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ISOTHERMAL DIFFERENTIAL SCANNING CALORIMETRY ON AN EXOTHERMIC PHENOMENON DURING THERMAL DECOMPOSITION OF HYDROMAGNESITE $4\ MgCO_3 \cdot Mg(OH)_2 \cdot 4\ H_2O$

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ABSTRACT

An exothermic phenomenon and a simultaneous rapid evolution of a small amount of carbon dioxide at ~500°C during thermal decomposition of hydromagnesite $4\ MgCO_3 \cdot Mg(OH)_2\ 4\ H_2O$ was studied by isothermal DSC—TG in a carbon dioxide atmosphere. It was quantitatively confirmed that the exothermic phenomenon was due to crystallization of $MgCO_3$ from the amorphous phase and that the evolution of carbon dioxide was due to decomposition of the $MgCO_3$ by the heat of crystallization (~3.4 kcal $mole^{-1}$).

INTRODUCTION

Thermal decomposition of hydromagnesite $4\ MgCO_3 \cdot Mg(OH)_2 \cdot 4\ H_2O$ proceeded via dehydration at 100—300°C and decarbonation at 350—650°C toward MgO. A sharp exothermic phenomenon was found at 500°C during the decarbonation process in carbon dioxide atmospheres with a simultaneous rapid evolution of a small amount of carbon dioxide [1—6].

The following assumptions were made and confirmed qualitatively in our previous papers [7—10].

(1) the exothermic phenomenon was attributed to the crystallization of $MgCO_3$ from the amorphous phase;

(2) the simultaneous rapid evolution of carbon dioxide was attributed to thermal decomposition of $MgCO_3$ by the heat of crystallization;

(3) this decomposition was strongly influenced by the heat transfer within the packed specimen.

These assumptions were confirmed quantitatively in the present work by the isothermal DSC—TG technique.

THEORY

It was assumed that the heat of crystallization from amorphous $MgCO_3$ into crystalline $MgCO_3$ was partially compensated by the heat of decomposi-

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tion; the resultant $MgCO_3$ crystal decomposed to MgO crystal and CO_2 gas. The overall process is the change of amorphous $MgCO_3$ (1 mole) into $MgCO_3$ crystal ($1-x$ mole), MgO crystal (x mole) and CO_2 gas (x mole). The enthalpy change of crystallization ($\Delta H_{\mathrm{cryst}}$) is given by

$$\Delta H_{\mathrm{cryst}} = H_{\mathrm{MgCO_3\ cryst}} - H_{\mathrm{MgCO_3\ amor}} \tag{1}$$

where $H_{\mathrm{MgCO_3\ cryst}}$ and $H_{\mathrm{MgCO_3\ amor}}$ are the enthalpy of the crystalline and amorphous $MgCO_3$, respectively. The enthalpy change of the decomposition ($\Delta H_{\mathrm{decomp}}$) is

$$\Delta H_{\mathrm{decomp}} = H_{\mathrm{MgO\ cryst}} + H_{\mathrm{CO_2\ gas}} - H_{\mathrm{MgCO_3\ cryst}} \tag{2}$$

where $H_{\mathrm{MgO\ cryst}}$ and $H_{\mathrm{CO_2\ gas}}$ are the enthalpy of MgO and carbon dioxide, respectively. The $\Delta H_{\mathrm{decomp}}$ is -22.9 kcal $\mathrm{mole^{-1}}$ at 800 K, $P_{\mathrm{CO_2}} = 1$ atm [11]. These relations are written as follows

$$\Delta H_{\mathrm{obs}} = \Delta H_{\mathrm{cryst}} + x\,\Delta H_{\mathrm{decomp}} \tag{3}$$

where ΔH_{obs} is the apparent heat of crystallization calculated from the peak area of the DSC; x was determined from the sudden weight loss in TG which was recorded simultaneously.

A small amount of intermediate decarbonation observed during the isothermal holding periods was neglected in this assumption.

EXPERIMENTAL

Specimen

Magnesium hydroxide carbonate G.R. (Merck, West Germany) was used as in our previous works [8—10]. The MgO : CO_2 : H_2O molar ratio determined by the compositional analysis (1.00 · 0.80 . 1.12) was very close to that of pure hydromagnesite (1.00 : 0.80 : 1.00).

The composition immediately before and after the exothermic phenomenon was calculated from the weight change. In this calculation, the dehydration was assumed to be completed prior to the decarbonation.

DSC—TG

Standard type DSC—TG, Rigaku Denki Co., Japan, was used in a carbon dioxide atmosphere. The specimen powder (~5—14 mg) was placed in an aluminum sample pan (~5 mmϕ × ~2.5 mm) and covered with an aluminum plate (~5 mmϕ). The cover was pressed with a pressing machine to enhance the thermal conductivity. The specimen was heated at a heating rate of ~10°C $\mathrm{min^{-1}}$ and held at a predetermined temperature (~470—500°C). The error in measurement was approximately ±5% of the absolute value.

RESULTS

Isothermal DSCs for the exothermic phenomenon of hydromagnesite at various holding temperatures are shown in Fig. 1. The time where the exo-

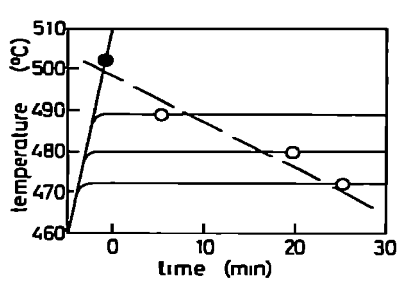
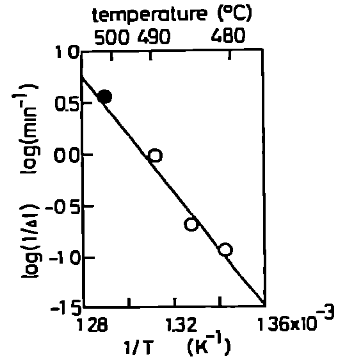
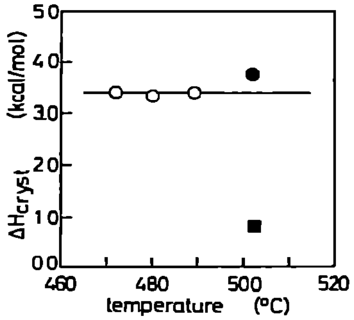


Fig. 1. Isothermal DSC for the exothermic phenomenon of hydromagnesite with various holding temperatures. ———, heating schedules; ●, an exothermic phenomenon with a sudden weight loss; ○, an exothermic phenomenon without a weight loss. Specimen weight: ~8 mg; atmosphere: carbon dioxide.

thermic phenomenon occurred decreased as the holding temperature increased. Crystallization of $MgCO_3$ was affected by the heating condition. The crystallization of $MgCO_3$ and the simultaneous sudden weight loss was observed at ~500°C when the specimen was heated-up continuously. The crystallization took place at a lower temperature in the isothermal condition.

The exothermal peak became sharper as the holding temperature increased. The half-width of the peak reflects the approximate rate of the crystallization. Negative logarithms of the half-widths (Δt (min)) are plotted against the reciprocal absolute temperatures of holding in Fig. 2 The activation energy calculated tentatively was ~56.8 kcal mole^{-1}. This value was much smaller than that determined from the DTA experiments of our previous work (~100—300 kcal mole^{-1}) [10]. Clearly, the rate-determining factor was very strongly influenced by the temperature.





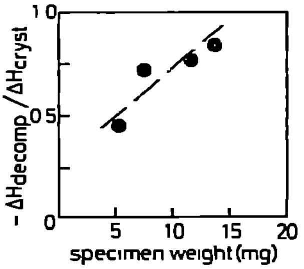


Fig. 2. The relation between log ($1/\Delta t$) and $1/T$ (Δt, half-width of DSC peak). ●, an exothermic phenomenon with a sudden weight loss; ○, an exothermic phenomenon without a weight loss. Activation energy: ~56.8 kcal mole^{-1}

Fig 3. The effect of crystallization temperature on heat associated with the exothermic phenomenon. ○, crystallization without decomposition $\Delta H_{cryst} = \Delta H_{obs} = \sim 3.4$ kcal mole^{-1}, ●, crystallization with decomposition $\Delta H_{cryst} = \Delta H_{obs} - x\ \Delta H_{decomp}$, ■, heat detected by DSC when the decomposition occurred (plotted tentatively) ΔH_{obs}.

Fig. 4. The effect of specimen weight on the heat which was consumed by decomposition of $MgCO_3$.

The assumption made in our previous papers [7—10] was supported quantitatively by DSC. The heats associated with the crystallization are plotted against the holding temperature in Fig. 3. The heat was approximately constant (~3.4 kcal mole^{-1}) when the crystallization of $MgCO_3$ occurred below 500°C. No rapid evolution of carbon dioxide took place in these cases; $\Delta H_{cryst} = \Delta H_{obs}$. When the specimen was heated-up continuously, a rapid evolution of carbon dioxide occurred simultaneously with the crystallization. The heat measured by DSC ($-\Delta H_{obs}$) was exceptionally small. The heat of crystallization calculated from eqn. (3) ($\Delta H_{cryst} = \Delta H_{obs} - x\ \Delta H_{decomp}$) agreed well with those measured at lower temperatures. The small difference was negligible due to the measurement errors in DSC and TG. This result clearly shows that the heat of crystallization was constant within the present experimental conditions. The exceptionally small heat of crystallization measured in a continuous heating mode was due to the consumption of heat by the decomposition.

Figure 4 shows the effect of specimen weight on the heat consumed by decomposition of $MgCO_3$. The ratio $-\Delta H_{decomp}/\Delta H_{cryst}$ increased as the specimen weight increased.

DISCUSSION

Rapid heating was necessary for the sharp exothermic phenomenon. When the specimen was heated rapidly, the crystallization temperature increased (Fig. 1). The rate of crystallization increased drastically at high temperature; activation energy was ~57 kcal mole^{-1}. The heat of crystallization further raised the specimen temperature. The specimen temperature increased to its decomposition point, since the heat could not disperse in a short period of time. A rapid evolution of carbon dioxide occurred only when the specimen was heated non-isothermally without being held at a constant temperature (Fig. 1).

The ratio $-\Delta H_{decomp}/\Delta H_{cryst}$ increased as the specimen weight increased (Fig. 4). The dispersion of the heat was difficult when a large amount of speciment was heated.

Suzuki and Ito [12] found evolution of carbon monoxide. Its amount was much greater than that expected from the equilibrium between carbon dioxide and oxygen. They explained the exothermic phenomenon by suggesting that the crystallization of $MgCO_3$ triggered an explosive combustion of carbon monoxide. However, the combustion of carbon monoxide cannot explain the exothermic phenomenon. The evolution of carbon monoxide was investigated in our previous paper [7]; the amount of carbon monoxide was ~1/1000 of the carbon dioxide evolved simultaneously. The heat of combustion of carbon monoxide ($CO + \frac{1}{2}\ O_2 = CO_2$) is 68 kcal mole^{-1} at 298—1300 K [11]. Assuming that the carbon monoxide burned during the exothermic phenomenon at ~500°C, the heat of combustion would be ~0.003 kcal mole^{-1} Mg. This was negligible compared with the heat of crystallization (~3.4 kcal mole^{-1}).

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REFERENCES

1 R M Dell and S.W. Weller, Trans Faraday Soc , 55 (1959) 2203.
2 N. Morandi, Mineral Petrogr. Acta, 15 (1969) 93.
3 H. Hashimoro, T Tomizawa and M. Mitomo, Kogyo Kagaku Zasshi, 71 (1968) 480.
4 W. Höland and K. Heide, Thermochim. Acta, 15 (1976) 287.
5 T. Tomizawa, S. Hara and H. Hashimoto, Yogyo Kyokai Shi, 84 (1976) 259.
6 Y. Sawada, K. Uematsu, N. Mizutani and M. Kato, J. Inorg. Nucl. Chem , 40 (1978) 979.
7 Y Sawada, K. Uematsu, N. Mizutani and M Kato, Thermochim. Acta, 27 (1978) 45.
8 Y. Sawada, K Uematsu, N Mizutani and M Kato, Nihon Kagaku Zasshi, 1 (1979) 57.
9 Y. Sawada, J. Yamaguchi, O. Sakurai, K. Uematsu, N. Mizutani and M. Kato, Thermochim Acta, 32 (1979) 277
10 Y. Sawada, J. Yamaguchi, O Sakurai, K. Uematsu, N. Mizutani and M. Kato, Thermochim. Acta, 33 (1979) 127.
11 I Barin and O. Knacke, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Heidelberg, 1973, pp. 163, 441 and 450.
12 J. Suzuki and M Ito, J. Jpn. Assoc. Mineral , Petrol Econ. Geol , 69 (1974) 275