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CRYSTALLIZATION OF ANODIC ALUMINA MEMBRANES STUDIED BY SIMULTANEOUS TG-DTA/FTIR

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Abstract

The thermal change of anodic alumina (AA), particularly the exothermic peak followed by the endothermic peak at ca 950°C was studied in detail by mainly using simultaneous TG-DTA/FTIR. The gradual loss of mass up to ca 910°C is attributed to dehydration. When heated at a constant rate by using TG-DTA, an exothermic peak with subsequent endothermic peak is observed at ca 950°C, but the exothermic peak becomes less distinct with decreasing heating rate. It has been found that gaseous SO_2 accompanying a small amount of CO_2 is mainly discharged at this stage. The reaction in this stage can be considered roughly in two schemes. The first scheme can be said collectively as crystallization, in which the migration of S or C trapped inside the crystal lattice of the polycrystalline phase (γ-, δ-, and θ-Al_2O_3, which presumably accompanies a large amount of amorphous or disordered phase) occurs. In the second scheme, the initial polycrystalline (+amorphous) phase crystallizes into a quasi-crystalline γ-Al_2O_3-like metastable phase after amorphization. Conclusively, after the distinct exo- and endothermic reactions, the amorphous phase crystallizes into γ-Al_2O_3, presumably accompanying small amount of δ-Al_2O_3. It is also found that, when maintained isothermally, the metastable phases undergo transformation into the stable α-Al_2O_3 at 912°C.

Keywords: alumina, catalyst carriers, γ-alumina, nanopores, simultaneous TG-DTA/FTIR, templates

Introduction

Anodic alumina (AA) is well known in the alumite technology, i.e., in the anodization of aluminum. This material consists of a thick (more than 100 μm) porous layer and a relatively thin (<1 μm) dense barrier layer, and, is recently attracting much attention as catalyst, catalyst support, gas filter, etc., because of the controllable unique pore structure consisting of hexagonal cylinders in the porous layer.

An as-prepared AA membrane is amorphous, but crystalline AA can be prepared by thermal treatment [1]. The present authors studied the basic thermal properties of an AA prepared from sulphuric acid electrolyte [2], and proposed its use as a standard

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for evaluating the surface roughness or porosity of samples having open pores. Detailed studies have been made on AA prepared from oxalic acid [3] and on polycrystalline alumina prepared in the form of powder from boehmite [4], but few thermal studies have been made on the transformation of AA prepared from sulphuric acid.

The thermal changes of an AA prepared from sulphuric acid was studied [2] by using TG-DTA and XRD. It was found that, when heated at a constant rate by using TG-DTA, the as-prepared amorphous AA changes into a polycrystalline phase (γ-, δ-, and θ-Al_2O_3) up to ca 910°C. This phase once corrupts to newly develop a metastable phase at temperatures around 910–960°C, mainly consisting of γ-Al_2O_3 phase accompanying δ-Al_2O_3. Then, this phase is maintained while increasing crystallinity up to ca 1240°C, at which the metastable γ-Al_2O_3 phase undergoes transition into a stable α-Al_2O_3. To further elucidate the reaction occurring at 910–960°C, detailed study was performed by using simultaneous TG-DTA/FTIR [5] developed by one of the present authors.

Experimental

Sample

An amorphous as-prepared alumina was prepared from sulphuric acid electrolyte by a method described previously [2]. The sample, denoted AA-25 hereinafter, is a 150 μm thick AA membrane having pores 25 nm in diameter. The SO_2 content as determined by EDS is 11%.

TG-DTA

High temperature simultaneous TG-DTA was performed on ca 5 mg of sample placed inside a Pt pan in 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}.

Simultaneous TG-DTA/FTIR

The simultaneous system consists of a TG-DTA 6200 module of Seiko SSC5200II TA system (Seiko Instruments, Inc.) connected to a JASCO FT/IR-620 Fourier-transform infrared spectrometer equipped with a MCT (mercury cadmium telluride) detector. This allows a high sensitivity run with a resolution of 2 cm^{-1} in single scan. A 1/16-inch stainless steel tube was used to connect the TG-DTA module and the FT-IR spectrometer system, and the system was optimized in such a manner that the gas evolved from the sample placed in the TG-DTA furnace may reach the FT-IR cell within 1 s. Thus, sampling was made every 14 s. Gaseous N_2 was flown as a carrier gas at the optimized flow rate of 175 ml min^{-1}.

TMA and dilatometry

TMA was performed on AA-25 to investigate the change perpendicular to the flat surface of the sample ca 0.15 mm in diameter. Sampling was performed each 1.0 s while flowing gaseous N_2 at a rate of 200 ml min^{-1}, and heating at a rate of 20 K min^{-1} (R.T. to 600°C) and 10 K min^{-1} (600 to 1500°C). Dilatometry was performed on the same sample, but the change in dimension was measured in the direction perpendicular to the walls of the cylindrical pores. The heating conditions were the same as in TMA, and the initial sample length was 5.19 mm.

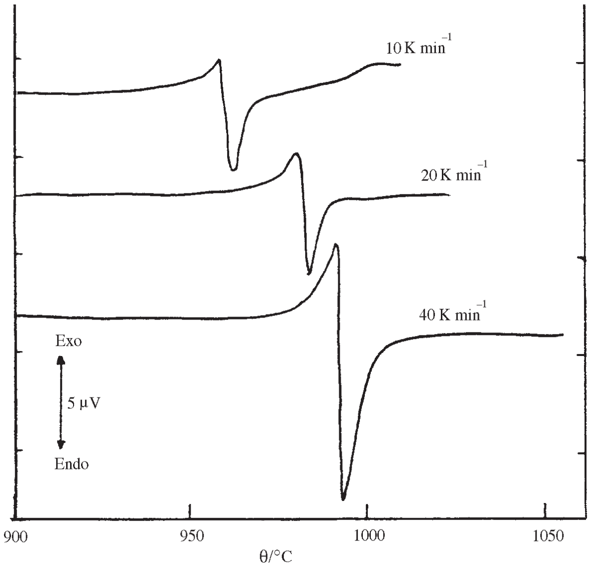

Fig. 1 DTA curves obtained under various heating rates of 10, 20 and 40 K min^{-1}

Results and discussion

TG-DTA

Figure 1 shows the DTA curves for the exothermic peak followed by endothermic peak at ca 950°C obtained by changing the heating rates to 10, 20 and 40 K min^{-1}. The temperature range of the peaks shifts to the higher side with increasing heating rate. Furthermore, the exothermic peak becomes less distinct with decreasing heating rate.

Table 1 shows the TG-DTA data for the exothermic and the subsequent endothermic peaks for AA-25 obtained by changing the heating rates to 2, 5, 10 and 20 K min^{-1}. The temperatures were plotted *vs.* the heating rates and the temperature for isothermal reaction was assumed by extrapolation to a heating rate of 0 K min^{-1}. Thus, the isothermal reaction temperature was assumed to be ca 910°C.

Table 1 TG-DTA data for anodic alumina (AA-25) obtained under various heating rates

	Heating rate/K min^{-1}			
	2	5	10	20
TG T_i/°C	922.2	939.7	948.1	957.0
TG T_f/°C	948.1	970.6	995.3	1000.0
Mass loss/%	8.7	8.5	8.6	8.6
DTA exo/°C	928.6	945.2	956.0	974.4
DTA endo/°C	933.0	949.8	961.2	976.0

Simultaneous TG-DTA/FTIR, TMA and dilatometry

The data can be obtained typically in a three-dimensional diagram; the change in IR spectra over 4000 to 400 cm^{-1} can be related to time. Thus, the change in IR spectra can be related to that in TG-DTA because the heating rate is maintained constant, e.g., at 10 K min^{-1}. The evolution of H_2O is confirmed by the band observed ca 1640 cm^{-1} over the entire temperature range from R.T. to ca 1240°C, which is in good agreement with the results reported by Maldilovich *et al.* [3]. More specifically, the evolution of H_2O at temperatures lower than ca 500°C is due to crystallization from the amorphous phase containing H_2O to a crystalline alumina; that in the temperature range of ca 500 to ca 940°C is attributed to the phase transformation of metastable alumina phases that constitute the polycrystalline phase; the final evolution of H_2O is mainly due to the loss of OH groups present in γ-Al_2O_3 during its transition into the stable α-Al_2O_3 phase which accompanies a distinct change in volume. A sharp band attributed to SO_2 appears at a time corresponding to ca 940°C. Figure 2 shows a slice taken from the three-dimensional diagram corresponding to ca 940°C. The absorption bands ca 3800 cm^{-1} are assigned to H_2O. The bands ca 2300 cm^{-1} are assigned to the stretching vibration bands of free CO_2. The high intensity band at 1367 cm^{-1} and the intense band at 1160 cm^{-1} are assigned to the SO asymmetric stretching vibration and the SO symmetric stretching vibration for gaseous SO_2, respectively.

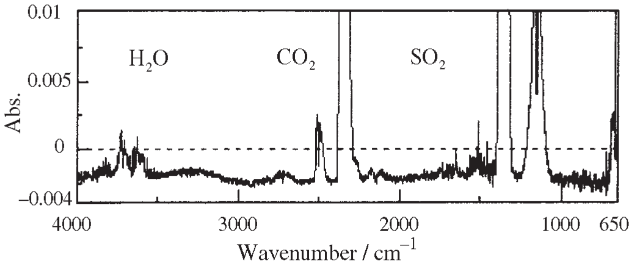

Fig. 2 FTIR spectrum obtained at 940°C by simultaneous TG-DTA/FTIR, showing gases evolved from the sample at the temperature

Figure 3 shows the change in intensity of bands assigned to CO_2 and SO_2 as described above with elevating temperature, which are superposed with the TG curve.

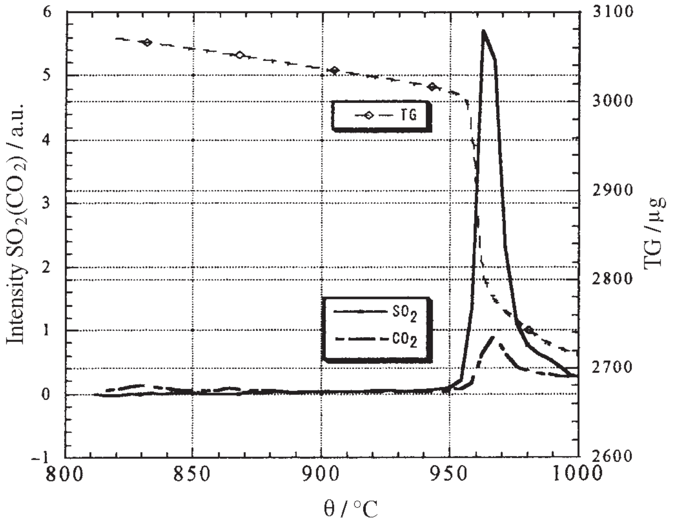

Fig. 3 IR absorption spectrum obtained for the gas discharged at ca 940°C, showing the presence of H_2O, CO_2, and SO_2

Since the absorbance is taken in arbitrary unit (AU), it should be noted that the intensity cannot be directly compared for different species. However, it can be understood that the loss of mass at ca 950°C and higher temperatures is attributed to the discharge of gaseous SO_2 and CO_2.

Figure 4 shows the change in intensity of bands assigned to CO_2 and SO_2 above with time in case the sample is maintained isothermally at 912°C. This time again, the

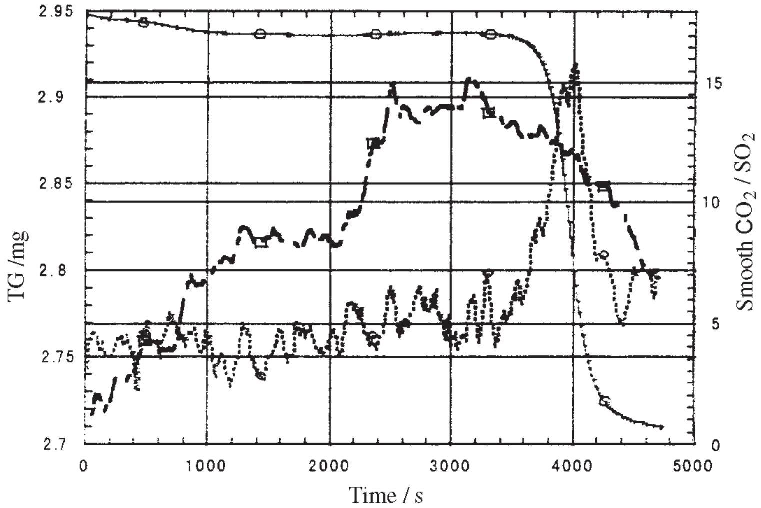

Fig. 4 Change in intensity of bands assigned to CO_2 and SO_2 with elevating temperature. TG curve is also shown in the figure. –□– Smooth CO_2, --●--Smooth SO_2

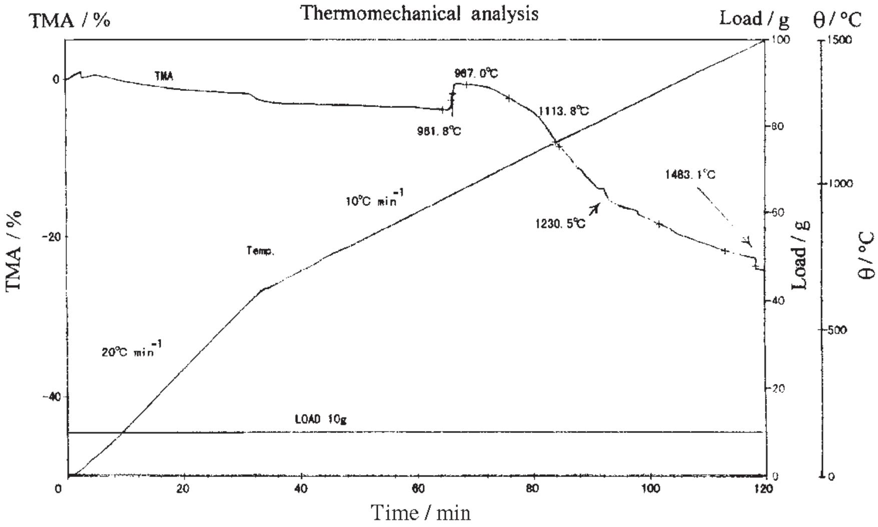

Fig. 5 Change in intensity of bands assigned to CO_2 and SO_2 with time for a sample maintained isothermally at 912°C

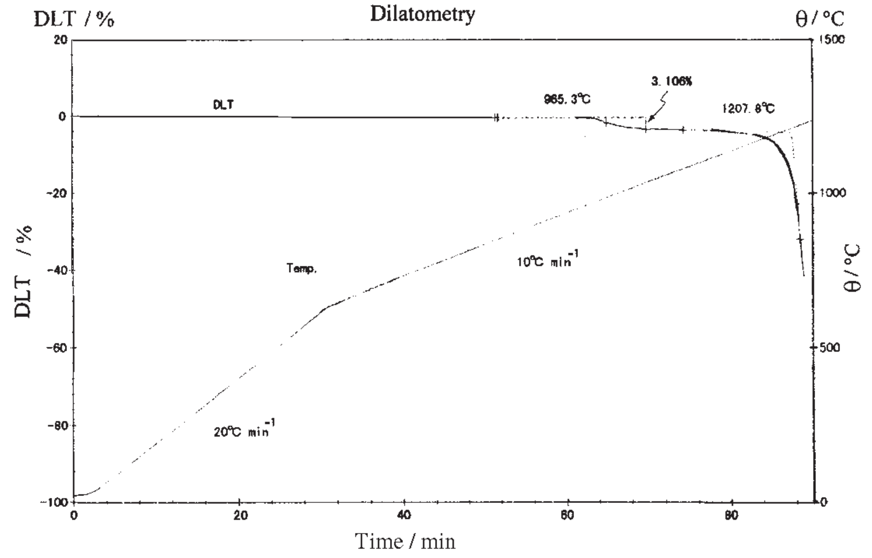

Fig. 6 TMA curve for the sample while heating at a rate of 20 K min^{-1} (R.T. to 600°C) and 10 K min^{-1} (600 to 1500°C)

absorbance is taken in AU. What is to be noted here is that CO_2 is discharged before the release of SO_2. This suggests that CO_2 and SO_2 are present in different sites. Furthermore, no exothermic peak was observed in DTA when kept isothermally. From these results, CO_2 presumably are present at sites near the surface, i.e., adsorbed on the surface of the membrane pores. After the CO_2 molecules undergo desorption, a path for sulfur (S) is provided to ease the migration and the release of S that is present in the deeper sites, i.e., presumably in the amorphous or disordered structure portions. Similar to the case of amorphous alumina prepared from oxalic acid [3], the exothermic reaction may be attributed to crystallization, comprising the following schemes: 1. the release of excess energy due to the decrease in entropy (crystallization of the amorphous phase contained in the polycrystalline γ-, δ-, and θ-Al_2O_3 phase); 2. the contraction which occurs with the release of impurity ions; and 3. the concentration of pure Al_2O_3 phase as a consequence of the migration of S. By taking the XRD identification results [6] into consideration, the subsequent endothermic reaction might correspond to the amorphization and the discharge of gaseous SO_2. TMA and dilatometry results (Figs 5 and 6) strongly support this. In TMA curve (Fig. 5), it can be seen that at ca 960°C, contraction occurs after a sharp expansion attributed to the release of a large amount of gas, however, the initial size is not lost to ca 1100°C. That is, the initial thickness of the sample at ca 900°C is still maintained up to ca 1100°C. On the other hand, dilatometry shows contraction only (Fig. 5), amouning to 3.106%. These facts strongly support that morphological change occurs at this stage.

Conclusions

The thermal change, particularly the exothermic and the subsequent endothermic reaction, of amorphous alumina prepared from sulphuric acid electrolyte was studied in detail by means of simultaneous TG-DTA/FTIR. It has been found that gaseous SO_2 accompanying a small amount of CO_2 is mainly discharged at this stage. The reaction which takes place in this stage occurs roughly in two schemes. The first scheme can be collectively denoted as crystallization, in which the migration of sulfur (S) or carbon (C) trapped inside the crystal lattice of the polycrystalline phase (γ-, δ-, and θ-Al_2O_3, which presumably accompany a large amount of amorphous phase) occurs. In the second scheme, some morphological change occurs; the initial polycrystalline (+amorphous) phase crystallizes into a quasi-crystalline γ-Al_2O_3-like metastable phase. Conclusively, after the distinct exo- and endothermic reactions, the disordered phase crystallizes into γ-Al_2O_3, presumably accompanying small amount of δ-Al_2O_3. It is also found that, when maintained isothermally, the metastable phases undergo transformation into the stable α-Al_2O_3 at 912°C.

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References

1 R. S. Alwitt and T. Kudo, J. Met. Finish. Soc. Jpn., 32 (1981) 226.
2 R. Ozao, M. Ochiai, Y. Ichimura, H. Takahashi, T. Takano and T. Inada, Thermochim. Acta, 352-353 (2000) 91.

3 P. P. Mardilovich, N. G. Govyadinov, N. I. Mukhurov, A. M. Rzhevsii and R. Peterson, J. Membrane Sci., 98 (1995) 131.
4 T. Tsukada, H. Segawa, A. Yasumori and K. Okada, J. Mater. Sci., 9 (1999) 549.
5 R. Kinoshita, Y. Teramoto, T. Nakano and H. Yoshida, J. Thermal Anal., 38 (1992) 1891.
6 R. Ozao, M. Ochiai, H. Yoshida, Y. Ichimura and T. Inada, submitted for publication in J. Therm. Anal. Cal.