Thermochimica Acta, 178 (1991) 109–115
Elsevier Science Publishers B.V., Amsterdam

EMANATION THERMAL ANALYSIS STUDIES OF SURFACE LAYER OF IRON OXIDE POWDERS PREPARED BY VARIOUS GRINDING TREATMENTS

TADAO ISHII, SHUICHI NAKANO and AKIRA YADA

Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060 (Japan)

(Received 19 June 1990)

ABSTRACT

In order to examine the effects of grinding treatment on the surface layer of powders, the new technique of emanation thermal analysis (ETA), using a method of surface impregnation with the ^{226}Ra nuclide, was applied in the range 25–1200 °C for characterization of the surface of five iron oxide powders (α-Fe_2O_3) with various preparation histories with regard to grinding treatment. The ETA results were compared with those obtained by the conventional methods: size distribution, BET surface, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The mechanochemical effects of grinding on the surface layer of the sample powders were evident as an increasing peak I and a pronounced peak IIa.

INTRODUCTION

The phase boundary reaction that takes place in the near-surface region of the powder plays an important role in the reactivity of fine powders. Therefore, in order to study the reactivity of powders, especially fine powders, it is necessary to follow the surface behavior of the powder during the reaction, on the basis of the effects on the near-surface region of the constituent powders under various conditions at high temperatures.

From the above standpoint, the first author has already reported on the applications of emanation thermal analysis (ETA) using ^{226}Ra as parent isotope for the thermal characterization of iron oxide and aluminum oxide powders [1–3], nickel oxide, copper oxide and magnesium oxide [4], zinc oxide [5] and titanium oxide [6], and for studying the surface reactivity of these oxide powders in the reaction systems TiO_2–$BaCO_3$ [6], Fe_2O_3–Al_2O_3 [7], Fe_2O_3–ZnO, Al_2O_3–ZnO and TiO_2–ZnO [8]. From this work, it was shown that the ETA method provides useful information on the thermal behavior of the near-surface region for both single powders and the reaction systems at high temperatures.

In this paper, the ETA technique, using a method of surface impregnation with the nuclide ^{226}Ra, was applied in the range 25–1200 °C for characterization of the near-surface region of iron oxide powders with various preparation histories with regard to grinding treatment. In a subsequent paper [9], the ETA studies will be extended to aluminum oxide powders in order to examine the effects of both grinding and sieving treatments on the surface layer of the powders.

EXPERIMENTAL

Materials

The iron oxide sample was prepared by calcining precipitates of FeOOH. The precipitates were obtained by adding 0.5 M NaOH solution to 0.1 M $Fe(NO_3)_2$ solution while stirring. After the precipitates had been dried at 50 °C for 24 h in an oven, ground in an agate mortar and sieved to pass through a 200 mesh sieve, the powders were calcined at 1200 °C for 2 h in air. The dried α-Fe_2O_3 samples thus obtained were ground during various times using a Fritsch Planetary-Micro-Pulveriser (P-7 type) equipped with a cylindrical agate vessel (12 ml volume) and four agate balls (12 mm diameter). Finally, five α-Fe_2O_3 samples, F1, F2, F3, F4 and F5, were prepared according to grinding time, 0, 30, 60, 300 and 600 min. These samples were characterized by ETA, in addition to the usual methods of size distribution, BET surface, X-ray diffraction (XRD) and SEM.

Apparatus and procedures

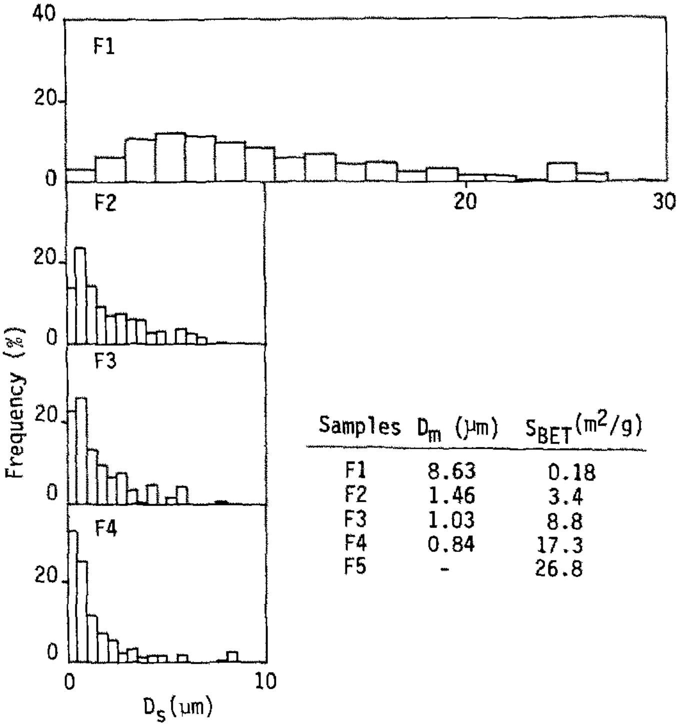
The size distributions of the sample powders were obtained automatically by means of the centrifugal sedimentation method (Horiba CAPA-300), using transmittance of light.

The apparatus for ETA was the Netzsch ETA403-STA409 instrument, which allows simultaneous ETA–DTA–TG measurements. The standard experimental conditions of ETA were as follows: sample weight, 100 mg; nitrogen carrier gas, flow-rate 50 ml min^{-1}; heating and cooling rates, 10 °C min^{-1}; threshold, 2 MeV; time constant, 100 s. The samples were labeled by a surface impregnation method using an aqueous ^{226}Ra solution (≈ 4 μCi ml^{-1}) and then dried under an infrared lamp without further washing of the surface of the labeled powders. Before being used for ETA studies, either in the first or in subsequent runs, the dried labeled samples were stored for periods in excess of one month so that radioactive equilibrium could be attained. The rates of radon release dF/dt (in cpm) were normalized to a weight of 100 mg of the labeled samples.

Interpretation of ETA curves

A comprehensive review of ETA has been presented by Balek [10]. An impregnation method was used for labeling the sample; ^{226}Ra nuclide was adsorbed onto the sample surface, and ^{222}Rn nuclide was thus embedded by the recoil energy. Once radioactive equilibrium had been reached in the dry labeled sample, ^{222}Rn was found to have been distributed in a surface layer less than 50 nm thick. Therefore, information obtained from the ETA experiments is related to the behavior of the near-surface of powders ($<$ 50 nm) during a temperature rise.

Balek [11] proposed that radon release from a dispersed solid with increase in temperature may be separated into three parts: (a) a recoil part, E_r, due to the energy that a radon atom gains during its formation by the decay of radium; (b) a diffusion part, E_p, due to diffusion via intergranular spaces, open pores, etc., of the dispersed powder; and (c) a diffusion part, E_d, due to the bulk diffusion of radon via the solid matrix of the dispersed powder. E_r is independent of temperature. E_p, which is dependent on temperature and on the dispersity or morphology of the powders, is negligible at room temperature. E_d is exponentially dependent on temperature and dependent on the effective surface area of the powder.



Samples	D_m (μm)	S_{BET}(m^2/g)
F1	8.63	0.18
F2	1.46	3.4
F3	1.03	8.8
F4	0.84	17.3
F5	-	26.8

Fig. 1. Size distributions, median diameters (D_m) and BET surfaces (S_{BET}) of samples subjected to various grinding treatments.

Matzke [12] has shown that gas release because of E_d starts at 40–50% of the absolute melting temperature, T_m, for a wide variety of ionic crystals with different lattice structures. The onset temperatures of gas release in the E_d part are similar to those of self-diffusion of the lattice ions, T_s. For the gas diffusion mechanism, the relation with self-diffusion indicates that the gas probably migrates via small vacancy clusters.

On the basis of the above, the characteristic peaks in the ETA curves observed in this work were grouped into two main stages: stage I, at temperatures lower than $T_s = (0.4–0.5)T_m$, and stage II, due to E_d at temperatures higher than T_s, 456–639°C for α-Fe_2O_3. The ETA peaks corresponding to stages I and II are hereinafter designated peaks I and II, respectively. In many cases, peak II was split into two peaks, IIa and IIb.

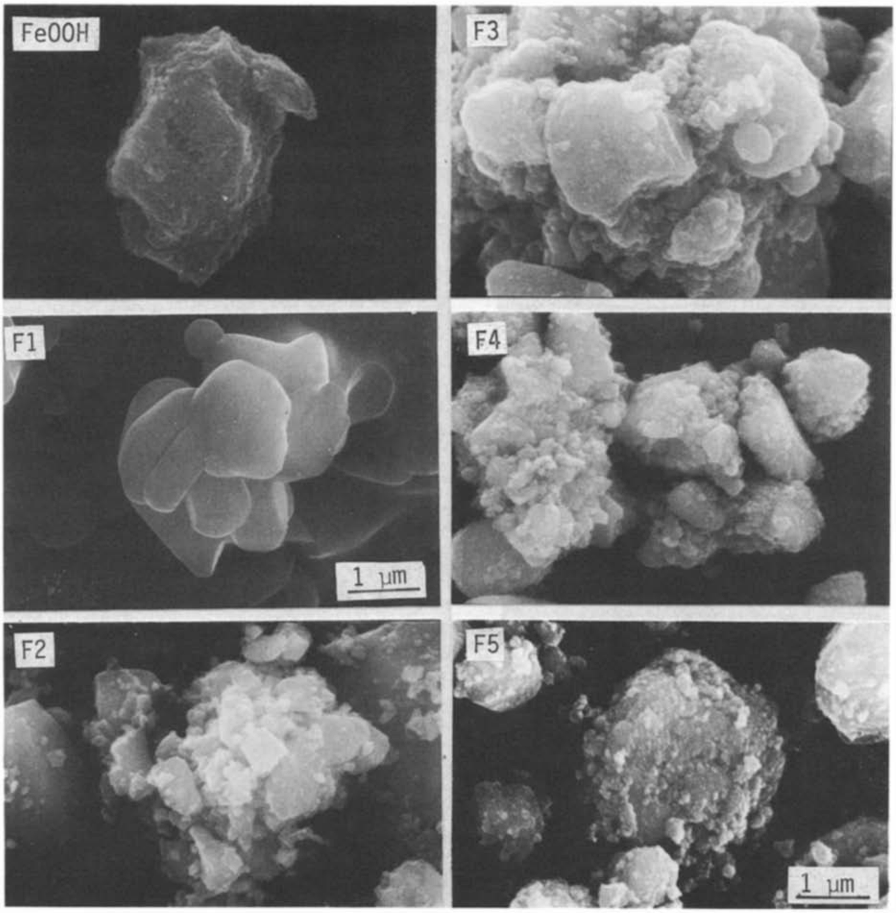


Fig. 2. Scanning electron micrographs of α-FeOOH and α-Fe_2O_3 powders with various grinding treatments. The scale bar applies to all mimicrographs.

RESULTS AND DISCUSSION

Size distribution

Figure 1 shows the size distribution of four samples, F1, F2, F3 and F4. The grinding times used were 0 min (F1), 30 min (F2), 60 min (F3) and 300 min (F4), respectively. From the results, the median diameters of the sample particles, D_m, were calculated. BET surfaces, S_{BET}, were also measured for these samples. A remarkable grinding effect appears for the sample ground for 30 min, F2, compared with the non-ground sample, F1.

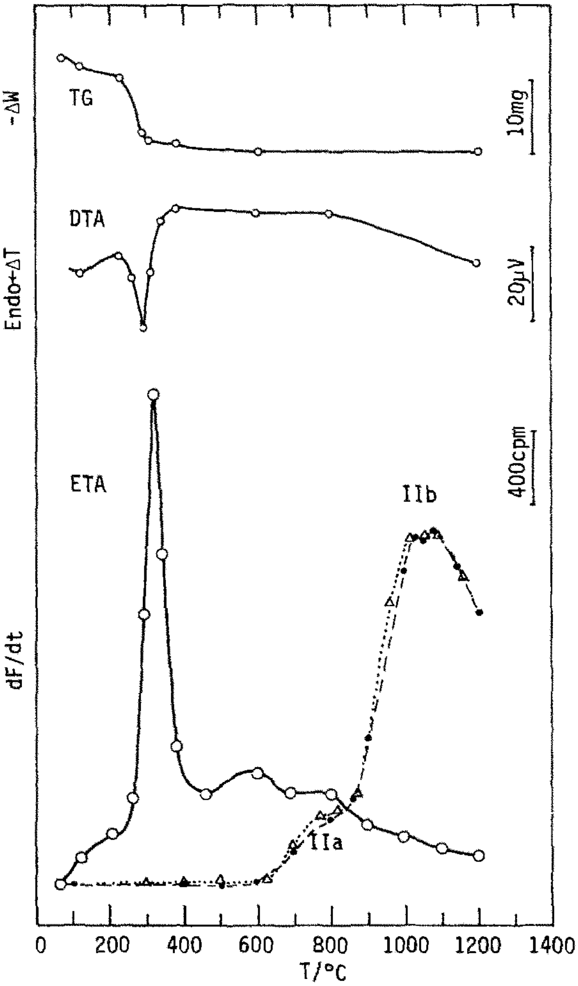


Fig. 3. ETA–TG–DTA curves for α-FeOOH powders. ○——○ run 1; ●— — —● run 2; △······△ run 3.

Scanning electron microscopy

Figure 2 shows the scanning electron micrographs of α-FeOOH and α-Fe_2O_3 powders with various grinding treatments. As shown in Fig. 1, a remarkable phenomenological change relative to the unground sample, F1, appears for the sample ground for 30 min, F2.

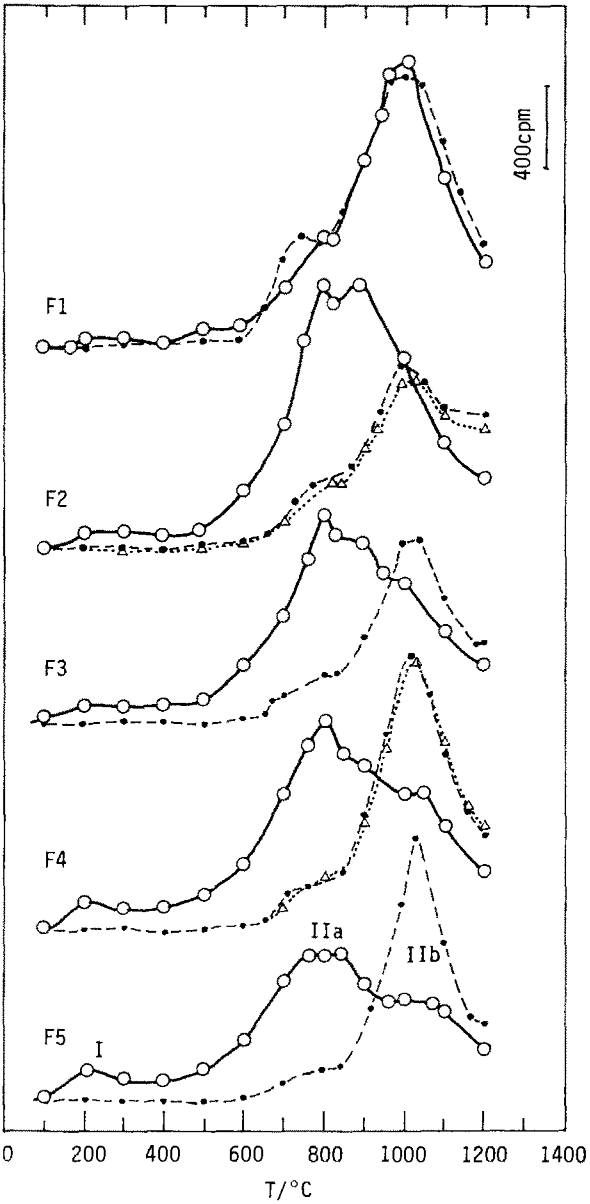


Fig. 4. ETA curves for α-Fe_2O_3 samples with various grinding treatments. ○———○ run 1; ●— — —● run 2; △· · · · · ·△ run 3.

Figure 3 shows the ETA–TG–DTA curves for α-FeOOH powder as a starting material in the range 25–1200 ° C. In the first heating run (run 1), the ETA peak at about 300 ° C corresponds to the changes of both the weight decrease in TG and the endothermic peak in DTA, which were caused by the decomposition to α-Fe_2O_3. In the second run (run 2) for the α-Fe_2O_3 which has been formed in run 1, the ETA peak at 300 ° C disappears and two peaks appear: peak IIa starting at about 600 ° C corresponding to the temperature T_s, reaching a shoulder-like maximum at 800 ° C, and peak IIb, reaching a maximum at about 1050 ° C. The ETA curves of the third run (run 3) agree with those of run 2. Thus, when α-Fe_2O_3 had been heated to 1200 ° C in run 1, it attained a thermally stable state. No change was observed between the TG–DTA curves of runs 2 and 3. It is thought that peak IIa corresponds to gas release from defect structures such as the grain boundary (dislocation) or the amorphous part present in the surface layer.

Figure 4 shows the ETA curves for α-Fe_2O_3 samples F1, F2, F3, F4 and F5. The ETA curve of F1 (without grinding treatment) is similar to that of run 2 in Fig. 3. The ETA curves in run 1 for F2–F5, which were prepared with various grinding times, show a significant difference from that for F1; an increasing peak I, and a pronounced peak IIa starting at about 500 ° C and reaching a maximum at about 800 ° C.

It is thought that these changes result from the mechanochemical effects of grinding on the ETA curves, and show a deterioration of the texture and an increase of the grain boundary (dislocation) or the amorphous part in the surface layer. All the curves in runs 2 and 3, however, lead to the ETA curve of F1, with a large peak IIb at 1000 ° C and peak IIa at 800 ° C as a shoulder.

These results show that ETA is applicable as a useful means of characterization of surface layers affected by mechanochemical effects.

REFERENCES

1 T. Ishii, Thermochim. Acta, 88 (1985) 277.
2 T. Ishii, Thermochim. Acta, 93 (1985) 469.
3 T. Ishii, Thermochim. Acta, 109 (1986) 227.
4 T. Ishii, Thermochim. Acta, 137 (1989) 293.
5 T. Ishii, React. Solids, 6 (1988) 1.
6 T. Ishii, React. Solids, 3 (1987) 85.
7 T. Ishii, React. Solids, 4 (1988) 327.
8 T. Ishii, React. Solids, 6 (1988) 11.
9 T. Ishii, T. Takemura, S. Nakado and A. Yada, Thermochim. Acta, 178 (1991) 117.
10 V. Balek, Thermochim. Acta, 22 (1978) 1.
11 V. Balek, J. Mater. Sci., 17 (1982) 1269.
12 H. Matzke, Can. J. Phys., 46 (1968) 6.