Preparation of Composite Microporous Glass Membrane on Ceramic Tubing*

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Porous thin glass membranes of which thickness is in the range of 5 to 23 μ m have been prepared on the surface of porous ceramic tubing by coating with metal alkoxide solution, drying, heating and acid leaching sequentially. Structure of the membranes was investigated by Scanning Electron Microscope, and found that pore size is in the range of 4 to 64nm.

Key words: Membrane, Composite membrane, Porous glass, Ceramic tubing, Gas separation, Metal alkoxide coating

Microporous glass membranes have advantages of their chemical and thermal stability as well as higher permeability over organic membranes. The preparation of the microporous glass was first patented by Hood & Nordberg¹⁾. A mixture of glass material was used in order to make a phase separable glass that results in the separation of an acid soluble phase and this phase can be removed by acid leaching. Thus, a microporous structure is obtained as an intermediate stage in the manufacturing of Vycor-brand glass. Commercially available microporous glass membrane, however, has some disadvantages, that is, 1st, their thickness is very thick of several mms and 2nd, it seems impossible to make them into a module which has large membrane area for commercial application.

We have tried to fabricate very thin microporous glass membrane on the surface of porous ceramic tubing of small diameter

Membrane Making Procedure

Thin layer of microporous glass was fabricated on the surface of porous ceramic tubing (supplied by TDK Co., Ltd.) using the method described by Sakka²⁾. The procedure is shown schematically on Fig.1. The compositions of metal alkoxide solutions which was used in the coating process onto the ceramic tubing, are listed on Table 1.

Porous ceramic tubing of which the dimensions

Fig.1 Procedure of Composite Porous Glass Membrane by Alkolate Method

* 多孔質セラミック円管上に微多孔ガラス薄膜を形成させた複合膜

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Fig.2 Sequential Change of Structure

were 2mm of outer diameter and 1mm of inner diameter was dipped in metal alkoxide solution from sealed end and pulled out with speed of 2mm/s. The solution coated on ceramic tubing was dried 1 minute or so at room temperature, then placed in electric furnace and heated at 550°C for 60 minutes then taken out to cool down. After the procedure of coating, drying and heating was repeated several times, the tubing was dipped in aqueous 3M HCl acid solution at 80°C for 6 hours to leach out acid soluble phase so as to make the membrane porous. The acid leached membrane washed by pure

Table1 Compositions of Alkoxide Solutions for Coating

Membrane	AA	AB1	AB2	AC1	AC2	AC3	AC4
	Quantity (g)						
Si(OC ₂ H ₅) ₄	25	25	25	25	25	25	25
C ₂ H ₅ OH	37.6	37.6	37.6	37.6	37.6	37.6	37.6
H ₂ O	23.7	23.7	23.7	23.7	23.7	23.7	23.7
HCl	0.3	0.3	0.3	0.3	0.3	0.3	0.3
H ₃ BO ₃	0	0	0	3.2	3.2	3.2	3.2
B ₂ O ₃	0	0.5	1.0	0	0	0	0
SiO ₂ /B ₂ O ₃	-	14	7.2	4	4	4	4
Coating times	10	15	15	15	7	5	2
Membr. Thickness (μm)	18	23	23	23	15	13	6

water at room temperature for more than 10 hours and dried at 80–100°C for over night.

Fig. 3 Cross Sectional View of Membrane

The Structure of Membrane

Using Scanning Electron Microscope (SEM), sequential change of the appearance of the structure of glass membrane during the course of membrane making was observed. Fig.2-a shows surface of ceramic tubing before coating. Fig.2-b shows surface of only one time coated glass layer of the alkoxide before the acid treatment process. The configuration of the glass layer is rough as same as virgin ceramic tubing but small pores which can be seen on the original ceramic tubing are disappeared. Fig.2-c shows surface of 15 times alkoxide coated glass membrane after acid treatment. There are pore of which sizes are in the order of several tenth μm to several μm , and are becoming smaller toward the inside of the membrane as shown on Fig.2-d.

The membrane thickness, which was measured on the SEM photo of the cross sectional view shown on Fig.3 as an example, is plotted against coating times on Fig.4. The thickness at 5 times was about $13\mu\text{m}$ and at 15 times about $23\mu\text{m}$. After the 5th times of coating, the increment of thickness is around $1\mu\text{m}$ for every coating.

Mean Pore Diameter

Permeation rate (P.R.) through porous media

Fig. 4 Increase of Membrane Thickness with Repeat of Coating

Fig. 5 Permeation Rate vs. Mean Pressure

is expressed by the Eq.1 in which the first term represents Knudsen flow and the second viscous flow. Where K_0 is permeation rate of Knudsen flow, η viscosity of the gas and B_0 geometric factor of membrane and $\bar{p}$ average pressure over

Table 2 Mean Pore Size of Pourous Glass Membrane

Coating Times	$\frac{\text{SiO}_2}{\text{B}_2\text{O}_3}$	Mean Pore Size [nm]
2	4	64.0
5	4	24.0
7	4	6.8
15	4	4.3
15	7	8.1
15	14	7.8

the membrane. Mean pore diameter of the porous media d_p is expressed by the Eq. 2⁴⁾

$$P.R. = K_o + (B_o/\eta)\bar{p} \quad (1)$$

$$d_p = (B_o/K_o)(16/3)(2RT/\pi)^{\frac{1}{2}} M^{-\frac{1}{2}} \quad (2)$$

Fig.5 shows a typical example obtained with pure methane gas, and gives d_p as 4.3nm. Mean

pore diameters for other membranes are listed on Table 2. When coating time increases, the mean pore diameter decreases for ($\text{SiO}_2 : \text{B}_2\text{O}_3 = 4:1$) membrane.

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