

THERMAL CHARACTERIZATION OF IRON OXIDE AND ALUMINUM OXIDE POWDERS
BY EMANATION THERMAL ANALYSIS

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ABSTRACT

Emanation thermal analysis (ETA) using a surface impregnation method of Ra-226 nuclide was applied for the thermal characterization of iron oxide and aluminum oxide powders with various preparation histories in the heating and grinding treatments.

INTRODUCTION

The role of the surface on the reactivity of powder increases with a decrease in particle size. The author has already reported on the applications of emanation thermal analysis (ETA) for the initial reactivity of metal oxide powders [1,2]. Further, the thermal characterization of iron oxide powders by ETA was reported [3].

In this paper, ETA using a surface impregnation method of Ra-226 nuclide was applied for the characterization of near-surface of iron oxide and aluminum oxide powders with various preparation histories in the heating and grinding treatments.

EXPERIMENTAL

The apparatus used for ETA is commercially available Netzsch device (ETA 403 - STA 409) for simultaneous ETA-TG-DTA measurements. The standard experimental conditions were as follows; sample weight of 100mg, N₂ carrier gas of 50ml/min, heating rate of 10°C/min, threshold of 2MeV, time constant of 300sec. The samples were labeled by a surface-impregnation method using Ra-226 solution (4μCi/ml) and dried without further washing the surface of labeled powders. Before being used for ETA experiments, in both first and repeated runs, the dried labeled-samples were stored respectively for the periods exceeding one month until a radioactive equilibrium state was reached.

Reagent grade commercial α -Fe₂O₃ (Kanto) and activated alumina (merck) were used as the starting materials. The ETA samples with various preparation histories are shown in Table 1. As an example, the sample No. F24 was prepared as follows; first the Fe₂O₃ powder (F2) compacted as a tablet was heated at 1300°C for 20hr in air,

then it was ground and sieved to obtaine a sive fraction between 100 and 150 mesh.

TABLE 1

Preparation methods of samples.

Sample No.	Preparation methods
F20	F2
F21	F2(-200+250 m)
F22	F2 - C(1300°C, 1hr, air) - G(+150 m)
F23	F2 - C(1300°C, 1hr, air) - G(-325 m)
F24	F2 - C(1300°C, 20hr, air) - G(-100+150 m)
F25	F2 - C(1300°C, 20hr, air) - G(-325 m)
A10	A
A11	A - C'(1300°C, 2hr, air) - G'(-325 m)

F2: α -Fe₂O₃, Kanto-GR, Test No. 308A1133.

A : activated alumina, Merck, -70+230 mesh.

(sample No. A11 was transfered to α -Fe₂O₃ during the preparation)

C . calcining in compacted tablet, rapid heating and cooling in air.

C' : calcining in dispersed powders, rapid heating and cooling in air.

G : grinding with a pestle, and sieving.

G' : grinding in acetone by ball-mill, and sieving.

m : mesh.

RESULTS AND DISCUSSION

When a state of radioactive equilibrium was reached in the dry labeled sample, Rn-222 gas is distributed in the surface layer smaller than 100nm thick [4]. On the basis of Balek's considerations [5], the radon release was grouped into three parts; (a) recoil part, E_r , due to the energy that radon atom gains during its formation by decay of radium, (b) a diffusion part, E_p , due to the diffusion in intergranular space, open pores, etc. of the dispersed powder and (c) a diffusion part, E_d , due to the bulk diffusion of radon in solid matrix of the dispersed powder. E_r is temperature-independent. E_p is dependent on temperature, and on dispersity or morphology of the powders. E_d is dependent on temperature. A gas release for E_d -part starts between 40 and 50% of the melting temperature, T_m (K), for a large variety of ionic crystals of different lattice structures [6]. The onset temperature of gas release for E_d -part is also similar to that of self-diffusion of matrix atoms. The characteristic changes in ETA curves obtained were observed in the following two stages; stage I due to E_p at temperature lower than $(0.4-0.5)T_m$, and stage II due to E_d at temperature higher than $(0.4-0.5)T_m$. The ETA peaks corresponding to the stages I and II are hereinafter represented by

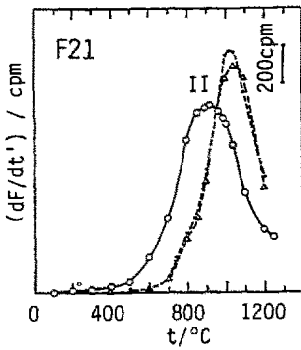


Fig. 1 ETA curves for Fe_2O_3 powder (F21).

-- : Repeated run.
 -△ : Third run.

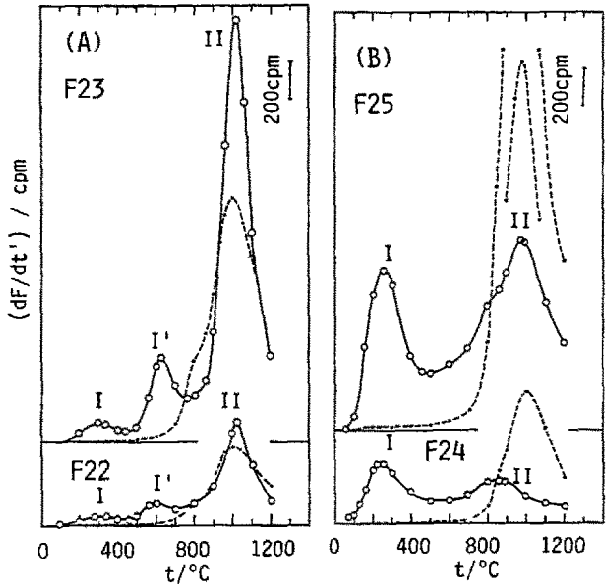


Fig. 2(A, B). ETA curves for Fe_2O_3 powders (F22, F23, F24, F25) of different particle sizes with heating and grinding treatments.

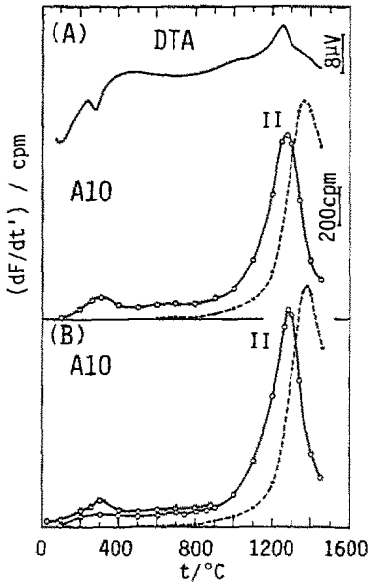


Fig. 3. (A), ETA-DTA curves for activated-alumina (A10), and (B), its stepwise tests.

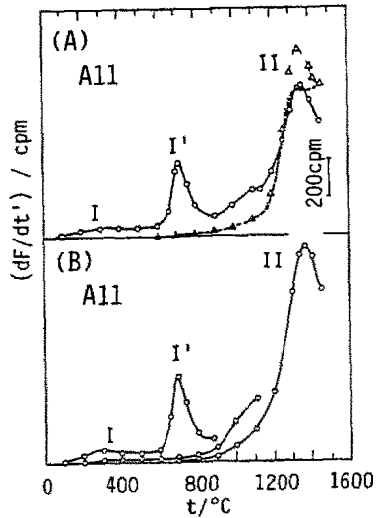


Fig. 4. (A), ETA curves for $\alpha\text{-Al}_2\text{O}_3$ (A11), and (B), its stepwise tests.

peaks I and II, respectively. The peak which appears at the temperature of about $(0.4-0.5)T_m$ was represented as peak I', because in the repeated run this peak shows a behavior similar to peak I. The temperature range of $(0.4-0.5)T_m$ is calculated as 456 - 639°C for $\alpha\text{-Fe}_2\text{O}_3$ ($T_m=1823\text{K}$) and 656 - 889°C for $\alpha\text{-Al}_2\text{O}_3$ ($T_m=2323\text{K}$).

Figs. 1 and 2 show the ETA curves for various Fe_2O_3 powders (F21 - F25). The curves obtained in first and repeated runs are represented by solid and dashed lines, respectively. The curves in first run greatly vary with the preparation history of sample, but in repeated run the curves lead to a single curve which has onset temperature of about 600°C and peak temperature of about 1000°C with a good reproducibility (see third run in Fig.1). Fig. 2 shows that in the first run peak I appears newly at 200 - 300°C as a result of mechanochemical effects which were caused by the grinding treatment of the preheated samples, and peak II at about 900°C (Fig.1) shifts to a higher temperature side (1000°C) as a result of an ordering effect of crystal lattice by the heating treatments. For peak I' at about 600°C, however, it is thought that both mechanochemical and ordering effects appear simultaneously at this temperature. These peaks I and I' disappear in the repeated run by the heating treatment.

Figs. 3 and 4 show the curves for activated alumina and $\alpha\text{-Al}_2\text{O}_3$, respectively. In general, the results show a behavior similar to that of Fe_2O_3 powders. For activated alumina (A10) in Fig. 3, peak II initiates at about 800°C with peak temperature of about 1270°C corresponding to the transition to $\alpha\text{-Al}_2\text{O}_3$ (see DTA curve). The ETA peak at about 300°C corresponds to the dehydration. In the repeated run, the curve leads to that of $\alpha\text{-Al}_2\text{O}_3$ with peak II at 1350°C. In the stepwise tests shown in Fig. 4(B), the peaks I and I' disappear successively, finally lead to a single peak II at 1350°C.

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