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Preparation and properties of porous alumina ceramics with uni-directionally oriented pores by extrusion method using a plastic substance as a pore former

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Abstract

Porous alumina ceramics with uni-directionally aligned pores were prepared by an extrusion method using 0–40 vol.% poly (vinyl acetate) (PVAC) as the pore former. A paste was prepared by mixing 25 mass% distilled water, 4 mass% methylcellulose, 8 mass% oleic acid and 0.8 mass% ammonium poly (carboxylic acid). This paste was molded into a 10 mm Ø body using a ram-type extruder, dried at room temperature for 24 h, calcined at 600 °C for 1 h and sintered at 1500 °C for 2 h in air. The PVAC added to the paste was homogeneously dispersed and formed particles 0.1–150 μm in size which extended in the extrusion direction and were converted to through-hole pores after sintering. The resulting pore size distribution in the samples was bimodal, centered at about 0.4 μm with a broad peak at about 70 μm dia. The resulting porous alumina ceramics showed high gas permeability because of their uni-directionally oriented through-hole pore structure.

Keywords: Al_2O_3; Porosity; Extrusion; Permeability

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1. Introduction

Porous ceramics for separation filters have become important for reducing various types of environmental pollution. One of the most important properties of porous ceramics for these applications is their permeability. Therefore, many attempts have been reported to prepare porous ceramics with high permeability by uni-directionally aligning the pores to enhance the permeability, using extrusion,[1–5] filament winding,[6,7] electrophoretic deposition,[8] biomimetic[9–13] and slip casting methods.[14] The extrusion method is particularly desirable because it avoids problems such as difficulties in mass-production, control of the porosity and pore size and limitation of the matrix. During extrusion, well-known alignment phenomena occur, especially for particles with a high aspect ratio. If such particles are used as pore formers, porous ceramics should be formed with a highly oriented microstructure similar to a lotus structure. We have succeeded in increasing the permeability of porous alumina ceramics by controlling the orientation of the through-hole pores by this method.[4] The resulting porous alumina ceramics have higher bending strengths than conventional-type porous ceramics because of the controlled microstructure.[4–7] On the other hand, the use of fibers with the extrusion method generates a considerable amount of CO_2 by decomposition of the pore formers. To avoid this generation of CO_2 which is harmful to the global environment, more eco-friendly processes must be developed.[15–19]

It is known that an extruded paste is elongated in the extrusion direction after passing through the convergent region of the extrusion die.[20] When the paste contains secondary phases, these also elongate in the extrusion direction[21,22] as shown schematically in Fig. 1. The secondary phases may be solids, liquids or gases, if they have plastic properties. Thus, water and/or air can be used as pore formers and their usage makes the process eco-friendly, since harmful gases are not generated during production. However, it is very difficult to control the paste rheology using water and/or air as the pore formers in an extrusion process. As a first approach, it may be possible to obtain valuable peaces of information by introducing an organic liquid phase as the pore former.

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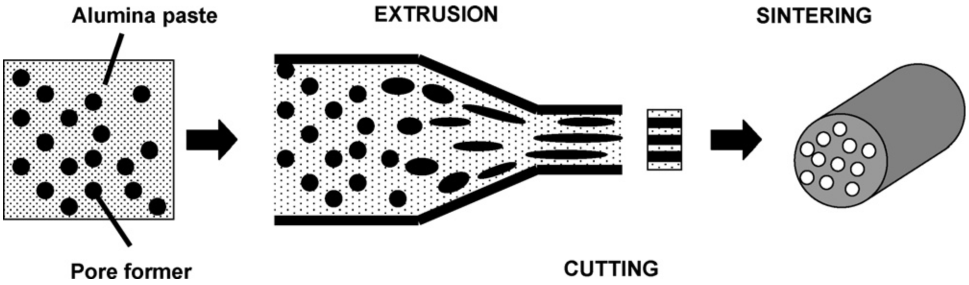

Fig. 1. Schematic illustration of the preparation of porous alumina ceramics with oriented cylindrical pores by the extrusion method.

In this fundamental study, porous ceramics with aligned through-hole pores were prepared using poly (vinyl acetate) (PVAC) with high plasticity as pore former, rather than organic fibers, in order to develop an eco-friendly process which would eventually use water and/or air as the pore former.

2. Experimental procedure

Poly (vinyl acetate) (M_w: 12,800, density: 1.19 g/cm^3, Sigma–Aldrich, USA) was chosen as the pore former because its melting point (35 °C) is only slightly above ambient temperature. High purity alumina (AHP-200, Nippon Light Metal, Japan) was mixed with 0–40 vol.% PVAC and 25 mass% distilled water, 4 mass% methylcellulose (SM-4000, Shin-Etsu Chemical, Japan), 8 mass% oleic acid (Wako Pure Chemical Industries, Japan) and 0.8 mass% ammonium poly (carboxylic acid) (D-305, Chukyo Yushi, Japan) using a planetary homogenizer[23] (AR-250, Thinky, Japan). Fig. 2 shows the schematic illustration of the planetary homogenizer. The starting materials were put into the centrifuge container and this centrifuge container was revolved while rotating. The revolution and rotation speed are 800 and 2000 rpm, respectively. During mixing, the temperature of the paste increased to about 60 °C due to friction between the alumina particles and the droplets of molten PVAC dispersed uniformly in the paste. The resulting paste was cooled to 30 °C in the container and molded into 10 mm Ø rods using a ram-type extruder (barrel: 30 mm Ø, die: 10 mm Ø × 20 mm) at 30 °C. The extruded green bodies were dried at room temperature for 24 h, calcined at 600 °C for 1 h and sintered at 1500 °C for 2 h in air.

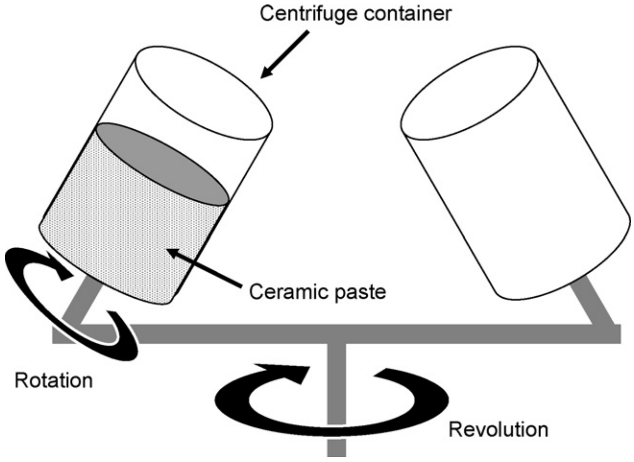

Fig. 2. Schematic illustration of planetary homogenizer.

The densities and porosities of the samples were measured by the Archimedes technique using water. The samples were sliced with a diamond cutter and the surfaces polished using commercial #1500 and #8000 emery. After polishing, the samples were ultrasonically washed for 10 min in distilled water and their microstructure was observed by a scanning electron microscope (SEM; JSM-5310, JEOL, Japan). The pore size distribution of the samples was measured by mercury intrusion porosimetry (Pascal 140 and Pascal 240, CE Instruments, Italy). The weight of the sample used for the measurement was 0.7 g. The contact angle and surface tension used in the calculation were 141.3° and 480×10^{-3} N/m, respectively.

The permeability of the porous ceramics was evaluated using Eq. (1):

$$\Delta P = \frac{\eta L}{\mu A} Q \tag{1}$$

where ΔP is the pressure drop between the entrance and exit of the sample, μ is Darchy's permeability, η is the dynamic viscosity of the fluid, A and L are the cross sectional area and thickness of the sample and Q is the flow rate. Samples 1.5 mm thick and 5 mm dia. were fixed in the center of an epoxy resin mold. ΔP and Q were measured using this equipment. The permeability was calculated from the slope of the line plotted for ΔP versus Q using Eq. (1). The dynamic viscosity η of nitrogen gas used for the calculation was 1.75×10^{-5} Pa s.

3. Results and discussion

3.1. Porosity

Fig. 3 shows the bulk density and porosity of the porous ceramics sintered at 1500 °C for 2 h. The bulk densities of the samples decreased from 3.77 to 2.39 g/cm^3 with increasing PVAC content, corresponding to a porosity increase from 5 to 40%. The closed porosity in the samples with 16 and 24% porosity was 5 and 3%, respectively. However, almost all the pores in the samples with $\geq$29% porosity were open pores. Since the porosity of the samples prepared without the pore former was 5%, the porosity of the sample prepared with 40% pore former is expected to be 45%, but the actual value (40%) was lower than expected. This is attributed mainly to the shrinkage of the samples during the sintering, but also to the dissolution of a small

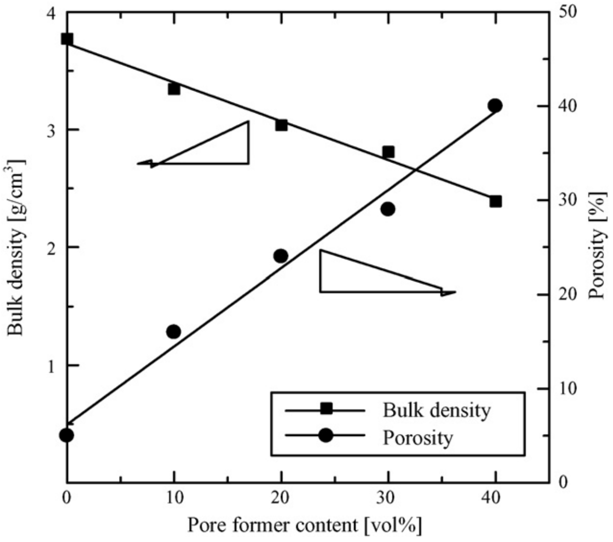

Fig. 3. Changes in bulk density and porosity of the extruded porous alumina ceramics as a function of pore former content.

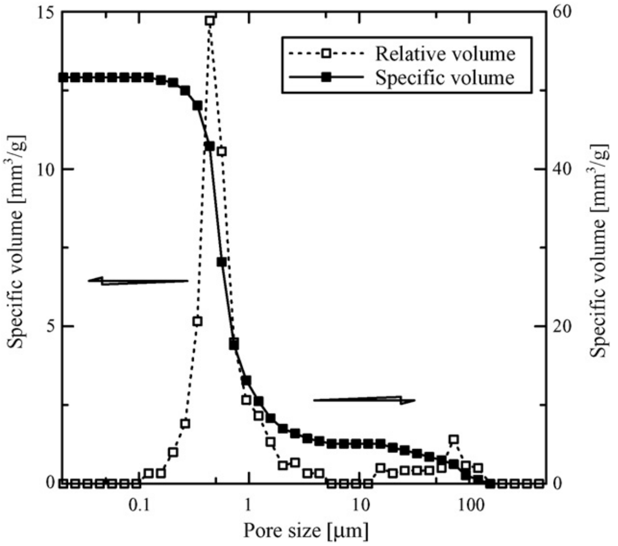

Fig. 5. Pore size distribution of the extruded porous alumina ceramics (10 vol.% PVAC).

amount of the PVAC into the poly (vinyl alcohol) and acetic acid. The sample shrank about 15% from the extruded body during sintering. The shrinkage isotropically occurred even in the extruded samples.

3.2. Pore size distribution

Figs. 4 and 5 show the pore size distributions of the non-extruded sample and extruded sample (containing 10 vol.% PVAC) sintered at 1500 °C for 2 h, respectively. The pore size distribution of the non-extruded sample was broad, with pore sizes ranging from 0.1 to 150 μm, thought to originate from the evaporation of PVAC particles. Thus, this pore size distribution is thought to indicate the particle size distribution of PVAC. This broad pore size distribution is related to the melting of the PVAC (mp 35 °C) by the heat generated during the mixing of the paste. By contrast, the pore size distribution of the extruded samples showed a sharp peak at 0.4 μm. It is considered that this difference in pore size compared with that of the non-extruded sample is due to the deformation of the pore former during the extrusion process. This change in pore size was observed in all the samples irrespective of their porosity (Fig. 6). The pore size distributions also show a broad peak at 20–150 μm, attributed to the large agglomerated particles of PVAC.

3.3. Microstructure

Fig. 7 shows SEM micrographs of the non-extruded porous ceramics (40% PVAC). The microstructures show both large spherical pores and small pores homogeneously distributed in

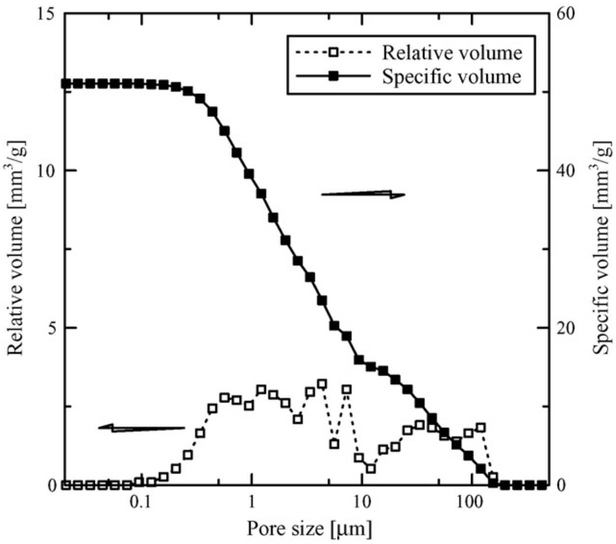

Fig. 4. Pore size distribution of the non-extruded porous alumina ceramics (10 vol.% PVAC).

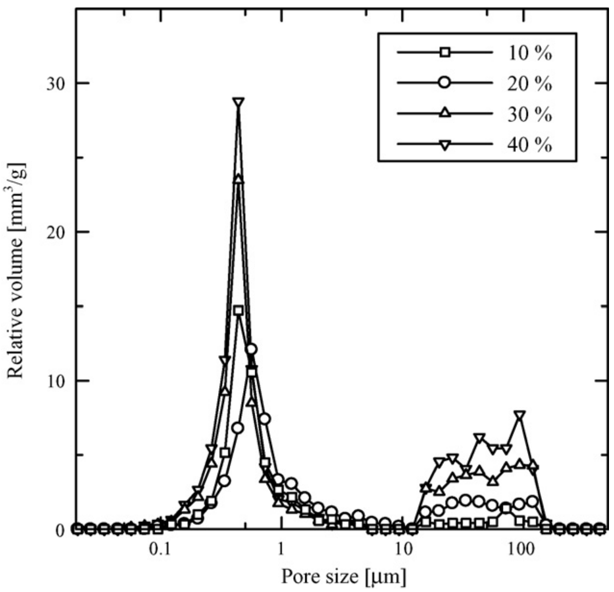

Fig. 6. Pore size distributions of the extruded porous alumina ceramics prepared with various pore former contents.

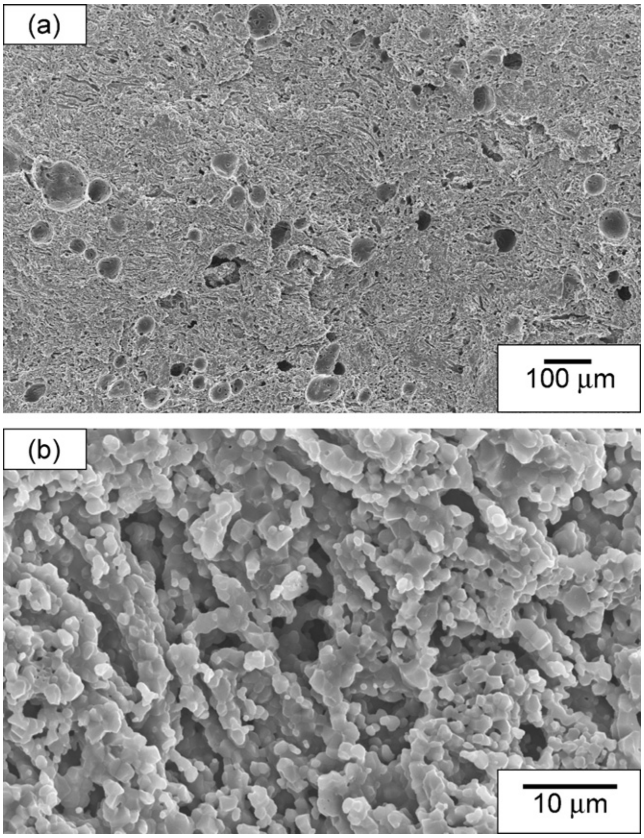

Fig. 7. SEM micrographs of cross section of the non-extruded porous alumina ceramics (40 vol.% PVAC) observed at low (a) and high (b) magnifications.

the matrix. The sizes of these pores range from 0.1 to 150 μm, in good agreement with the mercury porosimetry result.

Figs. 8 and 9 show SEM micrographs of the cross sections of the extruded porous alumina ceramics perpendicular and parallel to the extrusion direction, respectively. These SEM micrographs clearly show the presence of highly oriented continuous pores running parallel to the extrusion direction. The micrographs of the parallel cross section show two types of pore, some smaller than 1 μm and others of 50–100 μm size. The small pores correspond to the pore size distribution peak at 0.4 μm in Fig. 6 while the large pores correspond to the broad peak at 20–150 μm. This correspondence between the SEM observations and the mercury porosimetry indicates that the small pores are very uniform in size without a distinct hill-and-valley structure. This feature is unlike the porous alumina ceramics prepared by extrusion method using flammable fibers as pore formers, in which some pores correspond to the fiber diameter and others result from fiber contact.[1–5] The number of pores increases with increasing porosity, with all the extruded pores oriented to the extrusion direction. Therefore, the present porous ceramics closely conform to the desired microstructure and should have high gas permeability.

3.4. Gas permeability

Fig. 10 shows the relationship between the porosity and permeability of the present porous alumina ceramics and those prepared using fibers as pore formers.[5] The permeability of the present ceramics increases from 2.8×10^{-15} to 6.3×10^{-13} m^2 as the porosity increases from 16 to 40%. The permeability of the present sample with 40% porosity and an average pore size of 22.4 μm is slightly higher than that of comparable samples previously reported, prepared using fibers and displaying 39% porosity and 24 μm pore size (2.0×10^{-13} m^2).[5] To quantitatively evaluate the effect of the pore shape control, the observed permeability was compared with the permeability calculated using a capillary permeability model,[19] assuming a porous structure of uniform capillary tubes aligned parallel to the gas flow direction. This capillary permeability (μ_c) was calculated by the following Eq. (2):

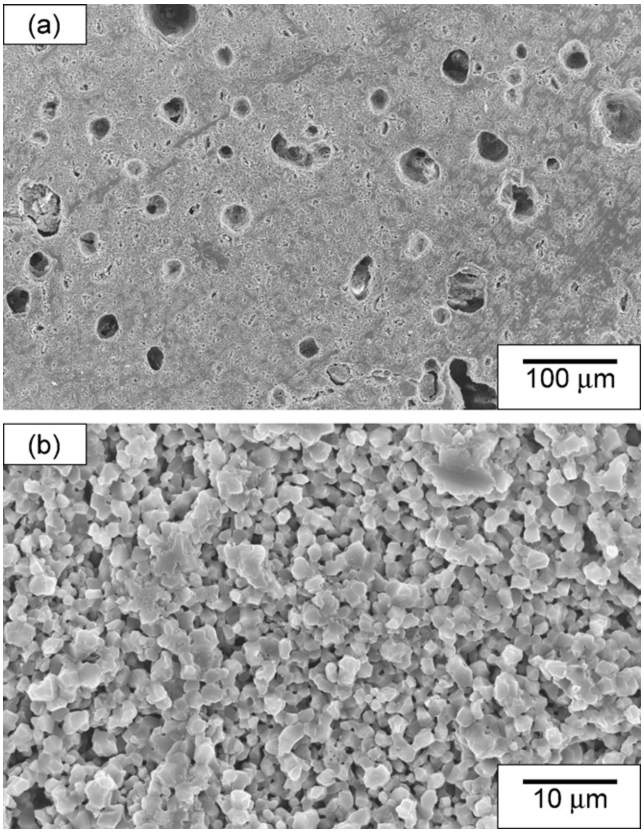

Fig. 8. SEM micrographs of cross sections of the extruded porous alumina ceramics (40 vol.% PVAC) perpendicular to the extrusion direction observed at low (a) and high (b) magnifications.

$$\mu_c = \frac{d^2}{32} P \qquad (2)$$

where d and P are the pore size and porosity. The pore sizes measured by mercury porosimetry were used in the permeability calculation, and were 6.4, 14.5, 20.7 and 22.4 μm for samples with porosities of 16, 24, 29 and 40%, respectively. The ideal permeability data calculated from Eq. (2) using these values are also shown in Fig. 10. The observed permeability values are only slightly lower than the calculated values for the ideal capillary model, and show a similar trend in the ideal permeability data as a function of porosity change. It is known that the permeability values of conventional porous alumina ceramics of random type

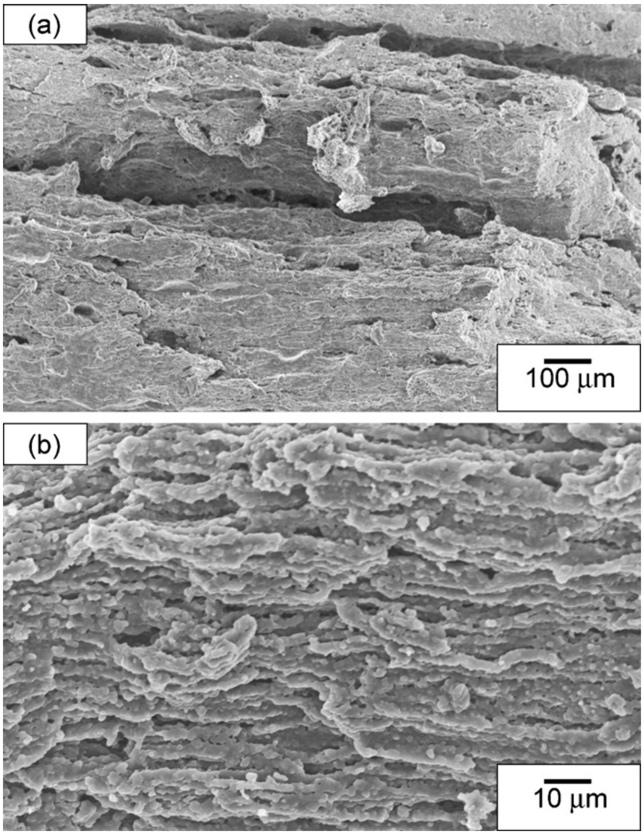

Fig. 9. SEM micrographs of cross sections of the extruded porous alumina ceramics (40 vol.% PVAC) parallel to the extrusion direction observed at low (a) and high (b) magnifications.

are about 10^3 times lower than the ideal value (Table 1). The permeability of such porous ceramics is drastically decreased by the larger and more complicated pathways than for the ideal capillary model. By contrast, the present porous alumina ceramics with uni-directionally aligned pores show only slightly lowered permeability from that of the ideal model. The long, straight pathways observed in the SEM micrographs appear to effectively enhance the gas permeability.

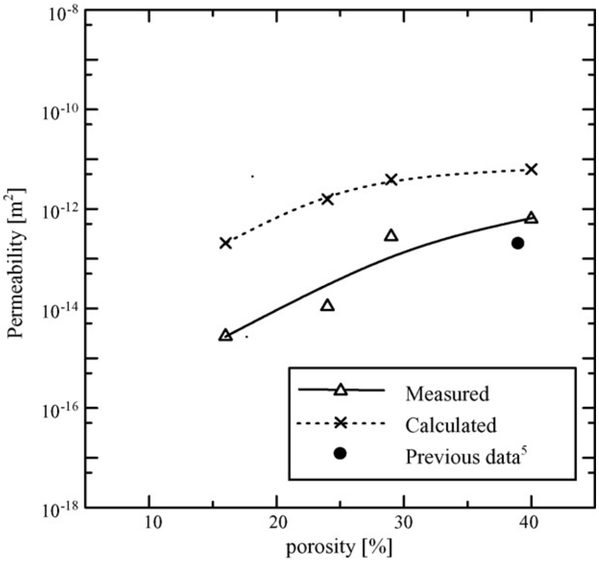

Fig. 10. Permeability of the extruded porous alumina ceramics as a function of porosity. The calculated values were obtained from Eq. (2).

Table 1
Comparison of permeability of porous alumina ceramics prepared by various methods

	Porosity (%)	Pore size (μm)	Permeability (m^2)	
			Measured value	Ideal value*
Extrusion (PVAC method)	40	22.4	6.3×10^{-13}	6.3×10^{-12}
Extrusion (Fiber method)[5]	39	38	3.9×10^{-13}	1.8×10^{-11}
Random type[5]	44	8.5	1.0×10^{-16}	9.9×10^{-13}
Foam[19]	62	85	1.0×10^{-13}	1.4×10^{-10}
Foam[19]	58	83	8.0×10^{-14}	1.2×10^{-10}

* Calculated from Eq. (2).

4. Summary

Porous alumina ceramics with pores extended in the extrusion direction were prepared using plastic PVAC as the pore former instead of flammable fibers as in previous work.[1–5] PVAC was homogeneously dispersed as small particles in the precursor pastes using a planetary homogenizer. The particle size of the PVAC ranged from 0.1 to 150 μm and the particles were elongated and connected by the extrusion process. These elongated PVAC particles were converted to through-hole pores after sintering at 1500 °C for 2 h. The pore sizes showed a bimodal distribution with peaks at 0.4 and 70 μm. The porosities of these porous alumina ceramics increased proportionally with increasing PVAC content, and the samples showed a high gas permeability owing to their uni-directionally pore oriented structure. These results suggest the possibility of developing other eco-friendly process using air and/or water as the pore formers.

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References

1. Isobe, T., Kameshima, Y., Nakajima, A. and Okada, K., Preparation and properties of porous alumina ceramics with oriented pores. *Key Eng. Mater.*, 2006, **318**, 689–692.
2. Isobe, T., Kameshima, Y., Nakajima, A., Okada, K. and Hotta, Y., Extrusion method using nylon 66 fibers for the preparation of porous alumina ceramics with oriented pores. *J. Eur. Ceram. Soc.*, 2006, **26**, 2213–2217.
3. Isobe, T., Kameshima, Y., Nakajima, A., Okada, K. and Hotta, Y., Effect of dispersant on paste rheology in preparation of porous alumina with oriented pores by extrusion method. *J. Porous Mater.*, 2006, **13**, 279–283.
4. Isobe, T., Tomita, T., Kameshima, Y., Nakajima, A. and Okada, K., Preparation and properties of porous alumina ceramics with oriented cylindrical pores produced by an extrusion method. *J. Eur. Ceram. Soc.*, 2005, **13**, 2006, **26**, 957–960.
5. Isobe, T., Kameshima, Y., Nakajima, A., Okada, K. and Hotta, Y., Gas permeability and mechanical properties of porous alumina ceramics with unidirectionally aligned pores. *J. Eur. Ceram. Soc.*, in press.

6. Zhang, G. J., Yang, J. F. and Ohji, T., Fabrication of porous ceramics with unidirectionally aligned continuous pores. *J. Am. Ceram. Soc.*, 2001, **84**, 1395–1397.
7. Zhang, G. J., Yang, J. F. and Ohji, T., Porous ceramics with fine unidirectionally aligned continuous pores. *Ceram. Eng. Sci. Proc.*, 2001, **22**, 183–189.
8. Nakahira, A., Nishimura, F., Kato, S., Iwata, M. and Takeda, S., Green fabrication of porous ceramics using an aqueous electrophoretic deposition process. *J. Am. Ceram. Soc.*, 2003, **86**, 1230–1232.
9. Ota, T., Takahashi, M., Hibi, T., Ozawa, M., Suzuki, S., Hikichi, Y. *et al.*, Biomimetic process for producing SiC “wood”. *J. Am. Ceram. Soc.*, 1995, **78**, 3409–3411.
10. Mizutani, M., Takase, H., Adachi, N., Ota, T., Daimon, K. and Hikichi, Y., Porous ceramics prepared by mimicking silicified wood. *Sci. Tech. Adv. Mater.*, 2005, **6**, 76–83.
11. Takase, H., Kinoshita, N., Hirashita, T., Miyazaki, H., Ota, T., Daimon, K. *et al.*, Porous Ceramics prepared by mimicking fossil woods. *Trans. Mater. Res. Soc. Jpn.*, 2000, **25**, 637–640.
12. Ota, T., Imaeda, M., Takase, H., Kobayashi, M., Kinoshita, N., Hirashita, T. *et al.*, Porous titania ceramic prepared by mimicking silicified wood. *J. Am. Ceram. Soc.*, 2000, **83**, 1521–1523.
13. Hirashita, T., Miyazaki, H., Takase, H., Kinoshita, N. and Ota, T., Porous titania ceramics prepared by mimicking silicified woods. *Ceram. Trans.*, 2001, **112**, 521–526.
14. Miyagawa, N. and Shinohara, N., Fabrication of porous alumina ceramics with uni-directionally-arranged continuous pores using a magnetic field. *J. Ceram. Soc. Jpn.*, 1999, **107**, 673–677.
15. Nagaoka, T., Tsugoshi, T., Hotta, Y., Sato, K. and Watari, K., Fabrication of porous alumina ceramics by new eco-friendly process. *J. Ceram. Soc. Jpn.*, 2005, **113**, 87–91.
16. Nagaoka, T., Iwamoto, Y., Kikuta, K. and Hirano, S., Forming and sintering of in situ alumina composite with hydraulic inorganic binder. *J. Am. Ceram. Soc.*, 2000, **83**, 1613–1616.
17. Nagaoka, T., Tsugoshi, T., Hotta, Y. and Watari, K., Fabrication of porous alumina-based ceramics with hydraulic inorganic binder. *J. Ceram. Soc. Jpn.*, 2004, **112**, 277–279.
18. Tomita, T., Kawasaki, S. and Okada, K., A novel preparation method for foamed silica ceramics by sol–gel reaction and mechanical foaming. *J. Porous Mater.*, 2004, **11**, 107–115.
19. Tomita, T., Kawasaki, S. and Okada, K., Effect of viscosity on preparation of foamed silica ceramics by a rapid gelation foaming method. *J. Porous Mater.*, 2005, **12**, 123–129.
20. Graczyk, J., Mansour, S. and Gleiβle, W., Extrusion properties of aluminum oxide. *Ind. Ceram.*, 2000, **20**, 188–190.
21. Khayat, R. E., Luciani, A. and Utracki, L. A., Boundary-element analysis of planar drop deformation in confined flow. Part 1. Newtonian fluids. *Eng. Anal. Bound. Elem.*, 1997, **19**, 279–289.
22. Khayat, R. E., Boundary element analysis of planar drop deformation in confined flow. Part II. Viscoelastic fluids. *Eng. Anal. Bound. Elem.*, 1998, **22**, 291–306.
23. Omura, N., Hotta, Y., Sato, K., Kinemuchi, Y., Kume, S. and Watari, K., Planetary homogenizing of Al_2O_3 slurries. *J. Ceram. Soc. Jpn.*, 2005, **113**, 753–757.