

THERMAL CHARACTERIZATION AND REACTIVITY OF METAL OXIDE POWDERS BY EMANATION THERMAL ANALYSIS USING Ra-226 PARENT ISOTOPE

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ABSTRACT

Emanation thermal analysis using Ra-226 parent isotope was successfully applied to the characterization of the near-surface and the initial reactivity of metal oxide powders with various preparation histories.

INTRODUCTION

A powder reaction generally starts with phase-boundary reactions followed by transport through the bulk of the newly formed phase. The importance of the phase-boundary reaction that takes place in a near-surface of the powders during the initial reaction step increases with decrease in particle size. In this paper, the usefulness of emanation thermal analysis (ETA) in studying the thermal behaviour of the near-surface of oxide powders under the working state at high temperatures is discussed on the basis of some experimental results selected from previous papers.

EXPERIMENTAL

Reagent-grade commercial chemicals were used for all starting materials without further chemical purification. The apparatus and conditions for ETA experiments were given in ref. 1. Sample powders were labelled by a surface-impregnation method using Ra-226 solution ($3\text{--}4 \mu\text{Ci ml}^{-1}$). Before being used for ETA experiments, in both first and repeated runs, the dried, labelled samples were stored for periods exceeding 1 month in order to attain the radioactive equilibrium state. The daughter inert gas atom, Rn-222, was introduced into a surface layer about 50 nm thick by recoil energy. In

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order to measure the reactivity of oxide powders, labelled (denoted by an asterisk) and non-labelled powders were mixed with acetone in an agate mortar. The non-labelled powder in the mixing system was hardly labelled by Ra-226 atoms adsorbed on the surface of the labelled powders. This means that the zones of effective chemical contact between particles are extremely small.

RESULTS AND DISCUSSION

Thermal characterization

The ETA curves of Fe_2O_3 [1–3], TiO_2 [2] and Al_2O_3 [1] powders with different preparation histories of heating and grinding treatments have been reported. The curves obtained from the ETA experiments may be correlated with the thermal behaviour of the near-surface of powder. The gas release steps have been discussed in detail by Balek [4] and Matzke [5].

The characteristic changes in the ETA curves for the above oxide powders were observed in the following three peaks: peak I, due to the diffusion in the intergranular space, open micro-pores, etc., at temperatures lower than $(0.4-0.5)T_m$, peak I', which appears at a temperature of about $(0.4-0.5)T_m$, and peak II, due to the bulk diffusion of radon in the solid matrix of the

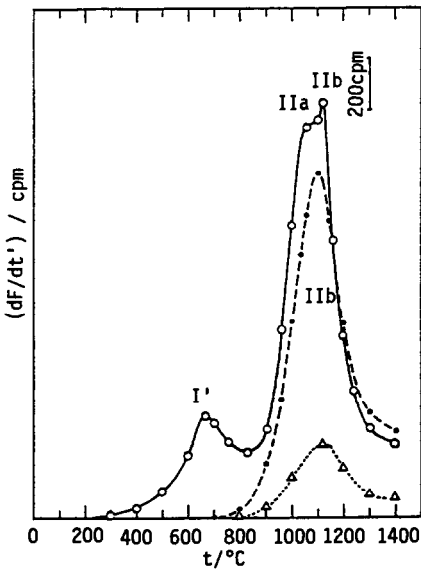


Fig. 1. ETA curves for antase and rutile. (○—○), first run; (●-----●), second run; (△·····△), third run.

powder at temperatures higher than $(0.4-0.5)T_m$, where T_m (K) is the melting temperature. The temperature $(0.4-0.5)T_m$ corresponds to the onset of self-diffusion of matrix atoms.

In general, the behaviour of the ETA peaks obtained can be summarized as follows. Both peaks I and I' appear by a mechano-chemical effect during the preparation of sample, and they disappear with heat treatment at relatively low temperatures. Peak II shifts to higher temperatures, and in some instances becomes small, on heat treatment. This behaviour of peak II results from the annealing causing lattice ordering and sintering causing a decrease in surface area, respectively.

As an example, the ETA curve of TiO_2 (anatase) is shown in Fig. 1 (solid line). Peaks I' and II appear in this sample. Peak II separates into two, IIa (anatase) and IIb (rutile), resulting from the anatase-rutile transition in the range $1000-1100^\circ\text{C}$. In repeated runs (dashed and dotted lines), only peak IIb, corresponding to rutile, appears, and its height decreases with repeated heat treatment.

Reactivity

In order to measure the initial reactivity of Fe_2O_3 and TiO_2 powders with different preparation histories, ETA has been applied to the Fe_2O_3 -ZnO and TiO_2 - BaCO_3 reaction systems [2]. As an example, TG-DTA-ETA curves of BaCO_3 alone and TiO_2 (rutile)- BaCO_3 systems are shown in Figs. 2 and 3, respectively.

For BaCO_3 alone (Fig. 2), the TG-DTA curves show that the decomposition of BaCO_3 to BaO and CO_2 is initiated at about 1000°C . A sharp endothermic peak at 820°C in DTA corresponds to the transition to

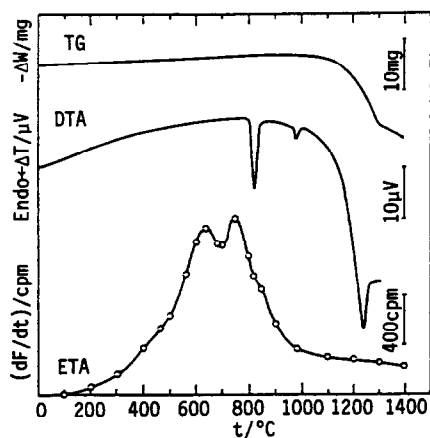


Fig. 2. TG-DTA-ETA curves for BaCO_3 .

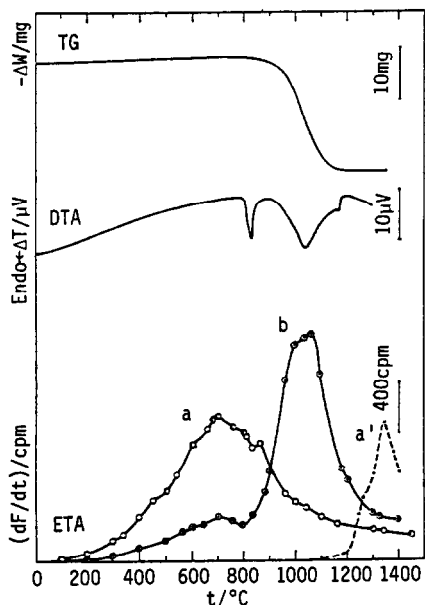


Fig. 3. TG-DTA-ETA curves for $\text{TiO}_2(\text{rutile})\text{-BaCO}_3$ systems. (a) Rutile- BaCO_3^* ; (b) rutile*- BaCO_3 ; (a') repeated run on rutile- BaCO_3^* . Asterisks denote the labelled samples.

$\beta\text{-BaCO}_3$. In the ETA curve, on the other hand, a large peak that is split into two parts appears at around 700°C . This suggests that a reconstruction of crystal lattice of BaCO_3 occurs at around 700°C which is much lower than the temperature of the initiation of BaCO_3 decomposition. An ETA peak corresponding to the transition to $\beta\text{-BaCO}_3$ appears as only a small shoulder.

For the $\text{TiO}_2(\text{rutile})\text{-BaCO}_3$ system (Fig. 3), the TG-DTA curves show that the decomposition of BaCO_3 is promoted and is initiated at about 800°C . The rutile sample used was prepared by calcining anatase at 1200°C for 1 h, and its ETA curve agreed very closely with that of the second run in Fig. 1. The high-temperature X-ray diffraction pattern for this system showed that the formation of BaTiO_3 is initiated at about 800°C , and this is fully consistent with the TG-DTA results. The ETA curves are indicated by two systems, (a) $\text{TiO}_2\text{-BaCO}_3^*$ and (b) $\text{TiO}_2^*\text{-BaCO}_3$. Both curves (a) and (b) differ from that of BaCO_3 alone and rutile alone, respectively. In curve (b), the appearance of a new peak at around 700°C probably means that some mutual interactions between TiO_2 and the disordered BaCO_3 occurred at around 700°C , and an amorphous intermediate was formed at the near-surface of powder in the initial reaction step, prior to the decomposition of BaCO_3 and recrystallization to the product BaTiO_3 . The large peak initiated at about 800°C corresponds to the behaviour of TG-DTA curves. Curve (a') is the result of a repeated run on (a), and corresponds to that of

the product. For the TiO_2 (anatase)– BaCO_3 system, the promoting effect on the decomposition of BaCO_3 was much greater than that of rutile.

The results described above suggest that ETA can provide useful information for considering the reactivity of solids in the initial reaction step.

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