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Note

THERMAL DECOMPOSITION OF BASIC BISMUTH CARBONATE UNDER HIGH PRESSURES OF CO_2 AND N_2 UP TO 50 ATM

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INTRODUCTION

Thermal decomposition of basic carbonates has been reported previously by the authors. Differential thermal analysis was performed systematically under high-pressure gas atmospheres of CO_2 and N_2 for the following hydroxycarbonates (double salts of the normal carbonate and the hydroxide):

$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ [1], $2PbCO_3 \cdot Pb(OH)_2$ [2]

$CuCO_3 \cdot Cu(OH)_2$ [3], $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ [4]

$2CuCO_3 \cdot Cu(OH)_2$ [3], $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ [5]

$2ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$ [3]

$2CoCO_2 \cdot 3Co(OH)_2 \cdot nH_2O$ [3]

In the present study, the investigation was extended to another kind of basic carbonate, i.e. oxycarbonates (double salts of the normal carbonate and the basic oxide): thermal decomposition of bismuth oxycarbonate $(BiO)_2CO_3$ under high-pressure gas atmospheres (CO_2 and N_2, 0–50 atm) was reported.

The decarbonation temperature increased remarkably at high CO_2 pressures. One-step decarbonation took place at $pCO_2 < 17$ atm to form mono-

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clinic Bi_2O_3. Two-step decarbonation took place at $pCO_2 > 17$ atm: the cause of two-step decarbonation was not clarified in the present paper. The influence of the self-generated atmosphere of CO_2 was explained successfully for the present results. The sample contained a small amount of water: the hydration process was open to question.

EXPERIMENTAL

Reagent grade basic bismuth carbonate (Wako Pure Chemical Industries, Ltd., Japan) was used. The powder X-ray diffraction showed the pattern of bismuth oxycarbonate (Bismutite: $(BiO)_2CO_3$, JCPDS 25-1464). The Bi_2O_3:CO_2:H_2 molar ratio (1.00 : 0.97 : 0.27) determined by the compositional analysis was slightly different from the ideal composition of $(BiO)_2CO_3$ (1.00 : 1.00 : 0.00): the state of the excess water was not investigated in the present study.

The experimental methods are similar to the previous reports [3–5]. A cover was placed onto the sample holder when examining the influence of the self-generated atmospheres.

RESULTS AND DISCUSSION

The results of DTA–TG in air (1 atm) showed a single endothermic peak at approximately 380°C with a corresponding weight loss. The X-ray diffraction of the decomposed sample showed the presence of monoclinic Bi_2O_3 (JCPDS 27-53). Evolution of CO_2 and a small amount of water vapor was expected from the composition of the sample. The results of differential thermal gas analysis (DTGA) [6] in He (1 atm) atmosphere supported this: a gas evolution was detected without a trap while no gas evolution was detected with an "Askarite (KOH)" trap, which eliminates CO_2 and H_2O.

However, the DTGA failed to detect the dehydration independently from the decarbonation. No distinct gas evolution was observed in CO_2 atmosphere (1 atm). No difference was observed in He atmosphere (1 atm) between the results with and without a P_2O_5 trap, which eliminates only H_2O. Therefore, no definite conclusion was possible as to the dehydration temperature, although the weight loss in TG (10.3%) was in excellent agreement with the value (10.2%) expected from the composition by which a simultaneous occurrence of the decarbonation and the dehydration was suggested.

The results of high-pressure DTA in CO_2 atmosphere are shown in Fig. 1. The decomposition temperature increased at high CO_2 pressure. Two endothermic peaks appear at high pressures above 17 atm. The X-ray diffraction of the sample quenched immediately after the first decomposition (endother-

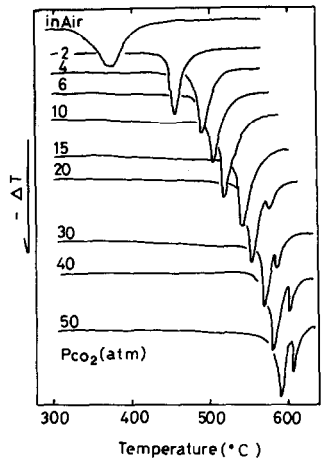

Fig. 1. The result of high-pressure DTA at various CO_2 pressures for bismuth carbonate: sample weight, 10 mg; heating rate, 15°C min^{-1}; atmosphere, CO_2 (up to 50 atm, overflowed).

mic peak in high-pressure DTA) revealed the mixture of $(BiO)_2CO_3$ and Bi_2O_3: no intermediate phase explaining the two-step decomposition was detected.

The relationship between the temperature of the endothermic peak and gas pressure is shown in Fig. 2. In CO_2 atmosphere, the decomposition

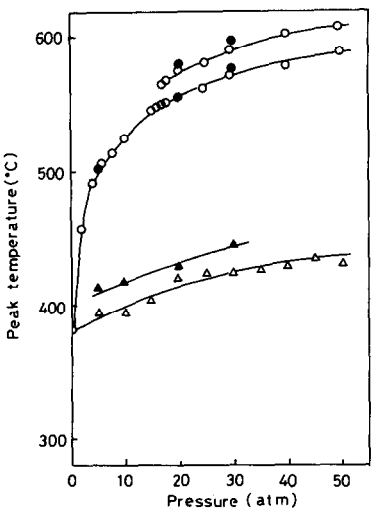

Fig. 2. The relationship between the temperature of the endothermic peak and the pressures of CO_2 and N_2 for basic bismuth carbonate: ● and ○, closed and open sample holders, respectively, in CO_2 atmosphere; ▲ and △, closed and open sample holders, respectively, in N_2 atmosphere.

temperature was remarkably affected by the pressure while no difference was observed between the result of the covered (closed) sample holder and that of the open one. In N_2 atmosphere, the influence of N_2 pressure was observed only slightly, while the difference between the sample holders was remarkable. These differences can be explained by the influence of the self-generated CO_2 atmosphere.

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