학술발표 I-ii

THE PREPARATION AND CHARACTERIZATION OF ALUMINA UF MEMBRANE BY SOL-GEL PROCESS

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ABSTRACT

Alumina UF membranes were prepared by sol-gel process and their gas permeabilities were characterized. Alumina MF membrane with average pore diameter about $0.12 \mu m$ and tubular shape was used as a support. Gas permeation measurements of helium and nitrogen gas exhibited the permeabilities of $1.58 \times 10E-6$ and $0.63 \times 10E-6$ cc $\cdot$ cm(STP)/$cm^2 \cdot$ sec $\cdot$ cmHg , respectively. The permeability ratio was 2.5. This means the gas permeation is fully governed by Knudsen diffusion mechanism.

I. Introduction

The sol-gel method is suitable for the preparation of ceramic membranes with micropores in the nanometer range. The sol was prepared via hydrolysis and peptization of metal alkoxides and then coated on porous support by dipping. In the process, it is essential to obtain boehmite (γ-AlOOH) as a precursor material, because it can be easily peptized with acids. The crystallite size of γ-AlOOH is determined by the heat treatment temperature and time, and the type of acid and its concentration during peptizing. Here we describe the preparation of γ-alumina membrane film on porous support and its permeability.

II. Experimental Procedure

Boehmite sols (γ-AlOOH) were prepared using aluminum alkoxide (Al(OR)3) as a precursor. The precursor was hydrolyzed and precipitated in excess water [100 mole water /alkoxide]. HNO3 was used for peptizing agent, where 0.05, 0.07, 0.1, 0.2 HNO3 / alkoxide was added for each solution to observe sol characteristics. And also DMF(Dimethylformamide) with 5 mole per alkoxide was added as DCCA (Drying Control Chemical Agent). With this sol we coated the alumina porous support by dip technique. This gel layer can be dried and calcined to form oxidic toplayer of controlled microstructure.

We measured the permeability of γ-Al2O3 membranes for He and N2 gas seperately using the system in Fig.1. Thickness and length of the membrane were $5-6\mu m$ and 3.2cm. Feed gas permeate the membrane with changing the pressure by line regulator. The permeation rate was measured by flowmeter.

III. Results and Discussion

III-1. Preparation of membrane

A. Effect of acid concentration

We presented the sol particle size changed by the amount of acid . The minimum mean particle size was obtained from the sol of 0.07 mole HNO3/alkoxide and its size was increased around that point as shown in Fig. 2. For 0.05 HNO3/alkoxide, it was not fully peptized and precipitated. The particles for sols with higher than 0.07mole were agglomerated each other, which resulted in the increase of particle size. A critical amount of certain acids must be introduced into the precipitates for peptization. In this step, agglomerates were broken up into the units of colloidal size. The peptization phenomenon is based on electrostatic interactions. Repulsion is caused by the electric double layer around the colloidal particles. For instance, with acid electrolyte, hydrogen ions are adsorbed at the particle surface and the redistribution of counterions causes the formation of double layer. 0.07 HNO3/alkoxide is critical amount for preparing the most stable boehmite sol.

B. Viscosity of sol with and without DCCA

The viscosities of the sols with and without DCCA were shown in figures 3-4 as a function of boehmite content. While the sols with 0.05, 0.07 HNO3/alkoxide and without DCCA exhibit gradually increase of viscosities, those of highly acidic sols increase drastically because the particles were agglomerated just after peptization. For sol with DCCA in Fig.4, even the viscosities for highly acidic sols increase gradually above middle stage unlike pure sol. This is the reason that the evaporation of water is suppressed for drying by adding DCCA, where DCCA act as a buffer against agglomeration of particles and then prevent sharp increase of sol viscosity. And also the variations of weight loss and boehmite content in sol with DMF as a funtion of drying time exhibited smooth curves as shown in Fig.5-6. Therefore we can see that the use of DCCA is effective to avoid crack formation in the drying process.

C. Pore properties as a function of acid concentration

Four boehmite monolithic gels varied acid concentration were calcined to 600°C for 1hr and the surface and pore properties were tested by BET method. The surface area and pore volume are shown in Fig.7. The pore volume and surface area go through a maximum at 0.07 mole acid concentration. The effect of acid concentration on the average pore sizes in shown in Fig.8. This pore morphology of the resultant alumina reflects the optimizing effect of acid concentration in sol.

D. SEM observation for a γ-Al2O3 membrane

Fig.9 is a SEM photo showing a cross-section of a asymmetric membrane which was coated with 5wt% AlOOH content sol and heat-treated at 600°C for 1hr. And Fig.10 shows a surface of substate before dipcoating. Its uniform microstructure is suitable for coating on the surface by sol-gel method. The thickness of first dipcoated membrane layer estimated from the SEM photo is about 5μm. The membrane layers were further examined by helium and nitogen permeability data at different pressures.

III-2. Gas Permeation

Fig.8 showed the permeabilities as a function of pressure difference ($\triangle$P) for helium and nitrogen. The Permeability(P) was defined as follows ;

$$P = \frac{V \cdot d}{A \cdot \triangle P}$$

where V is the volume of permeated gas per unit time
    A is the effective area of the membrane
    d is the thickness of membrane

In the range of UF alumina membrane, Knudsen diffusion and laminar flow may occur as gas permeation mechanisms at room temperature.   At atmospheric pressure the mean free path of gas molecules is in the order of 0.1μm.   This is considerably larger than the average pore diameter of our menbrane with pores in the order of a few nanometers. Therefore it can be assumed that the permeation mechanism is fully Knudsen diffusion. Actually it was proven that the permeability was independent of the pressure difference, as can be seen from Fig. 11.
The pore diameter of support itself is very large compare to that of coating layer. So, it cannot be applied for Knudsen diffusion mechanism, the permeability ratio of helium is similar to that of nitrogen. And also, the actual permeability ratio of supported membrane for helium and nitrogen is 2.51 when the ideal one is 2.65 in Knudsen region. The results mean that the permeation was completely governed by Knudsen diffusion mechanism and that the formation of membrane layer by sol-gel process was successfully carried out without pinholes or cracks.

IV. Conclusions

(1) A critical amount is needed to peptize the hydroxide for clear sol, the amount
  determines various properties of the membranes.   Mean particle size and viscosity
  of the sol exhibited a minimum at acid concentration of 0.07mole HNO3 /alkoxide.

(2) Low boehmite contents and low viscosity of sols are necessary to coat uniformly on
  the support and prepare a crack-free membrane.

(3) The pore properties of γ-Al2O3 are optimized at the 0.07mole acid concentration in
  sol.

(4) The permeability of supported membranes could be explained by Knudsen diffusion
  mechanism.

References

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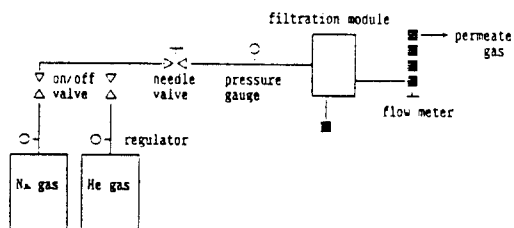8. K. Keiser & A. J. Burggraaf, Science Ceramics. 14, 551 .

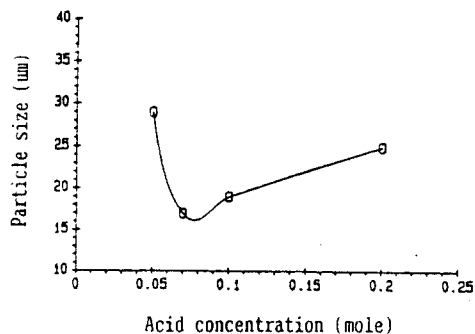Fig. 1 The schematic diagram of gas permeation unit

Fig. 2 Particle size in various acid
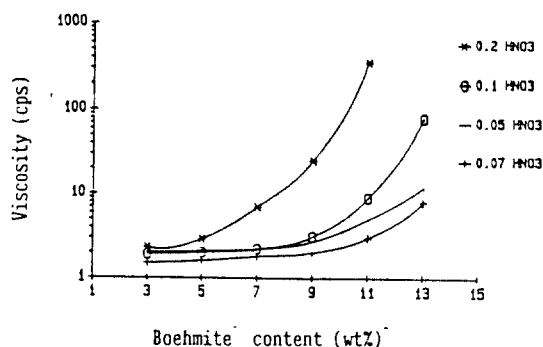concentration sols.

Fig. 3 Effect of Boehmite content on
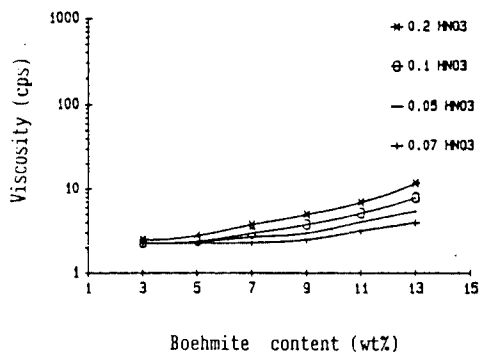Viscosity of pure sol.

Fig. 4 Effect of Boehmite content on
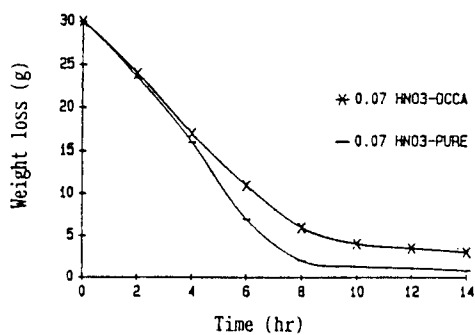Viscosity of DCCA sol.

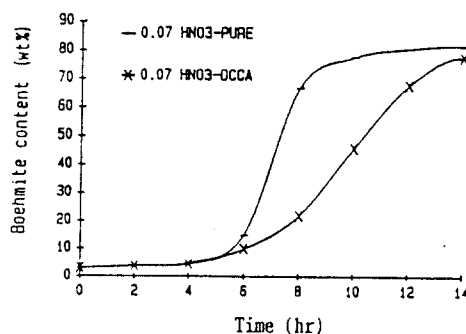Fig. 5 Weight loss of sol against
drying time at 90 C.

Fig. 6 Boehmite content in pure sol and DCCA sol
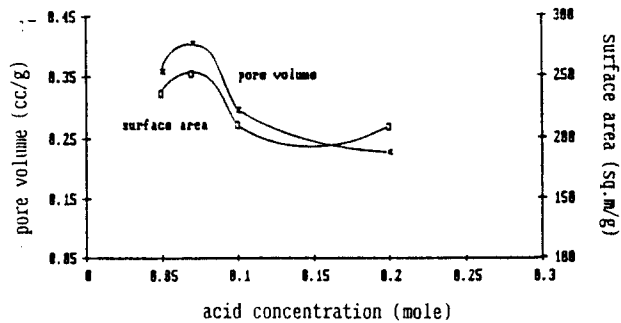against drying time at 90 C.

Fig. 7 Effect of acid concentration of sol
_ Surface area and pore volume of γ-alumina
heat-treated at 600°C for 1hr.
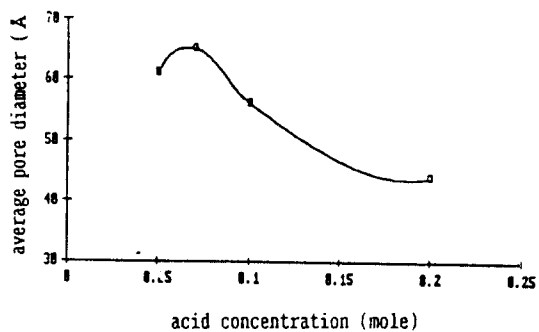
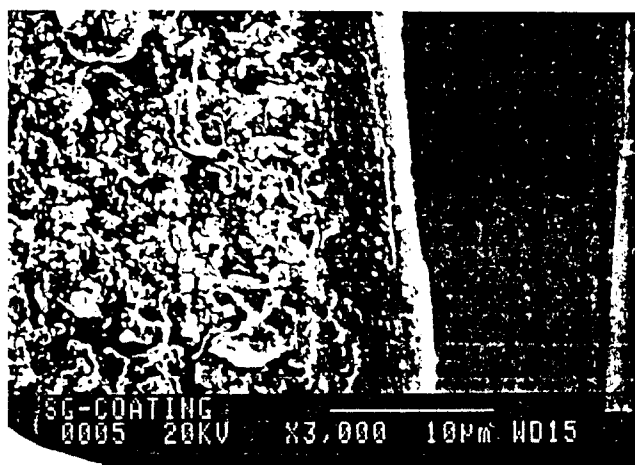

Fig. 8 Variation of γ-alumina pore size
with acid content
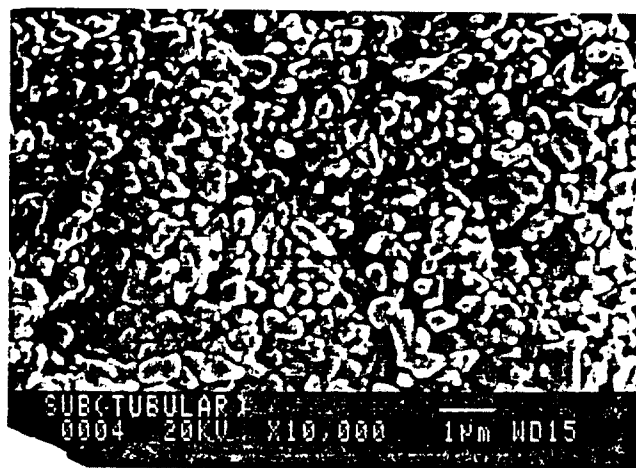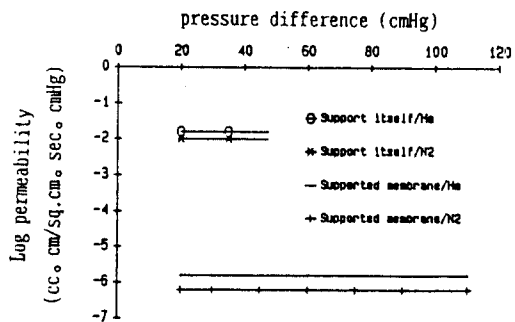

Fig. 9 Cross-section of supported
γ-alumina membrane

Fig. 11 Permeability of gases as a function
of pressure difference

Fig. 10 Surface state of substrate