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Note

ON THE TRANSITION TEMPERATURES OF $BaCO_3$ AND $SrCO_3$ AS DTA TEMPERATURE REFERENCE MATERIALS

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In the course of the temperature calibration work of our DTA apparatus, we noticed that the peak temperatures of $BaCO_3$ and $SrCO_3$ were slightly shifted in flowing CO_2 and N_2. In this note, the results of the examination of these behaviours are briefly described.

EXPERIMENTAL

The materials used in this study were as described.

(1) $BaCO_3$ and $SrCO_3$ from NBS-ICTA Standard Reference Material GM-760. T_p: $BaCO_3$, 819°C; $SrCO_3$, 938°C [1].

(2) Reagents $BaCO_3$ and $SrCO_3$ manufactured by Wako Pure Chemical Ind., Ltd., Osaka, Japan. These materials are used for comparison purposes with NBS-ICTA materials.

(3) Witherite from Settlingstone, Cumberland, England. Chemical composition; $BaCO_3$, 90.39; $SrCO_3$, 9.17; $CaCO_3$, 0.44. Strontianite from Drensteinfurt, Westfalia, Germany. Chemical composition: $BaCO_3$, 0.00; $SrCO_3$, 90.08; $CaCO_3$, 9.92.

In addition, in order to examine instrumental effects on the DTA peak shift, K_2CrO_4 (NBS-ICTA Standard Reference Material GM-760, $T_p = 673°C$ [1]) and high purity metallic silver are also used. The metallic silver has a melting point at about 960°C. The peak temperature of K_2CrO_4 is below while that of Ag is above the transition temperatures of $BaCO_3$ and $SrCO_3$.

DTA curves are recorded with a partially modified commercial apparatus incorporating a Pt–PtRh 13% thermocouple, a Pt micro sample pan (in the measurement of metallic silver, a micro pan of silica glass is used) and calcined alumina as a reference material, under the given conditions: sample weight, 5.0 mg (in the case of metallic silver, 15.0 mg); programmed heating rate, 10°C min^{-1}; DTA sensitivity, ± 50 μV. Under these conditions, the peak temperatures are reproducible within ± 1 K. Measurements are carried out in the mixing gas flow of CO_2 and N_2 in various CO_2/N_2 ratios, keeping

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the total flow rate at 100 ml min^{-1}. The gas flows upward past the sample pan. Only natural minerals are ground in an agate mortar and fractions finer than 325 mesh (43 μm) are used.

RESULTS AND DISCUSSION

The values of T_p for NBS-ICTA $BaCO_3$ are almost constant in the range 100–10% CO_2 in the CO_2/N_2 mixture, while slight decreases are detected in flowing N_2 (Fig. 1). Such behaviour is hardly recognizable in witherite. On the other hand, the values of T_p for the reagent $BaCO_3$ decrease continuously with decrease of CO_2 in the CO_2/N_2 ratio. Like NBS-ICTA $BaCO_3$, NBS-ICTA $SrCO_3$ also shows almost constant T_p values in the range 100–10% CO_2 in the CO_2/N_2 mixture (Fig. 2). However, in contrast with $BaCO_3$, an increase in T_p is observed for $SrCO_3$ in flowing N_2. Similar behaviour is evident in both the reagent $SrCO_3$ and strontianite. In the N_2 flow, strontianite shows the largest shift of T_p in the $SrCO_3$ group, while witherite shows the smallest shift in the $BaCO_3$ group. Furthermore, K_2CrO_4 and metallic silver clearly indicate that their T_p values are not affected by the CO_2/N_2 ratio (Fig. 3). This suggests that the temperature shifts found in the $BaCO_3$ and $SrCO_3$ groups could be attributed to the effects arising within the materials themselves, and not to the instrumental effects.

According to their DTA curves, $SrCO_3$ and $BaCO_3$ decompose at tempera-

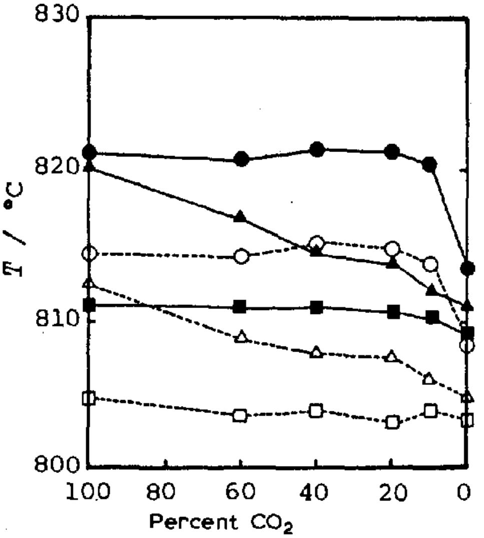

Fig. 1. T_e and T_p values for the $BaCO_3$ group at various percentages of CO_2 in CO_2/N_2 mixtures. ○●, NBS-ICTA $BaCO_3$; △▲, reagent $BaCO_3$; □■, witherite; - - - - - -, T_e; ———, T_p.

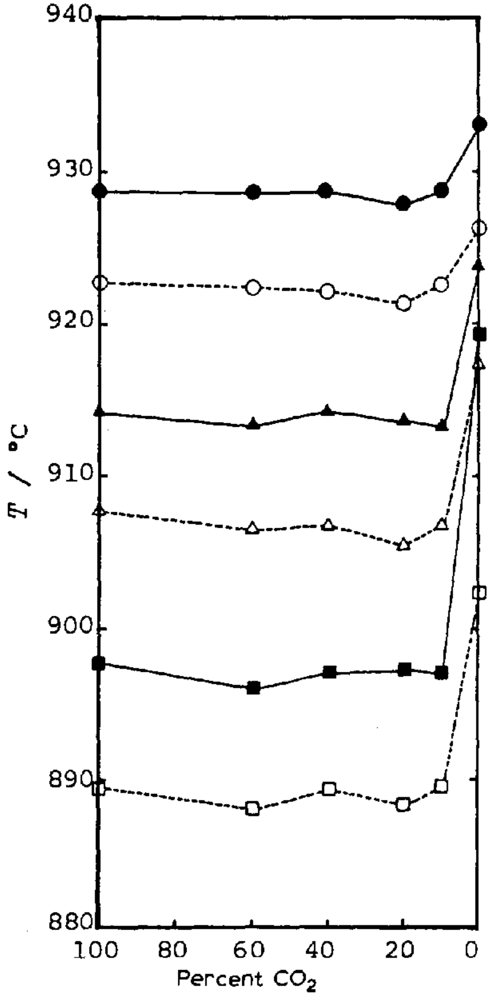

Fig. 2. T_e and T_p values for the $SrCO_3$ group at various percentages of CO_2 in CO_2/N_2 mixtures. ○●, NBS-ICTA $SrCO_3$; △▲, reagent $SrCO_3$; □■, strontianite; - - - - - -, T_e; ————, T_p.

tures above 1000°C (e.g.: $BaCO_3$, 1350°C; $SrCO_3$, 1000°C [2]). However, in air or in a flowing N_2 atmosphere having a low CO_2 partial pressure, it is highly probable, as suggested by some previous investigators [3,4], that the decompositions of $BaCO_3$ and $SrCO_3$ begin before their transitions. Although it is difficult to observe the base-line shift due to the preceding decomposition on the DTA curve of NBS-ICTA $SrCO_3$ in the N_2 flow [Fig. 4, curve (1)], the remarkable decrease of its peak area, compared with that in CO_2 [Fig. 4, curve (2)], strongly suggests that the decomposition begins just prior to the transition in N_2. In order to clarify this, TG curves are recorded in the N_2 flow. The curves of the $SrCO_3$ group clearly indicate

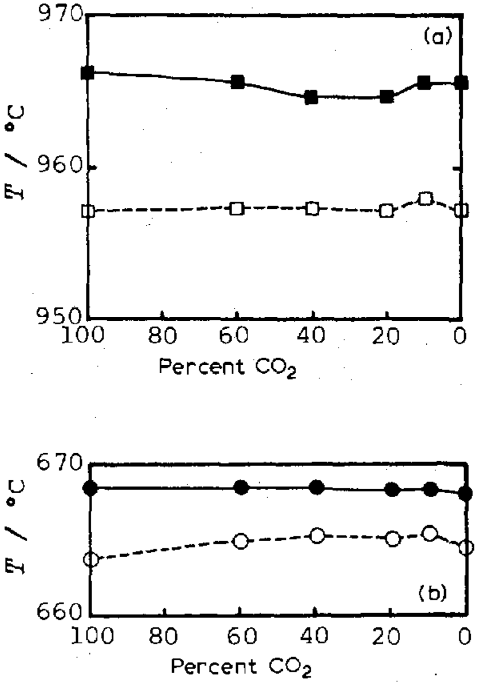

Fig. 3. T_e and T_p values for: (a), metallic silver; (b) NBS-ICTA K_2CrO_4 at various percentages of CO_2 in CO_2/N_2 mixtures. - - - - - -, T_e; ————, T_p.

that the decomposition begins at lower temperatures than its transition. On the other hand, the $BaCO_3$ group does not show any detectable weight loss in the temperature region around its transition.

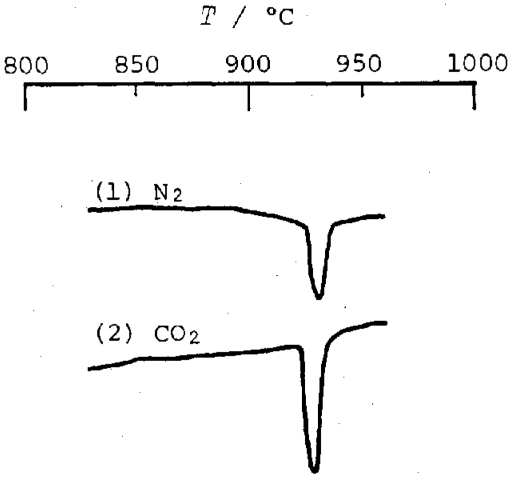

Fig. 4. DTA peaks of NBS-ICTA $SrCO_3$ in flowing N_2 and CO_2. (1), N_2; (2), CO_2.

Figure 5 shows the calculated equilibrium curves of the decomposition of $CaCO_3$ (calcite) (A), $SrCO_3$ (B) and $BaCO_3$ (C). The straight line, 1, representing 10% CO_2 in the CO_2/N_2 mixture intersects with curves B and C at higher temperatures than the transition of $SrCO_3$ and $BaCO_3$. This shows that their transition will take place at lower temperatures than the beginning of their decomposition in an atmosphere of 10% CO_2 in the CO_2/N_2 mixture. So their transition temperatures will remain constant in an atmosphere of more than 10% CO_2 in the CO_2/N_2 mixture, since their transitions are not affected by their decompositions. The observed constancy of T_p of $BaCO_3$ and $SrCO_3$ in the range 100–10% CO_2 in the CO_2/N_2 mixture could thus be explained.

Though both are expected thermodynamically to decompose at a fairly low temperature in the N_2 flow, it is observed that $SrCO_3$ decomposes at a lower temperature than its transition while $BaCO_3$ does not. The results may be explained using the assumptions that (1) $BaCO_3$ and $SrCO_3$ as well as $CaCO_3$ decompose at the temperature calculated thermodynamically and (2) CO_2 gas evolved from the sample during its decomposition is not completely exhausted even in the N_2 flow, but is accumulated in the immediate vicinity of the sample and makes the local partial pressure around the sample increase to a definite pressure (hereafter, it is expressed as the saturated CO_2 pressure).

When heated in the N_2 flow, the decomposition of the carbonate will start at a fairly low temperature with the formation of the saturated CO_2 pressure. Further decomposition will be delayed until the sample reaches a tempera-

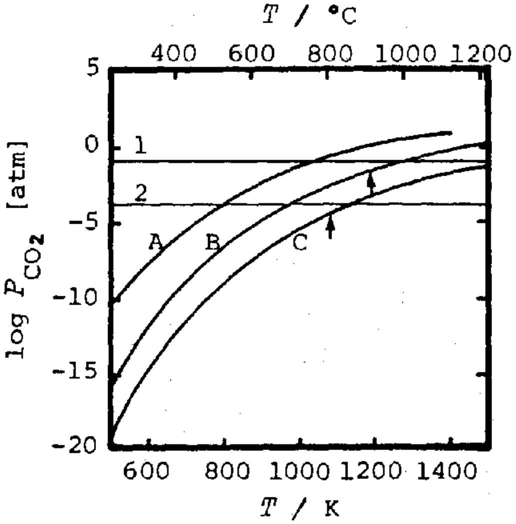

Fig. 5. Equilibrium decomposition CO_2 partial pressure vs. temperature curves of $CaCO_3$, $SrCO_3$ and $BaCO_3$. A, $CaCO_3$; B, $SrCO_3$; C, $BaCO_3$; 1, 10% of CO_2 in CO_2/N_2 mixture; 2, saturated CO_2 pressure; ↑, equilibrium transition temperature.

ture at which the equilibrium decomposition pressure of CO_2 exceeds the saturated CO_2 pressure. Above this temperature, the decomposition will proceed appreciably, giving a distinct shift from the base line to an endothermic side of the DTA curve. Therefore, from the temperature at which the endothermic peak due to the decomposition begins to form, it is possible to estimate the saturated CO_2 pressure equivalent to the equilibrium decomposition pressure at that temperature. Using $CaCO_3$, the temperature at which the endothermic peak begins to form is found to be 500°C, so the saturated CO_2 pressure could be estimated as $\log P_{CO_2} = -3.85$ (1.4×10^{-4} atm) from curve A in Fig. 5. TG measurement indicates that the temperatures at which decomposition begins for $SrCO_3$ and $BaCO_3$ are 730 and 850°C, respectively. These values are closely consistent with those indicated by the intersections of curves B and C with the straight line 2 representing the estimated saturated CO_2 pressure. This fact supports the foregoing assumptions that, in the decomposition of the carbonate, a definite CO_2 partial pressure is maintained in the immediate vicinity of the sample even in the N_2 flow and that the carbonates examined in this study obey the thermodynamic equilibrium condition when they decompose.

Since the line 2 in Fig. 5 lies between the equilibrium CO_2 pressures at the transition temperatures of $BaCO_3$ and $SrCO_3$, it is well understood that $SrCO_3$ begins to decompose before its transition in the N_2 flow, and that $BaCO_3$ does not. In the case of $SrCO_3$, the decomposition, immediately before and partly overlapped with the transition, proceeds inward from the surface of each particle, consuming a large part of the heat which is being supplied from the furnace. Therefore, the unreacted $SrCO_3$ will reach the transition temperature more slowly, compared with the case when the decomposition does not occur near the transition temperature. This delay will make the peak move to a higher temperature. With respect to the peak shift of $BaCO_3$, the interpretation is impossible at present, and further study will be necessary.

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