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Preparation and properties of porous alumina ceramics with oriented cylindrical pores produced by an extrusion method

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Abstract

Porous alumina ceramics with unidirectionally-oriented pores were prepared by extrusion. Carbon fibers of 14 μm diameter and 600 μm length to be used as the pore-forming agent were kneaded with alumina, binder and dispersing agent. The resulting paste was extruded, dried at 110 °C, degreased at 1000 °C and fired at 1600 °C for 2 h. SEM showed a microstructure of dispersed highly oriented pores in a dense alumina matrix. The pore area in the cross section was 25.3% with about 1700 pores/mm^2. The pore size distribution of the fired body measured by Hg porosimetry showed a sharp peak corresponding to the diameter of the burnt-out carbon fibers. The resulting porous alumina ceramics with 38% total porosity showed a fracture strength of 171 MPa and a Young's modulus of 132 GPa. This strength is significantly higher than the reported value for other porous alumina ceramics even though the present pore size is much larger.

Keywords: Extrusion; Porous ceramics; Mechanical properties; Al_2O_3

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1. Introduction

Porous ceramics are widely used as filters, catalyst carriers, separation membranes and bio-ceramics, and their preparation has been extensively studied. A conventional synthesis method is to partially sinter at low temperature with or without using a pore-forming agent.[1–4] Macroporous foamed ceramics with very high porosity can be prepared using the well-known sponge replica method.[5] Since the size and distribution of the pores formed in these ceramics is random, very high porosity is necessary to achieve high permeability. This, however, decreases the mechanical strength of the porous ceramic.[1–3] To address these problems, it is necessary to control the size and distribution of the pores.

Conventional partial sintering methods generally form pores of about 1 μm.[3] By contrast, the pore size in foamed ceramics is about 150 μm or greater.[5,6] Thus, an appropriate preparation method to form pores of several 10 μm is not yet available. The size distribution of the pores is also an important factor in the preparation of satisfactory porous ceramics. For example, pores running perpendicular to the flow direction are not useful in filter applications. A microstructure having unidirectionally aligned pores is preferable for applications requiring high permeability. Some attempts have been reported to fabricate porous ceramics with such microstructures.[7–9] Nakahira et al.[7] have fabricated porous alumina ceramics using an electrophoretic deposition method. The pores were formed by the gases generated from the electrode during electrophoretic deposition. The pore size obtained by this process was about 60 μm. Zhang et al.[8] have prepared porous ceramics using a filament winding method. They coated alumina slurry on cotton fibers and aligned the fibers to form bulk samples similar to the preparation of fiber-

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reinforced composites. Porous ceramics were then obtained by burning-out the fibers during sintering. The resulting pore size and porosity were 165 μm and 35%, respectively. Ota et al.[9] fabricated porous SiC ceramics with a wood-like microstructure using a biomimetic method in which tetraethyl orthosilicate was infiltrated into the pores of charcoal and fired at high temperature to form SiC.

Extrusion processes have been widely used for industrial manufacturing of various ceramics. This process is advantageous in the production of rods, tubes and honeycombs. It is also used for preparation of fiber-reinforced ceramic composites with microstructures in which the fibers are aligned unidirectionally, thereby improving the mechanical properties of the composite.[10,11] Such a highly oriented microstructure is obtained by the uniform convergent flow of the matrix, which induces the rearrangement of the fiber orientations in the extrusion die. Thus, it should be possible to prepare porous ceramics with unidirectionally aligned pores by extrusion method if flammable fibers are used as the pore-forming agent.

In this study, porous alumina ceramics with oriented pores were prepared by this extrusion method using an alumina paste containing carbon fibers and the mechanical properties of the resulting porous ceramics were evaluated.

2. Experimental procedure

High purity alumina (AA-07, Sumitomo Chemical, Japan) with an average particle size 0.7 μm was mixed with 52 vol% carbon fiber (M-115T, Kureha Chemical Industry, Japan) with an average diameter of 14 μm and length of 600 μm. The mixture was kneaded for 1 h with 4 mass% methylcellulose (400cP, Wako Pure Chemical Industries, Japan), 0.4 mass% ammonium poly-carboxylic acid (D-305, Chukyo Yushi, Japan) and 17.6 mass% distilled water. The resulting paste was molded using an extruder (EP-28, Ishikawa Toki Iron-works, Japan). A schematic diagram is shown in Fig. 1. The dimension of the extruder barrel and inner aperture was 50 and 10 mm, respectively, the conical die having an entrance angle 33.7°. The extruded green bodies were dried at 110 °C for 48 h in air. The specimens were then degreased at 1000 °C for 1 h and sintered at 1600 °C for 2 h in air.

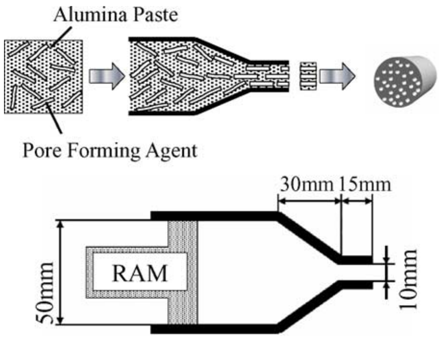

Fig. 1. Schematic illustration of the preparation of porous alumina ceramics with oriented cylindrical pores by the extrusion method, and a schematic sketch of the laboratory extruder used.

The relative density and porosity of the specimens was measured by the Archimedes technique using water. The pore size distribution of the samples was measured by mercury intrusion porosimetry (Auto Pore IV 9520, Shimadzu, Japan). The maximum injection pressure was about 400 MPa. The contact angle and surface tension used for the calculation was 130° and 485×10^{-3} N/m, respectively. The three-point bending strengths of the sintered specimens (2 mm × 2 mm × 10 mm) were measured with a span length of 8 mm and crosshead speed of 0.5 mm/min (AGS-5kND, Shimadzu, Japan). The average bending strength and Weibull modulus were obtained from measurements of 10 samples. Young's modulus was determined by an impulse excitation technique using a 1 mm × 7 mm × 100 mm billet. The surfaces were polished with 3 and 6 μm diamond pastes. The microstructure of the polished surface was observed using a scanning electron microscope (JSM-5310, Jeol, Japan).

3. Results and discussion

Fig. 2 shows SEM micrographs of cross sections of the porous alumina ceramics observed in directions perpendicular (a) and parallel (b) to the extrusion. The microstructures show alignment of highly oriented cylindrical pores parallel to the extruded direction. These pores have shapes which can be attributed to the carbon fibers. The average diameter of the pores obtained by the intercept method was 14 μm, in good agreement with the diameter of the fibers. The pore area in the cross section perpendicular to the extrusion (Fig. 2a) is 25.3% and the number of pores in the cross section is about 1700 pores/mm^2. By contrast, the pore area in the parallel section is 41.0%. The pore area of this cross section is calculated to be 50.3% by assuming continuous pores perfectly aligned parallel to the extrusion, i.e. $(25.3)^{1/2} \times 100\%$, giving an observed pore area ratio in this direction of 81.5%. This value indicates that the resulting sample has the necessary possibility for contact between the adjacent fibers to form continuous pores.

Fig. 3 shows the pore size distribution of the fired specimen, with a very sharp peak at 5.3 μm. This pore size is however smaller than that observed in the SEM photographs (Fig. 2). Since the pore size obtained by mercury intrusion porosimetry represents intersection size of the pore, this pore size is thought to correspond to pores generated by burnout of connected fibers. Table 1 lists the data for the present porous alumina ceramics. The bulk density is 2.47 g/cm^3 and the calculated relative density is 62%; of the 38% total porosity, 36% is due to open pores and only 2% to closed pores. The observed total porosity is lower than the fiber content of the starting paste (52%). This difference may be due to only the shrinkage during sintering process and the breaking of fibers during the kneading process. The 2% closed pores are thought to correspond to these broken fibers remaining in the

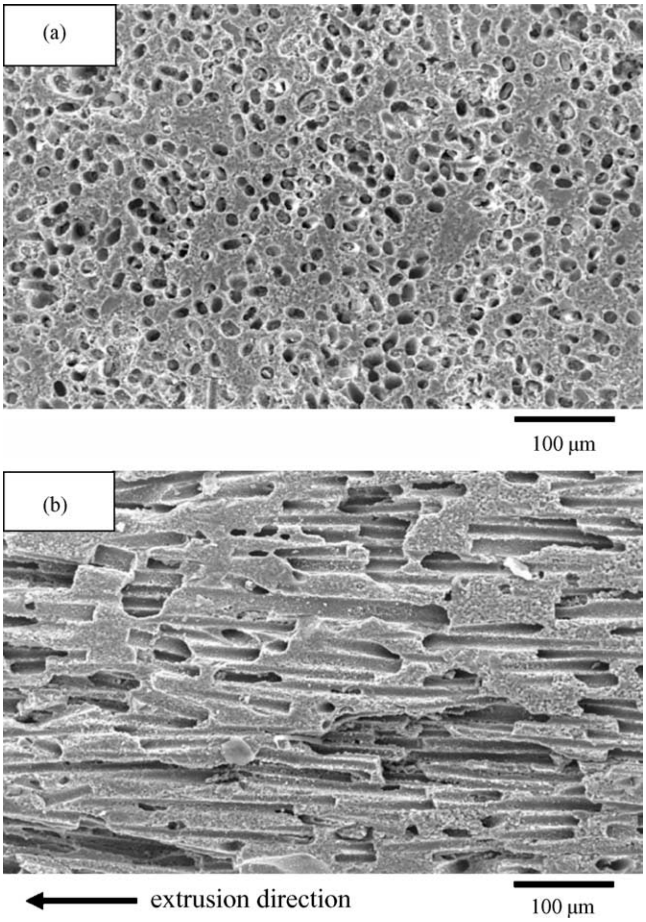

Fig. 2. SEM micrographs of cross sections of porous alumina ceramics, (a) perpendicular and (b) parallel to the extrusion direction.

specimen because the matrix alumina appears to be almost fully dense.

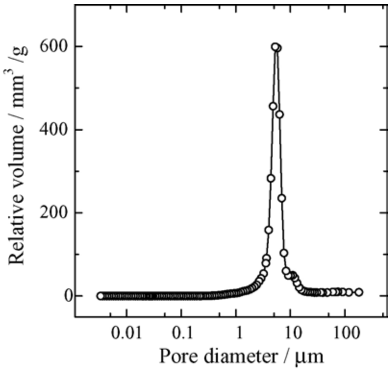

Fig. 3. Pore size distribution of the extruded porous alumina ceramic measured by Hg porosimetry.

Table 1
Properties of obtained porous alumina with oriented pores

Property	Value
Density	2.47 g/cm^3
Relative density	62%
Open porosity	36%
Closed porosity	2%
Pore size	14 μm
Pore number density	1700 pores/mm^2
Pore area (perpendicular)	25.3%
Pore area (parallel)	41.0%
Three-point bending strength	171 ± 19 MPa
Weibull modulus	9.28
Young's modulus	132 GPa

The average three-point bending strength of the porous alumina ceramics obtained from 10 samples is 171 MPa and the Weibull modulus is 9.28. The fracture strength is lower than that of fully dense alumina ceramics (380 MPa) because of the presence of the pores. Table 2 compares the mechanical properties of the present specimen with those prepared by hot isostatic pressing,[12] W/O-type emulsion method,[13] partial sintering of aluminum hydroxide[14] and of boehmite gel.[15] The porosities of all these samples are similar. However, the bending strengths obtained for these specimens differ according to the specimen size. Therefore, the effect of specimen size [16] was corrected using the following equation:

$$\frac{\sigma_a}{\sigma_b} = \left(\frac{S_b}{S_a}\right)^{1/m}$$

where, σ_a and σ_b are the bending strengths of specimens a and b, S_a and S_b are the effective surface areas of specimens a and b, and m is the Weibull modulus. The bending strength σ_a and the Weibull modulus (m) of the present porous alumina is $\sigma_a = 171$ MPa and $m = 9.28$, and the effective surface area S_a is 2 mm × 8 mm. Thus, the bending strength σ_b related to the effective surface area of the standard specimen size (3 mm × 4 mm × 30 mm) is calculated to be 137 MPa. The corrected strengths are listed in Table 2. The present material is stronger than the other reported materials even when compared with their corrected bending strengths. The effect of porosity on the mechanical properties of ceramics has been reported by many investigators.[17] The mechanical strength is also known to be influenced by pore size, with lower strengths at larger pore sizes. The pore size of the present porous alumina ceramics is apparently larger than those of other reported specimens. Nevertheless, the present specimens show a higher bending strength than the other specimens. This excellent fracture strength is thought to be due to the highly controlled microstructure, i.e. uniform pore size with unidirectional pore orientation.

The Young's modulus of the present porous alumina ceramics (132 GPa) is lower than that of dense alumina ceramics (386 GPa)[18] due to the presence of the pores. The decrease of the Young's modulus depends mainly on the sample porosity. Many reported studies have addressed the relationship between the porosity and Young's modulus of various porous ceramics.[1,3,18–20] Herakovich and Baxter[18] determined the relationship between the elastic properties and pore geometry by a generalized method using cells. They calculated the elastic modulus of the porous materials assuming four different pore shapes, sphere, cylinder, cube and cross. The pore shape which shows the highest elastic modulus is cylindrical

Table 2
Comparison of mechanical properties of porous ceramics prepared by various methods

	This study	Kinemuchi et al.[12]	Otoishi et al.[13]	Deng et al.[14]	Kawamura and Endo[15]
Porosity (%)	38	40	∼40	38	40
Average pore size (μm)	14	0.15	1–4	0.1	
Bending strength (MPa)	171	90–120	∼110	90	80
Bending strength (MPa) (standard specimen)	137	82–115	–	90	–

while the pore shape showing the lowest elastic modulus is spherical. The Young's modulus of porous alumina with 40% porosity assuming cylindrical and spherical pores is 230 and 130 GPa, respectively. The observed Young's modulus of the present sample (132 GPa) is lower therefore than that calculated by Herakovich and Baxter.[18]

The extrusion method has the advantage of being readily applicable to industrial production and could also be used for other types of porous ceramic such as apatite, zirconia, SiC and Si_3N_4. The pore size and porosity can be controlled by the diameter and fiber content of the ceramic powder mixture.

4. Conclusions

Porous ceramics with unidirectionally oriented pores were prepared by an extrusion method. The paste for extrusion was prepared by mixing alumina and carbon fibers with added dispersant and binder. The pore size observed from the SEM photographs of the sintered body was 14 μm, in good agreement with the original carbon fibers. The microstructure showed highly oriented pores running parallel to the extrusion direction. The resulting ceramics have a bending strength of 171 MPa (Weibull modulus of 9.28) and a Young's modulus of 132 GPa at 38% total porosity. This technique is widely applicable to the preparation of various porous ceramics, and the pore size and porosity can be controlled by the fiber diameter and fiber content of the ceramic powder mixture.

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