

THERMAL DECOMPOSITION OF BASIC COPPER CARBONATE, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$, IN CARBON DIOXIDE ATMOSPHERE (0–50 atm)

HIROSHI HENMI and TORU HIRAYAMA

Department of Industrial Chemistry, School of Engineering, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa-pre. 259-12 (Japan)

NOBUYASU MIZUTANI* and MASANORI KATO

Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152 (Japan)

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ABSTRACT

The thermal decomposition of basic copper carbonate, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$, was studied by high-pressure DTA under high-pressure carbon dioxide (0–50 atm).

The DTA–TG measurement in air showed that the peak temperature was influenced more by heating rate than by sample weight.

Decomposition via dehydration and decarbonation was rapidly finished in a single step, and no intermediate was found. The decomposition temperature was strongly influenced by the partial pressure of carbon dioxide. The decomposition temperature increased in the range $0 \text{ atm} < P_{\text{CO}_2} < 7 \text{ atm}$, but was nearly constant above $P_{\text{CO}_2} = 7 \text{ atm}$. Explaining these phenomena was approached by various considerations.

INTRODUCTION

Metal hydroxy carbonates (metal basic carbonates) are important in the wet corrosion of metals, weathering of materials, as raw materials for metal refining and ceramic processing, etc.

Most of the hydroxy carbonates are unstable at high temperatures. The thermal decomposition of these carbonates proceeds via dehydration and decarbonation to each metal oxide. This behavior is influenced by the antecedents of the sample, the packing conditions of the sample, the heating rate and atmosphere (the partial pressure of water vapor and carbon dioxide), etc.

Kato and Mizutani [1] already classified the hydroxy carbonates into three

* Author to whom all correspondence should be addressed.

categories by their thermal decomposition mechanism as follows.

(1) Evolution of all H_2O and CO_2 at the same temperature, e.g., basic carbonates of cobalt, nickel and copper.

(2) Evolution of all H_2O and part of CO_2 in subsequent steps which depends on partial pressure of CO_2 , e.g., basic carbonates of lead [2–7] and some lanthanides.

(3) Evolution of H_2O and CO_2 in different steps: in the first step all H_2O evolves and in the following steps CO_2 evolution occurs and is drastically affected by the partial pressure of CO_2 , e.g., basic magnesium carbonate [8].

In this report, the phenomenon for the thermal decomposition of the basic copper carbonate is described. Cuprous carbonate, Cu_2CO_3 , is reported in the literature, but doubted to exist. The natural salt does not have the composition of the cupric carbonate, CuCO_3 , but usually exists as compound salts, like $\text{CuCO}_3 \cdot \text{K}_2\text{CO}_3 \cdot n\text{H}_2\text{O}$. Generally, "copper carbonate" means basic copper carbonate. Basic copper carbonate (hydroxy copper carbonate) is naturally produced as azurite, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ or malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$.

Zivkovic et al. [9] studied the thermal decomposition of $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ with DTA at a heating rate of 5°C min^{-1} in atmospheric air. The decomposition was initiated at 220°C and ended at approximately 300°C . The product of the thermal decomposition of basic copper carbonate was CuO .

The TG study of Uzunov and Klissurski [10], at a heating rate of 5°C min^{-1} in atmospheric air, showed that basic copper carbonate decomposed at $290\text{--}300^\circ\text{C}$.

Brown et al. [11] studied the thermal decomposition of malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, with TG, DTA and EGA at a heating rate of $10^\circ\text{C min}^{-1}$ in He gas. Decomposition via dehydration and decarbonation occurred in a single step in which water and carbon dioxide were lost simultaneously at 380°C . The results of X-ray powder diffraction showed that the product of decomposition was exclusively tenorite, CuO .

In this study, the thermal decomposition of basic copper carbonate, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$, was studied by high-pressure DTA in the P_{CO_2} range $0\text{--}50$ atm. No study has systematically reported the effect of carbon dioxide pressure on the thermal decomposition of basic copper carbonate.

EXPERIMENTAL

Samples

Reagent grade basic copper carbonate (Kanto Chemical Co., Japan) was used as the sample. The $\text{CuO}/\text{CO}_2/\text{H}_2\text{O}$ molar ratio ($1.00:0.47:0.97$), determined by compositional analysis, was approximately equal to the ideal

$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ composition (1.00 : 0.50 : 1.00). Powder X-ray diffraction showed the pattern of malachite (JCPDS 10-399).

The sample is shaped like a 2- μm agglomerate of submicron particles.

Differential thermal analysis and thermogravimetry

The DTA-TG measurement (Type M8076 instrument, Rigaku Denki Co., Japan) was carried out in air for studying the relationship between heating rate and peak temperature (sample weight, 10 mg; heating rate, 2.5, 10, 15 and 20°C min⁻¹), and the relationship between sample weight and peak temperature (heating rate, 10°C min⁻¹; sample weight, 5, 10 and 17 mg).

High-pressure differential thermal analysis

The thermal decomposition was studied with a high-pressure DTA apparatus which was designed and constructed by the authors. The sample was heated under various pressures of carbon dioxide (P_{CO_2} : 0–50 atm) at a heating rate of 15°C min⁻¹, to 500°C. The atmosphere in the sample chamber was changed from air to CO₂ by filling with pure carbon dioxide up to 5 kg cm⁻² and discharging three times before heating. Carbon dioxide was then passed through this chamber (about 100 ml min⁻¹) to remove the gases rapidly evolved on thermal decomposition.

X-ray powder diffraction

Identification of the sample was carried out with an X-ray diffractometer (Type 2171, Rigaku Denki Co., Japan) with a Cu target and a monochromator.

Scanning electron microscopy

Basic copper carbonate as starting material and copper oxide formed by the thermal decomposition were observed by SEM (JSM-T200, JEOL).

RESULTS

Figure 1 shows typical DTA-TG curves and the X-ray diffraction analysis. Basic copper carbonate changed to copper oxide at about 295°C (in air; heating rate, 15°C min⁻¹; sample weight, 10 mg). Decomposition via dehydration and decarbonation rapidly finished in a single step. No intermediate was found.

Figure 2 shows the relationship between heating rate and peak temperature (in air). The peak temperature increased as the heating rate increased.

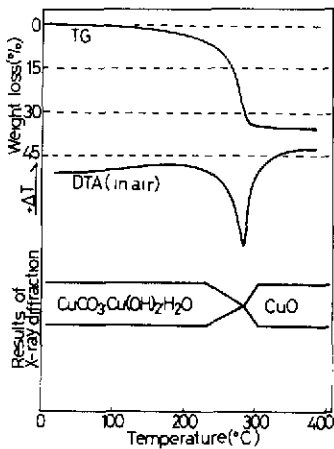


Fig. 1. Typical DTA-TG curves and X-ray diffraction analysis.

Figure 3 shows the relationship between sample weight and peak temperature (in air). The peak temperature slightly increased as the sample weight increased. It seemed that the peak temperature was influenced by more heating rate than by sample weight.

Figures 4 and 5 show the DTA diagrams at various carbon dioxide pressures and the relationship between partial pressure of carbon dioxide and peak temperature, respectively. The CO_2 pressure strongly affected the thermal decomposition. As P_{CO_2} increased, the peak temperature increased, the peak profile became more narrow and sharp, and the apparent peak area decreased.

The decomposition temperature increased as the partial pressure of carbon dioxide increased in the range $0 \text{ atm} < P_{\text{CO}_2} < 7 \text{ atm}$, but was nearly constant above $P_{\text{CO}_2} = 7 \text{ atm}$.

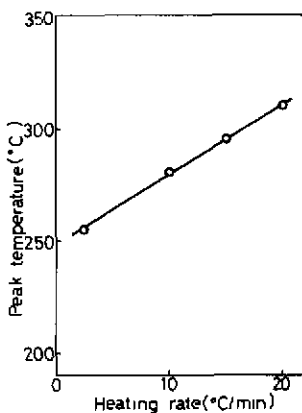


Fig. 2. Relationship between heating rate and peak temperature.

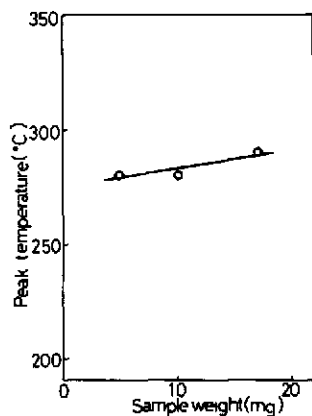


Fig. 3. Relationship between sample weight and peak temperature.

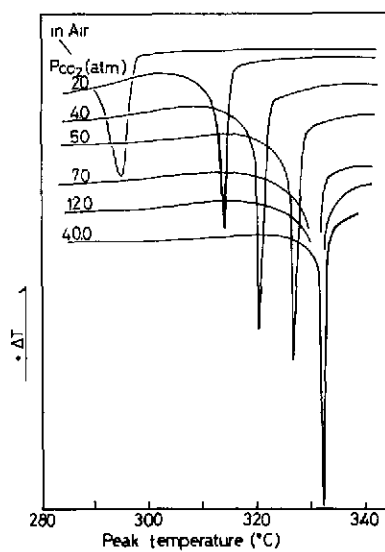


Fig. 4. DTA diagrams at various carbon dioxide pressure.

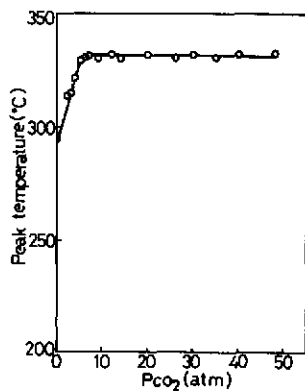


Fig. 5. Relationship between partial pressure of carbon dioxide and peak temperature.

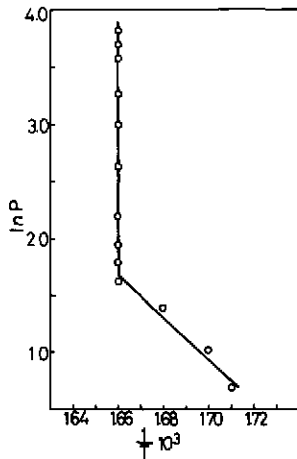


Fig. 6. Plot of $\ln P$ vs. $1/T$.

Figure 6 shows the van't Hoff plot of the relationship between decomposition temperature and P_{CO_2} .

The SEM photographs (Figs. 7 and 8) show basic copper carbonate as the starting material and copper oxide formed by the thermal decomposition of basic copper carbonate, respectively.

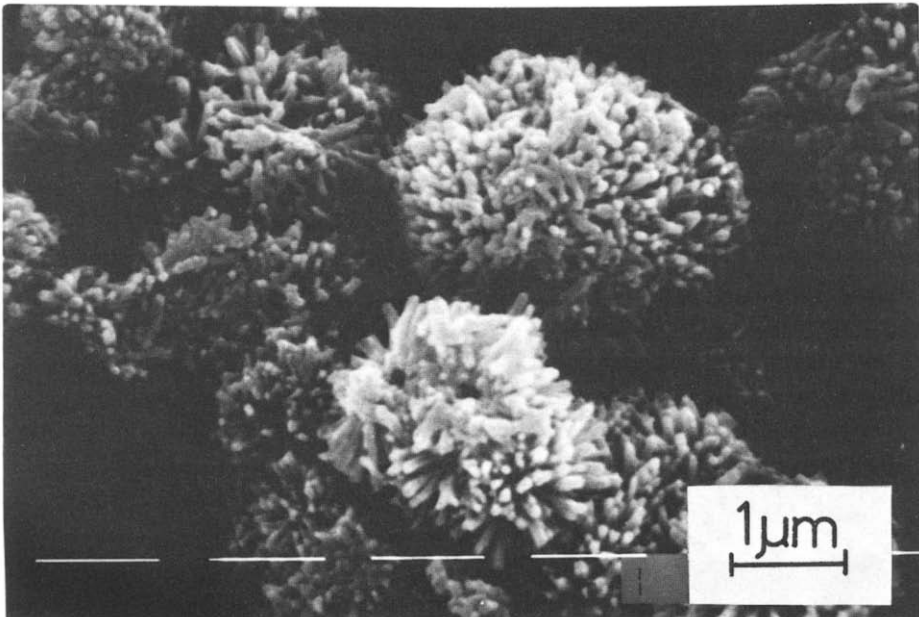


Fig. 7. SEM micrograph of basic copper carbonate.

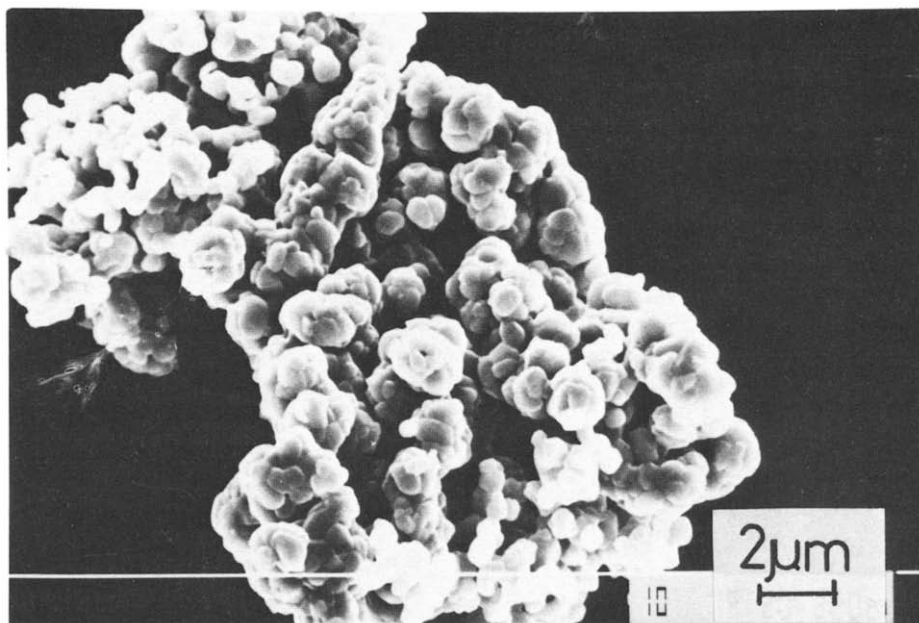


Fig. 8. SEM micrograph of copper oxide.

DISCUSSION

The decomposition mechanism is considered to be the first step of the above-mentioned classification, as follows.



The existence of anhydrate and intermediates such as malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) and Azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) were neither formed by X-ray diffraction nor recognized from the DTA and TG curves.

If the reaction is given by eqn. (1), the decomposition temperature is affected by P_{CO_2} and $P_{\text{H}_2\text{O}}$ according to eqn. (2).

$$\ln P_{\text{CO}_2} P_{\text{H}_2\text{O}}^2 = -\Delta H/R(1/T) \quad (2)$$

where ΔH is the enthalpy change of decomposition. Figure 6 shows the van't Hoff plot of this reaction. This plot is divided into low- and high-pressure regions. The apparent enthalpy change is estimated to be $36.4 \text{ kcal mol}^{-1}$ for $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ or $18.2 \text{ kcal mol}^{-1}$ for CuO from the straight line in the low-pressure region.

Table 1 gives the standard enthalpy changes for some reactions similar to this decomposition. The standard enthalpy change of the above reaction is $10\text{--}12 \text{ kcal mol}^{-1}$ of CuO .

Here, we assume a model like Fig. 9. The decomposition curves only affected by P_{CO_2} and $P_{\text{H}_2\text{O}}$ are assumed to be curves (A) and (B), respec-

TABLE 1

Standard enthalpy change for some reactions, from ref. 12

Reaction	ΔH_{298}^0	
	per mole of reactant	per mole of CuO
$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \rightarrow 2\text{CuO} + \text{CO}_2 + \text{H}_2\text{O}$ (malachite)	24.2	12.1
$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \rightarrow 3\text{CuO} + 2\text{CO}_2 + \text{H}_2\text{O}$ (azurite)	31.3	10.4
$\text{CuCO}_3 \rightarrow \text{CuO} + \text{CO}_2$	12.1	12.1
$\text{Cu}(\text{OH})_2 \rightarrow \text{CuO} + \text{H}_2\text{O}$	12.1	12.1
$\text{H}_2\text{O}(\text{solid}) \rightarrow \text{H}_2\text{O}(\text{vapor})$	10.5	10.5

tively. When the partial pressure of water vapor is constant at $P_{\text{H}_2\text{O}}$ (initial $P_{\text{H}_2\text{O}}$), the decomposition temperature is T_a . The decomposition temperature from T_0 to T_a depends on P_{CO_2} from 0 to P_{C_a} , but does not depend on P_{CO_2} above P_{C_a} . The decomposition temperature above P_{C_a} is only affected by $P_{\text{H}_2\text{O}}$. That is, the decomposition temperature is considered to be constant although P_{CO_2} may be higher than P_{C_a} (curve T_0-C_a-a). If the partial pressure of the water vapor is able to be controlled at $P_{\text{H}_2\text{O}}$, or $P_{\text{H}_2\text{O}}$, the decomposition curves (T_0-C_b-b or T_0-C_c-c), which depend on the partial pressure of water vapor, may be obtainable.

The decomposition temperature in the region $7 \text{ atm} < P_{\text{CO}_2} < 50 \text{ atm}$ was nearly constant although P_{CO_2} increased. Generally, in the measurement of DTA, the melt reaction is indicated as the endothermic peak during the heating step. To confirm that the sample does not melt before it decomposes, the sample was heated above the temperature at which the endothermic peak appeared and was cooled continuously. The experiments were carried out at $P_{\text{CO}_2} = 6$ and 20 atm, respectively. A change in the DTA curve during the

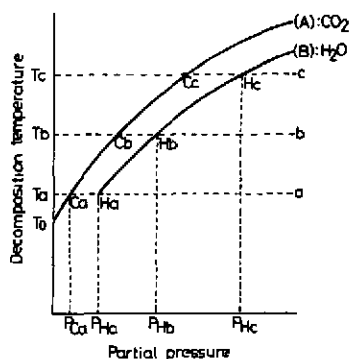


Fig. 9. Schematic diagram of the relationship between partial pressure and decomposition temperature.

cooling step was not found. The melt reaction did not occur. It was clear that the melt phenomenon was irrelevant for a constant peak temperature.

The above-mentioned explanations are incomplete and further study to elucidate this behavior is necessary.

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