

Thermotreatment and Chemical Resistance of Porous Alumina Membrane Prepared by Anodic Oxidation

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Abstract—Porous alumina membranes were prepared by anodic oxidation of aluminum in an aqueous solution of oxalic acid. The thermal and chemical stabilities of porous alumina membranes were investigated by thermal analysis and corrosion test. Alumina membranes prepared in oxalic electrolyte had fairly good thermal stability, but they reacted with boiling water to form boehmite, which blocked pores on the surface of the membrane. For acid and alkali resistance, the membranes were estimated to have chemical stability in aqueous acidic and alkaline solution at $1 < \text{pH} < 12$. On the other hand, pore size and its distribution were not changed at the time of thermal treatment. Polycrystalline alumina membrane obtained by thermal treatment for 3 h at 900 °C could suppress corrosion reaction and enhance their resistance in acid and alkaline solution.

Key words: Anodic Oxidation, Oxalic Acid, Amorphous Alumina Membrane, Boehmite Polycrystalline Alumina Membrane, Corrosion Resistance, Acid and Alkali Resistance

INTRODUCTION

Although polymeric membranes for ultra-filtration or reverse osmosis are being widely used for simple water treatment, owing to their low price and good functions in separation and purification, their thermal and chemical stability are so poor that they are not proper to use for separation processes at high temperature. In other words, their pore structures were destroyed, losing their function due to softening phenomena of polymer at high temperature. However, membranes made of inorganic materials have good chemical, thermal and mechanical stability, long lifetime, feasibility of cleaning and reconstruction, and small damage by microbes. Thus, extensive efforts have been made to establish manufacturing methods of inorganic membranes. Inorganic membranes on the market are usually prepared by slip-casting or sol-gel method, and have relatively broad pore diameter distribution. In addition, the pressure gradient through the membrane is large owing to the tortuous nature of pore structure [Larbot et al., 1986; Leenaars and Burggraaf, 1985; Winston Ho and Sirkar, 1991].

On the other hand, it is known that amorphous porous alumina membranes prepared by anodic oxidation have uniform pore diameter and distribution, high pore density, and straight pore structure. But application of the membranes is limited because they react with water over 80 °C which leads to blockage of the pores, and they have little resistance to acid and alkali attack [Korean Aluminum Surface Treatment Cooperation, 1993]. In addition, it is known that dissolution of amorphous porous alumina membranes prepared by anodic oxidation begins at $\text{pH} < 5.0$ and $\text{pH} > 8.2$, and dissolution is complete at $\text{pH} < 4.2$ and $\text{pH} > 9.9$ with enough time. It is necessary to solve the problems of

dissolution of the membranes in aqueous acidic and alkaline solutions to improve membrane performance without change of pore diameter as well as pore structure. It is known that amorphous anodic oxides crystallize at about 830-840 °C, which corresponds to the boehmite series that is formed at lattice and surface structure [Mardilovich and Rzhetskii et al., 1995; Mardilovich et al., 1995; Hsieh et al., 1988].

Therefore, in this study, porous alumina membranes were prepared by anodic oxidation of 99.8% aluminum plate, and their thermal and chemical stability were investigated. For these purposes, thermal analysis and corrosion test in boiling water, acid or alkaline solution were carried out for both amorphous and polycrystalline membranes. From these experiments, we intend to present the fundamental data necessary to apply the porous alumina membranes to a separation process or catalytic reaction at high temperature.

EXPERIMENTAL

The schematic flowchart for preparation of porous alumina membrane from aluminum plate is presented in Fig. 1. As shown in Fig. 1, porous alumina membrane was prepared through a series of pre-treatments (such as thermal oxidation, chemical polishing, and electrochemical polishing), anodic oxidation, and dissolution of aluminum plate and barrier layer successively. And then the prepared membrane was treated at high temperatures. Corrosion resistance and acid and alkali resistance of both thermally treated and untreated membranes were observed.

1. Materials

The aluminum plate used in this study has 99.8% purity (size: $30 \times 70 \times 0.6$ mm). Ultra-pure water (resistance = $1.8 \text{ M}\Omega \cdot \text{cm}$) was prepared (Elga Stat Co.) and used for preparation of aqueous solution or cleaning. Various acids of special grade were supplied by Ducksan or Junsei.

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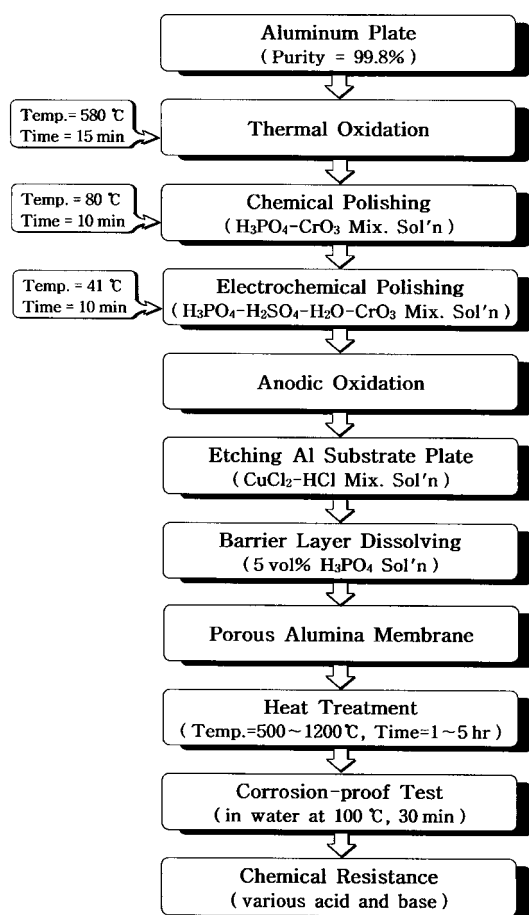


Fig. 1. Schematic diagram of experimental procedure.

2. Preparation of Porous Alumina Membrane

Prior to anodic oxidation, sample was washed by ultrapure water after it was cleaned by acetone to eliminate the impurities on the surface. After washing, thermal oxidation was executed for 15 min at 580 °C to make better formation of pores. Subsequently, chemical polishing was carried out in 3.5 vol% aqueous H₃PO₄ solution containing 45 g CrO₃/l for 10 min at 80 °C and then electrochemical polishing was performed in solution of H₃PO₄-H₂SO₄-H₂O (7:2:1) containing 35 g CrO₃/l for 10 min at 40 °C under 2.87 A constant current. The sample was cleaned with ultrapure water and acetone at the end of every stage of pre-treatment procedures in order to remove solution from sample. Finally, after only one side of sample was sealed, anodic oxidation was carried out on this sample.

Porous alumina membrane was prepared by anodic oxidation under constant current mode of 30 mA/cm² current density and 150 C/cm² cumulative charge density at 20 °C with 10 wt% oxalic electrolyte. Cooling water was circulated through the jacket of the reactor in order to maintain a constant reaction temperature. As anodic oxidation was carried out, electrolyte was stirred constantly to eliminate heat that was generated from the reactor. The distance between the sample and a titanium counter electrode was 5 cm. Experimental apparatus used in this anodic oxidation experiment was the same as designed in previous papers [Lee et al., 1998].

In order to separate porous alumina membrane from the an-

odized sample, aluminum substrate plate on the back of sample was etched by being contacted with the aqueous solution of 0.1 M CuCl₂ and 20 wt% HCl. Because this process accompanied a large exothermic reaction, the sample was etched under cooling air flow.

Since porous alumina membrane prepared by anodic oxidation consists of double geometric structure: porous layer on the barrier layer, it is essential to dissolve the barrier layer beneath porous layer of alumina plate to be used as a membrane. So, the barrier layer of the porous alumina membrane was dissolved in 5 wt% aqueous H₃PO₄ solution.

Pore diameter and thickness of alumina membrane prepared in this study were 55 nm and 66 μm, respectively.

3. Thermal and Chemical Resistance of Porous Alumina Membrane

Porous alumina membrane prepared by anodic oxidation was tested for thermal and chemical resistance to see whether it could be used as the membrane for separation or catalytic reaction at high temperature.

3-1. Heat Treatment

After the porous alumina membrane was prepared in oxalic electrolyte, the membrane was heat treated for 1-5 h at 500-1,300 °C to investigate its thermal stability against warping as well as the change of pore structure.

3-2. Corrosion Test

The corrosion test of both uncalcined alumina membrane and the calcined membrane was carried out by putting both membranes into boiling distilled water for 30 min.

3-3. Acid and Alkali Resistance Test

To estimate the chemical resistance of both untreated alumina membrane and alumina membrane thermally treated for 3 h at 900 °C, experiments were carried out under the conditions of Table 1. Pieces of these membranes were put into both 20 ml aqueous acidic and alkaline solution for 180 min and then were picked out every 30 min to analyze the changes of pore structure using SEM. Moreover, the above experiments were repeated with varying the pH of both aqueous HCl and NaOH solution under the same temperature.

Aqueous acidic solutions of pH<4 [0.01 N HNO₃, 0.1 N H₂SO₄] and alkaline solutions of pH>9 [0.01 N NaOH, 0.1 N NaOH] were chosen in order to estimate the chemical stability of both membranes. In addition, these experiments were repeatedly carried out with various kinds of strong acid [0.1 N HNO₃, 0.1 N

Table 1. Test conditions for resistance to acid and base

	Solutions	Temp. [°C]	Time [min]
Acid	0.1 N HCl	20, 30, 40	30-180
	0.01 N HCl	20	30-180
	0.001 N HCl	20	30-180
	0.1 N HNO ₃	20	30-180
	0.1 N H ₂ SO ₄	20	30-180
Base	0.1 N NaOH	20, 30, 40	30-180
	0.01 N NaOH	20	30-180
	0.001 N NaOH	20	30-180
	0.01 Ca(OH) ₂	20	30-180

H₂SO₄] and alkali [0.01 N Ca(OH)₂] solution.

4. Instrumental Analysis

4-1. Thermal Analysis (TG-DTA)

In order to examine dehydration behavior, weight loss and phase transition of porous alumina membrane, thermal analysis was performed in raising temperature at a rate of 10 °C/min to 1,300 °C using STD 2960 of TA Instrument [U.S.A.].

4-2. ICP Analysis

The amount of aluminum ions released from porous alumina membrane into both aqueous acidic and alkaline solution at various reaction temperature was estimated using an Optima 300 DV of Perkin Elmer Co. after the calibration curve was established with aluminum standard solution and values within 0.3% of RSD (relative standard deviation) were selected.

4-3. X-Ray Diffraction Analysis

The crystal structures of porous alumina membranes were analyzed by using the Geiger flex Model-3A of Rigaku (Japan) Co., and measurement conditions were the same as Table 2.

4-4. SEM Analysis

The extent of surface damage, layer thickness and pore size of porous alumina membrane after experiments, such as thermal treatment and chemical resistance and corrosion test, was examined using JSM-5800 of JEOL Co. (Japan).

Table 2. Measurement conditions of X-ray analysis

Target	Filter	Load	Start angle	End angle	Scan speed
Cu	Ni	30 kV, 15 mA	10 °	80 °	4 °/min

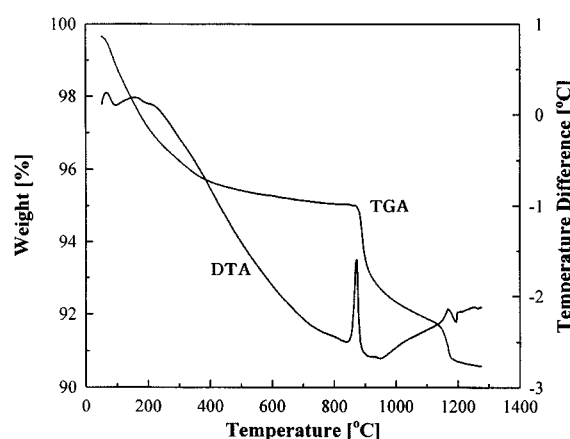


Fig. 2. TGA-DTA curve of porous alumina membrane prepared in oxalic acid.

RESULTS AND DISCUSSION

1. Thermal Characteristic of Porous Alumina Membrane

Fig. 2 shows the TG-DTA results for prepared alumina membrane. In the DTA curve, the strong exothermic peak at about 870 °C was caused by the transition of amorphous alumina into crystal (θ , δ -Al₂O₃), and the endothermic peak at 1,200 °C indicated the transition of α -Al₂O₃. From TG analysis, on the other hand, the weight loss of about 3% up to 200 °C was caused by moisture removal and the weight loss at 200-400 °C by removal of anions that existed in porous layers after anodic oxidation. In

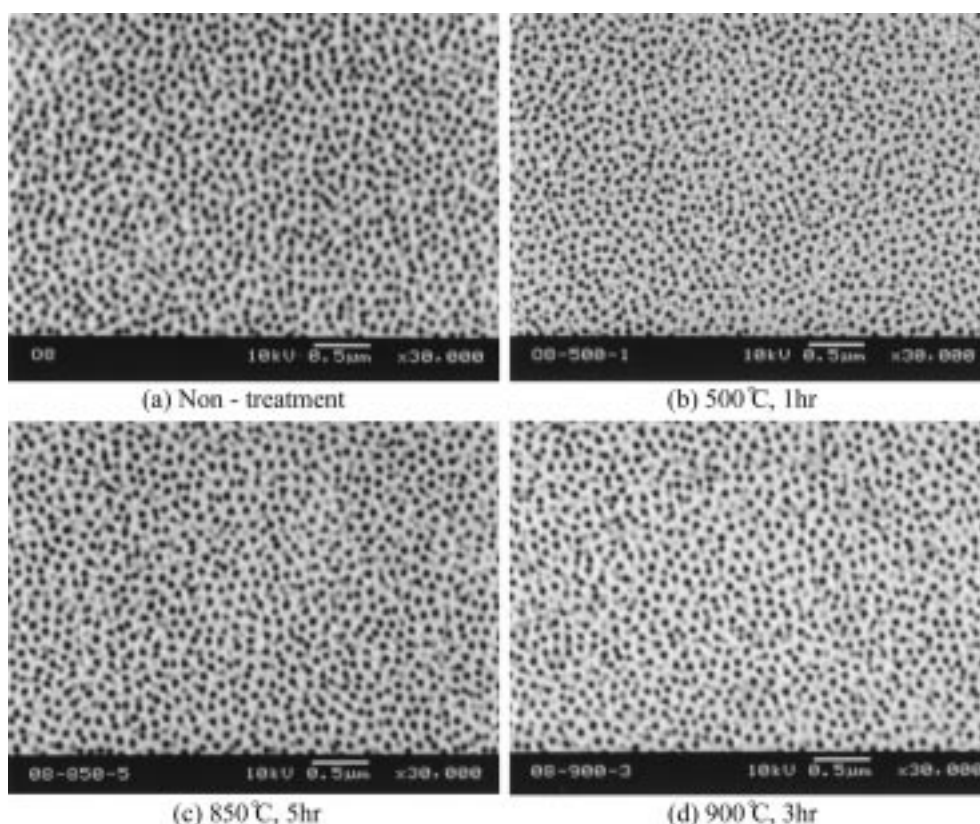


Fig. 3. SEM photographs of porous alumina membrane according to calcined temperature and time.

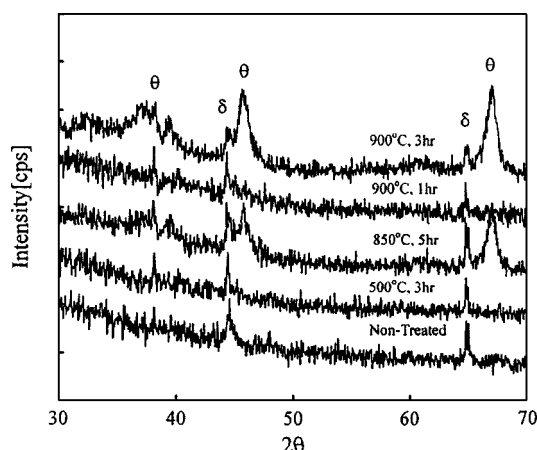


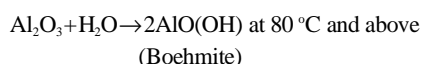
Fig. 4. X-ray diffraction patterns of porous alumina membrane according to calcined temperature.

addition, the weight loss due to phase transition into crystal was observed at 870 and 1,200 °C. On the basis of these results, amorphous porous alumina membranes were calcined at 500, 850, 900, 1,200, and 1,300 °C, respectively. These heat treatments revealed that warping did not take place at 1,200 °C and below, but it was found above that temperature. Therefore, it can be said that amorphous alumina membrane is thermally stable up to 1,200 °C.

Fig. 3 shows SEM photographs of porous alumina membranes heat treated for 1 h at 500 °C, for 5 h at 850 °C and for 3 h at 900 °C, respectively. As shown in Fig. 3, there was no difference in pore diameter and distribution before and after heat treatment. So it was found that although amorphous porous alumina membrane was calcined, its pore diameter and distribution did not change, which leads this membrane to be used for separation at high temperature without losing its properties. On the other hand, Fig. 4 shows the results of XRD analysis that ascertained the crystallinity according to temperature of heat treatment. As shown in Fig. 4, the membrane calcined for 3 h at 900 °C has polycrystallinity of θ and δ - Al_2O_3 [Mardilovich et al., 1995]. These results coincide with the results of TG-DTA as shown in Fig. 2.

2. Corrosion Test of Porous Alumina Membrane

A corrosion test of porous alumina membrane was carried out in boiling water, and SEM photographs of its surface before and after corrosion test were presented in Fig. 5. Fig. 5(a) shows SEM photograph of the sample before corrosion test indicating well-developed pores of alumina membrane. But Fig. 5(b) shows that pores were blocked owing to the reaction of alumina membrane with boiling water. This is due to the fact that prepared alumina membrane undergoes the corrosion reaction that alumina membrane transforms into boehmite as following equation [Korean Aluminum Surface Treatment Cooperation, 1993].



Therefore, alumina membrane prepared by anodic oxidation is not proper to be used without any treatment in a high temperature reactor in which water vapor is generated.

To investigate the effects of heat treatment on corrosion re-

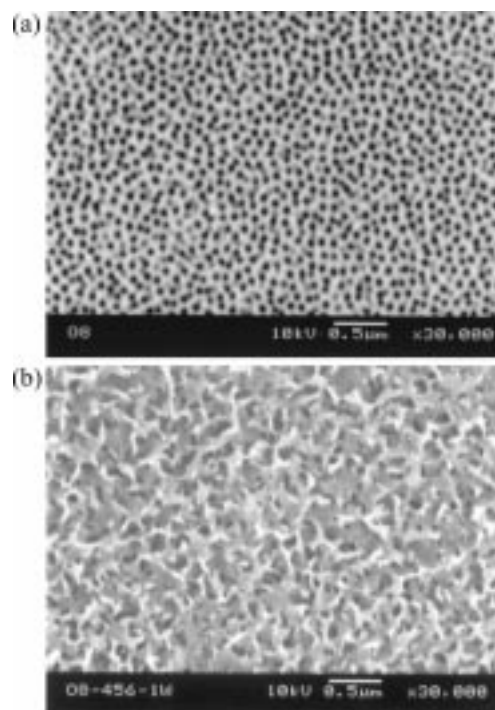


Fig. 5. SEM photographs of porous alumina membrane (a) before and (b) after corrosion test [Temp.: 100 °C, Reaction time: 30 min].

action, the membranes which were calcined at 500, 850 and 950 °C, respectively, were reacted with boiling water for 30 min and SEM photographs of surfaces of membrane were presented in Fig. 6. As shown in Fig. 6(a) and (b), corrosion reaction proceeded to block pores in the case of alumina membranes heat treated for 1 h at 500 °C and for 5 h at 850 °C, respectively, but in the case of the membrane that was heated for 3 h at 900 °C, corrosion was not observed on the surface. This result is due to the chemical stability induced by the phase transition of amorphous alumina membrane into polycrystalline alumina membrane, such as θ and δ - Al_2O_3 , as shown in Fig. 4 of XRD analysis. Thus, the corrosion reaction on the surface of prepared alumina membrane could be suppressed by thermal treatment for 3 h at 900 °C and it is thought that such membrane is to be used in a high temperature reactor.

3. Acid and Alkali Resistance Test of Porous Alumina Membrane

3-1. Effect of Reaction Temperature

In order to ascertain stability of amorphous porous alumina membrane against acidic solution, a definite amount of porous alumina membrane was put into both 0.1 N HCl and 0.1 N NaOH solution, which are maintained at 20, 30 and 40 °C, respectively, and then the results of ICP analysis that measured content of aluminum ions dissolved in each aqueous solution according to reaction temperature were shown in Fig. 7. As described in Fig. 7, the content of aluminum ions dissolved in both aqueous HCl and NaOH solution was increased as reaction time become longer. In addition, as reaction temperature increased, the content of aluminum ions dissolved from porous alumina membrane in each aqueous solution was increased and rate of dissolution was in-

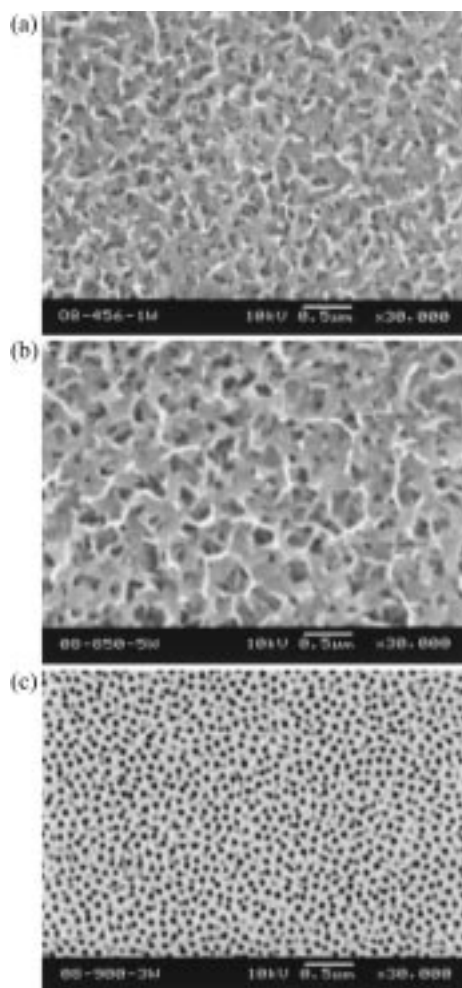


Fig. 6. SEM photographs of porous alumina membrane according to calcined temperature and time.

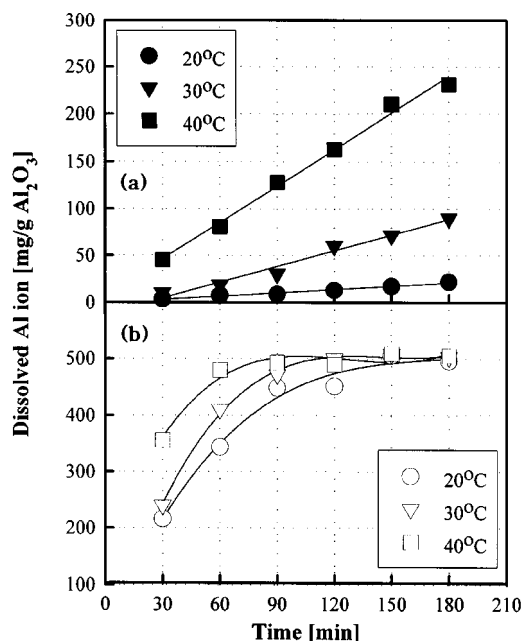


Fig. 7. Variation of amount of dissolved Al ion from porous alumina membrane in various temperature (a) in 0.1 N HCl solution (b) in 0.1 N NaOH solution.

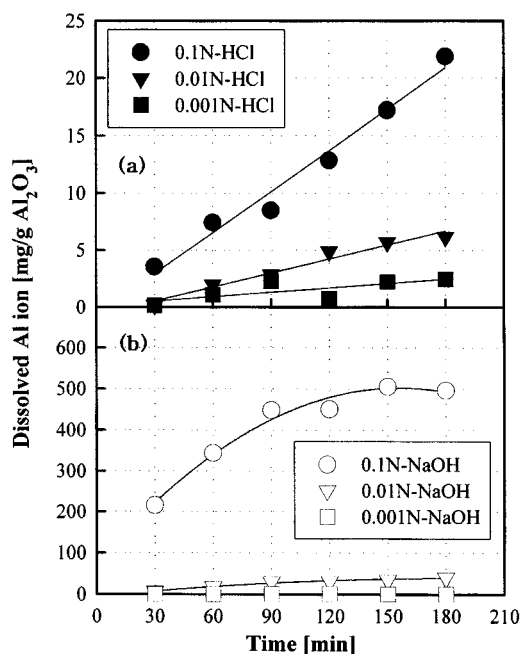


Fig. 8. Variation of amount of dissolved Al ion from porous alumina membrane in various concentration of (a) HCl solution (b) NaOH solution [Temp.: 20 °C].

creased. These phenomena take place due to increase in activities of both aqueous HCl and NaOH solution with reaction temperature. On the other hand, the content of aluminum ions dissolved in aqueous NaOH solution was higher than that dissolved in aqueous HCl solution. And it increased linearly until 90 min, but after 90-120 min it remained constant regardless of reaction temperature. This tendency is due to the dissolution of most porous alumina membrane in aqueous NaOH solution. Therefore, it can be thought that although porous alumina membrane prepared in oxalic electrolyte was not chemically stable in aqueous alkaline solution at pH=13, it has some chemical stability against aqueous acidic solution at pH=1.

3-2. Effect of Acid & Alkali Concentration

Fig. 8 shows the results of ICP analysis that measured the content of aluminum ions dissolved in aqueous solution after amorphous alumina membrane was put into each 0.1, 0.01 and 0.001 N HCl and NaOH solution at 20 °C.

As shown in Fig. 8(a), the content of aluminum ions dissolved in aqueous HCl solution increased linearly with reaction time and also with concentration of aqueous HCl solution. Particularly, rate of dissolution was higher in 0.1 N aqueous HCl solution. However, only 20 mg per 1 g of porous alumina membrane dissolved in aqueous HCl solution for 3 h reaction time. SEM photographs according to reaction time revealed that pore structure of porous alumina membrane was not affected by dissolution. On the other hand, as shown in Fig. 8(b), the content of aluminum ions dissolved in aqueous NaOH solution increased with reaction temperature at all concentrations of aqueous NaOH solutions and it increased linearly in both 0.01 N and 0.001 N aqueous NaOH solutions like aqueous acidic solution. And also, when the amount of aluminum ions dissolved in both 0.01 N and 0.001 N aqueous NaOH solution was close to that in aque-

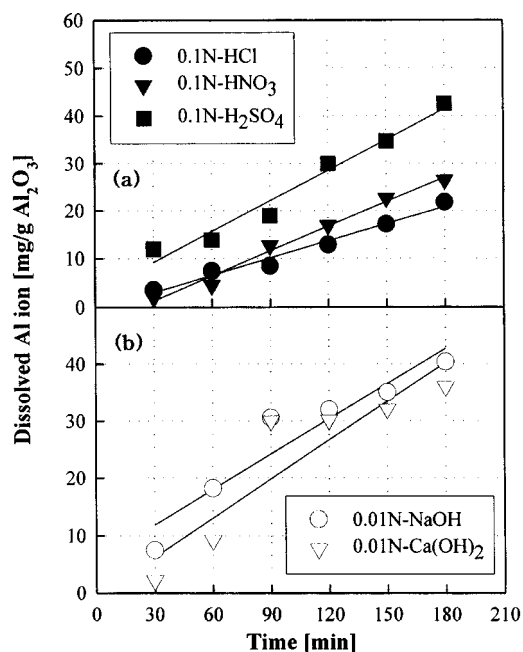


Fig. 9. Variation of amount of dissolved Al ion from porous alumina membrane (a) in various acid solution (b) in various base solution [Temp.: 20 °C].

ous HCl solution. The surface of porous alumina membrane after dissolution experiment in 0.01 N aqueous NaOH solution was observed with SEM which revealed that there was no change of pore structure on this surface. So, it is thought that porous alumina membranes have chemical stability against aqueous NaOH solution up to pH=12 at 20 °C.

3-3. Effect of Kinds of Acid & Alkali

The effects of kinds of acids and alkalis were investigated with 0.1 N HNO₃, 0.1 N H₂SO₄ and 0.01 N Ca(OH)₂ solutions. Fig. 9 described the content of aluminum ions dissolved from amorphous alumina membrane in both 0.1 N acidic and 0.01 N alkaline solution at 20 °C as a function of reaction time. As shown in Fig. 9, the content of aluminum ions dissolved in both aqueous acidic and alkaline solution increased linearly with reaction time. However the content of aluminum ions dissolved in each aqueous solution was very small. Actually, when the surface of this alumina membrane was observed with SEM according to reaction time, pore structure had not been changed.

3-4. Effect of Heat Treatment

To investigate acid resistance of polycrystalline alumina membrane obtained by thermal treatment for 3 h at 900 °C, the membrane was put into both 0.1 N HCl and 0.01 N NaOH solution, and the content of aluminum ions in both aqueous acidic and alkaline solution was presented in Fig. 10. Experimental method was the same as described in the previous section. As shown in Fig. 10(a) and (b), the released amount of aluminum ions from polycrystalline alumina membrane was about 1.5-4 times as small as that from amorphous alumina membrane regardless of aqueous acidic and alkaline solution, and the rate of dissolution decreased remarkably. This improvement of chemical stability against acid and alkali is due to the phase transition of the membrane from amorphous into polycrystalline phase by thermal treatment. On

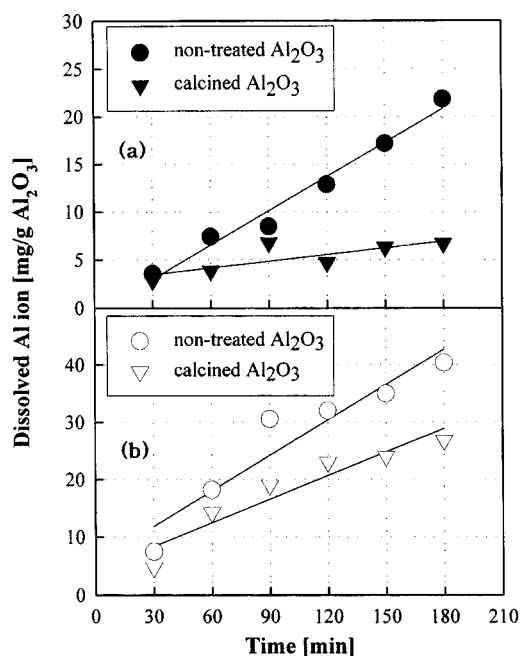


Fig. 10. Variation of amount of dissolved Al ion from porous alumina membrane (a) in 0.1 N HCl solution (b) in 0.01 N NaOH solution [Temp.: 20 °C].

the other hand, as ascertained in Fig. 7, the release of aluminum ions from alumina membrane thermally treated for 3 h at 900 °C was not affected seriously by reaction temperature. In addition,

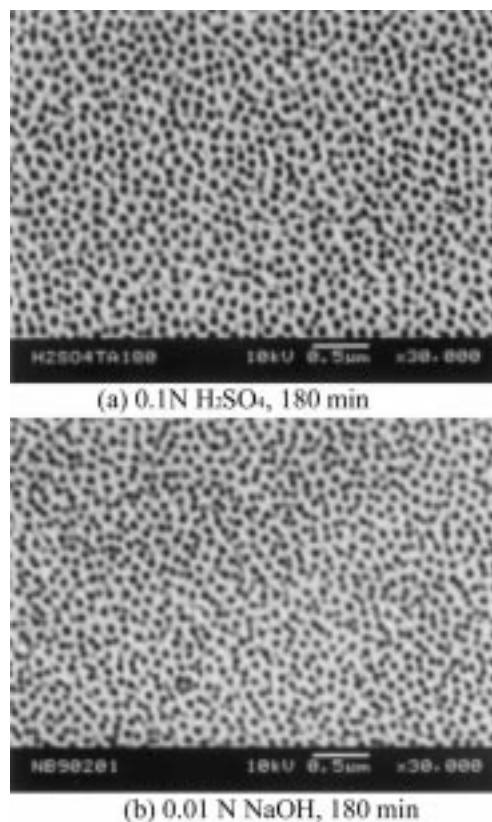


Fig. 11. SEM photographs of calcined porous alumina membrane after acid and alkali-proof test [Temp.: 20 °C].

polycrystalline alumina membrane had more chemical stability against acid than amorphous alumina membrane at 30 °C and above. So, it is thought that alumina membrane can be used in stronger acidic and alkaline condition through thermal treatment.

To ascertain the extent of corrosion of calcined alumina membrane in both 0.1 N H₂SO₄ and 0.001 N NaOH solution at 20 °C, SEM photographs of its surface obtained from each aqueous solution were presented in Fig. 11. As shown in the photographs, pore structure of porous alumina membrane did not change greatly even though it passed 3 h reaction time.

Therefore, the porous alumina membrane prepared in this study has good stability against aqueous acidic as well as alkaline solution at pH=12 and below.

CONCLUSIONS

The following conclusions could be obtained by investigating thermal and chemical stability of porous alumina membrane prepared by anodic oxidation of aluminum plate in oxalic electrolyte.

The membranes were thermally stable since pore diameter of porous alumina membrane prepared in this study was not changed in the temperature range from 500 to 1,200 °C and warping did not take place. The amorphous porous alumina membrane reacted with boiling water to form boehmite, causing corrosion and blocking the pores. On the other hand, polycrystalline alumina membrane obtained by thermal treatment for 3 h at 900 °C did not show corrosion. In addition, through experiments with porous alumina membrane prepared by above method using various aqueous acidic and alkaline solutions, it was found that the membrane had chemical stability at 1 < pH < 12 at 20 °C.

From these conclusions, it is thought that porous alumina membrane can be applied as a catalytic membrane or a gas separation membrane at high temperature.

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REFERENCES

- Hsieh, H. P., Bhawe, R. R. and Fleming, H. L., "Microporous Alumina Membranes," *J. Membrane Sci.*, **39**, 221 (1988).
- Korean Aluminum Surface Treatment Cooperation, "Aluminum Surface Treatment," (1993).
- Larbot, A., Fabre, R. R., Guizard, C. and Cot, L., "Inorganic Membranes Obtained by Sol-Gel Techniques," *J. Membrane Sci.*, **39**, 203 (1988).
- Lee, C. W., Chang, Y. H. and Hahm, Y. M., "Preparation of Porous Alumina Membrane by Anodic Oxidation in Sulfuric Acid," *HWAHAK KONGHAK*, **36**, 653 (1998).
- Lee, C. W., Hong, Y. H., Chang, Y. H. and Hahm, Y. M., "Preparation of Inorganic Ultrafiltration Membrane by Anodic Oxidation in Oxalic Acid," *J. of Kor. Ind. and Eng. Chem.*, **9**(4), 536 (1998).
- Leenaars, A. F. and Burggraaf, A. J., "The Preparation and Characterization of Alumina Membranes with Ultrafine Pores. 2. The Formation of Supported Membranes," *J. Colloid Interface Sci.*, **105**, 27 (1985).
- Mardilovich, P. P., Govyadinov, A. N., Mukhurov, N. I., Rzhevskii, A. M. and Paterson, R., "New and Modified Anodic Alumina Membranes Part I. Thermotreatment of Anodic Alumina Membranes," *J. Membrane Sci.*, **98**, 131 (1995).
- Mardilovich, P. P., Govyadinov, A. N., Mukhurov, N. I. and Paterson, R., "New and Modified Anodic Alumina Membranes Part II. Comparison of Solubility of Amorphous (normal) and Polycrystalline Anodic Alumina Membranes," *J. Membrane Sci.*, **98**, 143 (1995).
- Winston Ho, W. S. and Sirkar, K. K., *Membrane Handbook*, 391 (1991).