

MORPHOLOGICAL AND STRUCTURAL CHANGE OF NANO-PORED ALUMINA MEMBRANE ABOVE 1200 K

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Abstract

The transition and the change in pore morphology of a porous alumina membrane prepared by anodically oxidizing aluminum in sulfuric acid were studied mainly by TG-DTA, TMA, dilatometry and TEM. At ca. 1243 K, TMA showed an expansion followed by contraction; the CO₂ and SO₂ gases were quickly discharged, and the pore morphology of the as-prepared porous membrane (ca 150 μm-t, with pores ca 25 nm in diameter and containing ca 11% by mass of SO₂) showed an abrupt change, but the pores were retained to ca. 1573 K. Sulfur incorporated in the membrane was lost in two stages, i.e., at ca 1243 K and in a range up to 1373 K. Isothermal measurements revealed the complex crystallization of the amorphous phase into polycrystalline phase.

Keywords: alumina polymorphs, anodic alumina, mesoporous membrane, nanopores, TMA

Introduction

Porous alumina membranes can be obtained by anodically oxidizing aluminum in oxalic acid, chromic acid, sulfuric acid, etc. This material has been applied to various fields such as catalysts, catalyst supports, gas filters, etc. More recently, it has attracted much attention because of its potential use as templates for preparing devices. Well-known in the art are clay mesoporous structures [1], but most of them are prepared from silicates using pillaring reactions of lamellar solids. The porous alumina membranes referred here are prepared by a different approach, i.e., by using electrochemical reaction well known as anodization of aluminum, and without incorporating any organic species into the structure. Thus, the diameter of the cylindrical pores is controllable by simply adjusting the applied voltage.

The as-prepared membrane obtained here is amorphous; but in some reports, anodic alumina is denoted as pseudo-boehmite (AlOOH) phase [2]. Gamma-alumina develops from the amorphous phase by heating and dehydration.

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Concerning porous alumina membranes, detailed studies have been made on the commercially available ones prepared from oxalic acid [3]. However, few studies have been made on those prepared from sulfuric acid. Thus, the present authors have recently made studies [4] on the transformation of alumina membranes prepared from sulfuric acid. However, morphological change with temperature is important in practical application, and this is yet to be studied, particularly the pore morphology. This paper reports on the morphological change of the cylindrical pores of the alumina membrane and on the detailed reaction with increasing temperature by mainly using simultaneous TG-DTA, TMA, dilatometry and TEM.

Experimental

Sample

An amorphous as-prepared alumina obtained by anodizing aluminum in sulfuric acid electrolyte was used as the sample [4]. This sample, denoted AA-25, is about 150 μm in thickness and has cylindrical pores about 25 nm in diameter. The as-prepared sample contains about 11% by mass of SO_2 as determined by EDS [4].

Simultaneous TG-DTA

High temperature simultaneous TG-DTA was performed on ca 5 mg of sample placed in a Pt pan inside a horizontal type furnace of SII TA system EXSTAR 6000 TG-DTA6300 manufactured by Seiko Instruments Inc. Gaseous N_2 was flown at a rate of 100 mL min^{-1} . The sample was held isothermally at 1183 K (sample temperature). Furthermore, quenched samples were obtained at 1185, 1373, 1523, and 1723 K. These samples were subjected to TEM observation.

TEM observation

For TEM observation, samples were prepared in the following manner. Sample fractions were each subjected to size reduction. A micromesh (i.e., a 3-dimensionally wo-

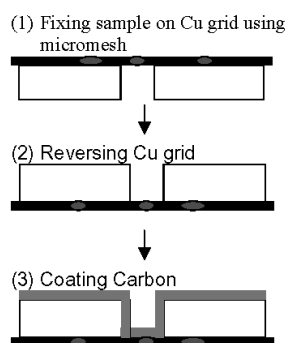


Fig. 1 Schematically shown method for preparing samples for TEM observation

ven special polymer) was placed on a copper grid to fix the size-reduced sample, and the grid was reversed for carbon coating (Fig. 1). TEM observation was carried out by using JEOL transmission microscope model JEOL 2000FX.

TMA and dilatometry

TMA was performed using TMA4130S (manufactured by MAC Science Co., Ltd.) in a flow of gaseous N_2 at a rate of 200 mL min^{-1} at a heating rate of 20 deg min^{-1} (from r.t. to 873 K) and 10 deg min^{-1} (from 873 to 1773 K), while applying load of 10 g against the planar surface of the sample $150 \mu\text{m}$ in thickness. Sampling was made every 1.0 s. Isothermal measurement was made at 1213 K by heating the sample to the temperature at a rate of 10 deg min^{-1} .

Dilatometry was performed on a sample fraction 5.19 mm in length by using TD5200S (manufactured by MAC Science Co., Ltd.) in a flow of gaseous N_2 at a rate of 200 mL min^{-1} at a heating rate of 20 deg min^{-1} (from r.t. to 873 K) and 10 deg min^{-1} (from 873 to 1773 K).

Results and discussion

Figure 2 is the transmission electron micrograph of the as-prepared anodic alumina showing the pore morphology of the sample. It can be seen that the cylindrical pores

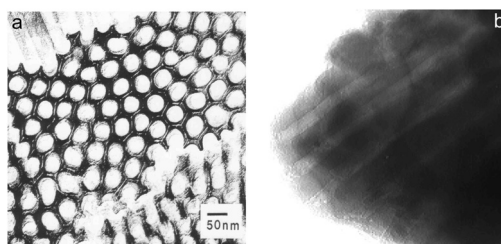


Fig. 2 Transmission electron micrograph showing pore morphology of as-prepared anodic alumina: a – planar section, b – cross section

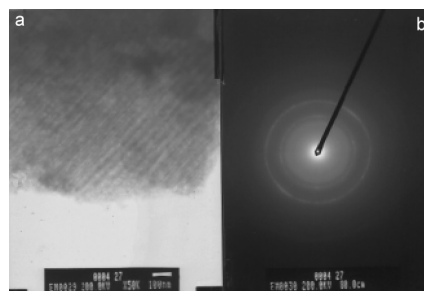


Fig. 3 a – Transmission electron micrograph of samples obtained at 912°C. b – The selected area diffraction pattern photograph corresponding to (a)

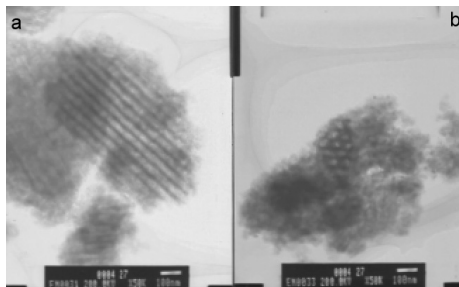


Fig. 4 Pore morphology of the sample at 912°C observed by TEM (given in negative film): a – Cross section view of the cylindrical mesopores, b – Plan view of the mesopores

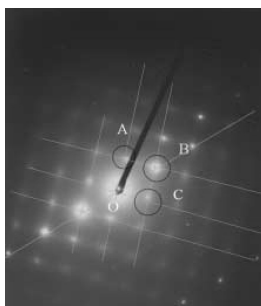


Fig. 5 Diffraction of sample obtained at 1100 °C, showing clear presence of γ - Al_2O_3 crystallites

have honeycomb cross section about 25 nm in diameter. At this stage, however, the X-ray diffractograms show amorphous patterns [7].

Figures 3 and 4 show transmission electron micrographs for samples obtained at 1185 K (Figs 3 and 4; note that are presented in negative films for the sake of clarity). Similarly, the TEM observation was performed on samples obtained at 1373 K. Diffraction patterns are also given for the corresponding temperatures. At 1185 K, the initial honeycomb pore morphology is still observed, but the pore diameter is slightly increased and falls in a range of from 28 to 35 nm. The diffraction pattern shows the presence of θ -alumina with $d=0.139$ and 0.2 nm (Figs 3a and 3b). At 1373 K (1100°C), it is confirmed that the pores are still present, but the pores differ in diameter to yield 14, 18, 29, and 38 nm. In the diffraction shown in Fig. 5, spots A, B, C are assigned as (220), (400), and (2 $\bar{2}$ 0) of the cubic γ - Al_2O_3 , with the beam incident from the (008) direction. This indicates that well-developed crystallites of γ - Al_2O_3 are present at this stage. Since a size of at least 17 nm is necessary for a γ - Al_2O_3 crystallite to undergo transformation into a θ - Al_2O_3 crystallite [5], presumably the size of θ - Al_2O_3 crystallites is about 20 nm. This signifies that the cylindrical pore walls consist of 2 to 3 crystallites in the direction in parallel to the plane of the membrane. In other micrographs, there are phases with $d=0.142$ and 0.2 nm, suggesting the presence of γ -, θ -, and δ -alumina phases. These results are again in conformity with the previous results suggesting the development of a polycrystalline phase. Thus, cylin-

drical pores were observed to be present up to a temperature of 1523 K (1250°C), however, clear spots begin to develop to suggest the formation of α -alumina crystals.

Figure 6 shows the results obtained by TMA and dilatometry superposed. It can be seen that the sample once shows an abrupt expansion in the direction perpendicular to the plane of the membrane, contracts rapidly, and expands again in a short temperature range of about 1223 K. This is in good agreement with the TG-DTA results obtained previously [6]; i.e., sharp exothermic reaction immediately followed by a sharp endothermic reaction with loss of mass of about 8.6 % occurs with heating. It is confirmed previously [4] by simultaneous TG-DTA/FTIR that impurities incorporated in the membrane are discharged in two steps. The change in TG-DTA curve corresponds to the discharge of gaseous CO_2 immediately followed by the discharge of gaseous SO_2 , at which a quasi-crystalline phase is developed. Thus, the rapid expansion corresponds to the development of gaseous SO_2 , and the contraction corresponds to the loss of volume for the gaseous phase. This can also be confirmed from Fig. 7, in which the average linear expansion coefficients in the direction perpendicular to the plane (TMA) and in the direction perpendicular to the pore wall (DLT) are shown. At temperatures higher than ca 1213 K, the linear expansion coefficients are the same in the directions in parallel with and perpendicular to the plane of the membrane. Since nearly isotropic contraction proceeds after discharge of gaseous SO_2 up to ca 1373 K, the gradual contraction possibly corresponds to the development of a new polycrystalline or quasi-crystalline phase. This supports the previous interpretation that amorphous anodic alumina becomes polycrystalline at about 1243 K, at which temperature γ -, θ -, and δ -alumina phases are identified [6].

In Fig. 8 is shown the isothermally obtained TMA at 1213 K (940°C) to investigate the expansion-contraction scheme observed in TMA. The expansion (indicated by numeral 1 in the figure) corresponds to an exothermic reaction, and the contraction (2) corresponds to an endothermic reaction. According to TEM-EDS observation (at a resolution of 10 nm), sulfur is found to be uniformly distributed in anodic alumina

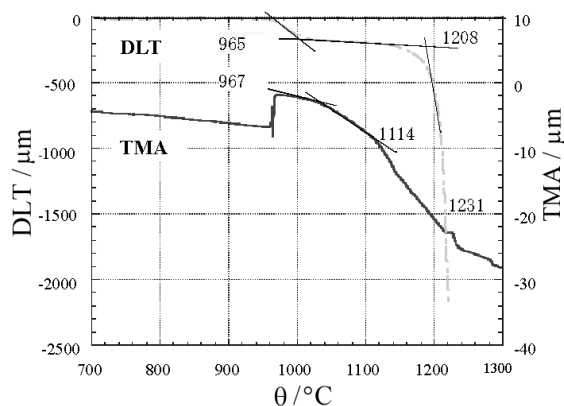


Fig. 6 TMA and dilatometry curves (700–1000 °C)

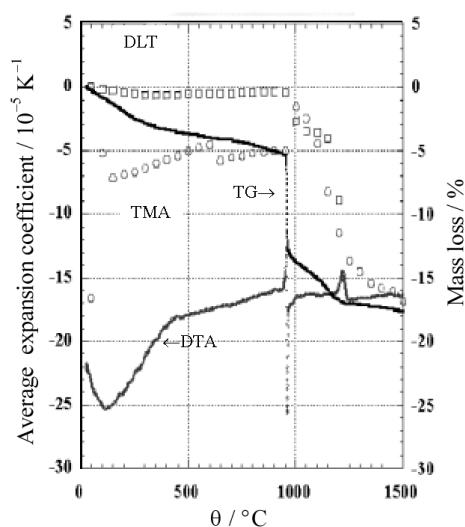


Fig. 7 Average expansion coefficient obtained by TMA and DLT, superposed on TG-DTA curves (Note that the heating rate was changed at 600 °C). □: DLT, O: TMA

[4], this indicates that the expansion is due to the disordering caused by the diffusion of sulfur atoms in due course of developing polycrystalline alumina. The contraction subsequent to the expansion corresponds to the discharge of SO_2 , which is also supported by the endothermic reaction suggesting desorption. Although kinetic analysis was performed, the reaction could not be assigned to a simple nucleation or crystal growth reaction. Hence, the expansion and contraction may involve diffusion, nucleation, gas expansion, desorption, and the destruction of the micropores that are inherent in the pore walls. However, note that the cylindrical mesopores are still retained even after the release of gaseous SO_2 .

Conclusions

The pore morphology of porous alumina membrane prepared from sulfuric acid was studied by means of TMA and TEM. The phases and the pores of the as-prepared alumina membrane change with heating as follows:

Phase change of anodic alumina	AA → Alumina (polycrystalline; γ -, θ -, δ -)	Discharge CO_2 , migration of sulfur in amorphous phase	Release SO_2 , development of quasi-crystalline phase	Quasi-crystalline phase → development of γ - Al_2O_3
Pore diameter /nm	28–35	–	–	14–38
Temperature / K	< 1183	ca 1243 (Ex)	ca 1243 (En)	ca 1373

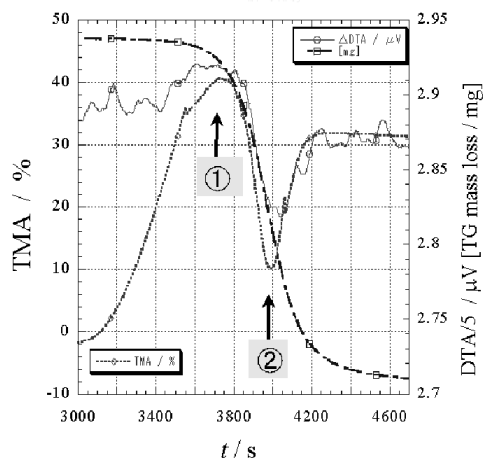


Fig. 8 TMA results obtained isothermally, superposed on isothermal TG-DTA curves

It has been found that the pores are retained to a temperature as high as 1573 K. The pore diameter greatly changes with the discharge of impurities in gaseous phase, and at temperatures higher than ca 1243 K, the pore walls contract with elevating temperature as the alumina loses impurities to crystallize into a pure alumina phase. At 1373 K, well-developed crystallites of γ - Al_2O_3 were found to be still present, although this phase at such a high temperature is not reported so far in powder samples.

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