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Separation–permeation performance of porous Si_3N_4 ceramics composed of columnar β-Si_3N_4 grains as membrane filters for microfiltration

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The separation–permeation performance of porous silicon nitride (Si_3N_4) ceramics (consisting of columnar grains connected at random in three dimensions) as membrane filters was evaluated, and compared with commercial Al_2O_3 membranes having a three-layer structure. Si_3N_4 membranes separate particles with diameters much less than their pore diameters. The permeability of Si_3N_4 membranes with separability values the same as those of the Al_2O_3 membranes was about 1.3–2.4 times as large as the Al_2O_3 membranes. Dead-end filtration examination, using Al_2O_3 particles with a particle size distribution, indicated that the Si_3N_4 membrane filtration mechanism obeyed the cake filtration mechanism although the particle size was smaller than the pore size of the Si_3N_4 membranes.

1. Introduction

Porous ceramics have been used as new membrane filters for various filtration uses, such as microfiltration and ultrafiltration, due to their excellent properties, such as high heat resistance and high chemical resistance. Most of the commercial ceramic membranes, such as aluminum oxide (Al_2O_3) [1] and titanium oxide (TiO_2) [2], are produced by semisintering the green bodies of ceramic powders. It is widely known that the use of monolithic ceramics as membrane filters leads to a high pressure drop due to their low porosities. Therefore, commercial ceramic membranes are designed to have multilayer-structure (i.e. a thick support layer and a thin characteristic layer) to reduce the pressure drop in filtration [3]. However, a complicated production process is essential to produce ceramic membranes with multilayer-structure, resulting in high production costs.

Silicon nitride (Si_3N_4) ceramics have great promise for engineering applications due to their excellent properties, such as high strength, high fracture toughness, high thermal shock resistance and high chemical resistance [4]. Recently, we reported that porous Si_3N_4 sintered ceramics with both high porosity and high strength could be fabricated by the powder metallurgy process [5]. In this report, we report the separation–permeation performance of porous Si_3N_4 ceramics as membrane filters for microfiltration, compared with commercial Al_2O_3 membranes.

2. Experimental procedure

2.1. Materials

Fig. 1 shows a typical scanning electron microscope (SEM) image of porous Si_3N_4. The porous Si_3N_4 consists of columnar β-Si_3N_4 grains connected at random in three dimensions. Porous Si_3N_4 sintered bodies with porosities of about 50% were used for evaluation as membrane filters. Their typical mechanical and thermal properties are shown in Table I.

Tubular Si_3N_4 membranes (outer diameter, 10 mm; thickness, 1 mm; length, 100 mm) with three kinds of pore size distributions (specimens No. 4–6) were used to evaluate their separation–permeation performance. For comparison, commercial Al_2O_3 membranes (specimens No. 1–3) with three-layer structure (outer diameter, 10 mm; thickness, about 1.5 mm; length, 100 mm) were also evaluated. Table II shows the thickness of the three layers determined from SEM images of the cross-sections of the membranes. Fig. 2 shows the cumulative pore size distributions of the Si_3N_4 membranes measured by mercury porosimetric analysis, compared with Al_2O_3 membranes. The pore size distributions of the Al_2O_3 membranes show those of characteristic layers.

2.2. Evaluation of separation–permeation performance

2.2.1. Separability and permeability

Separability was measured by dead-end filtration at a filtration pressure of 0.1 MPa using aqueous suspensions of polyethylene particles, i.e. Latex, with uniform diameters of 0.05–1.0 μm. Their concentration was 0.1 kg m^{-3} (100 p.p.m.). Suspensions of 100 ml were filtered with tubular membranes, one terminal of which was closed with epoxy resin. Separability was calculated from the variation in absorbance of the suspensions before and after filtration using absorbance spectrophotometric analysis.

TABLE I Typical properties of porous Si_3N_4 ceramics

Properties	Values
Porosity, %	50
Flexural strength, MPa	200
Thermal expansion coefficient, K^{-1}	2.1×10^{-6}
Thermal shock resistance, ΔT, °C	1000

TABLE II Thickness of ceramic membranes

Specimen No.	Material	Characteristic layer (μm)	Intermediate layer (μm)	Support layer (μm)
1	Al_2O_3	80	140	1350
2	Al_2O_3	60	160	1350
3	Al_2O_3	60	150	1440
4	Si_3N_4	1000	0	0
5	Si_3N_4	1000	0	0
6	Si_3N_4	1000	0	0

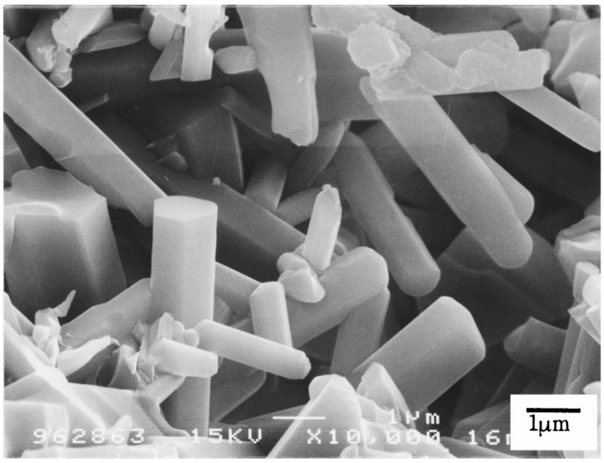

Figure 1 Typical microstructure of porous Si_3N_4 ceramics.

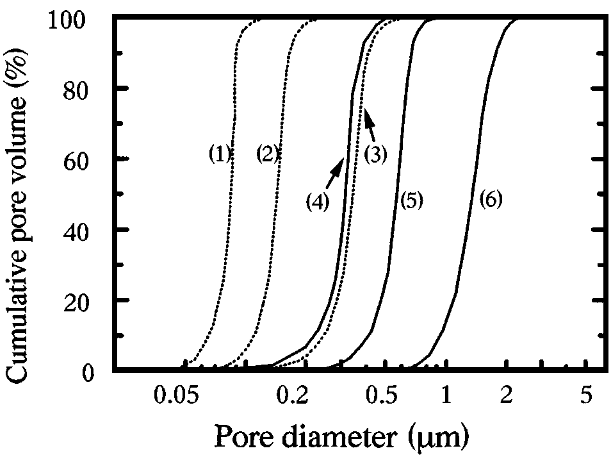

Figure 2 Pore size distributions of ceramic membranes: solid (specimens No. 4–6) and broken lines (specimens No. 1–3) represent Si_3N_4 and Al_2O_3 membranes, respectively.

The permeability of pure water was also measured by dead-end filtration at filtration pressures of 0.05–0.15 MPa.

2.2.2. Analysis of the filtration mechanism

Filtration of an Al_2O_3 suspension was carried out to analyse the filtration mechanisms of Si_3N_4 and Al_2O_3 membranes. The Si_3N_4 membrane (specimen No. 6) and the Al_2O_3 membrane (specimen No. 3), which had equivalent separability as demonstrated later, were used. An aqueous suspension of Al_2O_3 particles with a median diameter of 0.5 μm (AKP-50) was prepared, and was then filtered at a filtration pressure of 0.1 MPa by dead-end filtration. Its concentration and amount were 4 kg m^{-3} and 500 ml, respectively.

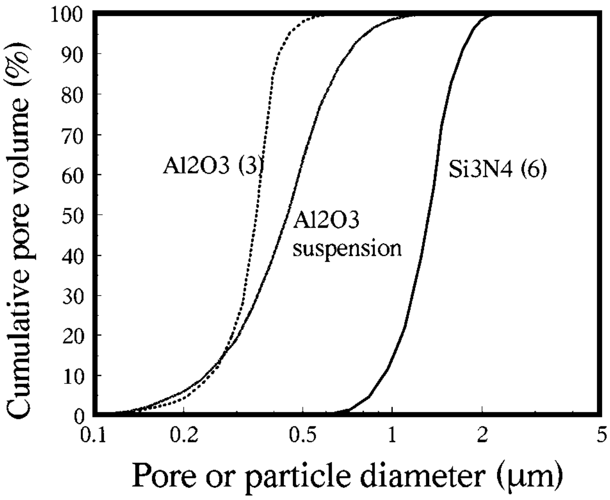

Figure 3 Relation between the particle size distribution of Al_2O_3 suspension and the pore size distributions of Al_2O_3 (specimen No. 3) and Si_3N_4 (specimen No. 6) membranes.

Fig. 3 shows the relation between the particle size distribution of the suspension and the pore size distributions of Si_3N_4 and Al_2O_3 membranes. Where, the particle size distribution was measured by laser Doppler method, the relation between particle size and the pore sizes of both membranes was contrastive: in the case of the Si_3N_4 membrane, most proes were larger than the particle sizes; in the case of the Al_2O_3 membrane most pores were smaller than the particle sizes. Filtration time and cumulative permeance were measured, and filtration behaviour was analysed using some equations proposed for dead-end filtrations.

3. Results and discussion

3.1. Separability and permeability

Table III summarizes the separability of both ceramic membranes. The separability of Al_2O_3 membranes depended seriously on their maximum pore diameters. The separability decreased drastically when the diameters of the particles were smaller than the maximum

TABLE III Separability of ceramic membranes

		Separability (%)			
		Latex diameter (μm)			
Material	Specimen No.	0.5	0.2	0.1	0.05
Al_2O_3	1	99<	99<	99<	65
	2	99<	99<	29	13
	3	99<	65	22	0
Si_3N_4	4	99<	99<	99<	93
	5	99<	99<	97	40
	6	99<	98	98	a

[a]Not measured.

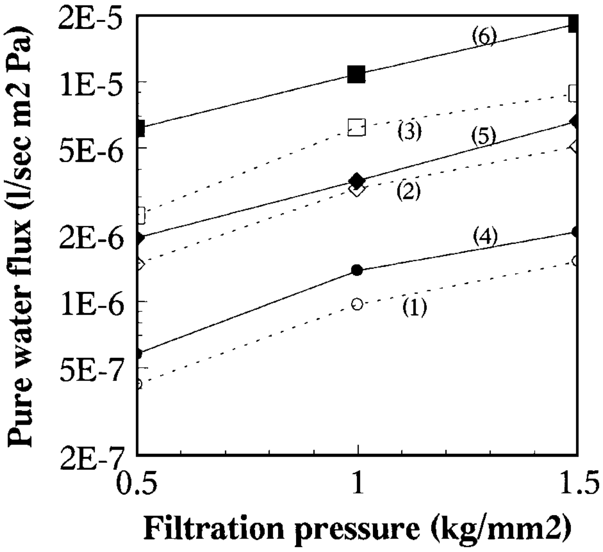

Figure 4 Pure water flux of Al_2O_3 and Si_3N_4 membranes.

pore diameters. This indicates that separation using Al_2O_3 membranes occurs by a sieve effect on the membrane surface. However, the Si_3N_4 membranes separated Latex particles much smaller than the maximum pore diameter of the membrane. Furthermore, the separability did not decrease drastically with decreasing particle diameter. The Latex particles are highly dispersed in the suspension and their concentration is not large enough to form a thick cakelike layer on the surface of the membrane. Therefore, we consider that the high separability of Si_3N_4 membranes cannot be ascribed only to the sieve effect.

Thus, the separability of the three kinds of Si_3N_4 membranes (specimens No. 4–6), corresponds to that of the Al_2O_3 membranes (specimens No. 1–3), respectively. This suggests that Si_3N_4 membranes with pore diameters much larger than those of Al_2O_3 membranes can be chosen for the separation of particles with constant diameters. Fig. 4 shows a comparison of the pure

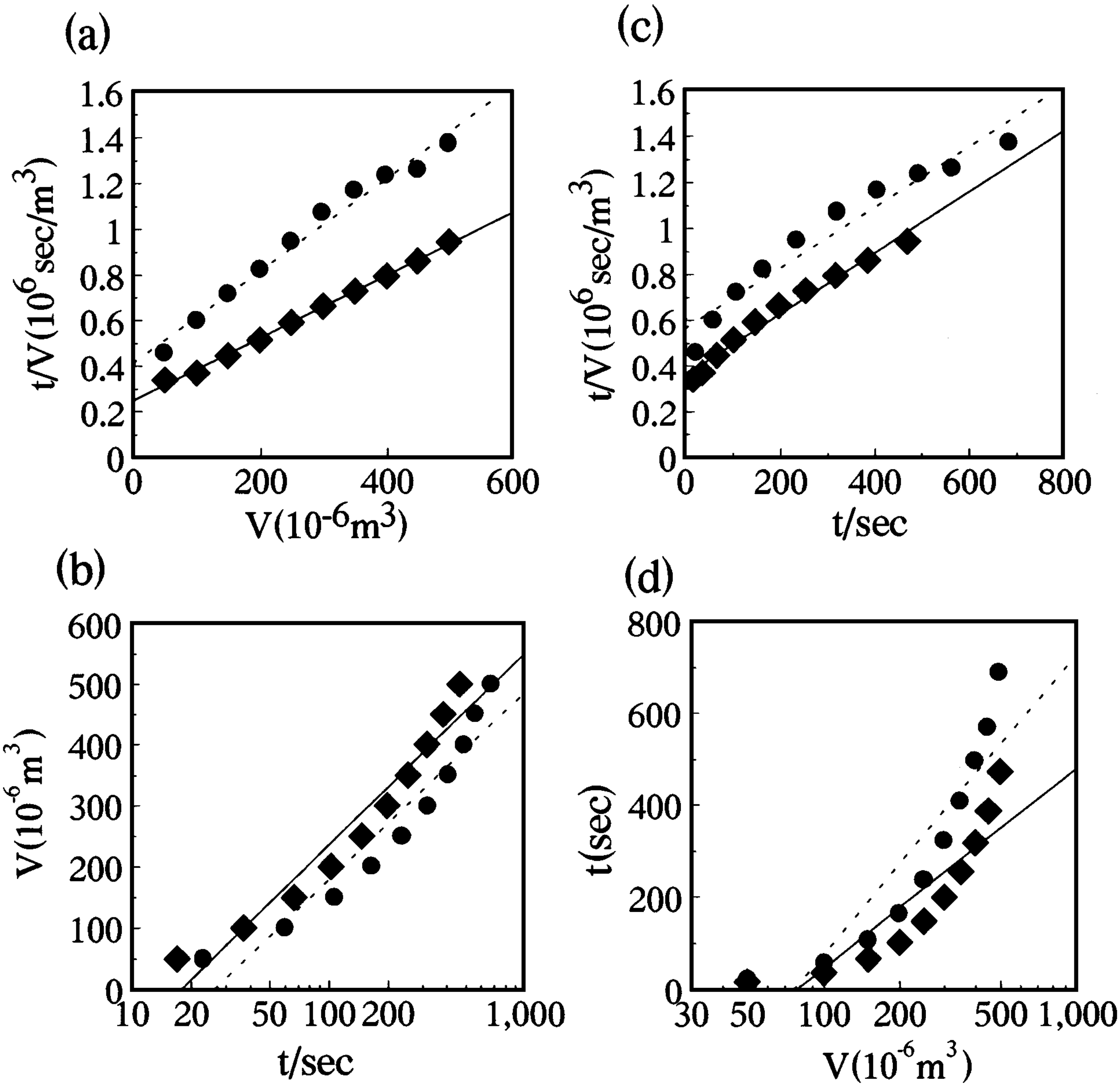

Figure 5 Various plots for analysis of the filtration mechanisms of Al_2O_3 (●) and Si_3N_4 (◆) membranes: (a) V versus t/V, (b) ln t versus V, (c) t versus t/V, and (d) ln V versus t plots.

water flux of Al_2O_3 and Si_3N_4 membranes. In spite of monolayer-structured membranes, the permeances of the Si_3N_4 membranes were 1.3–2.4 times as large as those of the Al_2O_3 membranes. The high permeability of the Si_3N_4 membranes is probably caused not only by their high porosity but also by their peculiar microstructure. However, such filtration behaviour of the Si_3N_4 membranes commonly suggests that inner filtration rather than cake filtration may occur. Therefore, analysis of the filtration mechanism is necessary.

3.2. Analysis of the filtration mechanism

The following equation is proposed for some dead-end filtration mechanisms [6]

$$d(dt/dV)/dV = d^2t/dV^2 = b(dt/dV)^n \qquad (1)$$

Where, t, V and dt/dV are filtration time, permeance and filtration resistance, respectively. The n value varied from 0 to 2.0. In the case of $n = 0$, filtration is governed by the cake layer mechanism operative on membranes, i.e. cake filtration. In the case of $n = 1.0$ to 2.0, filtration is governed by the decrease in pore diameter, which is caused by occupancy of the pores by filtered particles, i.e. inner filtration. In particular, where $n = 1.5$ standard inner filtration occurs, and is a common feature of practical filtration. Integration of Equation 1 at each n value gives

$$n = 0 \qquad t/V = (K_c/2)V + 1/Q_0 \qquad (2)$$

$$n = 1.0 \qquad K_iV = \ln(1 + K_iQ_0t) \qquad (3)$$

$$n = 1.5 \qquad t/V = (K_s/2)t + 1/Q_0 \qquad (4)$$

$$n = 2.0 \qquad K_bV = Q_0[(1 - \exp(-K_bt))] \qquad (5)$$

Where, K_c, K_i, K_s and K_b are constants; and Q_0 is the initial flux. Accordingly, the filtration mechanism can be determined from the linearity in the V versus t/V, ln t versus V, t versus t/V and ln V versus t plots.

Fig. 5 shows a comparison of the plots for Al_2O_3 (specimen No. 3) and Si_3N_4 (specimen No. 6) membranes having the same separability. With the Al_2O_3 membrane, clear linearity cannot be seen in V versus t/V plot (Fig. 5a). Considering the relation between the particle size distribution of the Al_2O_3 suspension and the pore size distribution of the Al_2O_3 membrane, there is a possibility that many particles are separated by inner filtration. In practice, linearity is seen at the initial time up to about 100 s in the t versus t/V plot (Fig. 5c). Therefore, filtration may proceed by inner filtration at the initial time, then it may shift to cake filtration.

On the other hand, there can be seen a linearity higher than that of Al_2O_3 in the V versus t/V plot (Fig. 5a), using the Si_3N_4 membrane–although almost all the particles are less than the pore sizes of the membrane. Thus, filtration almost seems to proceed by cake filtration using the Si_3N_4 membrane. Similarly to the Al_2O_3 membrane, however, we cannot negate inner filtration at the initial time, since there might be a linearity at the initial time up to about 100 s in the t versus t/V plot (Fig. 5c). Such cake filtration, despite the pore sizes being larger than the particle sizes, is probably caused by the peculiar microstructure; the pore form of the Si_3N_4 membranes is seriously different from that of the Al_2O_3 membranes. We consider that the pore size distributions of the Si_3N_4 membranes measured by mercury porosimetric analysis do not correspond to actual pore size distributions of the membranes; conventional filtration theory cannot be applied directly to the structure of porous Si_3N_4 consisting of columnar grains connected at random in three dimensions. Membranes having such a microstructure possibly have slit-like pores.

4. Conclusions

The separation–permeation performance of porous Si_3N_4 ceramics composed of columnar grains connected at random in three dimensions as membrane filters, was evaluated compared with commercial Al_2O_3 membranes with three-layer structure. We can conclude:

1. The Si_3N_4 membranes can separate particles with diameters less than their pore sizes in dead-end filtration using Latex particles.
2. Filtration with Si_3N_4 membranes obeyes the cake filtration mechanism although the size of filtered particles is smaller than the pore size of the membranes.

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