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DSC study of alumina materials — applicability of transient DSC (Tr-DSC) to anodic alumina (AA) and thermoanalytical study of AA

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Abstract

Thermo-analytical studies were performed on two types of porous anodic alumina (AA) membranes prepared from sulfuric acid. Both samples were 150 μm in total thickness; the first sample AA-1 consists of a 50 μm thick layer having 10 nm diameter pores and a 100 μm thick layer of 25 nm diameter pores, and the second sample AA-2 consists only of 25 nm pores. From the high temperature DSC run, the AA membranes as received were found to undergo dehydration up to 350°C where they exhibit a plateau, and at ca. 970°C, they yield a sharp exotherm immediately followed by a distinct endotherm.

The apparent C_p values obtained by Tr-DSC at 350°C differed depending on the contact area of the samples with the sample pan or on the impurity content. The contact area depends on the pore diameter that is a function of applied voltage, and the impurity content similarly depends on the applied voltage. It is therefore presumed that Tr-DSC is advantageous in that it is a quick and handy method in obtaining apparent C_p as a parameter to identify samples differing in the properties which depend on the voltage applied at the preparation.

In addition, the thermal changes obtained on the present AA membranes were found to be different from those obtained by oxalic acid known in the literature. That is, the present AA membranes exhibit a sharp exothermic reaction followed by a broad endothermic reaction apparently attributed to an amorphous to polycrystalline (AA $\rightarrow$ γ-+δ-Al_2O_3) transition, and, a exothermic reaction at ca. 1400°C, presumably due to the final transformation from the metastable ccp polycrystalline alumina to the most stable phase, i.e., the hcp α-Al_2O_3. The transformation temperatures are higher than those of AA prepared from oxalic acid by 150–300°C. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Anodic alumina; Gas filter; DSC; γ-Alumina; Phase transition

1. Introduction

The use of a heat-flux DSC having sufficiently high reproducibility and reliability (precision and accuracy) is effective for acquiring thermodynamic properties of materials and for detecting thermochemical changes. The present authors, moreover, found that it enables detection of morphological differences in certain types of materials (e.g., etched electrolytic aluminum electrodes [1], pentaerythritol powder compacts [2]). In particular, the findings above has been obtained by using the DSC signal in transient state (the

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signal obtained in a short period of time less than one minute on starting heating). This method, which we denote as transient DSC (Tr-DSC), is especially effective for obtaining information on morphological differences of heterogeneous materials, e.g., porous materials having internal distribution in thermal conductivity.

Anodic alumina (AA) membranes are promising for the preparation of ceramic membranes and membrane sieves and numerous studies have been made [3] because their pore morphology and active layer thickness are fully controllable. It is also known that the properties of the AA membranes greatly differ depending on the electrolyte used in anodization; for instance [4], the thickness of the acid contaminated region in the cell wall increases in the order of chromic acid<phosphoric acid<oxalic acid<sulphuric acid, but that the rate of membrane formation increases in the same order. Thus, Inada et al. [5] have established a method of applying pulsed voltages to control the pore structure and to prepare composite membranes having branched pore structure from sulfuric acid. This method is advantageous in that it enables rapid formation of AA membranes and that the AA membranes thus formed exhibit selectivity in gas species (gaseous CO_2 and N_2) depending on their pore structure. Thus, the AA membranes of this type are promising materials for use as gas filters at high temperatures, and particularly, for the separation of gaseous CO_2.

Concerning their thermal change, a detailed study had been reported by Mardilovich et al. [6] on a membrane prepared from oxalic acid. However, no thermoanalytical study has been made on an AA prepared from sulfuric acid. Furthermore, such a porous material characteristics may cause a change on the overall thermal conductivity or thermal diffusivity as compared with a material having a dense structure; hence, it is interesting to apply Tr-DSC to rapidly and simply detect the morphological difference [7].

The present paper shows the results obtained by applying Tr-DSC to AA. In particular, the results obtained by Tr-DSC are compared with those obtained on the same DSC while modulating temperature. In the present study, we obtained the data by using a DSC apparatus using a novel type Oval Sensor to eliminate instrumental temperature lag. Furthermore, we show the thermal changes of the AA membrane prepared from sulfuric acid.

2. Experimental

2.1. Sample preparation

The sample was prepared in accordance with a well established method described by Inada et al. [5]. Specifically, a 0.2 mm thick Niraco 99.999% pure aluminum (Al) plate, which was degreased in ethanol and rinsed, was electrochemically polished, and was subjected to anodization in a special cell using sulfuric acid as the electrolyte. This cell was constructed in such a manner that only one side of the Al plate be in contact with a H_2SO_4 1 mol dm^{-3} aqueous solution, while the other side be brought into contact with distilled water. A platinum wire was used as the cathode. The pore structure was controlled by changing the applied voltage. Thus, a sample (sample AA-1) having a total thickness of ca. 150 μm and consisting of two layers differing in pore diameter and thickness, i.e., a 100 μm thick layer with 25 nm diameter pores and a 50 μm thick layer with 10 nm pores, was obtained by applying 25 V for 6 h and 10 V for 17 h. Another 150 μm thick sample (sample AA-2) consisting only of 25 nm diameter pores was prepared by applying 25 V for 8 h. The pore sizes and the layer thickness are already identified in [5]. After rinsing the thus anodized Al plates, the back side Al substrate was removed by using a 20 wt.% HCl solution of 1 M $CuCl_2$. The remaining Al was thoroughly dissolved by using 9 vol.% bromine methanol. Thus were obtained porous alumina membranes. The pore density for AA-1 (on the surface) and AA-2 was found to be 17×10^{14} and 5×10^{14} m^{-2}, respectively (see schematically drawn plan view shown in Fig. 1).

As the thermal contact between the sample and the sample pan is critical, the disks as received were carefully cut into smaller disks 4.5 mm in diameter by using a laser beam cutter. The burrs were removed by using soft tweezers.

In addition to AA samples above, a 4 mm diameter sapphire (alumina) disk (10.09 mg) commonly used as a reference material for use in DSC was used as a comparative sample.

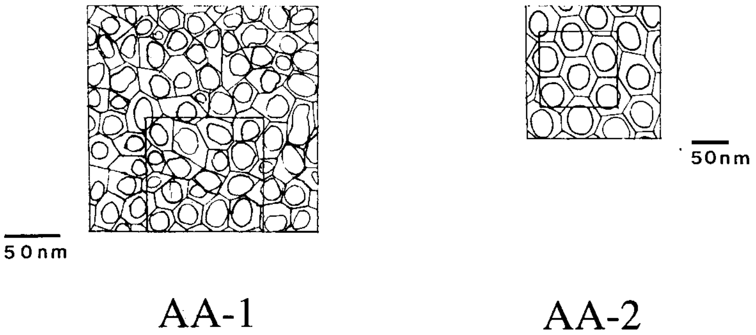

Fig. 1. Schematically drawn plan view of anodic alumina membranes AA-1 and AA-2. The squares drawn in the figure each have the same area of 100×100 nm^2. Both samples are 150 μm in total thickness, but AA-1 consists of a 50 μm thick layer having 10 nm diameter pores and a 100 μm thick layer of 25 nm diameter pores, whereas the second sample AA-2 consists only of 25 nm pores.

3. DSC measurements

3.1. High temperature DSC run

To obtain the overall view of the thermal change of the sample, the cut waste of AA-2 (19.92 mg) was subjected to high temperature DSC run using TA system EXSTAR 6000, DSC 6300 (Seiko Instruments) under the conditions as follows. Temperature range: 30–1500°C; heating rate: 20 K min^{-1}; sample pan: Pt pan; reference material: α-Al_2O_3 (20.00 mg); furnace atmosphere: gaseous Ar 200 ml min^{-1} flow; atmosphere of the heat sink: gaseous N_2 50 ml min^{-1} flow.

3.2. Tr-DSC

TA system EXSTAR 6000, DSC6200 (Seiko Instruments) equipped with Oval Sensor was used for the measurement. The resolution and sensitivity of the system were evaluated in accordance with the method described in [8] by using 4,4′-azoxyanisol, and are 0.17 and 4.04, respectively. Two 4.5 mm Ø disks were used for both AA-1 (10.88 mg) and AA-2 (10.00 mg). Sample pans were carefully selected to have the same weight (15.66 mg). For Tr-DSC, DSC curves were obtained by maintaining the sample at 350°C, and then, temperature was raised at a rate of 20 K min^{-1}. At least two scans were made on each sample to assure the repeatability. This temperature was selected, firstly, based on the results obtained by high temperature DSC. As is shown in the results below, a plateau is observed on the DSC curve (Fig. 2) at 350°C; apparently, adsorbed water is removed at this temperature. Secondly, the experimental conditions are the same as in our previous reports.

3.3. DSC with temperature modulation

While setting the base temperature to 350°C, temperature modulation was applied at a programmed temperature amplitude of 2°C and at frequencies of 0.01 and 0.02 Hz for a duration of 15 min for AA-1, and the data thus obtained were processed by using the application software DSC_OSC_Cp [9]. To assure repeatability, at least two scans were performed on each sample. Thus were obtained ‘apparent’ C_p for the samples. To eliminate instrumental effects, calibration on time constant was calibrated and set at τ=4.75, and the values were normalized using the C_p obtained for sapphire pellet.

4. Results and discussion

4.1. Phase transformation of AA

As described above, AA-2 is a sample consisting of 150 μm thick layer with uniform pores 25 nm in diameter, and the pore density was found to be 5×10^{14} m^{-2} (see Fig. 1). Fig. 2 shows the DSC curve obtained on coarse fractions of AA-2. A broad endothermic peak, apparently attributed to the desorption of adsorbed water, is observed up to about 350°C. A small exothermic peak is observed at ca. 600°C, but this is attributed to the mechanical breakdown (formation of cracks and breakage) of the

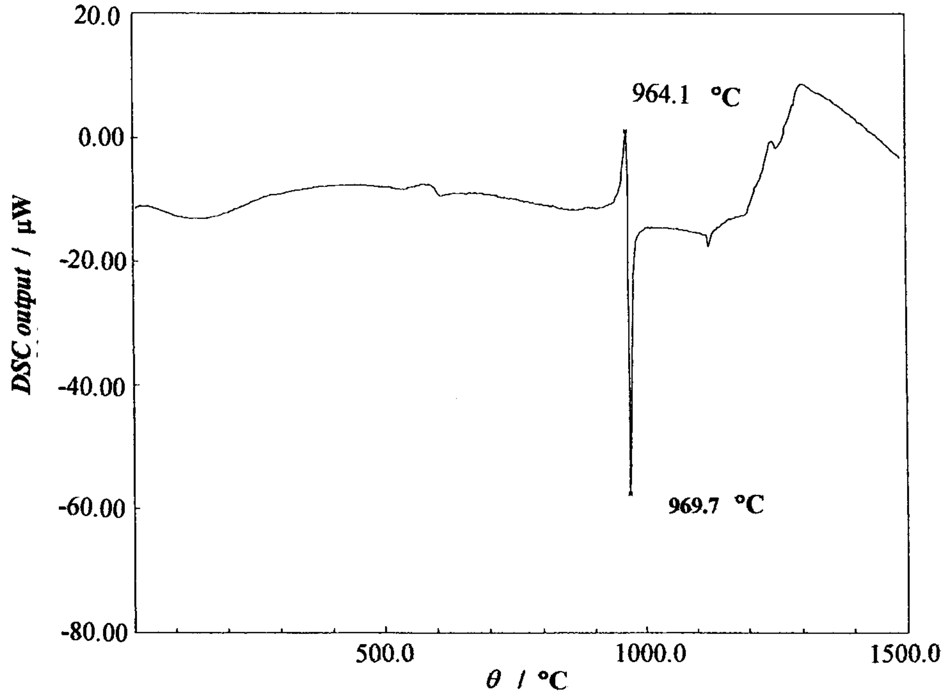

Fig. 2. High temperature DSC curve of AA-2.

sample. A sharp exothermic peak and a successive distinct endothermic peak is observed at around 960–970°C, suggesting transformation and a subsequent crystallization. An exothermic reaction is observed to initiate at ca. 1300°C, yielding a peak at 1400°C.

Mardilovich et al. [6] report TG-DTA curve in the temperature range of RT to 950°C for an AA obtained from oxalic acid. They separately determined the content of carbon and hydrogen incorporated in AA as impurities with changing temperature. They report gradual weight loss up to 820°C, and an exothermic and a subsequent sharp endothermic reaction which occur in a narrow temperature range of 820–840°C. This reaction accompanies a loss in weight attributed to the crystallization of AA into γ-Al_2O_3. It is well known that the electrolyte ions are incorporated in AA during their production [4]. In the case of oxalic acid, the impurities incorporated in AA are carbon, hydrogen, and oxygen. Mardilovich et al. [6] showed that carbon incorporated as an impurity is lost in the crystallization to γ-Al_2O_3. They also showed that hydrogen is incorporated predominantly as hydroxyl (OH–) groups on the surface of alumina. This hydrogen was lost gradually with increasing temperature up to ca. 1200°C. Furthermore, they identified transformation of γ-Al_2O_3 to δ-Al_2O_3 at ca. 950°C, and a small part of δ-Al_2O_3 underwent transformation to θ-Al_2O_3 at ca. 1050°C. That is, their sample were in

Table 1
Thermal change of AA

Phase	AA → γ-Al_2O_3	$\gamma \rightarrow \delta$	$\gamma \rightarrow \delta$ (Tr θ)	$\delta,\theta \rightarrow \alpha$
From oxalic acid electrolyte[a]	820–840	~950	~1050	ca. 1100
From sulfuric acid electrolyte	ca. 970	970~1250 (metastable modifications)	97 0~1250 (metastable modifications)	ca. 1250~

[a] [6].

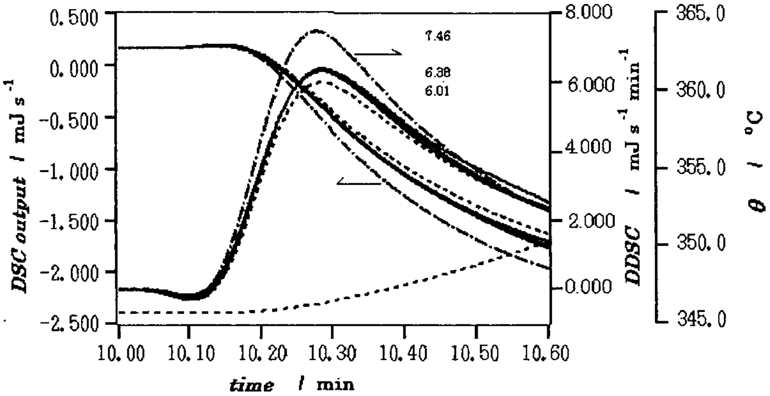

Fig. 3. DSC and derivative DSC (DDSC) curves in transient state of AA-1 (dotted line), AA-2 (solid line), and sapphire (dot-and-dash lines).

polycrystalline state at temperatures higher than 1050°C (see Table 1).

The phase transformation of AA obtained from sulfuric acid is presumably similar to that obtained from oxalic acid, except that the transformation temperatures from the amorphous state to a γ-Al_2O_3 (970°C) and from γ-Al_2O_3 to the polycrystalline state (970$\sim$1250°C) are higher for the present AA membranes, as summarized in Table 1. This suggests that the present AA membranes are resistant to higher temperatures. Further study to elucidate the details for these thermal changes are under way and the results are to be described elsewhere [10].

4.2. Tr-DSC results

Fig. 3 shows the result of DSC curves and derivative of DSC (DDSC) of dehydrated AA-1 and AA-2. Those for sapphire is also given as a control. Thus, the peak values reduced to the same sample weight were directly read from DDSC, and are used as Tr-DSC values (7.46, 6.38, 6.01 mJ s^{-1} min^{-1} for sapphire, AA-1, and AA-2, respectively). Further, C_p values for the samples were calculated therefrom by assuming thermal conductivity is the same and by using the C_p for sapphire as a standard. The thus obtained C_p values are given in Table 2. The 'apparent' C_p obtained by applying temperature modulation at frequencies of 0.01 and 0.02 Hz to AA-1 were 0.80 and 0.81 (J K^{-1} g^{-1}), respectively. In Table 3 [11] are given C_p values for known materials related to amorphous alumina or AA. It can be seen that C_p obtained for the AA samples is far lower than those of known materials.

Tr-DSC values [1] stands for an approximation of 1/*R*, where *R* (J^{-1} s K) is the thermal resistance which depends on the instrument and the thermal diffusivity of the sample. From dimensional analysis, it can be readily understood that *R* is the reciprocal of *K* value in Eq. (5) of Wunderlich et al. [12], where *K* is the calibration constant. The value of Tr-DSC can be used as the approximation of 1/*R* or *K* if the programmed heating rate is constant for all the samples and assume that the averaged heating rate over some period of time, say, 1 min, is maintained constant. Then, by dividing Tr-DSC (J s^{-1} min^{-1}) of all the samples by

Table 2
Apparent C_p, obtained by Tr-DSC (Peak height read from DDSC, the temperature of the peak, and repeatability are also given)

Sample	Apparent C_p (J K^{-1} g^{-1})	Peak height (MJ s^{-1} min^{-1})	Temperature (°C)	Repeatability (%, deviation)
Sapphire	1.04	7.46	350.7	±0.0
AA-1	0.89	6.38	350.7	±0.0
AA-2	0.84	6.01	350.7	±0.0

Table 3
Heat capacity of AA related materials (at 500 K)[a]

AA related materials		C_p ($J K^{-1} mol^{-1}$)	MW ($g mol^{-1}$)	C_p ($J K^{-1} g^{-1}$)	Relative C_p Sapphire=100 (%)
Sapphire	α-Al_2O_3	106.142	101.961	1.041	100
Polycrystalline alumina	γ-Al_2O_3	111.046	101.961	1.089	105
Polycrystalline alumina	δ-Al_2O_3	109.244	101.961	1.071	103
Diaspore	$Al_2O_3 \cdot H_2O$	113.303	119.977	0.944	91
Boebmite	$Al_2O_3 \cdot nH_2O$	138.365	119.977 (n=1)	1.153	111
Gibbsite	$Al_2O_3 \cdot 3H_2O$	260.496	156.007	1.670	160
Amorphous alumina	$Al(OH)_3$	135.495	78.004	1.737	167

[a] All data taken from [11].

a constant heating rate of, for instance, 20 K min^{-1}, the relative ratio of the resultant values ($J s^{-1} K^{-1}$) does not change. In this context, Tr-DSC value is an *approximation* and the advantage of using it is its convenience for quick analysis. The approach in Wunderlich et al. [12] is to give accurate values for C_s (i.e., the heat capacity of the sample system, or more specifically, that of the sample plus pan) by using modulated differential scanning calorimetry (MDSC). Thus, if the heat capacity of the sample pan is known, the accurate heat capacity of the sample can be obtained. Yet, C_s values obtained by MDSC is not free from deviations in case the sample has poor thermal conductivity or diffusivity [13]. Our approach is to provide a quick and simple method for identifying samples differing in thermal transmitting properties which may be related to, e.g., heterogeneity or the difference in morphology. If C_s is the same for all samples, Tr-DSC values depend only on R, and if the same conditions and instrument are used, R is a sample-dependent value.

As discussed in Section 4.1 above, the AA samples studied herein may differ in heat capacity; i.e., Tr-DSC values may not represent the R values only, so C_s values change accordingly. However, if the difference detected by Tr-DSC is influenced by the heat capacity only, it is possible to obtain accurate values for C_s by applying MDSC. The apparent heat capacity values obtained by MDSC are 0.81 or 0.80 ($J K^{-1} g^{-1}$), as described above, and are similar to that obtained by Tr-DSC. Thus, the difference between the samples depending on the sample preparation, i.e., the sample-dependent parameters, can be detected by Tr-DSC. Fig. 4 gives the SO_3 content of the samples determined by TEM-EDS as a function of the applied voltage [14]. As described above, it is well established that the pore size and the impurity content depend on the anodization potential. From Fig. 4, the SO_3 content for AA-1 and AA-2 can be obtained in accordance with the equation: $W_{SO_3}=0.39V+4.17$, where W_{SO_3} is the concentration of SO_3 expressed by % and V is the applied voltage (V). Thus, SO_3 content for AA-1 and AA-2 can be obtained as 11.96 and 13.92%, respectively.

Fig. 5 shows the change of SO_3 content (%) or the contact area between the sample and the pan (%) as a function of apparent C_p obtained by Tr-DSC. SO_3 content for sapphire is taken as 0%, and the contact area between sapphire and the pan is taken as 100% by assuming that the sapphire disk has a sufficiently smooth surface capable of attaining perfect contact with the sample pan. From the relation shown in Fig. 5, the contact area, y, can be obtained by

$$y=-673.37C_p^2+1388.7C_p-615.87 \quad (R^2=1) \tag{1}$$

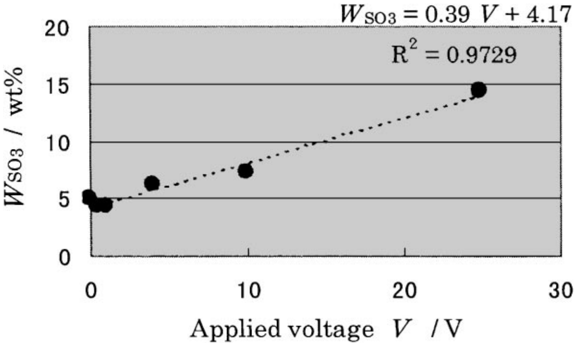

Fig. 4. SO_3 content of AA samples determined by TEM-EDS as a function of applied voltage [14].

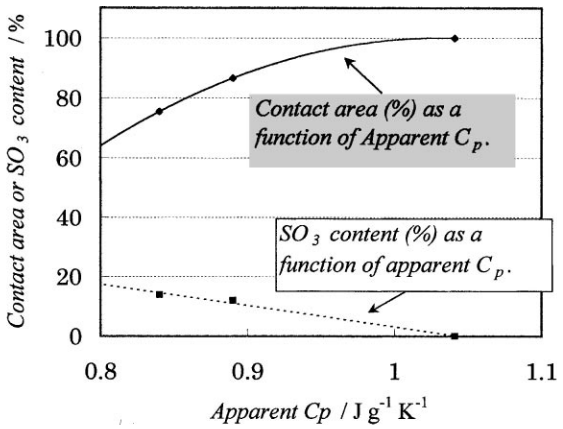

Fig. 5. Contact area (%) between the sample pan and the sample as a function of apparent C_p obtained by Tr-DSC (solid line), and SO_3 content (%) of the sample obtained as a function of apparent C_p obtained by Tr-DSC (broken lines).

where C_p is the apparent C_p obtained by Tr-DSC. Similarly, the SO_3 content, W_{SO_3}, can be obtained by

$$W_{SO_3} = -71.482C_p + 74.645 \quad (R^2 = 0.9876) \tag{2}$$

5. Conclusion

Tr-DSC has the potential to give a parameter for identifying AA differing in preparation. The apparent C_p obtained by Tr-DSC is related to the contact area y between the sample and the pan or the SO_3 content W_{SO_3} by Eqs. (1) and (2), respectively. Although it is not fully elucidated that Tr-DSC values directly represent the pore structure, the impurity content and pore structures can be related to the pulse voltage applied during preparation; more specifically, the impurity content and the pore structure are both functions of the applied voltage. Thus, the values obtained by Tr-DSC can be related to the voltage applied to the sample, and may be used as a parameter for identifying the preparation conditions. A further detailed study is under way.

DSC curve was obtained for an AA sample prepared from sulfuric acid. The results are summarized below, and they suggest that AA samples undergo phase transformation up to 1500°C in the following sequence: (a) at ca. 970°C, DSC shows a sharp exothermic peak accompanied by a broader endothermic peak, presumably due to the crystallization from amorphous state to γ-Al_2O_3, (b) at ca. 1250°C, DSC yields a smaller exothermic peak, apparently attributed to a less distinct phase change from the phase obtained at 970°C to a polycrystalline alumina phase; and (c) at temperatures higher than ca. 1300°C, the metastable polycrystalline alumina phase undergoes the final transformation into the stable α-Al_2O_3.

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