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Extrusion method using nylon 66 fibers for the preparation of porous alumina ceramics with oriented pores

Toshihiro Isobe [a], Yoshikazu Kameshima [a], Akira Nakajima [a], Kiyoshi Okada [a,*], Yuji Hotta [b]

[a] *Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro, Tokyo 152-8552, Japan*
[b] *Advanced Manufacturing Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Anagahora, Shimo-Shidami, Moriyama-Ku, Nagoya 463-8560, Japan*

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Abstract

Porous alumina ceramics with unidirectionally oriented pores were prepared using an extrusion method. The paste for extrusion was prepared by mixing alumina and nylon 66 fibers with binder and dispersant. The resulting paste was extruded, dried at room temperature, and after removal of the binder at 600 °C, fired at 1500 °C for 2 h. The pore size in the sintered body, determined from SEM micrographs, was 16 μm, corresponding to the size of the burnt-out nylon 66 fibers. The degree of orientation of the cylindrical pores was evaluated from SEM micrographs to be highly aligned to the extrusion direction. The orientation of the pores decreased with increasing fiber loading because of strong interaction between the fibers. The pore size distribution of the extruded samples showed a peak at 16 μm corresponding to the cylindrical pore diameter and also at 4 and 6 μm corresponding to the pores formed by connection of the fibers.

Keywords: Extrusion; Fibers; Al_2O_3; Membranes; Porous ceramics

1. Introduction

Porous ceramics are used as filters, catalyst carriers and insulators at high temperature. One of the most important applications of porous ceramics is as ceramic filters for use under severe conditions, i.e. high temperatures and high concentrations of corrosive substances. High collection efficiency, permeability, mechanical properties, chemical and abrasion resistance and thermal stability are required for these applications. Most porous ceramics have good mechanical properties, chemical and abrasion resistance and thermal stability. However, they do not display superior collection efficiency and permeability properties. In particular, high permeability is a most important property for filters because this property determines the pressure drop in the filter during the separation process. Since the permeability is reported to depend strongly on the microstructure of the porous ceramic,[1,2] it is necessary to control the size, distribution and connectivity of the pores to improve the permeability. Since the size and distribution of the pores formed in ceramics is usually random, very high porosity is necessary to achieve high permeability. This however lowers the mechanical strength of porous ceramics. Therefore, porous ceramics with unidirectionally aligned pores are necessary to achieve high permeability while maintaining good mechanical properties. Some attempts have been reported to fabricate porous ceramics with unidirectionally aligned pores using electrophoretic,[3] filament winding,[4] biomimetic[5–7] and slip casting methods.[8] The porous ceramics prepared by these methods showed excellent microstructures but presented some problems such as difficulties in mass-production, limitations in matrix ceramics and difficulty in controlling in the pore size. On the other hand, extrusion is widely used in the ceramic industry for the mass-production of porcelains and honeycombs, and also for the preparation of fiber-reinforced ceramic composites.[9–11] The mechanical properties of these composites are found to be enhanced by aligning the fibers

* Corresponding author. Tel.: +81 3 5734 2524; fax: +81 3 5734 3355.
E-mail address: kokada@ceram.titech.ac.jp (K. Okada).

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using extrusion. Such highly oriented pores in the microstructure can be obtained by a uniform convergent flow of the matrix, which induces the rearrangement of fiber orientations in the extrusion die. Thus, porous ceramics with unidirectionally aligned cylindrical pores should be formed by extrusion when combustible fibers are used as the pore formers.

We have prepared porous alumina ceramics with unidimensionally aligned pores using carbon fibers by an extrusion method to produce ceramics with highly oriented pores[12] and excellent bending strengths. However, some of the carbon fibers are broken during the kneading process, suggesting that more soft and flexible fibers may be effective in improving this break down. In this study, porous alumina ceramics with oriented cylindrical pores were prepared by the extrusion method using nylon 66 fibers. The degree of pore orientation and pore size in the resulting porous alumina ceramics was evaluated.

2. Experimental procedure

High purity alumina powder (AKP-30, Sumitomo Chemical, Japan) with an average particle size of 0.4 μm was mixed with 0–35 vol.% nylon 66 fibers (Chubu Pile Industries, Japan) with an average diameter of 19 μm and length of 800 μm. The mixture was kneaded with 40 mass% distilled water, 4 mass% methylcellulose (SM-4000, Shin-Etsu Chemical, Japan) and 0.8 mass% ammonium poly-carboxylic acid (D-305, Chukyo Yushi, Japan) for 1 h. The resulting paste was dried in vacuum to a moisture content of 30 mass% and molded using a single screw vacuum extruder (FM-20E, Miyazaki Iron works, Japan). A schematic figure of the extruder is shown in Fig. 1. The dimension of the extruder barrel and inner aperture was 20 and 5 mm, respectively, and the distance after the end of the convergence region was 25 mm. A breaker plate with 14 holes, 4 mm in diameter was installed. It was set at the end of the screw at a position where the motion of screw changes from helical to axial, to break up aggregated powders and fibers. The screw speed was 1/3 Hz. The extruded green bodies were dried at room temperature for 24 h, then freed from the binder by holding at 600 °C for 1 h and sintered at 1500 °C for 2 h.

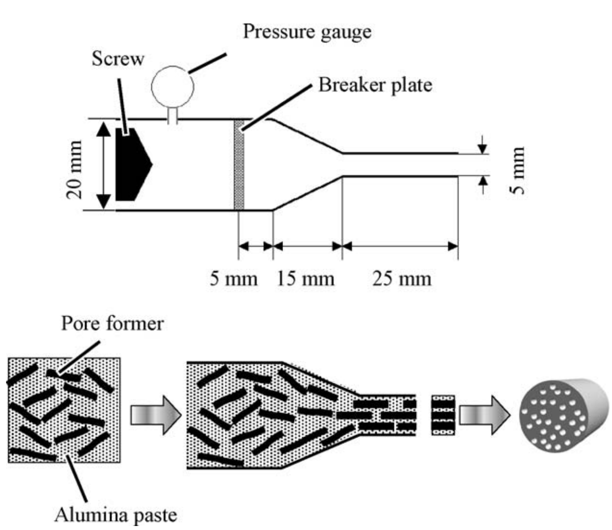

Fig. 1. Schematic sketch of a laboratory extruder and schematic for obtaining porous alumina ceramics with oriented cylindrical pores by the extrusion method.

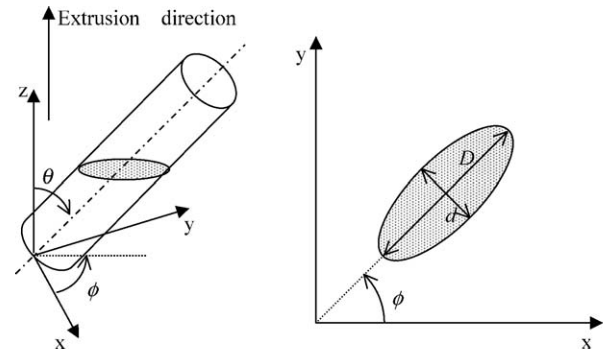

Fig. 2. Schematic representation of the relation between the fiber orientation angle (θ) and the corresponding cross-sectional parameters.

The density and porosity of the samples was measured by the Archimedes technique using water. The microstructures of the polished surfaces of the samples were observed by scanning electron microscope (JSM-5310, Jeol, Japan). The average pore size (pore diameter) was evaluated by the intercept method using cross-sectional SEM micrographs in directions both perpendicular and parallel to the extrusion. The orientation angle (θ) of the cylindrical pores was calculated by a general technique used for fiber composites.[13] The orientation angle (θ) was defined with respect to the extrusion direction and calculated by Eq. (1):

$$\cos\theta = \frac{d}{D} \qquad (1)$$

where D is the maximum diameter of the elliptical pores observed by SEM and d is the diameter of the fibers as shown in Fig. 2. In total, more than 300 pores/sample were used in the calculation of θ.

The pore size distribution of the samples was measured by mercury intrusion porosimetry (Pascal 140 and Pascal 240, CE Instruments, Italy). The samples used for the measurements were sliced to thicknesses of 0.5, 1.2 and 10 mm but the total sample weights were adjusted to be approximately equal for the three samples. The contact angle and surface tension used for the calculation were 141.3° and 480×10^{-3} N/m, respectively and are the recommended values for the instruments used.[12]

3. Results and discussion

3.1. Porosity

Fig. 3 shows the relationship between the fiber contents and porosities of the porous alumina ceramics. The porosity

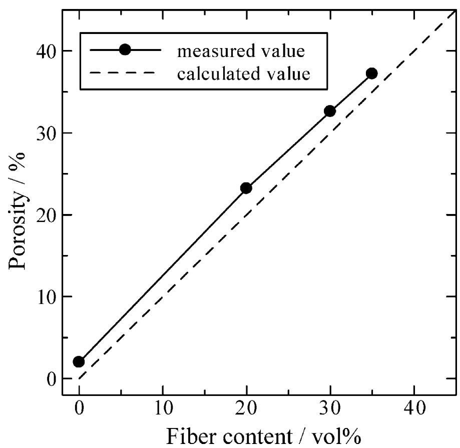

Fig. 3. Relationship between fiber content and porosity of the samples sintered at 1500 °C for 2 h.

of the sample without pore formers was <2% but the porosity increased proportionally with increasing fiber loading. It is thus considered that the added nylon 66 fibers are mostly converted to pores after sintering, as expected. This is different from the results obtained with carbon fiber loading, which showed decreased porosities due to breaking of the fibers during processing.[13]

3.2. Microstructure of porous alumina ceramics

To evaluate the effect of fiber orientation by the extrusion process, it is necessary to calculate the fiber orientation angle in the samples before and after extruding. Fig. 4 shows a SEM micrograph of the cross section of the non-extruded sample sintered at 1500 °C for 2 h. The cylindrical pores in the microstructure formed by burn-out of the fibers appear to adopt a random three-dimensional orientation. Fig. 5 shows the frequency distribution of the orientation angle (θ) of the pores obtained from the SEM micrograph. The calculated distribution of θ assuming random orientation is indicated by the dotted line which does not show a constant frequency at all angles because the number of fibers between θ and $\theta + \Delta\theta$

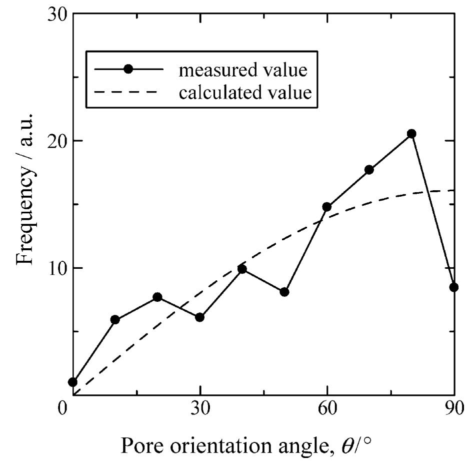

Fig. 5. Observed and calculated pore orientation angle distribution data for the non-extruded sample sintered at 1500 °C for 2 h.

is proportional to the angle θ.[14] Therefore, a lower orientation angle produces a lower frequency. The measured distribution of θ is in agreement with the calculated distribution, indicating random pore distribution in the non-extruded sample.

Fig. 6 shows SEM micrographs of the cross-section of the extruded porous alumina ceramics perpendicular (a) and parallel (b) to the extrusion direction. The microstructures

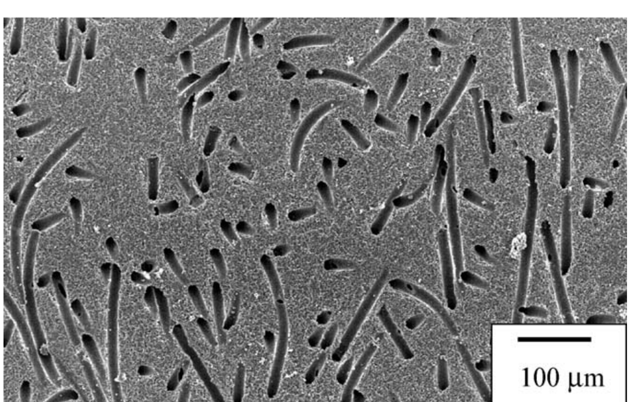

Fig. 4. SEM micrograph of cross-section of the non-extruded sample after sintering at 1500 °C for 2 h.

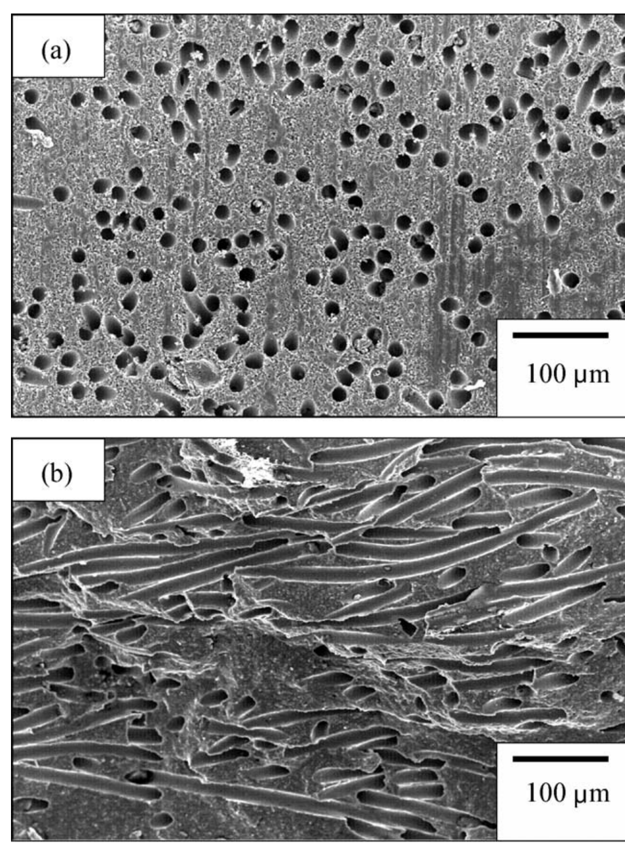

Fig. 6. SEM micrographs of cross sections of porous alumina ceramics (a) perpendicular and (b) parallel to the extrusion direction. The fiber content is 30%.

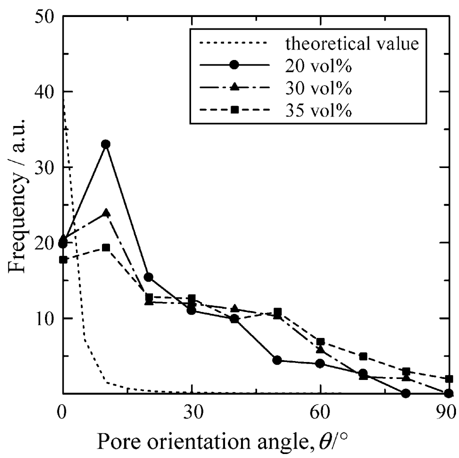

Fig. 7. Frequency distributions of orientation angle of the porous alumina ceramics with various porosities together with data calculated from Eq. (2).

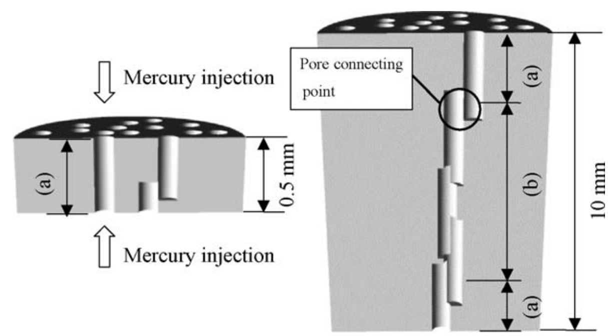

Fig. 8. Schematic pore models in the samples of different thickness. The pores in the regions (a) and (b) are attributed to pores corresponding to the fiber diameter and pore connecting point, respectively.

show highly oriented cylindrical pores parallel to the extrusion direction. These pore shapes can be attributed to the fiber shape. The average observed pore diameter was 16 μm. Fig. 7 shows the distribution of the pore orientation angle in the extruded sample. Pore orientation is clearly seen in the extruded sample compared with the random orientation of the non-extruded sample. Hine et al.[14] has described the relationship between the extrusion ratio and orientation angle in a single fiber by Eq. (2):

$$\tan\theta = \lambda^3 \tan\theta' \qquad (2)$$

where θ' and θ are the orientation angle before and after extrusion and λ is the extrusion ratio. The theoretical data calculated using this equation are also shown in Fig. 7 by a dotted line. The observed distribution data show a similar tendency to the theoretical data, with fair agreement between the two. The difference may be mainly due to a strong interaction between the fibers, this effect increasing with increasing fiber content. Thus, the peak height of the orientation angle decreases with higher fiber loadings.

3.3. Pore size distribution

The pores in the present samples are thought to be connected with the fibers because of their high degree of orientation and relatively high fiber loading. To achieve high permeability, the pore size formed by connection of the fibers is important as is the pore size determined by the nylon 66 fibers. This pore size can be determined by mercury porosimetry, which gives the smallest constricted size of the pores even if larger pores are present in the depths of the smallest constrictions.[15] Samples of thickness of 0.5, 1.2 and 10 mm were prepared to confirm this. Fig. 8 shows schematic pore models for the different thickness of samples. The 0.5 mm thick sample is thinner than the fiber length (800 μm) and almost all the pores go through the sample with few pore junctions. The pore size measured by the mercury injection is almost the same as the fiber diameter in this sample. By contrast, the thickest sample (10 mm) is much thicker than the fiber length and contains pores connected by many junctions. The mercury porosimetry measurement determines only the pores open to the surface (a), which are found to have a pore size corresponding to the fiber diameter. Most of the other pores present inside of the sample (in region (b)) have a bottle neck shape with a measured pore size corresponding to the pore necks formed by the fiber connections. This sample therefore has only a small number of pores of the fiber size but has a large number of pores of a size corresponding to the fiber connections.

Fig. 9 shows the pore size distributions of samples with 23% porosity. The pore size distribution of the porous alumina ceramics of 0.5 mm thickness shows a peak at 16 μm. These pores are thought to be formed by fiber burn-out but have shrunk slightly during sintering from their initial 19 μm in diameter. This shrinkage ratio coincides with that of the sample matrix. By contrast, the thickest sample (10 mm) clearly shows a peak at 4 μm but only a very small peak at 16 μm, which cannot be seen at this scale. The porous alumina ceramic with a thickness of 1.2 mm shows two peaks, at 6 and 16 μm. These results indicate that the pores formed in the 0.5 mm sample arise mainly from burn-out of single fibers because the thickness of the sample is less than the

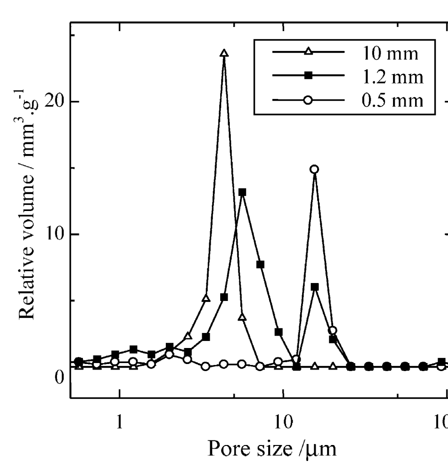

Fig. 9. Pore size distributions of the three samples of different thickness.

length of the fibers (<800 μm in this experiment), giving better pore connectivity. The lack of pore connections in this sample is expected to result in very good pore orientation and high permeability. When the samples are thicker than the fiber length (1.2 and 10 mm), the pores are connected by more pore connections and/or intersections. The number of smaller pores formed by the pore connections increases with increasing sample thickness. It is therefore, thought that the peak at 16 μm corresponds to the pores formed by burn-out of fibers and those at 4 and 6 μm correspond to the pores formed by the fiber connections. The pore size distributions of the samples with 33 vol.% porosity also show similar results.

4. Summary

Porous ceramics with unidirectionally oriented pores were prepared by an extrusion method using combustible nylon 66 fibers as the pore formers. The pore orientation of the resulting ceramics was investigated. The nylon 66 fibers were 19 μm in diameter and 800 μm in length and were kneaded with alumina powder, binder and dispersant. The observed cylindrical shaped pores showed a high degree of orientation running parallel to the extrusion direction. The average size of the pores in the sintered body was determined from SEM micrographs to be 16 μm in diameter and was close to the fiber diameter. The orientation of the cylindrical pores evaluated from the orientation angle was clearly higher in the extruded samples than the random orientation found in the non-extruded samples. Higher fiber loadings decreased the degree of pore orientation due to increasing interaction between the fibers. The pore size distribution measured by mercury porosimetry showed a peak at 16 μm corresponding to the pores formed by burn-out of the nylon 66 fibers and also showed peaks at 4 and 6 μm corresponding to the pores formed by burn-out of contacting fibers.

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