel freeze casting route

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**Abstract**

In traditional aqueous slurry freezing casting processing, the growth method of ice crystals is hard to control, resulting in the uncontrollable pore's morphologies of the porous ceramics. In the experimental, the pure $Al_2O_3$ sol was used to substitute water as a medium for preparing ceramic slurry. With $Al_2O_3$ sol addition, it becomes easy to control the microstructure and pore's morphologies of the porous $Al_2O_3$ ceramics via adjusting of the solid loading, composition of the ceramic slurries, as well as the cooling methods. The SEM micrographs showed that the sol-contained ceramic slurry combined with freeze casting processing can easily prepare the porous $Al_2O_3$ ceramics with different pore sizes and different morphologies. The porous $Al_2O_3$ ceramics prepared from 70 wt.% to 90 wt.% solid loading sol-contained $Al_2O_3$ slurries and sintered at 1500 °C for 2 h have open porosities from 81.7% to 64.6%.


*Keywords:* Alumina; Freeze casting; Slurry; Microstructure

## 1. Introduction

Ceramics with different pore sizes and porosities have drawn much attention due to their unique properties such as low density, low thermal conductivity, high temperature stability and chemical corrosion resistance, low dielectric constant, etc. Porous ceramics have been widely used in separation, catalytic supports, adsorbents, and so on [1–3]. The distribution of pore size, pore shape and volume of the void space in porous ceramics directly relate to their ability to perform the desired function in particular applications and the controllable pore size and morphology as well as the pore distribution might also enlarge their applications in different areas. Compared to other ceramic processing methods, the freeze casting is an easy, cost effective and environmental friendly processing, which has been used in porous ceramics preparation [4–18]. Fukasawa et al. [5] used freeze casting to prepare porous silicon nitride with unidirectionally aligned channels, Deville et al. [11] fabricated hydroxyapatite ceramics with lamellar and cellar pores, which exhibited high compressive strength. Ren et al. [8] prepared gradient pore $TiO_2$ sheets by a novel freeze-tape-casting process. Many factors induce the microstructures and properties of porous ceramics prepared by the freeze casting, such as, the solid loading, the organic additives, solvent, freezing rate, sintering conditions, and so on. In aqueous ceramic slurry freezing casting, ice plays the role of a template. How to control the size, shape and morphology of ice formed *in situ* is directly related to microstructure and properties of porous ceramics. However, many papers published on this topic are mainly focus on how to control the ceramic porosity by adjusting solid loading of slurry, only a few reports are related to control the microstructure and porous morphology of ceramics by tuning the composition and organic additives of slurries [19,20]. In the experiment, the $Al_2O_3$ sol solution was used to replace pure water to prepare sol-contained $Al_2O_3$ slurry. The sol contain ceramic slurry was first frozen to green body, which was then lyophilized to remove ice via sublimation. The porous $Al_2O_3$ ceramics were obtained after sintering at different temperatures. The solid

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Table 1
The formulation of the sol-contained $Al_2O_3$ slurries used in the experiment.

| Name | $Al_2O_3$ from powder (g) | $Al_2O_3$ from sol (g) |
|---|---|---|
| 90 wt.% | 90 | 10 |
| 85 wt.% | 85 | 15 |
| 80 wt.% | 80 | 20 |
| 75 wt.% | 75 | 25 |
| 70 wt.% | 70 | 30 |

loading, sol contraction as well as the cooling method effect on the microstructure, pore's morphology and porosity of $Al_2O_3$ ceramics were investigated.

## 2. Experimental procedure

α-$Al_2O_3$ powder (Showa Denko Co. Ltd. Japan, 160SG-1) was first dispersed in $Al_2O_3$ sol (alumina-sol 520; Nissan Chemical Industries, Japan) via ball-milling 24 h without any other organic additive to break agglomerate to get the well-dispersed sol-contained $Al_2O_3$ slurry. The TG analysis results indicated that $Al_2O_3$ sol contained about 16 wt.% pure $Al_2O_3$. In the experiment, the sol-contained $Al_2O_3$ slurry, such as 80 wt.% slurry, means that 80 wt.% $Al_2O_3$ is from $Al_2O_3$ powder and 20 wt.% $Al_2O_3$ is from $Al_2O_3$ sol. Table 1 shows the composition of slurries used in the experiment. The sol-contained $Al_2O_3$ slurry was then poured into a mould and frozen (Fig. 1 is the schematic illustrating diagram of the freeze casting sol-contained $Al_2O_3$ slurry in liquid nitrogen). Finally, the frozen green body was moved into a lyophilizer to remove ice via sublimation. The specimen were then sintered to the resetting temperature with a heating and a cooling rate of 5 °C/min. Open porosity and density were determined by Archimedes method in distilled-water, the pore size of the specimen was measured by the mercury porosimetry (Model PoreSizer 9320, Micromeritics, US) and microstructures and morphology were observed by scanning electron microscopy (SEM; Model JSM-5600, JEOL, Ltd., Tokyo, Japan).

## 3. Results and discussion

### 3.1. Microstructure of the $Al_2O_3$ sol derived ceramics

Fig. 2 shows the scanning electron microscope (SEM) image of the pure $Al_2O_3$ sol sintered at 1300 °C for 2 h. The commercial available $Al_2O_3$ sol was first frozen in liquid nitrogen, the frozen green body was then lyophilizated and subsequently sintered at 1300 °C. It is obvious that the phase separation happened and many uniform pore channels are clearly seen. While the sol-solution is freezing, the growing ice crystals expel the $Al_2O_3$ sol to form sol walls and ice rods, which are oriented in the direction parallel to the movement of the freezing front. The phase separation of $Al_2O_3$ sol is the important factor to adjust the pore size and pore morphology due to the $Al_2O_3$ sol is helpful to form the porous frame. Compared to the pure water, $Al_2O_3$ sol addition can improve the interconnectedness of porous materials.

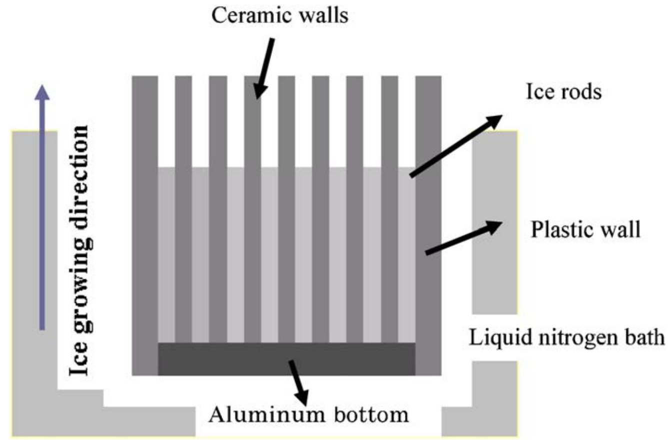


Fig. 1. The schematic illustrating diagram of the freeze casting sol-contained $Al_2O_3$ slurry in liquid nitrogen.

### 3.2. The effect of freeze method and the solid loading of the sol-contained slurries on the microstructure of the $Al_2O_3$ ceramics

As temperature decrease, the phase separation makes the $Al_2O_3$ sol-contained slurry to two phases, one is ice, the other one is the sol-contained $Al_2O_3$ wall. After sintering, except for the pores formed from the ice sublimation, the wall of the sol-contained $Al_2O_3$ is also possible to be pores, resulting in the porous microstructure.

In order to evaluate the cooling direction effects on the microstructure of the pores, two cooling methods were performed in the experiment, one is to use the mould whose cylinder is made of plastic and bottom is made of aluminum; the other one is to pour the $Al_2O_3$ slurry into liquid nitrogen directly. Fig. 3 is the SEM images of sol-contained 75 wt.% $Al_2O_3$ slurry frozen in different directions. Firstly, the sol-contained $Al_2O_3$ slurry was poured into the mould shown in Fig. 1. With temperature decrease, the thermal energy is mainly transmitted in one direction due to aluminum whose thermal conductivity coefficient is higher than that of plastic, therefore,

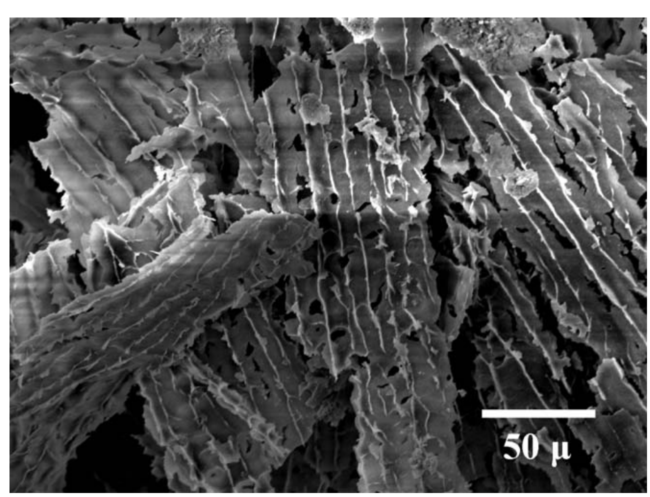


Fig. 2. SEM image of $Al_2O_3$ decomposed from pure $Al_2O_3$ sol and sintered at 1300 °C for 2 h.

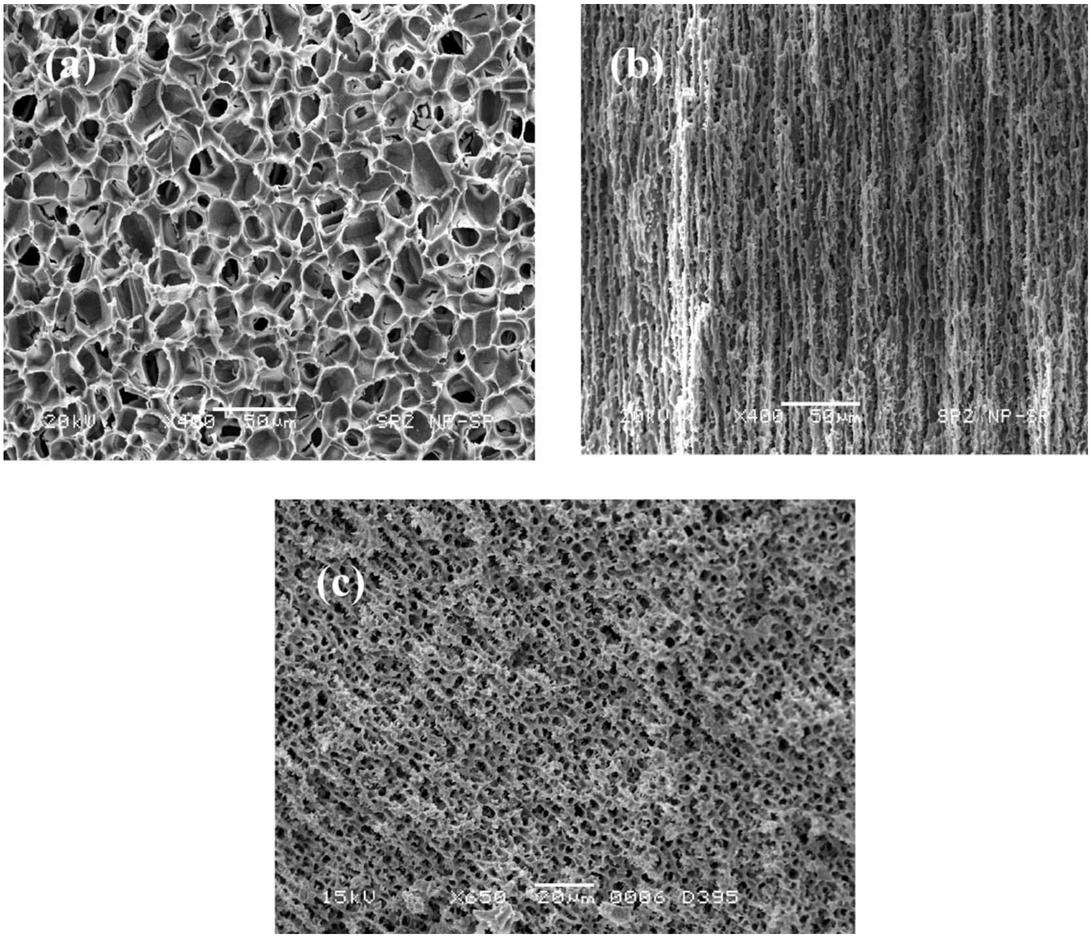


Fig. 3. Cross section SEM images of sol-contained 75 wt.% $Al_2O_3$ slurry frozen in different directions (1300 °C, 2 h): (a) perpendicular to the cooling direction; (b) parallel to the cooling direction; (c) immersion liquid nitrogen.

the ice grows in one direction, resulting in the unidirectional microstructure of the alumina ceramics. The SEM of Fig. 3(a) taken from the cross section of the specimen, which is parallel to the cooling direction, showed that the pores uniformly distribute on the fracture surface. Fig. 3(b) is also the SEM image taken from fracture surface which is perpendicular to the cooling direction. Because the ices growth in one direction, the uniformly pores channel formed after ice sublimation and green body sintering, the result further proved that the ice is growth in one direction. The same sol-contained $Al_2O_3$ slurry was directly poured into liquid nitrogen, after the same treatments, the SEM image of the specimen shown in Fig. 3(c) is totally different. The SEM micrograph of porous $Al_2O_3$ has a three-dimensional reticulate porous microstructure. The result is attributed to the sol-contained $Al_2O_3$ slurry immersed in liquid nitrogen, which is a fast heat exchange process and the cooling rate is the same in all directions. Therefore, the ices unidirectional growth were restrained, resulting in the three-dimensional reticulate porous microstructure.

Except for the cooling method, many other factors, such as, solid loading, the concentration of sol, sintering temperature, etc. have also great effects on the microstructure of the $Al_2O_3$ ceramics. Fig. 4 shows the SEM images of the porous $Al_2O_3$ with different solid loadings. The differences are not only the porous microstructure but also the pore size and morphology. With the variation of the solid loading of the sol-contained slurry, the microstructures and pore morphology shown in Fig. 4(a) and (b) are different. Fig. 4(a) is consist of porous channels and porous ceramic walls. However, Fig. 4(b) has a typical three-dimensional reticulate porous microstructure.

Fig. 5 shows the typical pore size distribution of the 85 wt.% $Al_2O_3$ specimen sintered at 1300 °C. It is clear that there are main two kinds of pores in the specimen, one is the porous channels which are formed from ice sublimation, the pore sizes are about 3.45, 5.72, 13 μm, respectively; the another one is the small pores in the walls, which is formed from the particle accumulation and its size is about 0.192 μm.

### *3.3. The density and porosity of the porous $Al_2O_3$ sintered at different temperatures*

Fig. 6 shows the density and porosity of the porous $Al_2O_3$ sintered at different temperatures. With the increase of solid loading, the density is increase and the porosity is decrease linearly. In fact, the freeze casting can prepare much high porosity materials with bimodal and controllable pore size and pore morphology. The porous $Al_2O_3$ ceramics prepared from 70 wt.% solid loading sol-contained $Al_2O_3$ slurries and sintered

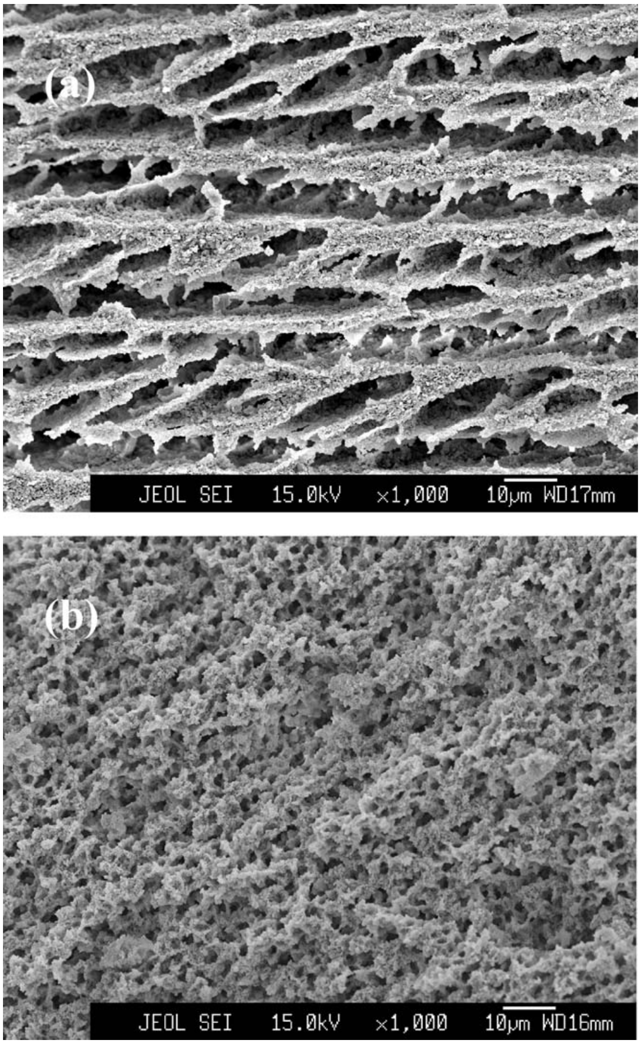


Fig. 4. SEM images of porous $Al_2O_3$ prepared from different $Al_2O_3$ solid loading slurries (1300 °C, 2 h) (a) 85 wt.% $Al_2O_3$; (b) 90 wt.% $Al_2O_3$.

at 1500 °C for 2 h has open porosity 81.7%, it means that the freeze casting processing can be used to prepare high porosity ceramics.

The sol-contained slurry freezing casting processing presents a simply way to prepare materials with aligned,

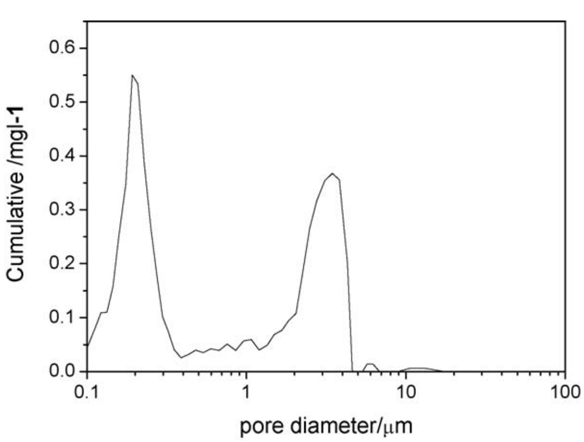


Fig. 5. Pore size distribution of 85 wt.% $Al_2O_3$ sintered at 1300 °C for 2 h.

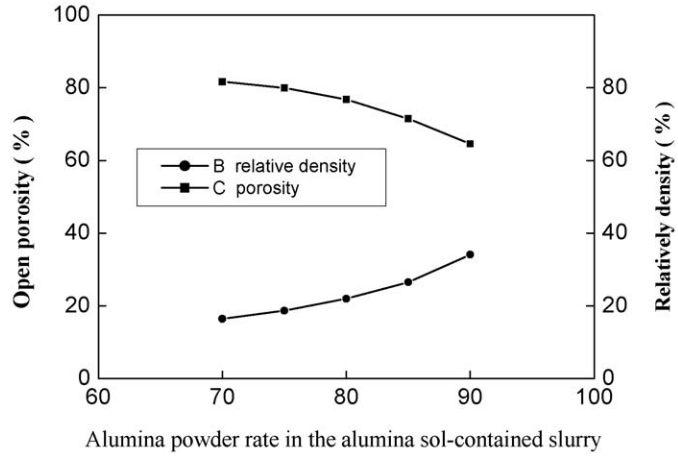


Fig. 6. Open porosity and relative density of the porous $Al_2O_3$ sintered at 1500 °C for 2 h.

bimodal, three-dimensional pores. There are many additional advantages associated with the processing, the method avoids to use organic filler to form pores, and can easily prepare any shape and large components, the special bimodal porous microstructure may find different applications in catalysts, biomaterials, and tissue engineering. The porous materials with aligned pore channels can be used as scaffold for never cell growth in bone replacement. Of course, the method can be also used to prepare other porous ceramics, such as $SiO_2$, $ZrO_2$, hydroxyapatite, $Si_3N_4$, SiC, mullite, and also used to prepare metal porous materials and porous composites.

## 4. Conclusions

By using $Al_2O_3$ sol to replace water, the microstructure and pore's morphology of porous $Al_2O_3$ can be easily modified because the sol is helpful to control the ice growth method. The SEM micrographs showed that $Al_2O_3$ ceramics with aligned, bimodal, three-dimensional porous were prepared by the modified freeze casting processing. The porous $Al_2O_3$ ceramics prepared from 70 wt.% to 90 wt.% solid loading sol-contained $Al_2O_3$ slurries and sintered at 1500 °C for 2 h have open porosities from 81.7% to 64.6%.

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