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PREPARATION OF γ-ALUMINA MEMBRANES FROM SULPHURIC ELECTROLYTE ANODIC ALUMINA AND ITS TRANSITION TO α-ALUMINA

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Abstract

Gamma-alumina membrane was prepared from anodic (amorphous) alumina (AA) obtained in a sulphuric acid electrolyte. The transformation scheme, i.e., the crystallization to form metastable alumina polymorphs and the final transition to α-Al_2O_3 with heating was studied by TG-DTA and X-ray diffraction (XRD) using fixed time (FT) method. When heating at a constant rate, the crystallization occurred at 900°C or higher and the final formation of α-Al_2O_3 occurred at 1250°C or higher, which temperatures were higher than the case of using anodic (amorphous) alumina prepared from oxalic acid electrolyte. Relative content of S of the products was obtained by transmission electron microscope (TEM)-energy dispersive spectroscopy (EDS). The proposed thermal change of anodic alumina membrane prepared from sulphuric acid is as follows:

1. At temperatures lower than ca 910°C: Formation of a quasi-crystalline phase or a polycrystalline phase (γ-, δ- and θ-Al_2O_3);
2. 910–960°C: Progressive crystallization by the migration of S toward the surface within the amorphous or the quasi-crystalline phase, forming S-rich region near the surface;
3. 960°C: Change of membrane morphology and the quasi-crystalline phase due to the rapid discharge of gaseous SO_2;
4. 960–1240°C: Crystallization of γ-Al_2O_3 accompanying δ-Al_2O_3; and
5. 1240°C: Transition from γ-Al_2O_3 (+tr. δ-Al_2O_3) into the stable α-Al_2O_3.

The amorphization which occurs by the exothermic and the subsequent endothermic reaction suggests the incorporation of SO_3 groups in the quasi-crystalline structure.

Keywords: crystallization, γ-alumina, nanoporous membrane, phase transition, quasi-crystalline phase, TEM-EDS, TG-DTA

Introduction

Gamma-alumina (γ-Al_2O_3) is attracting attention as catalyst, catalyst carriers, etc. because of its mesoporous nature, and extensive studies have been made thereon [1–2]. In general, γ-Al_2O_3 is manufactured from pseudoboehmite powder consisting of fine particles, and the importance of the crystallinity of the starting powder has been in-

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vestigated [3]. It is also known that γ-Al_2O_3 is a metastable phase and undergoes phase transition to the stable α-Al_2O_3, and that the transition temperature is influenced by the method of preparation [4, 5] and the impurities incorporated therein [5, 6]. Recently, Saito *et al.* [7] reported that the addition of amorphous SiO_2 elevates the transition temperature.

A γ-Al_2O_3 membrane can be prepared by the thermal treatment of an amorphous as-prepared anodic alumina (AA) [8]. Such membranes are widely used as catalysts, catalyst supports, gas filters, etc. Furthermore, because of the controllable unique pore structure consisting of hexagonal cylinders in the porous layer, there is recently proposed a use as a mold for preparing plastic devices having strictly controlled morphology in the nanometer size. Thus, membranes maintaining the pore structure to a higher temperature are more advantageous. It is also necessary to know their changes with increasing temperature.

Further, although extensive studies have been made on AA prepared from various types of electrolytes [9], the exact transformation scheme from the as-prepared amorphous material to the metastable alumina polymorphs and to the final α-Al_2O_3 is not yet established.

Thus, with an aim to obtain anodic alumina membranes resisting to higher temperatures, an AA membrane having 25-nm diameter pores and 150 μm in thickness prepared from sulphuric acid electrolyte according to the method previously [10] was thermally treated to prepare a γ-Al_2O_3 membrane. The thermal transformation from AA to α-Al_2O_3 was investigated by using TG-DTA and X-ray diffraction (XRD).

Experimental

Sample

An amorphous as-prepared alumina was obtained from sulphuric acid electrolyte by a method described previously [10]. The sample, denoted AA-25 hereinafter, is a 150 μm thick AA membrane having pores 25 nm in diameter. Further, an AA membrane having the same morphology was prepared from oxalic acid electrolyte (containing oxalic acid at a concentration of 0.3 mol dm^{-1}) by applying constant voltage of 25 V to use as a control. This sample is denoted as AA-Oxa hereinafter.

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}.

XRD identification of products

XRD measurements were performed by using High Power X-ray Diffractometer (18 kW) MXP18SRA (manufactured by MAC Science Co. Ltd.). Fixed time (FT) method was used to detect weak diffraction signals and to obtain a resolved diffraction profile. The slit system was 1° DS-1° RS-0.3 mm SS, and the radiation was monochromatized by using a curved graphite monochromator (CuK_{α_1} radiation: 0.154050 nm). Thus, scanning from 10 to 70° was performed over a time duration of 20 h at 0.01°/step and a scaling time of 100 s/step, and at a power of 30.0 kV–300 mA.

Relative sulphur content determination by transmission electron microscope (TEM)

Relative content of sulphur (S/Al+S) was determined by TEM-energy dispersive spectroscopy (EDS) using JEOL transmission electron microscope Model JEM-2000FX.

Results and discussion

TG-DTA of AA membranes

Figure 1a shows the TG-DTA result of the AA membrane prepared from sulphuric acid (AA-25). A gradual mass loss is observed up to 600°C, which is attributed to the loss of water confirmed by TG-DTA/FTIR. This is described in detail elsewhere [11]. An exothermic peak followed by a sharp endothermic peak is observed at around 960 to 970°C, accompanying a mass loss of 8.6%. After a gradual loss of mass of about 3% in total from 970 to ca 1200°C, an exothermic reaction is observed at ca 1250°C. This loss of mass is in agreement with the SO_3 content determined previously by TEM-EDS [10].

Figure 1b shows the TG-DTA curve for an AA prepared from oxalic acid (AA-Oxa) provided as a comparative example. Typically, an AA prepared from oxalic acid yields an exothermic peak at 700 to 900°C accompanying a mass loss of about 3 to 4%. Further, a broad exothermic peak is observed to occur from

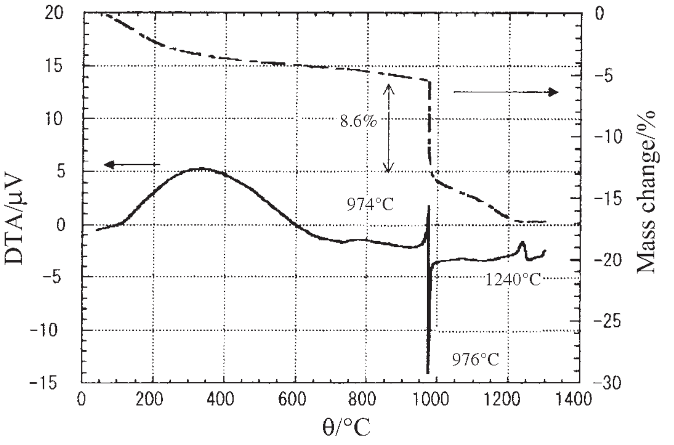

Fig. 1a TG-DTA curve of the AA membrane prepared from sulphuric acid (AA-25)

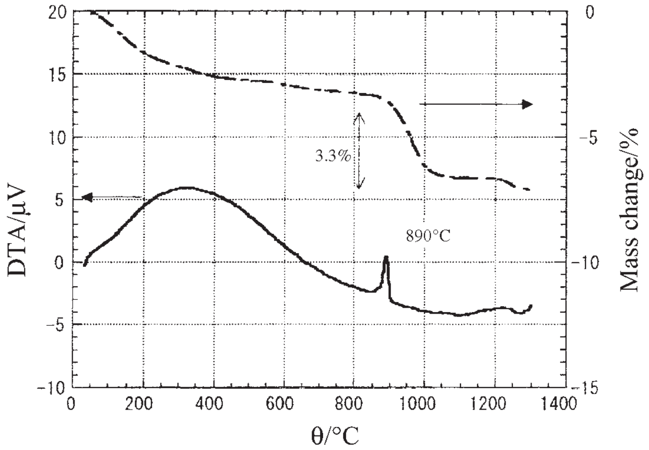

Fig. 1b TG-DTA curve of an AA membrane prepared from oxalic acid (AA-Oxa) provided as a control

1100–1200°C. It can be seen that AA-Oxa shows a typical thermal change for AA membranes prepared from oxalic acid known in the literature [12].

X-ray identification of products

Figure 2 shows the temperatures at which products were subjected to XRD phase identification. Namely, products were obtained before and after the exo-endothermic

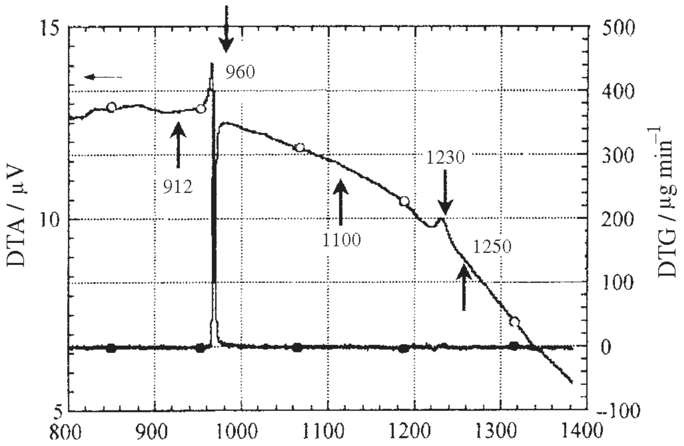

Fig. 2 Temperatures at which products were subjected to XRD phase identification, indicated on a DTA curve

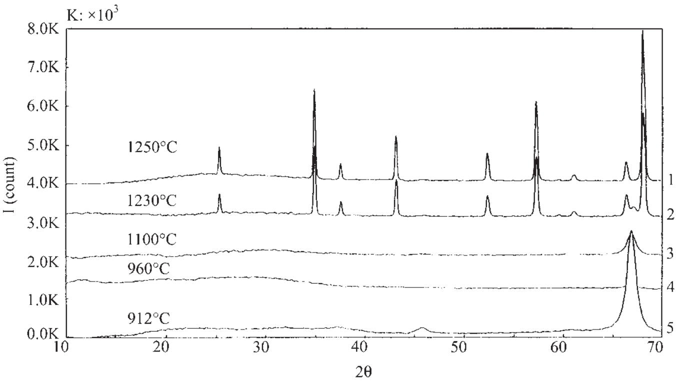

Fig. 3a XRD patterns for all of the products obtained at the temperatures indicated in Fig. 2

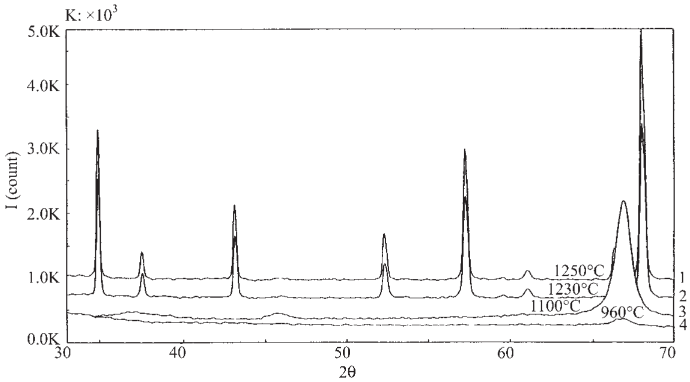

Fig. 3b XRD patterns of the overlapped portions for the products obtained at 960 and 1100°C

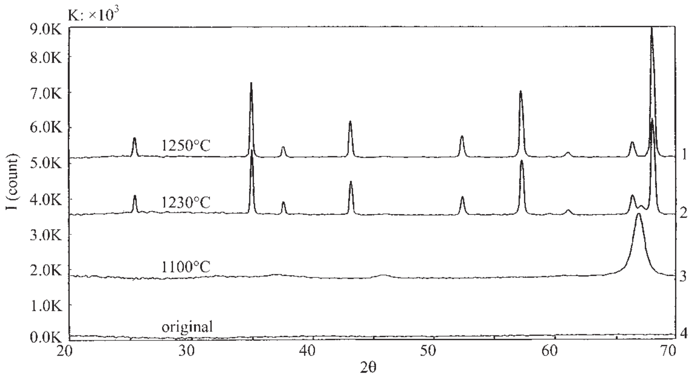

Fig. 3c XRD pattern of the original amorphous AA

peak (912 and 960°C, respectively), during the gradual loss of mass at 1100°C, at the exothermic reaction (1230°C), and after the final exothermic reaction (1250°C).

Figure 3a shows the XRD patterns for all of the products above. It can be seen that a polycrystalline phase is formed before the first exo-endothermic peak, but that rearrangement (amorphization) occurs during the peaks at ca 950°C, and that a reconstruction of a phase proceeds during heating up to ca 1200°C. The overlapped portions for the products obtained at 960 and 1100°C are clarified in Figs 3b and 3c. The XRD pattern for the as-prepared sample given in Fig. 3c for reference confirms that there is no crystalline phase developed in this stage.

Figure 4 shows the relative sulphur content (S/(Al+S)) for the products obtained at temperatures of ca 800, 960, 1100, 1250 and 1450°C. The data are plotted together with the TG curve. It can be seen that the loss of S is in close relation with the loss of mass, but that there still remains some quantity of S even at 1100°C. The sample becomes devoid of S at temperatures higher than 1250°C.

Table 1 summarizes the products obtained in each temperature. Since the XRD pattern for the products obtained in 960°C is similar to that obtained in 1100°C, the identification is made in the same manner as for the 1100°C product. It can be seen that at 912°C, the peaks fit for all of the metastable alumina polymorphs, i.e., γ-, δ-, and θ-Al_2O_3. After the exothermic and the successive endothermic reaction, it can be seen that mainly γ-Al_2O_3 develops accompanied by a small amount of δ-Al_2O_3. During the progressive loss of mass up to the exothermic peak at 1230°C, γ-Al_2O_3 remains to the final transition into the stable α-Al_2O_3. Thus, referring to Fig. 4 and Table 1, in AA-25, the polycrystalline or the quasi-crystalline phase (γ-, δ- and θ-Al_2O_3) first develops within the membrane, and while gradually losing S from presumably the amorphous phase by discharging gaseous SO_2, the corruption of the entire structure occurs at ca 960°C with the large discharge of SO_2. During this stage, S presum-

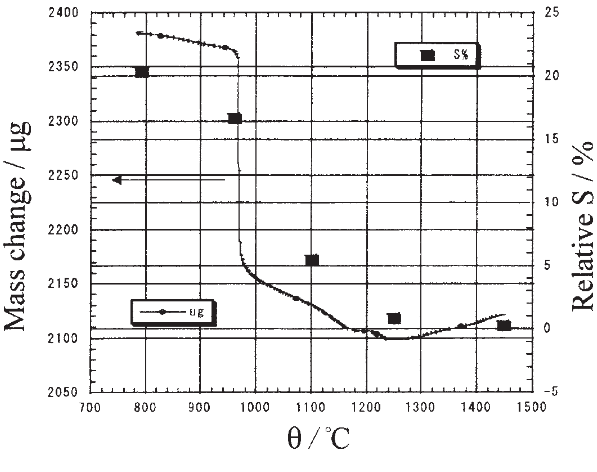

Fig. 4 Relative sulphur content (S/(Al+S)) for the products obtained by TEM–EDS at temperatures of ca 800, 960, 1100, 1250 and 1450°C

ably migrates in the quasi-crystalline phase to cause amorphization, and becomes concentrated near the surface. Then, gradual crystallization into γ-Al_2O_3 phase occurs accompanied by the formation of a small amount of δ-Al_2O_3. At 1230–1250°C, γ-Al_2O_3 undergoes the final transition to form the stable α-Al_2O_3 phase. This thermal change is different from that reported for AA membranes prepared from oxalic acid [12]; i.e., crystallization from AA to γ-Al_2O_3 (ca 820–840°C), transition from γ-Al_2O_3 to δ-Al_2O_3 with trace amount of θ-Al_2O_3, and the final transition from polycrystalline phase to α-Al_2O_3 (1100°C).

Table 1 XRD peaks (*d*-spacing and relative intensity) for the products obtained at each temperature and PDF data for alumina polymorphs

1250°C		1230°C		1100°C		912°C	
d(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0	*d*(Å)	I/I_0
		4.5669	1				
				4.156	8		
3.5131	15	3.5091	20				
		2.7493	2	2.784	9	2.831	44
2.5679	59	2.5665	70				
				2.436	5		
2.3933	8	2.3914	14	2.424	11	2.423	32
2.0960	28	2.0952	36				
				1.982	8	1.978	27
1.7465	17	1.7459	20				
1.6071	52	1.6065	59				
				1.542	9		
1.5163	3	1.5161	5			1.520	24
1.4079	12	1.4079	18			1.406	72
		1.3945	5	1.399	100	1.399	100
1.3777	100	1.3773	100				

Figure 5 shows the change in free energy values with increasing temperature [13]. Although it is natural to presume a transformation scheme from γ-Al_2O_3 to δ-Al_2O_3, and then to θ-Al_2O_3, the difference between the energy level is small, and since the crystallization occurs at far higher temperatures than AA-Oxa where the difference is further minimized, it is quite acceptable that the AA membrane does not show distinct transition scheme as in AA-Oxa. The unique transformation scheme is presumably attributed to the incorporation of SO_3 groups within the quasi-crystalline structure, the migration of which to form a S-rich region in the surface increases the movement of the quasi-crystalline structure.

Table 1 Continued

α (10–173)			γ (10–425)			δ (16–425)			θ (11–517)		
d(Å)	range	I/I_0	*d*(Å)	range	I/I_0	*d*(Å)	range	I/I_0	*d*(Å)	range	I/I_0
			4.56		40	4.570		12	4.50		60
						4.070		12			
3.479	3.459~3.499	75									
			2.80	2.60~3.00	20	2.728	2.708~2.748	30	2.85	2.65~3.05	80
									2.72	2.62~2.82	80
2.552	2.542~2.562	90				2.601	2.588~2.628	25			
						2.460	2.440~2.480	60			
2.379	2.369~2.389	40	2.39	2.29~2.49	80	2.402	2.382~2.432	16	2.43	2.33~2.53	80
			2.28	2.18~2.38	50	2.279	2.259~2.299	40	2.31	2.21~2.41	60
2.085	2.065~2.105	100				1.986	1.966~2.006	75	2.24	2.14~2.34	60
			1.977	1.957~1.997	100	1.953	1.933~1.973	40	2.01	1.91~2.11	80
1.740	1.720~1.760	45									
1.601	1.581~1.621	80									
									1.54	1.44~1.64	60
			1.520	1.500~1.540	30	1.517	1.497~1.537	16			
1.404	1.394~1.414	30				1.407	1.387~1.427	50	1.40	1.30~1.50	60
			1.395	1.375~1.415	100	1.396	1.376~1.416	100	1.39	1.37~1.41	100
1.374	1.364~1.384	50									

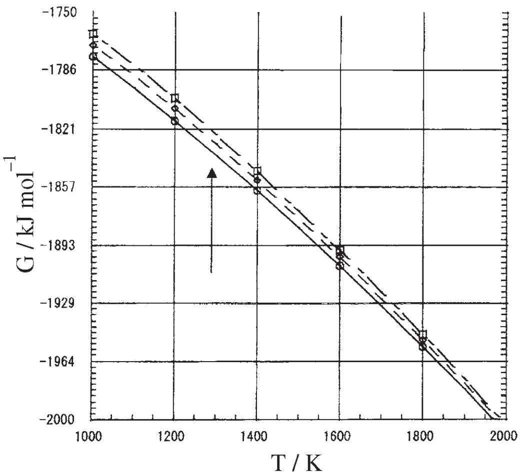

Fig. 5 Change in free energy values for selected alumina polymorphs (γ-, δ and θ-Al_2O_3) with increasing temperature

Conclusions

The crystallization of the as-prepared amorphous alumina and the final transition from the metastable γ-Al_2O_3 to α-Al_2O_3 both occur at higher temperatures than those of amorphous alumina prepared from oxalic acid.

The thermal change of anodic alumina membrane prepared from sulphuric acid can be summarized as follows:

1. At temperatures lower than ca 910°C: Formation of a quasi-crystalline phase or a polycrystalline phase (γ-, δ- and θ-Al_2O_3);
2. 910–960°C: Progressive crystallization by the migration of S toward the surface within the amorphous or the quasi-crystalline phase, forming S-rich region near the surface;
3. ca 960°C: Change of membrane morphology and the quasi-crystalline phase due to the rapid discharge of gaseous SO_2;
4. 960–1240°C: Crystallization of γ-Al_2O_3 accompanying δ-Al_2O_3; and
5. ca 1240°C: Transition from γ-Al_2O_3 (+tr. δ-Al_2O_3) into the stable α-Al_2O_3.

The amorphization which occurs by the exothermic and the subsequent endothermic reaction suggest the incorporation of SO_3 groups in the amorphous phase or in the quasi-crystalline structure.

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