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THERMAL CHARACTERIZATION OF IRON 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 near-surface of iron oxide powders with various preparation histories in the heating and grinding treatments. Peaks I and II appeared at the temperature regions lower and higher than 0.4 - 0.5 T_m, respectively, where T_m is a melting temperature (K) of powders. Further, peak I' appeared at the temperature region of 0.4 - 0.5 T_m. The appearance of peak I was explained by the mechanochemical effects due to the grinding treatment, and it disappeared in the repeated run. The shift of peak II 900°C to 1000°C in the repeated run was explained by the ordering effect of crystal lattice due to the heating treatment. The behavior of peak I' was complicated.

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 application of ETA for the initial reactivity of metal oxide powders (refs.1 and 2). On the other hand, it is a well-known fact that the reactivity of powder indicates a complex behavior in connection with the preparation history of powder. However, in the characterization of powders with the different preparation histories, one of the major problems is that a difficulty arises in pursuing the surface behavior of powders under the working condition at high temperature.

In this paper, emanation thermal analysis (ETA) using a surface-impregnation method of Ra-226 nuclide was applied for the characterization of near-surface of iron oxide powders with various preparation histories in the heating and grinding treatments. ETA is a dynamic technique used for the detection of radioactive inert gas (Rn) which is released from activated powders during a controlled temperature program (refs.3 and 4).

EXPERIMENTAL

The apparatus used for ETA is commercially available Netzsch device (ETA 403-STA 409 type) for simultaneous ETA-TG-DTA measurements. The standard experimental conditions were as follows: sample weight of 100 mg, N_2 carrier gas of 50 ml/min, heating rate of 10 °C/min, threshold of .2 MeV, time constant of 300 sec. The samples were labeled by a surface impregnation method using Ra-226 solution

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(4 µCi/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 Fe_2O_3 was used without further chemical purification. The ETA samples with various preparation histories are shown in Table 1. As an example, the sample No. F7 was prepared as follows; first the Fe_2O_3 powder compacted as a tablet was heated at 1300°C for 1 hr in air, then ground and sieved to obtain a sieve fraction between 100 and 150 mesh.

TABLE 1

Preparation methods of Fe_2O_3 samples.

Sample No.	Preparation methods
F1	F
F2	F(-100+150 m)
F3	F(-500 m)
F4	F - C'(1200°C, 1hr, N_2)
F5	F - C'(1320°C, 1hr, N_2)
F6	F(+250 m) - C(1300°C, 1hr, air) - G(-150+325 m)
F7	F - C(1300°C, 1hr, air) - G(-100+150 m)
F8	F - C(1300°C, 1hr, air) - G(-325 m)
F9	F - C(1300°C, 20hr, air) - G(-100+200 m)
F10	F - C(1300°C, 20hr, air) - G(-400+500 m)

F: Fe_2O_3, Kanto-GR, No.603A1162.
C: calcination in compacted tablet, rapid heating and cooling in air.
C': calcination in dispersed powders, controlled heating and cooling rates of 10°C/min in N_2.
G: grinding, with a pestle.
m: mesh.

RESULTS AND DISCUSSION

Interpretation of ETA curves

By use of an impregnation technique for labeling the sample, Ra-226 nuclide is adsorbed on the sample surface and Rn-222 nuclide is formed by its alpha-decay and introduced into the surface layer of the sample by recoil energy. When a state of radioactive equilibrium was reached in the dry labeled sample, Rn-222 gas is distributed in the surface layer smaller than about 100 nm thick (ref.3). Therfore, the informations obtained from the ETA experiments may be correlated with the behavior of near-surface of about 100 nm thick.

On the basis of Balek's considerations (ref.5), the radon release was grouped with a rise in temperature into three parts; (a) 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. Total emanating power, E, can be expressed as follows:

$$E = E_r + E_p + E_d. \qquad (1)$$

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 and expressed as follows:

$$E_d = K \cdot \exp(-\Delta H/2RT), \qquad (2)$$

where ΔH is the activation energy of radon diffusion in solid matrix. Matzke (ref.6) has shown that E_d-part of gas release starts between 40 and 50% of the melting temperature, T_m(K), for a large variety of ionic crystals of different lattice structures. The onset temperature of gas release for this E_d-part is also similar to that of self-diffusion of the matrix atoms.

For the ETA curves obtained, the stages in gas release during a linear temperature increase were grouped according to the temperatures of 0.4 - 0.5 T_m at which the self-diffusion of matrix atoms and the bulk diffusion of radon start. The characteristic changes in ETA curves 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 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.

ETA curves of Fe_2O_3 powders

Figs. 1 - 4 show the ETA curves for various Fe_2O_3 powders (F1 - F10) with different preparation histories in the heating and grinding treatments. All curves are represented as a gas release rate, dF/dt' (cpm, count per minute), per 100 mg of labeled sample against temperature (°C). In addition, the curves obtained in first and repeated runs are represented by solid and dashed lines, respectively.

In spite of the samples prepared from the same starting material, the curves obtained in the first run greatly vary in connection with their preparation histories. However, all the curves in the repeated run lead to a single curve which has the onset temperature of about 600°C and the peak temperature of about 1000°C. In the first runs, as a rule, peak I appears newly at 200 - 300°C as a result of a mechanochemical effect which was caused by the grinding treatment of the preheated samples, and peak II at about 900°C shifts to a higher temperature side

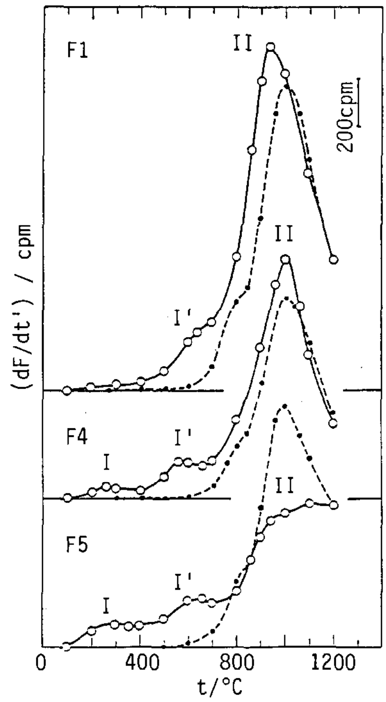

Fig. 1. ETA curves of Fe_2O_3 powders (F1, F4, F5) with different heating treatments.

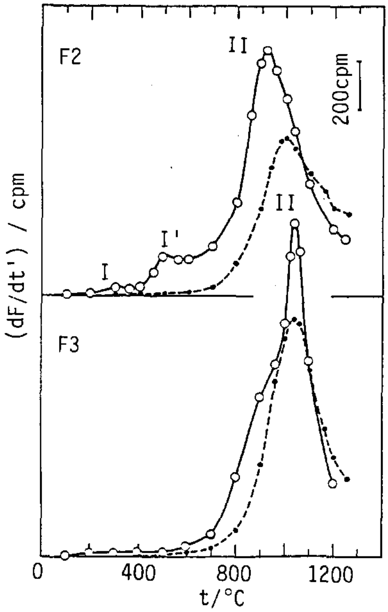

Fig. 2. ETA curves of Fe_2O_3 powders (F2, F3) with different particle sizes.

(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 not an easy matter to give a simple consideration of this subject. Because, it is thought that both mechanochemical and ordering effects appear simultaneously at this temperature region.

Fig. 1 shows the ETA curves for Fe_2O_3 samples with different heating treatments. F1 is for the starting material. F4 and F5 are the samples preheated at 1200 and 1300°C for 1 hr in flowing N_2 atmosphere, respectively, by use of the controlled heating and cooling rate of 10 °C/min, without a special grinding treatment. In F4 sample, the marked ordering effect appears for peak II, but the mechanochemical effect is little found for peak I. For F5 sample, it was thought from the TG result of 3.2% weight loss that the reduction of Fe_2O_3 to Fe_3O_4 occured during the heating treatment above 1200°C in N_2 atmosphere in the sample preparation. Peaks I and I' for F4 and F5 samples may be due to other thermal effects different from a simple mechanochemical effect by the grinding treatment.

Fig. 2 shows the effects of particle size for F1 sample. For large size fraction (F2), very little peak I and the pronounced peak I' appear. This is probably

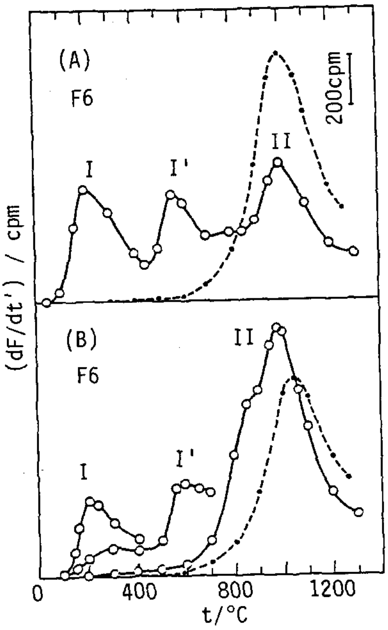

Fig. 3. (A); ETA curves for Fe_2O_3 powder (F6) with heating and grinding treatments, and (B); its stepwise ETA tests.

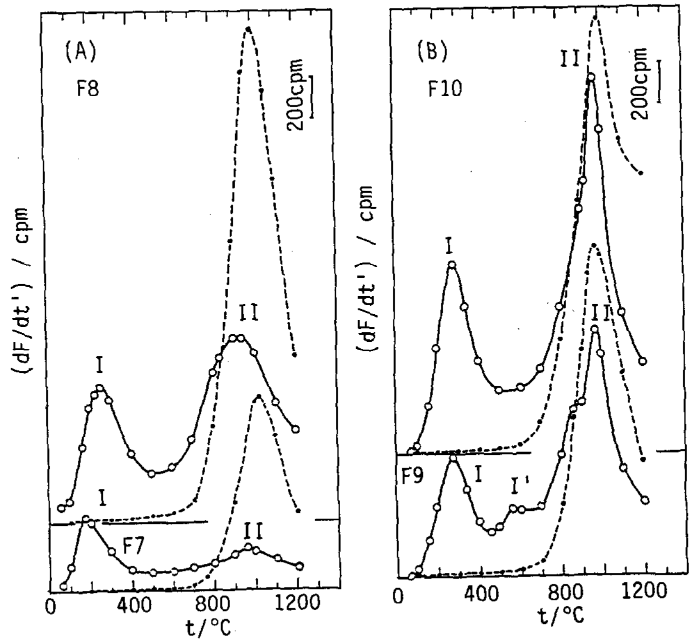

Fig. 4(A, B). ETA curves for Fe_2O_3 powders (F7, F8, F9, F10) of different particle sizes with heating and grinding treatments.

due to that the secondary particles produced by an agglomeration of the primary particles concentrate in this fraction. While, for the small size fraction (F3), peaks I and I' disappear, and peak II splits into two peaks at about 900°C (as a shoulder) and about 1000°C. The appearance of the peak at 1000°C means that the ordered particles as a primary particle concentrate in the small size fraction.

Fig. 3(A) shows the ETA curves of F6 sample which was prepared by the grinding treatment after the large size fraction (+250 mesh) of F1 sample was heated at 1300°C for 1 hr in air. The mechanochemical effects appear as peak I at about 200°C and peak I' at about 470°C, and the ordering effect of crystal lattice appears as peak II at 1000°C. Fig. 3(B) is the results of a stepwise test of F6 sample. Peaks I and I' become small by heating up to 400 and 700°C, respectively. This means that the mechanochemical effect is easily eliminated by a sintering effect in the heating treatment. While, peak II shifts step by step to a higher temperature side with the heating treatments.

Figs. 4(A and B) show the ETA curves of different size fractions with different heating and grinding treatments. The samples of large size fraction (F7 and F9) show low emanating power compared with that of small size fraction (F8 and F10). This is due to a difference of the surface area of samples. A remarkable mechanochemical effect appears in peak I at 200 - 300°C, but the effect of these treatments on the peaks I' and II is not the simple one.

These results described above suggest that the effects of the heating and grinding treatments on the ETA curves of oxide powders are very complicated, but ETA is an interesting tool in the study of the thermal characterization of the near-surface of powders under the working condition at high temperature.

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