Pore structure of porous ceramics synthesized from water-based slurry by freeze-dry process

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A unique porous ceramic with complex pore structure was synthesized by the freeze-dry process. A water-based ceramic slurry was frozen while controlling the growth direction of ice, and sublimation of the ice were generated by drying it at a reduced pressure. By sintering this green body, a porous ceramic with complex pore structure was obtained, where macroscopically aligned open pores exceeding 10 μm in size contained minute pores of about 0.1 μm in their internal walls. Wide control of the porosity was possible by changing the concentration of the starting slurry. The pore size distribution as well as the microstructure were substantially affected by the freezing and sintering temperatures. Optimization of the synthesis conditions was investigated in order to obtain the desired pore structure. © *2001 Kluwer Academic Publishers*

1. Introduction

Porous ceramics with open pore structure are expected to be used as filters and supports for catalysts or absorbents. Since high permeability and large surface area are required for these applications, it is essential to control pore structure (shape, morphology, orientation, etc.) as well as porosity, pore size and its distribution in these materials.

A number of conventional methods have been used to fabricate porous ceramics for various purposes. One of the most common techniques is that of firing a ceramic powder compact with an organic material, which is burned out during sintering [1, 2]. Acid leaching, a cost-effective method, has also been widely employed [3, 4]. However, these methods are disadvantageous in certain respects, notably they are harmful to the environment, applicable only to a limited range of materials, and pore structure cannot be controlled. Although ceramic foam is known to be useful because of large surface area and high permeability as well as wide applicability, it has shortcomings, namely low strength, low machinability and the problem posed by pyrolysis of the polymer foam [5–9]. Furthermore, these conventional methods are subject to a certain limitation respecting microscale control of pore structure.

Recently, a freeze-dry process, a novel method of providing a highly porous material with well-controlled pore structure, has been proposed [10, 11]. For example, a highly oriented porous ceramic with high porosity exceeding 90% has been obtained from a metal salt solution by using this technique [12]. Although the mechanical reliability is still poor, the excellent fluid permeability and large surface area suggest that this material may be a promising candidate for application as a filter or a catalytic support.

In the work reported in this paper, using the freeze-dry process, we attempted to fabricate porous ceramics with a unique microstructure from a water-based slurry of ceramic powder. Although aluminum oxide was used, the technique developed in this study is applicable to ceramics of all kinds. Compared to the freeze-dry processes using chemical solutions, this method has several advantages, that is, small sintering shrinkage, simple sintering control, widely controllable porosity, and relatively good mechanical properties. In addition, this process, which uses little other than water, is environmentally friendly. Porous ceramics with complex pore structure were obtained, where aligned macroscopic open pores contained a dendrite structure and minute pores were in internal walls. The effects of slurry concentration, freezing temperature of the slurry and sintering temperature on the pore structure were investigated.

2. Experimental procedure
2.1. Sample preparation
Alumina powder (Showa-Denko, Al-160SG4) was mixed with a small amount of dispersant (Toa-Gosei Chemicals, Alon A-6114) in distilled water. The mixture was ball-milled with nylon balls for about 20 hours. Different slurry concentrations of 28.0–45.0 vol% were prepared. These slurries were de-aired by stirring in a vacuum desiccator.

The slurry was poured into a cylindrical container and only the container bottom face was immersed in a refrigerant in a freezing bath as shown in Fig. 1. The container was composed of two parts: the container bottom made of metal with high thermal conductivity and the side of resin or fluorocarbon polymer. Ethanol was used as the refrigerant and its temperature was controlled at $-20°C$, $-50°C$ and $-80°C$. The top of the container was open so that the upper surface of the slurry would meet atmosphere at room temperature. Thus, ice was stimulated to grow macroscopically in the vertical direction and ceramic particles piled up between the columns of the ice. Microscopic branch-like ice also formed from this macroscopic ice. After the slurry completely froze, the container was put into a drying vessel and was dried for about one day at a reduced pressure.

The samples were carefully taken out of the container. The green bodies were set into an alumina crucible and sintered at various temperatures in the range from 1400°C–1600°C for 2 hours in air.

2.2. Characterization
Rheological properties of the slurry were evaluated by R-type viscometer (Toki Ind., RC-500). The relative density was determined from the mass and dimensions of the sintered bodies. The porosity was calculated by subtracting the relative density from 100%. The shrinkage was defined as the change in diameter of the samples before and after sintering. The pore size distributions of the sintered body were measured by mercury porosimetry (Shimadzu, Autopore 9220). The microstructure of the cross section perpendicular or parallel to the macroscopic ice growth direction was observed by a scanning electron microscope (SEM; JEOL, JSM-5600).
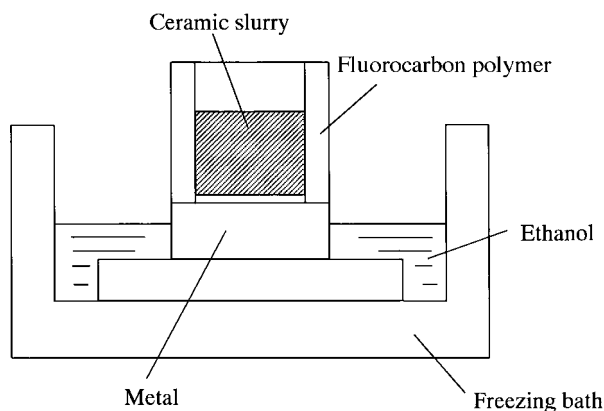

Figure 1 Schematic of freezing process. The container was composed of two parts: the container bottom made of metal with high thermal conductivity and the side of fluorocarbon polymer. Only the container bottom face was immersed in a refrigerant in a freezing bath.

3. Results and discussion
3.1. Shrinkage and porosity
The rheology measurements showed pseudo-plastic behaviors of the slurries, indicating homogeneous dispersion of the powder. The shrinkage and the porosity as a function of slurry concentration at different sintering temperatures are shown in Figs 2 and 3, respectively. The slurry concentration strongly affected the porosity but scarcely affected the shrinkage. This indicates that the porosity results from the water amount of the slurry and then can be widely controlled by the slurry concentration. On the other hand, the shrinkage of the sample is determined almost entirely by the intrinsic shrinkage of alumina itself, irrespective of the slurry concentration, and is for all practical purposes not controlled by it.
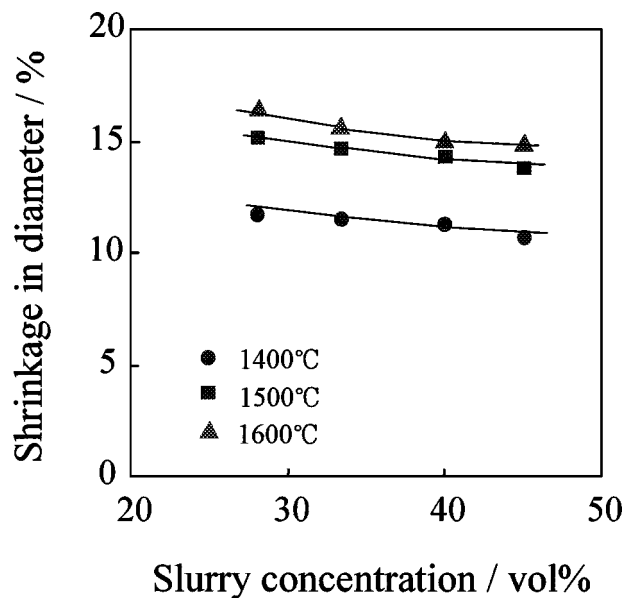

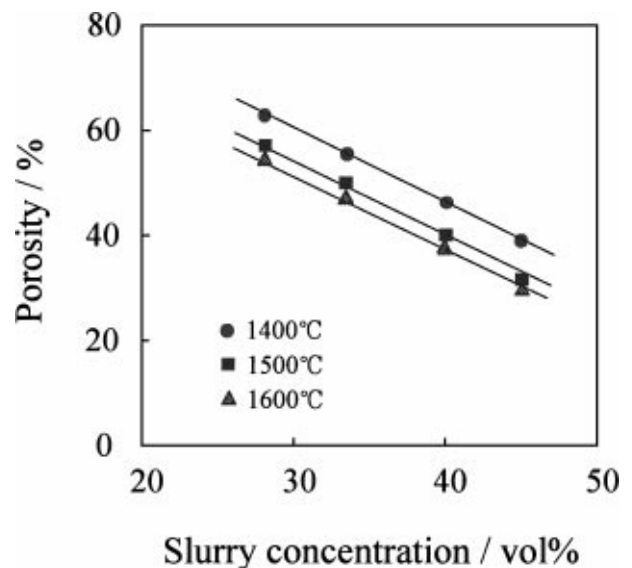*Figure 2* Shrinkage in diameter as a function of slurry concentration and sintering temperature.

Figure 3 Porosity of the sintered bodies as a function of slurry concentration and sintering temperature.
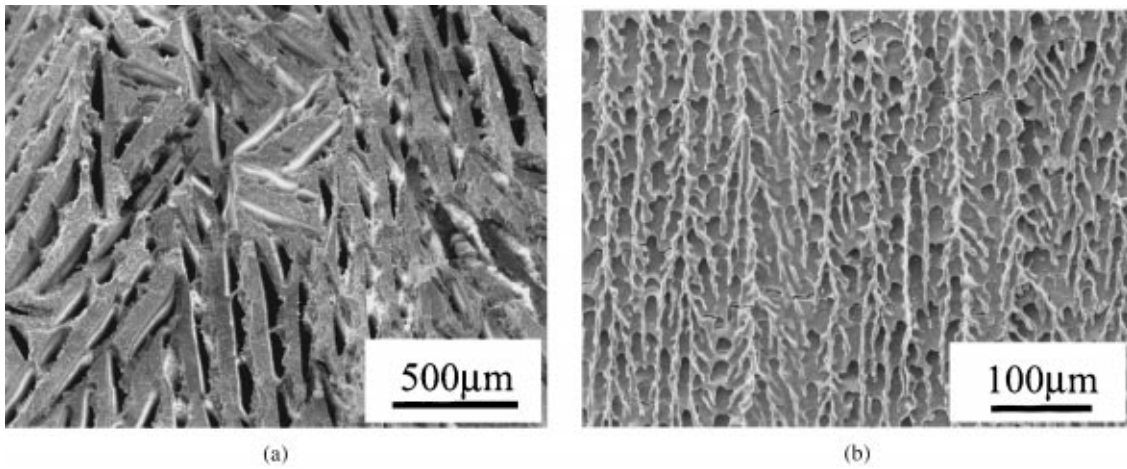
Figure 4 The microstructures of porous ceramics for the 28 vol% sample sintered at 1500°C. All the samples fabricated by freeze-dry process showed such a characteristic microstructure. (a) cross section perpendicular to the macroscopic ice growth direction (b) cross section parallel to the macroscopic ice growth direction.

3.2. Pore structure and pore size distribution

After freeze-dry, it was observed that macroscopic open pores had uniformly formed over the entire sample. These pores were generated from sublimation of the ice and were aligned along its macroscopic growth direction. Fig. 4a and b show microstructures of the cross sections perpendicular and parallel to the
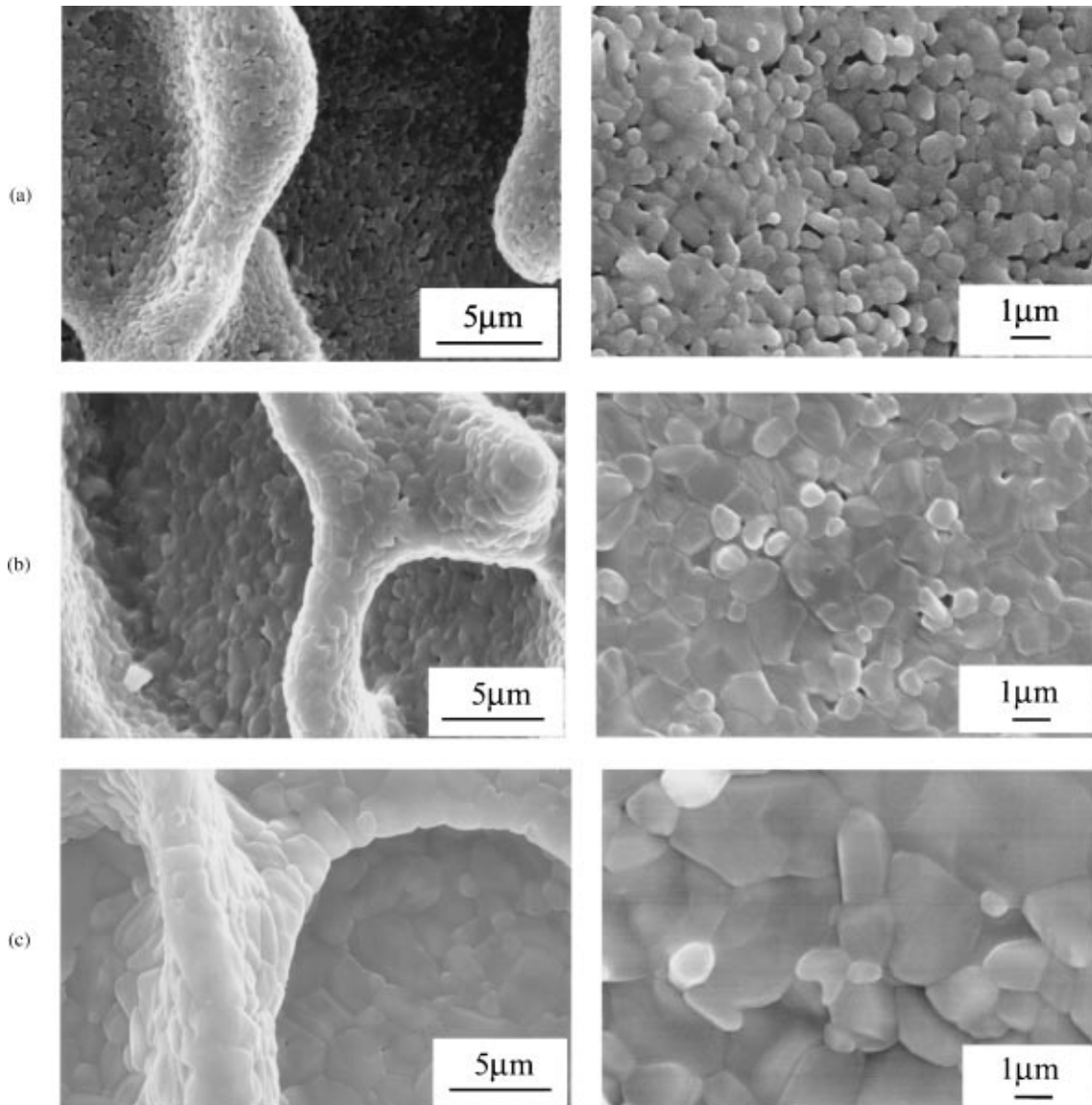

Figure 5 SEM micrographs of the internal wall microstructure for the 28.0 vol% samples sintered at (a) 1400°C (b) 1500°C and (c) 1600°C. The minute pores were observed in the dendrite structure. The grain growth of alumina matrix occurred with increasing sintering temperature.

macroscopic ice growth direction for the 28 vol% sample sintered at 1500°C, respectively. All the samples obtained by this method showed such peculiar microstructures. A dark area with flat shape in Fig. 4a is an open pore. The macroscopic open pores isolatedly existed in the alumina matrix, and were aligned along the ice growth direction. Fig. 4b shows an internal wall of the macroscopically aligned pore. The dendrite structure was formed, with pleat-shaped tracing of the microscopic ice formation.

SEM micrographs of the internal wall microstructure for the 28.0 vol% samples sintered at 1400°C, 1500°C and 1600°C are shown in Fig. 5. Fig. 5 is a magnification of the pores existing in the dendrite structure. It should be noted that the microstructure also had minute pores of sub-micron dimension.

The pore size distributions for the 28 vol% samples sintered at the different temperatures are shown in Fig. 6. The samples sintered at 1400°C showed a distribution which obviously had two peaks. One peak was above 40 μm, and the other was around 0.1 μm. In fact, both sizes of the pores were identified in the above microstructural observation (Fig. 5). These minute pores disappeared as the sintering proceeded at higher temperature. In fact, substantial grain growth of alumina matrix was observed with increasing sintering temperature (Fig. 5). These minute pores most likely formed due to the traces of the ice left between the alumina grains.

The peak pore size, porosity and specific surface area determined by mercury porosimetry are listed in Table I. The peak pore size is the pore diameter of a peak in the distribution. The porosity given by mercury porosimetry was almost the same as that calculated from the relative density. Therefore, it is reasonable to suppose that most of the pores are open ones. Although the slurry concentration had little effect on the minute pore size, the higher concentration tended to result in macroscopic pores of smaller size. The minute pore is most likely depends on the starting powder. The materials composed of such a complex pore structure are useful as support materials for catalysts and absorbents, etc. It is possible to enlarge the specific surface area further by controlling the pore structure as well as selecting the starting materials, and a study of this is in progress.

TABLE I Physical properties determined by mercury porosimetry. The peak pore size is the pore diameter of a peak in the pore distribution

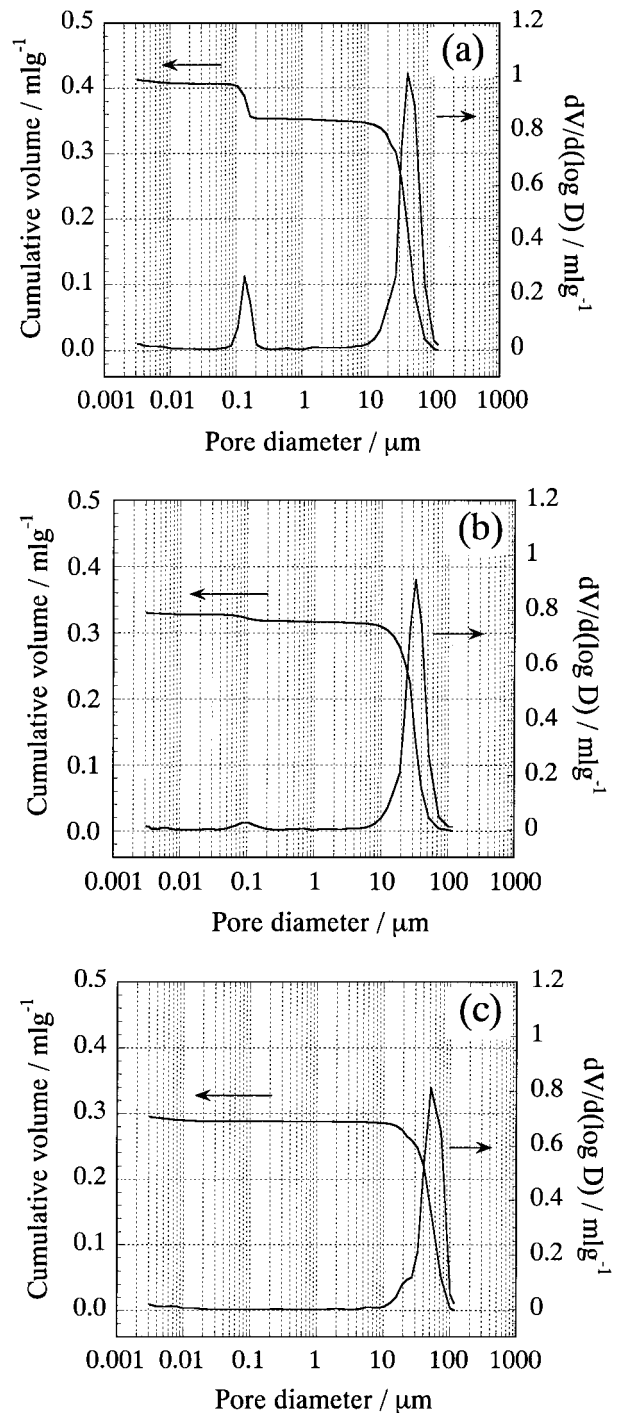| Slurry concentration (%)	Sintering temperature (°C)	Peak pore size (μm)	Porosity (%)	Specific surface area (m²/g)
28.0	1400	0.15, 40	61.3	7.1
28.0	1500	0.10, 32	55.8	2.6
28.0	1600	51	52.8	4.9
33.3	1400	0.12, 30	49.4	4.0
33.3	1550	31	46.5	3.3
33.3	1600	40	45.8	3.8
40.0	1400	0.10, 22	45.8	5.5
40.0	1500	20	37.9	1.8
40.0	1550	21	36.0	1.3
45.0	1400	0.10, 20	40.0	1.5

Figure 6 Pore size distributions for the 28.0 vol% samples sintered at (a) 1400°C (b) 1500°C and (c) 1600°C. The minute pores of about 0.1 μm size disappeared as the sintering proceeded at higher temperature.

3.3. Effect of freezing temperature on pore structure

The microstructure and pore size distribution of the samples frozen at −20°C and −80°C for the case of 28 vol% and 1400°C are shown in Figs 7 and 8, respectively. Fig. 7 is the micrograph which observed the sample from the top. In spite of the same porosity of 61.6%, a remarkable difference was seen in the microstructure between the two materials. The macroscopic pore size of the sample frozen at −80°C was about a half of that of the sample frozen at −20°C. Thus, it has been found that the pore size is controllable by changing the freezing temperature, without changing the porosity. It is true that the temperature gradient in upper
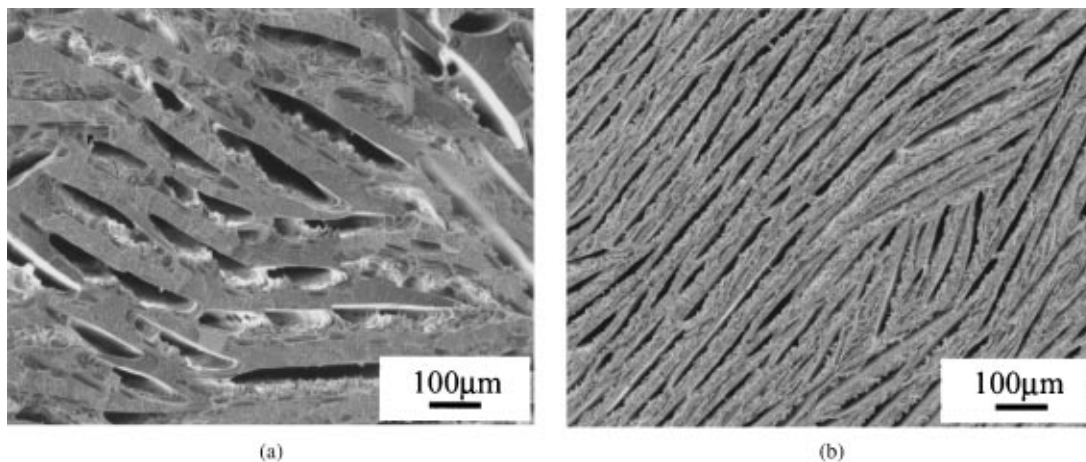
(a)   (b)

Figure 7 The microstructures of the samples in the case of 28 vol% and 1400°C. (a) frozen at −20°C (b) frozen at −80°C. Both materials had the same porosity of 61.6%.

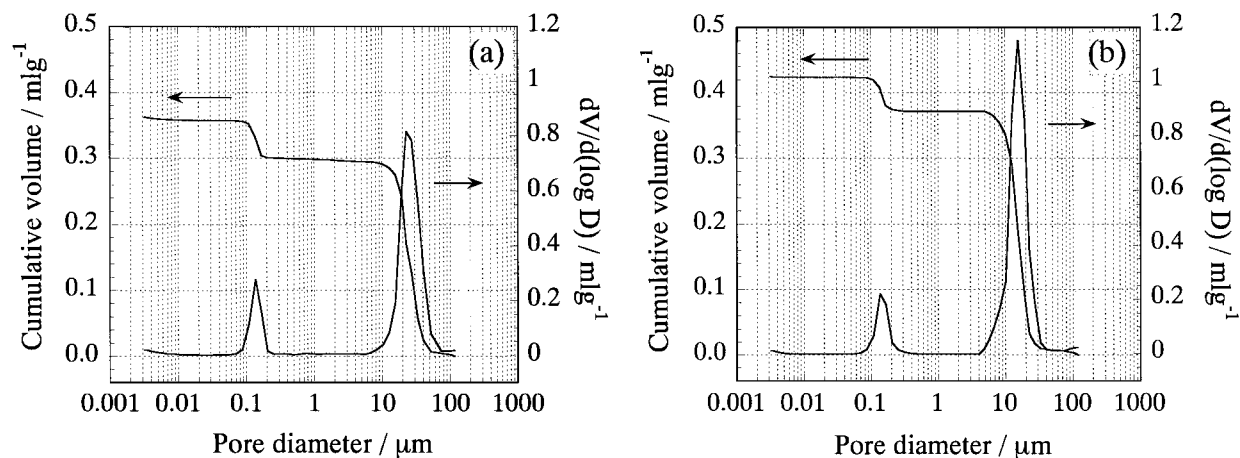*Figure 8* Pore size distribution of the samples in the case of 28 vol% and 1400°C. (a) frozen at −20°C (b) frozen at −80°C.

part and lower of the sample can become one of the parameters which control pore structure of the porous ceramic.

On the other hand, phase separation and nucleation and growth of the ice are also important issues to control pore structure, because they determine the size and the structure of the columnar ice in the freezing process of the slurry. On these effects, it is future research subject.

The fabrication technique described here is applicable to other kinds of ceramics such as silicon nitride and silicon carbide. Furthermore, the use of water-based slurry without organic binder is preferable with respect to environmental considerations.

4. Conclusions

Porous alumina with a complex pore structure was synthesized by the freeze-dry process for water-based slurries. Pores were formed by unidirectional freezing of the slurry and sublimation of the ice at a reduced pressure. Consequently porous ceramics were obtained where macroscopically aligned open pores exceeding 10 μm in size contained minute pores of about 0.1 μm in their internal walls. It was found that the pore structure was controllable by selecting the slurry concentration, the freezing temperature of the slurry and the sintering temperature. Besides, this fabrication technique was advantageous in terms of applicability to other materials and environmental friendliness.

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