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THERMAL DECOMPOSITION OF BASIC CARBONATES OF COPPER, ZINC AND COBALT UNDER HIGH PRESSURES

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ABSTRACT

The thermal decomposition of some basic carbonates (basic zinc and cobalt carbonates, synthesized malachite, natural malachite and natural azurite) was studied by DTA–TG, DTGA and high-pressure DTA. The thermal decomposition of basic carbonates was carried out under CO_2 and N_2 atmospheres, and the dependence of decomposition temperature on atmospheric pressure is presented and discussed.

The relationship between CO_2 pressures and peak temperatures is classified into two groups: (1) the peak temperatures increased up to a comparatively low pressure, but became nearly constant above that pressure; (2) the peak temperatures depended on pressure to a comparatively high pressure.

INTRODUCTION

Basic carbonates evolve CO_2 and H_2O on heating, but both CO_2 and H_2O are not always evolved at the same time. Their dehydration and decarbonation processes are not only affected by the kinds of carbonates, but also by the heating conditions, especially the kind of gas and its pressure.

The thermal decomposition of hydrozincite, or basic zinc carbonate, $2ZnCO_3 \cdot 3Zn(OH)_2$, finished completely around 370 °C, and the total weight loss was 23.0% as follows [1–3]:

$$2ZnCO_3 \cdot 3Zn(OH)_2 \rightarrow 5ZnO + 2CO_2 + 3H_2O$$

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The thermal analysis of cobalt carbonate, $CoCO_3 \cdot nH_2O$ showed endothermic peaks of dehydration at 85°C and decarbonation at 341°C [4]. Synthesized basic cobalt carbonates, $4CoCO_3 \cdot 5Co(OH)_2 \cdot 5H_2O$ and $4CoCO_3 \cdot 5Co(OH)_2 \cdot H_2O$, decomposed to Co_3O_4 in nitrogen gas and to CoO in vacuum, respectively. All of the water of crystallization of $4CoCO_3 \cdot Co(OH)_2 \cdot 5H_2O$ was lost between 100 and 180°C. In the temperature region 180–240°C, dehydration and decarbonation of $4CoCO_3 \cdot 5Co(OH)_2$ occurred simultaneously to give Co_3O_4 [5]. $2CoCO_3 \cdot Co(OH)_2 \cdot nH_2O$ decomposed with weight losses of ~ 5% from room temperature to 188°C and 22% from 188 to 230°C, and formed the stable phase Co_3O_4 above 230°C [6]. During thermal decomposition of basic cobalt carbonates, the final products differed according to the kind of gas of the atmosphere. For instance, basic cobalt carbonate decomposes to cobalt oxide, CoO, without air (in vacuum). Synthesized malachite, $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$, decomposed to CuO at about 295°C in air [7]. Natural malachite, $CuCO_3 \cdot Cu(OH)_2$, decomposed at 380°C in a single step and lost water and CO_2 simultaneously. Natural azurite lost weight in two steps corresponding to two DTA peaks at 320–335 and 390–395°C. These two steps involved the loss of both water and CO_2 [8].

However, the above experiments did not show the kinds of gases evolved using EGA. On decomposition with the evolution of two or more different kinds of gas, it is important to elucidate the kinds of gas in EGA to understand the correct decomposition process. Furthermore, on changing the atmosphere and its pressure, different decomposition products appear or the complex decomposition process is separated into some elementary steps.

In this study, the decomposition process of some basic carbonates was studied by using DTA–TG, DTGA (differential thermal gas analysis) and high-pressure DTA of CO_2 and N_2. The behavior of dehydration and decarbonation is discussed and summarized.

EXPERIMENTAL

Samples

The basic carbonates used were basic zinc carbonate, $2ZnCO_3 \cdot 3Zn(OH)_2$ H_2O; basic cobalt carbonate, $2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O$; synthesized malachite, $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ (Reagent Grade, Kanto Chemical Co., Japan); natural malachite, $CuCO_3 \cdot Cu(OH)_2$ (from Katanga, Zaire, Iwamoto Mineral Co., Japan); and natural azurite, $2CuCO_3 \cdot Cu(OH)_2$ (from North Korea, Iwamoto Mineral Co., Japan).

Differential thermal analysis and thermogravimetry

A Rigaku Denki type M8076 DTA–TG apparatus was used.

High-pressure differential thermal analysis and evolved gas analysis

The experimental method is similar to that previously reported [9].

X-ray powder diffraction

The sample was identified by a Rigaku Denki type 2171 X-ray diffractometer with Cu target and monochromator.

RESULTS

Basic zinc carbonate

Mechanism

Figure 1(A) shows the typical DTA–TG and DTGA curves. DTA shows the sharp endothermic peak at ~ 260°C. The TG curve has a single-step weight loss (28%), which is in agreement with the theoretical one (28.2%).

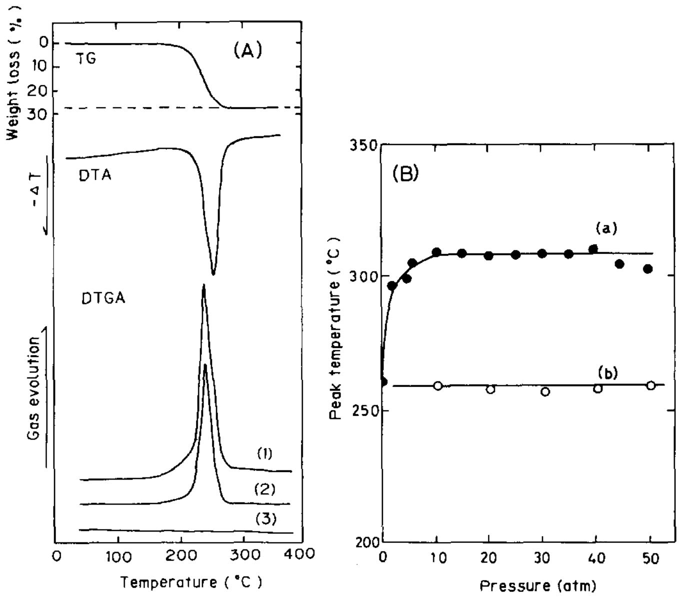

Fig. 1. (A) DTA–TG and DTGA for the thermal decomposition of basic zinc carbonate. DTA–TG: sample weight, 10 mg; heating rate, 10°C $\min^{-1}$. DTGA: sample weight, 5 mg; heating rate, 10°C $\min^{-1}$; carrier gas He, 20 ml $\min^{-1}$; (1) without trap; (2) with P_2O_5 trap; (3) with ascarite trap.

(B) Relationship between CO_2 and N_2 pressures and peak temperatures for basic zinc carbonate: (a) under CO_2; (b) under N_2.

The DTGA curve without trap (1) shows a single peak corresponding to the DTA and TG curves. This sharp peak indicates evolution of the gas. DTGA curve (2), obtained by using a P_2O_5 trap which can absorb only water, is similar to DTGA curve (1), but the peak area of curve (2) is less than that of curve (1). Furthermore, DTGA curve (3), obtained by using the ascarite trap which can absorb both water and CO_2, shows no peak.

From the above, the thermal decomposition of basic zinc carbonate, $2ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$, proceeds with simultaneous evolution of water and CO_2 in a single step:

$$2ZnCo_3 \cdot Zn(OH)_2 \cdot H_2O \rightarrow 5ZnO + 2CO_2 + 4H_2O$$

Under high pressures

Figure 1(B) shows the relationship between CO_2 and N_2 pressures and peak temperatures. The decomposition temperatures increased as CO_2 pressures increased in the range from 0 to about 10 atm, but were nearly constant above 10 atm of CO_2, and also over the whole range of N_2 pressures.

Basic cobalt carbonate

Mechanism

Figure 2(A) shows typical DTA–TG and DTGA curves. The TG curve shows two steps consisting of weight losses (about 8.3%) from room temperature to 239°C and (about 21.7%) from 230 to 280°C. The DTA curve shows two endothermic peaks at about 50 and 250°C. In DTA, curve (1) shows a first peak from room temperature to 200°C and a second peak from 200 to 265°C. The first peak is due to the evolution of water as this peak was missing when a P_2O_5 trap was used as shown in curve (2), and the second peak is based on the evolution of both water and CO_2 because in DTGA curve (2) with the P_2O_5 trap a smaller peak appeared in comparison with DTGA curve (1) without this trap, and the evolved gases were completely absorbed by the ascarite trap.

From the above results, the thermal decomposition of basic cobalt carbonate, $2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O$, proceeds with dehydration of water of crystallization in the first step and both dehydration and decarbonation of the anhydride in the second step.

$$2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O \rightarrow 2CoCO_3 \cdot 3Co(OH)_2 + nH_2O$$

$$2CoCO_3 \cdot 3Co(OH)_2 + 5/2O_2 \rightarrow 5/3Co_3O_4 + 2CO_2 + 3H_2O$$

Under high pressures

Figure 2(B) shows DTA diagrams at various CO_2 pressures. The peak profile became more sharp as CO_2 pressures increased.

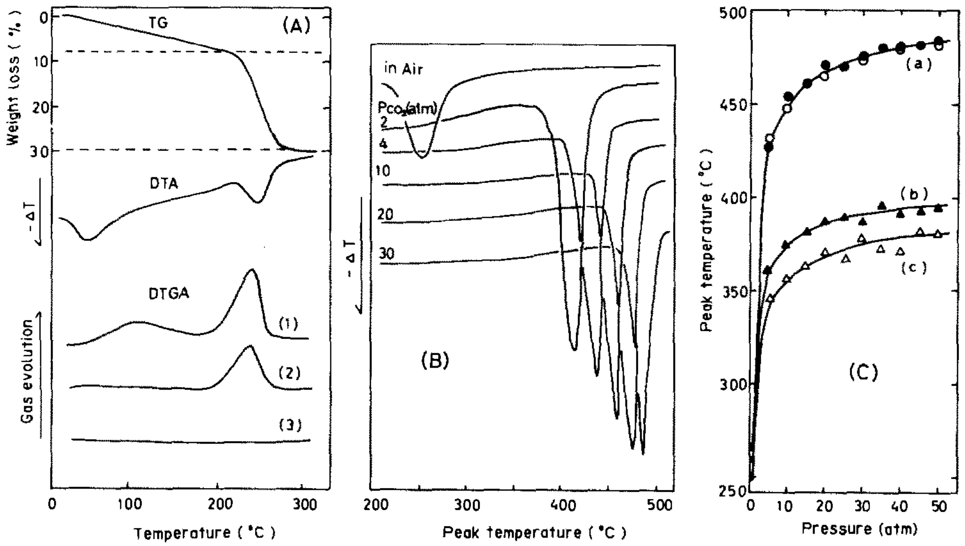

Fig. 2. (A) DTA–TG and DTGA for the thermal decomposition of basic cobalt carbonate. DTA–TG: sample weight, 10 mg; heating rate, 10°C $\min^{-1}$. DTGA: sample weight, 5 mg; heating rate, 10°C $\min^{-1}$; carrier gas He, 20 ml $\min^{-1}$; (1) without trap; (2) with P_2O_5 trap; (3) with ascarite trap.

(B) DTA diagrams of basic cobalt carbonate at various CO_2 pressures.

(C) Relationship between CO_2 and N_2 pressures and peak temperatures for basic cobalt carbonate: (●) closed sample holder under CO_2; (○) open one under CO_2; (▲) closed one under N_2; (△) open one under N_2.

Figure 2(C) shows the relationship between CO_2 and N_2 pressures and peak temperatures, which were obtained from the DTA curves using the open sample holder (without cover) and the closed one (double covers). The decomposition temperatures increased as CO_2 and N_2 pressures increased. A difference in decomposition temperature due to the sample holders (a) did not occur under CO_2 pressures but occurred under N_2 [(b) and (c)].

Basic copper carbonates

Mechanism

Typical DTA–TG and DTGA curves of synthesized malachite, natural malachite and natural azurite are shown in Figs. 3(A), (B) and (C), respectively. Decomposition behaviors of these samples are mutually similar, but the decomposition temperatures are different.

Decompositions of each sample finished in a single step with evolution of CO_2 and H_2O at the same time and gave CuO. The weight losses of 33, 28 and 31% for each sample, respectively were similar to each theoretical value, which can be expected from rational formula.

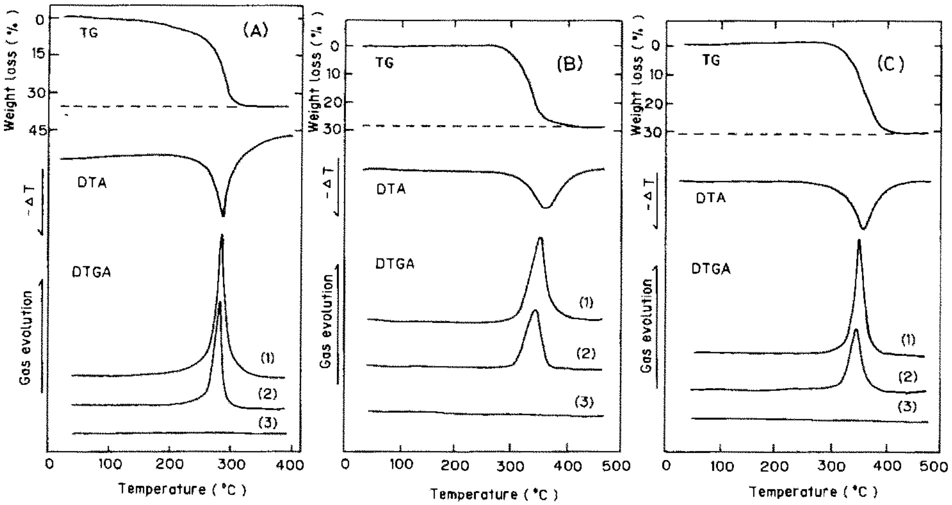

Fig. 3. DTA–TG and DTGA for the thermal decomposition of basic copper carbonates. DTA–TG: sample weight, 10 mg; heating rate 10°C min^{-1}. DTGA: sample weight, 5 mg, heating rate, 10°C min^{-1}; carrier gas He, 20 ml min^{-1}; (1) without trap; (2) with P_2O_5 trap; (3) with ascarite trap. (A) Synthesized malachite, (B) natural malachite, (C) natural azurite.

Under high pressures

Figures 4(a), (b) and (c) show the relationship between CO_2 pressures and peak temperatures for natural malachite, natural azurite and synthesized malachite, respectively. The relationship between N_2 pressures and peak temperatures for synthesized malachite is shown in Fig. 4(d). The decom-

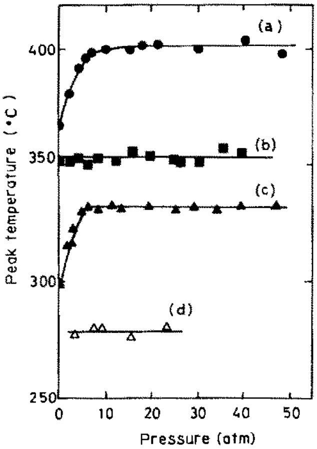

Fig. 4. Relationship between CO_2 (closed symbols) and N_2 (open symbols) pressures and peak temperatures for natural malachite (a), natural azurite (b), and synthesized malachite (c) and (d).

position temperatures for (a) and (c) increased as CO_2 pressure increased until a certain pressure of CO_2. However, above this pressure, the decomposition temperatures became almost constant. The decomposition temperatures for (b) and (d) were nearly constant, even if CO_2 pressures increased.

DISCUSSION

With respect to the phenomena under CO_2 pressures, the relationship between CO_2 pressures and peak temperatures can be classified as follows:

Type (1). The peak temperatures increase in the comparative low pressure region but become nearly constant above low pressures; e.g. basic carbonates of zinc and copper. Natural azurite has almost constant peak temperatures at all pressures.

Type (2). The peak temperatures depend on the pressures to the comparatively high pressure; e.g. basic carbonates of nickel and cobalt, in particular it seems that the peak temperatures for basic cobalt carbonate still increase above 50 atm.

In the case of N_2 pressures, the peak temperatures for samples belonging to type (1) do not depend on N_2 pressure, but those belonging to type (2) do depend on N_2 pressure. The schematic diagram for these relationships is shown in Fig. 5. This is not a strict classification, but is useful for understanding the tendency of decomposition behavior. A greater accumulation of data and more study are needed to elucidate these phenomena.

The closed holder is filled with CO_2 and H_2O evolved from the sample, but the open one is not filled with them, because evolved CO_2 and H_2O are removed by flowing gases. However, when the closed and open holders are used under CO_2 atmosphere the peak temperatures are the same, but they differ under N_2 atmosphere. That is, the closed holder forms a self-generated atmosphere. This indicates that when the evolution of CO_2 and H_2O

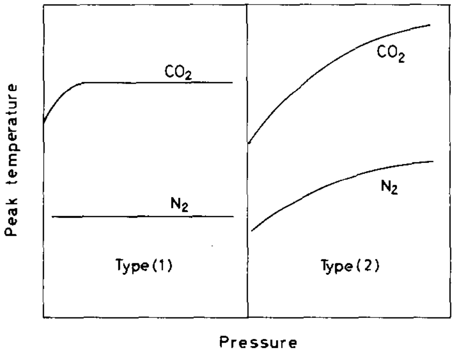

Fig. 5. Schematic diagram for relationship between CO_2 and N_2 pressures and peak temperatures.

TABLE 1

Phenomena for thermal decomposition of basic carbonates in air and CO_2 atmospheres

Sample	Decomposition process in air	Decomposition temperature of anhydride in air (°C)	Decomposition type under high pressure	Region of pressure dependence on peak temperature (atm)
Basic nickel carbonate, $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ [9]	$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O \rightarrow NiCO_3 \cdot 2Ni(OH)_2 + 4H_2O$ $NiCO_3 \cdot 2Ni(OH)_2 \rightarrow 3NiO + CO_2 + 2H_2O$	300	(2)	~ 35
Basic zinc carbonate, $2ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$	$2ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O \rightarrow 5ZnO + 2CO_2 + 4H_2O$	260	(1)	~ 10
Basic cobalt carbonate, $2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O$	$2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O \rightarrow 2CoCO_3 \cdot 3Co(OH)_2 + nH_2O$ $2CoCO_3 \cdot 3Co(OH)_2 + 5/6O_2 \rightarrow 5/3Co_3O_4 + 2CO_2 + 3H_2O$	250	(2)	> 50
Natural malachite, $CuCO_3 \cdot Cu(OH)_2$	$CuCO_3 \cdot Cu(OH)_2 \rightarrow 2CuO + CO_2 + H_2O$	365	(1)	~ 10
Natural azurite, $2CuCO_3 \cdot Cu(OH)_2$	$2CuCO_3 \cdot Cu(OH)_2 \rightarrow 3CuO + 2CO_2 + H_2O$	350	(1)	~ 0
Synthesized malachite, $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$	$CuCO_3 \cdot Cu(OH)_2 \cdot H_2O \rightarrow 2CuO + CO_2 + 2H_2O$	295	(1)	~ 7

occurs simultaneously, the thermal decomposition temperature under CO_2 and N_2 atmospheres is not always influenced by the self-generated atmosphere formed by H_2O evolved from the sample, but is influenced by that formed by evolved CO_2.

The processes of evolution of CO_2 and H_2O in air and the decomposition phenomena of anhydride under high pressures are summarized in Table 1. The decomposition temperatures of carbonates of nickel and zinc are about 400 and 300°C, and those of hydroxides of nickel and zinc are about 230 and 125°C, respectivey. The decomposition temperatures, 300 and 260°C, of basic carbonates of nickel and zinc are in between those of carbonates and hydroxides, respectively.

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