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EMANATION THERMAL ANALYSIS STUDIES OF SURFACE LAYER OF ALUMINUM OXIDE POWDERS PREPARED BY VARIOUS GRINDING AND SIEVING TREATMENTS

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ABSTRACT

In order to examine the effects of both grinding and sieving treatments on the surface layer of powders, the technique of emanation thermal analysis (ETA) was applied in the range 25–1450 °C for characterization of the near-surface region of 24 aluminum oxide powders (α-Al_2O_3) with various preparation histories with regard to grinding and sieving. The effects of pulverizer material, grinding time and particle size on the ETA curves were discussed. The ETA behavior was greatly affected, in addition of grinding effects, by the dispersion phenomena of particles resulting from the sieving treatments. These results made complex the relationship between the ETA curve and the preparation history of fine powders. However, it was concluded that the ETA technique is one of the interesting methods for characterizing the surface layer of fine powders subjected to various grinding and sieving treatments.

INTRODUCTION

In the preceding paper [1], the thermal characterization of the surface layer of various iron oxide powders, each prepared by a different grinding regime, was carried out by emanation thermal analysis (ETA) using ^{226}Ra as a parent isotope.

In the present paper, in order to examine the effects of both grinding and sieving treatments on the surface layer of powders, the ETA technique was extended to aluminum oxide powders.

EXPERMIMENTAL

Materials

Aluminum oxide (α-Al_2O_3) as a starting material was prepared from commercial activated alumina (Merck reagent grade, −70 to +230 mesh)

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TABLE 1

Preparation methods of samples. Grinding for 30 min; unsieved

Sample No.	Pulverizer material	Grinding procedure	Fig. No. of SEM	Fig. No. of ETA
A1	Alumina	Dry	8	1
A2	Alumina	Wet	8	1
A3	Tungsten carbide	Dry	8	1
A4	Tungsten carbide	Wet	8	1

by calcining at 1300°C for 3 h. The major part of this material (69.5%) belonged to the size fraction exceeding 20 μm in diameter.

The dried α-Al_2O_3 powders thus obtained were ground during various times using a Fritsch Planetary-Micro-Pulverizer (P-7 type) equipped with a cylindrical vessel (12 ml volume) and four balls (12 mm diameter). Two kinds of pulverizer material, alumina and tungsten carbide, and two grinding procedures, dry and wet, were used for preparing the samples for ETA. In many cases in this work, an alumina pulverizer and dry grinding were used. The preparation methods for the sample powders are shown in Table 1 (for Al–A4) and Table 2 (for A5–A24).

TABLE 2

Preparation methods of samples. Alumina pulverizer and dry-grinding

Sample No.	Grinding time (min)	Particle size (μm)	Fig. No. of SEM	Fig. No. of ETA
A5	0	unsieved		2
A6	0	32–45		2
A7	0	20–32		2
A8	0	10–20		2,4
A9	0	5–10		2,5
A10	0	−5		2,6
A11	30	32–45	9	
A12	30	20–32	9	
A13	30	10–20	9	4
A14	30	5–10	9	5
A15	30	−5		6
A16	60	10–20		4
A17	60	5–10		5
A18	60	−5		6
A19	180	unsieved		3
A20	180	32–45		3
A21	180	20–32		3
A22	180	10–20		3,4
A23	180	5–10		3,5
A24	180	−5		3,6

The pulverized samples, dispersed in water containing a small amount of dispersant medium, were sieved to various size fractions using an Automatic-Micro-Sieve apparatus (Shodex PS, Model PS-2), which enables the particles to be effectively sieved under application of suction and ultrasonic vibration. The samples thus ground and sieved into the various size fractions are shown in Table 2. A5–A10 are unground, and A5 and A19 are unsieved samples.

These samples were further characterized by scanning electron photomicroscopy in part, and ETA. The apparatus and procedures for ETA studies were described in the preceding paper [1].

RESULTS AND DISCUSSION

Emanation thermal analysis

The interpretation of ETA curves has been described in the preceding paper [1]. The characteristic peaks in ETA curves observed in this work were

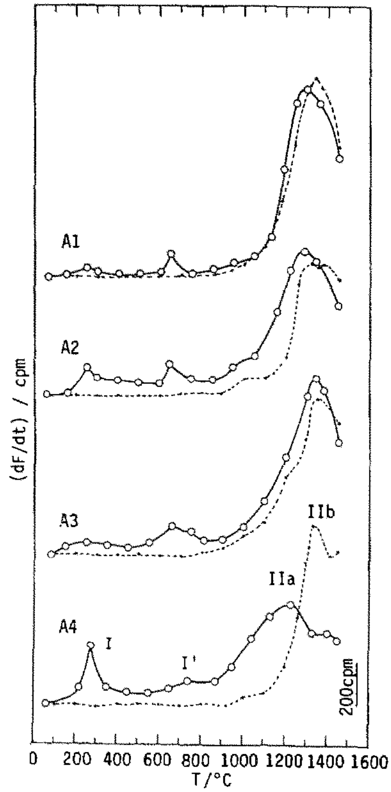

Fig. 1. ETA curves for unsieved aluminas (A1–A4) prepared by using pulverizers made of different materials and two grinding procedures (Table 1). A 30 min grinding period was used for all samples. o——o run 1; ●– – –● run 2.

grouped into two main stages: stage I at temperatures lower than $T_s = (0.4-0.5)T_m$, and peak II due to E_d at temperatures higher than T_s. Parameters T_s and T_m indicate the starting temperatures (in K) of self-diffusion of the lattice ions and melting point (K) of the samples, respectively. T_s was calculated as 656–889 °C for α-Al_2O_3. The ETA peaks corresponding to stages I and II are hereinafter represented by peaks I and II, respectively. In many cases, peak II was split into two peaks, IIa and IIb. The peak which appears at temperatures near T_s was represented as peak I′, which is considered to be due to amorphous–crystalline transition.

The curves obtained in the first run (run 1) and a subsequent run (run 2) are represented by solid and dashed lines, repectively. In general, these peaks, I, I′ and II, appear variably in run 1, corresponding to the effects of grinding and sieving. In run 2, however, the curves become typical of α-Al_2O_3, with a simple peak IIb at 1300–1350 °C starting at about 800 °C; there is no peak corresponding to stage I. Therefore, it is thought that the

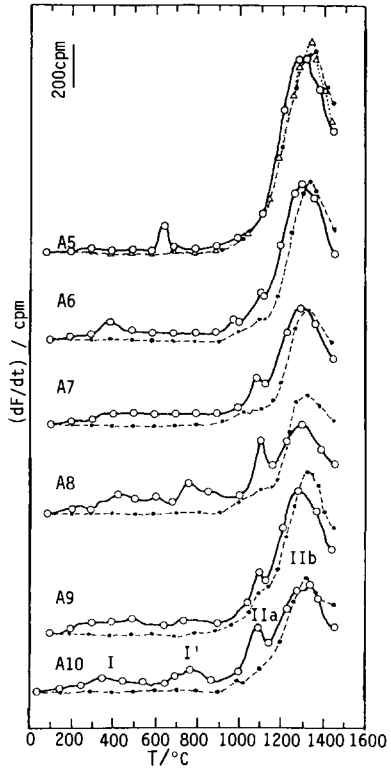

Fig. 2. ETA curves for unground aluminas (A5–A10) sieved to various particle sizes (Table 2). ○——○ run 1; ●– – –● run 2; △- - - - - -△ run 3.

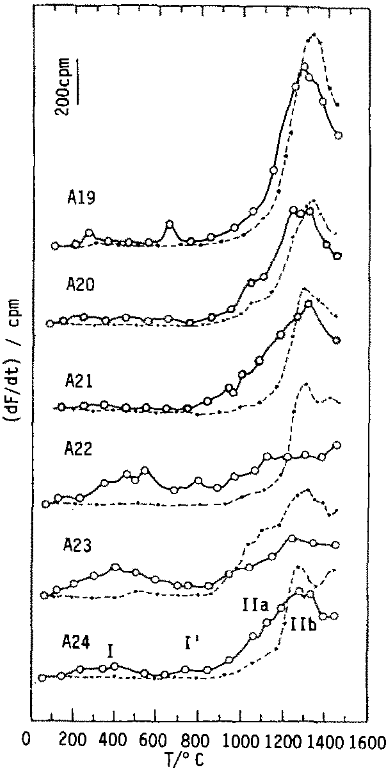

Fig. 3. ETA curves for aluminas (A19–A24) sieved to various particle sizes after grinding for 180 min using an alumina pulverizer (Table 2). o———o run 1; ●– – –● run 2.

effects of preparation methods of the samples on the surface layer appear as a variation of the ETA peaks in the first run.

Figure 1 shows the ETA curves for the unsieved aluminas (A1–A4) which were, respectively, ground by using two pulverizers made of different materials, alumina and tungsten carbide, and by two grinding procedures, dry and wet. A grinding time of 30 min was used for all the samples. A marked effect of grinding methods on the ETA curves appears in run 1, in the order A4 > A2 > A3 > A1, compared with the curve of the original alumina sample, A5 (unground and unsieved) shown in Fig. 2. In run 2 (dashed line), all the curves become typical of α-Al_2O_3 by the disappearance of peaks I, I′ and IIa, resulting from the annealing effects of the surface layer during run 1. The subsequent experiments were carried out with use of an alumina pulverizer and dry-grinding for preparing the ground samples.

Figures 2 and 3 show the ETA curves of the samples prepared by sieving to various size fractions after the use of two grinding times, 0 and 180 min, respectively. In Fig. 3 an alumina pulverizer and dry-grinding were used. Comparison of the two unsieved samples, A5 (Fig. 2) and A19 (Fig. 3), having different grinding times shows that no significant difference appears

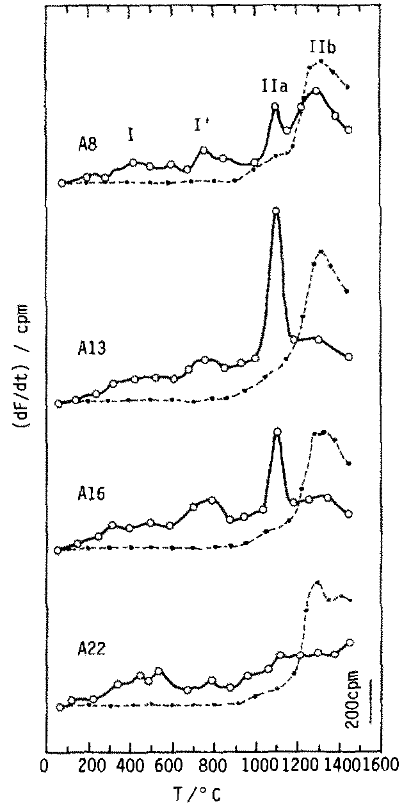

Fig. 4. ETA curves for aluminas (A8, A13, A16 and A22) sieved to 10–20 μm size after grinding for various times using an alumina pulverizer (Table 2). ○——○ run 1; ●– – –● run 2.

in the ETA curves. However, the curves for the samples of different size fractions differ greatly from one another, with a tendency to a decreasing peak IIb and increasing peaks I and IIa, despite the use of the same grinding conditions. These results mean that the ETA behavior is greatly affected, in addition to grinding effects, by the dispersion phenomena of the particles resulting from the sieving treatments.

Figures 4–6 show the effects of the grinding times on the ETA curves for the samples in the same size fraction. These results show, in an analogous manner with that considered in Figs. 1–3, that the relationship between the ETA behavior and the preparation histories such as grinding and sieving to obtain fine powders is very complex. However, the ETA curves for the different samples obtained in the same batch of labeling with the isotope have very good reproducibility, and it is considered that ETA is one of the more interesting new methods for characterizing the surface layer of fine powders.

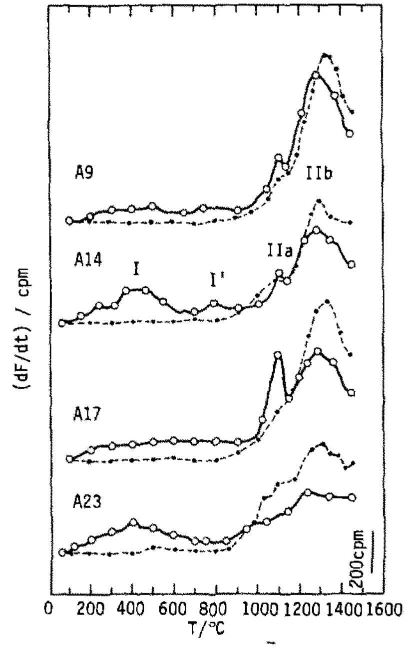

Fig. 5. ETA curves for aluminas (A9, A14, A17 and A23) sieved to 5–10 μm size after grinding for various times using an alumina pulverizer (Table 2). ○——○ run 1; ●– – –● run 2.

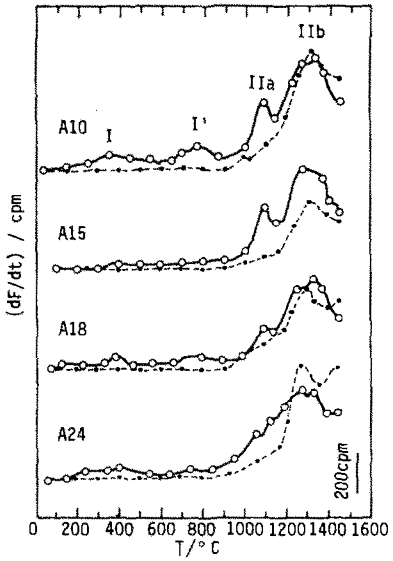

Fig. 6. ETA curves for aluminas (A10, A15, A18 and A24) sieved to −5 μm size after grinding for various times using an alumina pulverizer (Table 2). ○——○ run 1; ●– – –● run 2.

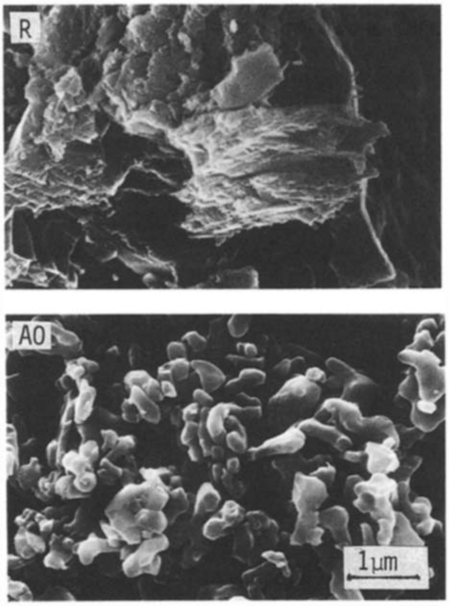

Fig. 7. Scanning electron micrographs of activated alumina (R) as a raw material and α-Al_2O_3 (A0) as a starting sample. The scale bar applies to both photographs.

Scanning electron photomicrography (SEM)

Figure 7 shows SEM photographs of activated alumina (R) as a raw material and α-Al_2O_3 (A0) as the starting alumina, which is unsieved and unground.

Figure 8 shows SEM photographs of aluminas (A1, A2, A3 and A4) which were not sieved but underwent 30 min of grinding. Two scale bars are used, 10 μm for the A-series and 1μm for the B-series. Grinding effects appear in the A-series, corresponding to the ETA behavior in Fig. 1, but no clear relationship is identifiable for the B-series.

Figure 9 shows SEM photographs of aluminas (A11, A12, A13 and A14) which were sieved to various size fractions. A grinding time of 30 min was used for all the samples. Two scale bars are used, 100 μm for the A-series and 1 μm for the B-series. The sieving effects appear clearly in the A-series.

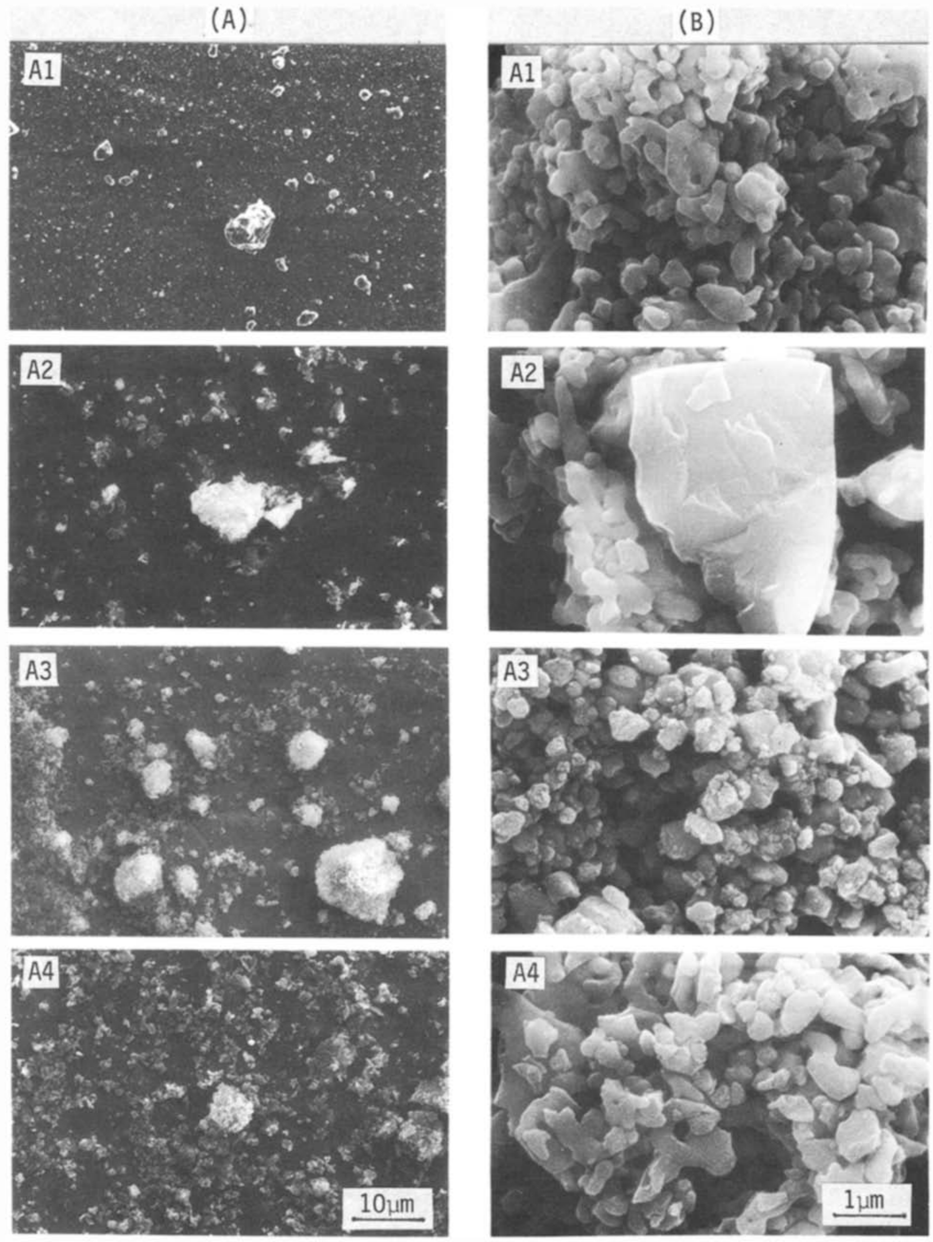

Fig. 8. Scanning electron micrographs of aluminas (A1, A2, A3 and A4). Two scale bars are used, 10 μm for all four photographs in the A-series and 1 μm for all four photographs in the B-series.

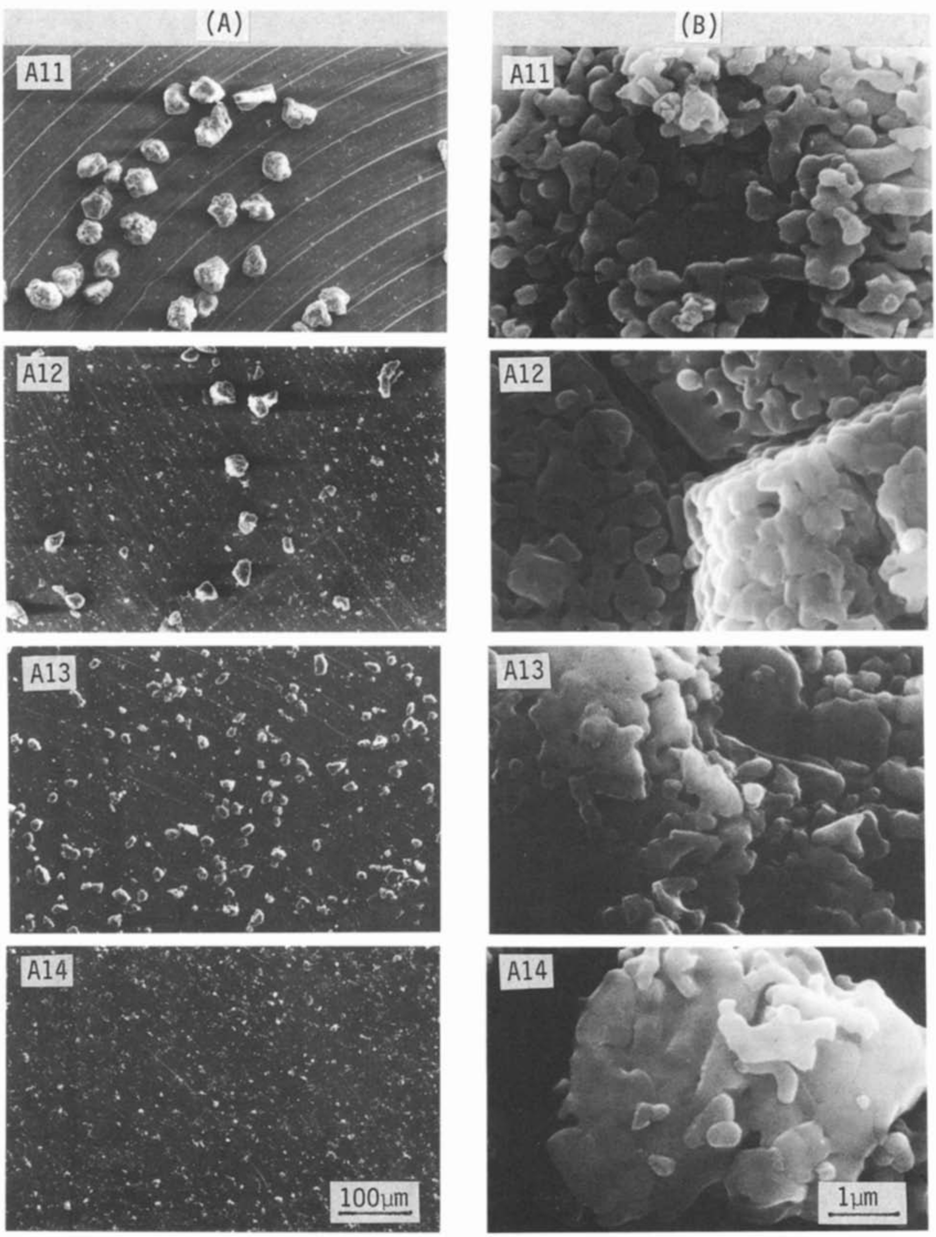

Fig. 9. Scanning electron micrographs of aluminas (A11, A12, A13 and A14). Two scale bars are used, 100 µm for all four photographs in the A-series and 1 µm for all four photographs in the B-series.

REFERENCE

1 T. Ishii, S. Nakano and A. Yada, Thermochim. Acta, 178 (1991) 109.