

Thermal decomposition of silver carbonate Part 4. High pressure differential thermal analysis under an atmosphere of carbon dioxide ^a

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Abstract

The thermal decomposition of silver carbonate was investigated by DTA under a high pressure atmosphere of carbon dioxide (1–40 atm). Three endothermic peaks were observed. The peak temperature (approximately 200 °C) of the first was independent of the partial pressure of carbon dioxide, which supports the conclusions of our previous papers that the first peak is attributed to the phase transition of the silver carbonate from the normal to the high temperature form. The second endothermic peak at 200–400 °C shifted to the higher temperature range with increasing pressure of carbon dioxide until it combined with the third endothermic peak at approximately 440 °C. The second peak can be attributed to decarbonation of the silver carbonate on the surface of the specimen to form silver oxide, while the interior remains undecomposed. The peak temperature of the third endothermic peak was independent of the pressure of the carbon dioxide. The third peak was attributed to the decarbonation of the remaining carbonate and the simultaneous reduction of the oxide to metallic silver. The decomposition mechanism is discussed.

INTRODUCTION

In our previous paper [1] three endothermic peaks were observed in the DTA of silver carbonate (Ag_2CO_3) in carbon dioxide (1 atm). In subsequent studies using a high temperature X-ray diffractometer and a cyclic DSC in a carbon dioxide atmosphere (1 atm) [2,3], the first peak, at approximately 200 °C, was attributed to the phase transition of the silver carbonate from the normal [4] to the α phase [5] via the β phase [6].

The second endothermic peak at approximately 255 °C in a carbon

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dioxide flow (1 atm) was attributed to surface decarbonation of the silver carbonate, while the interior of the specimen remained undecomposed [1], because a simultaneous evolution of carbon dioxide was detected by differential thermal gas analysis [7] and the X-ray diffraction spectra of silver carbonate (normal phase [4]) and silver oxide (Ag_2O) [8] were detected in the specimen quenched after the endothermic phenomenon. It was estimated in our previous paper [1] that the temperature of the decarbonation depends on the partial pressure of carbon dioxide, so that the second endothermic peak will overlap with the first in a static air atmosphere.

The third endothermic peak was attributed to the decarbonation of the remaining carbonate and the simultaneous reduction of the oxide at both the surface and in the interior to form metallic silver, because a simultaneous evolution of carbon dioxide and oxygen was observed by DTGA. It was interesting that little difference was observed between the peak temperature (416°C) in the static air atmosphere and that (414°C) in a carbon dioxide flow (1 atm) although accompanying decarbonation.

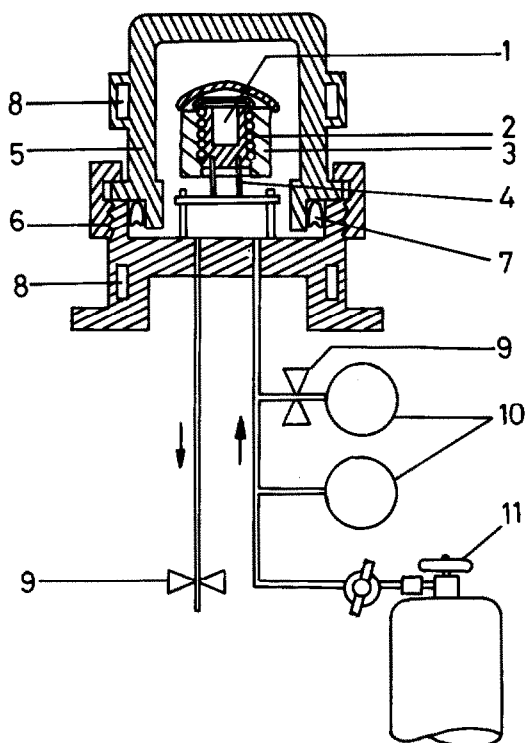


Fig. 1. Construction of the high pressure DTA equipment: 1, alumina bobbin in which the DTA measuring cell is installed as shown in Fig. 2; 2, platinum heater; 3, alumina fibres; 4, alumina pipe; 5, high pressure vessel (100 mm outer diameter); 6, screw for fixing the high pressure vessel; 7, U-shaped packing ring made of rubber; 8, cooling water tubes; 9, valves; 10, pressure gauges (10 and/or 100 kg cm^{-2}); and 11, gas cylinder (carbon dioxide).

In the present study, the dependence of these peak temperatures on the partial pressure of carbon dioxide was investigated with high pressure DTA (1–40 atm) in order to discuss the decomposition mechanisms.

EXPERIMENTAL

Specimens

Reagent grade silver carbonate, (Wako Pure Chemical Co. Ltd. Japan), was used: its X-ray diffraction pattern showed Ag_2CO_3 (normal form [4]) with no other phase being detected. The specimens were used for high pressure DTA after grinding the aggregated powders for a few seconds.

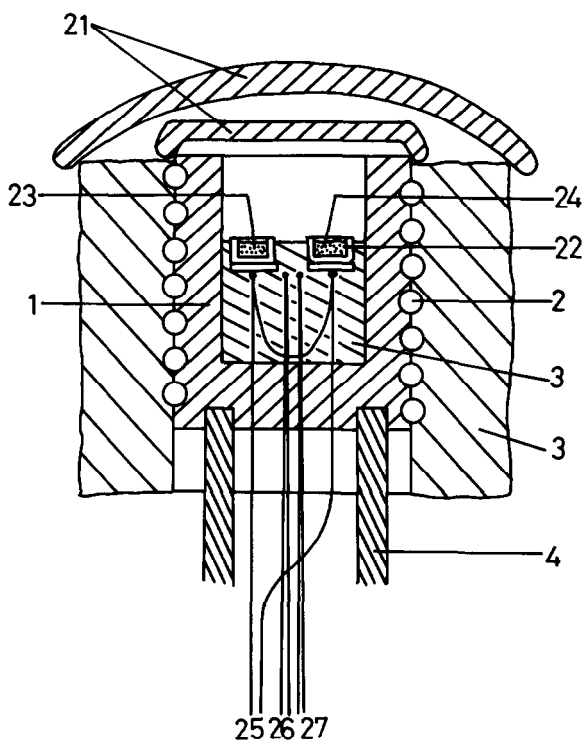


Fig. 2. Construction of the measuring cell of the high pressure DTA equipment: 1, alumina bobbin; 2, platinum heater; 3, alumina fibres; 4, alumina pipe; 21, alumina cap; 22, DTA specimen container; 23, specimen (approximately 600 mg); 24, reference (alumina); 25, thermocouple for DTA measurement (Pt–Pt/Rh13%); 26, thermocouple for temperature measurement (Pt–Pt/Rh13%); and 27, thermocouple for temperature control (Pt–Pt/Rh13%).

High pressure DTA

The construction of the high pressure DTA equipment and its measuring cell are shown in Fig. 1 and Fig. 2 respectively. The pressure vessel was reported previously [9]; the other components were reconstructed. A d.c. amplifier, a PID-type temperature controller (Rigaku) and an $X-t$ pen recorder were connected to the measuring cell. The DTA measurements were performed in an air (1 atm) and a carbon dioxide atmosphere (1–40 atm). The heating rate was $10^{\circ}\text{C min}^{-1}$. The temperature was calibrated with the melting points of indium, tin, lead and zinc.

RESULTS

The results of the high pressure DTA and the dependence of the endothermic peak temperatures on the partial pressure of carbon dioxide are shown in Fig. 3 and Fig. 4 respectively. The temperature (approximately 200°C) of the first endothermic peak was independent of pressure. This supports the hypothesis proposed in our previous papers [1–3] that the first endothermic peak is attributed to the phase transition of the silver carbonate.

The temperature for the second endothermic peak shifted to the higher temperature range at higher partial pressures of carbon dioxide until the second peak overlapped with the third peak at approximately 40 atm. The dependence of the peak temperature on the pressure of carbon dioxide can

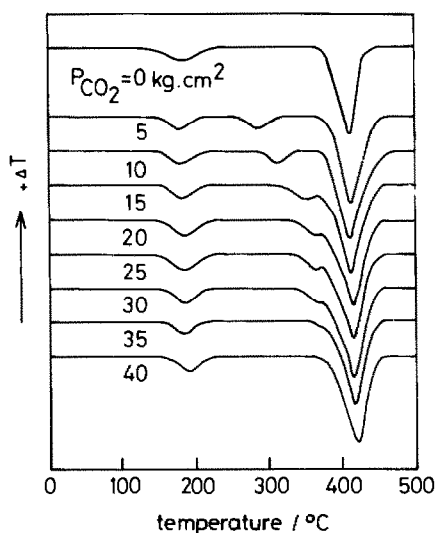


Fig. 3. Results of high pressure DTA for silver carbonate: atmosphere, air for $P_{\text{CO}_2} = 0 \text{ kg cm}^{-2}$ and carbon dioxide for the others; specimen weight, approximately 600 mg; heating rate, $10^{\circ}\text{C min}^{-1}$.

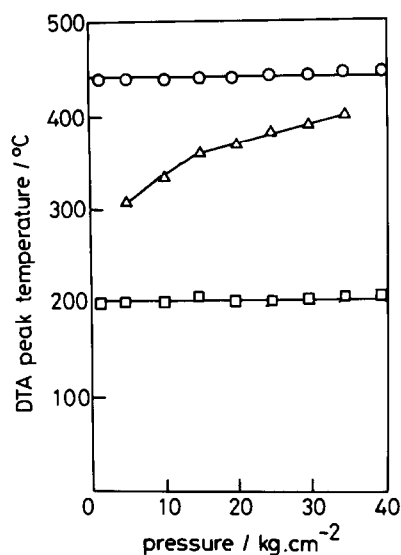


Fig. 4. Dependence of DTA peak temperature on partial pressure of carbon dioxide for the thermal decomposition of silver carbonate: □, the first endothermic peak which was attributed to the phase transition of silver carbonate; △, the second endothermic peak which was attributed to decarbonation; and ○, the third endothermic peak which was attributed to the simultaneous decarbonation and reduction to form metallic silver.

be understood qualitatively by the decarbonation reaction. The present results support the explanation in our previous paper [1] that the second endothermic peak is coincident with the first endothermic peak in a static air atmosphere.

The temperature for the third endothermic peak was independent of the partial pressure of carbon dioxide. A shoulder or a small peak at 360–380 °C observed in the previous DTA or DTGA studies [1] was not detected, probably because a larger specimen (600 mg) was needed to obtain reproducible results in high pressure atmospheres.

DISCUSSION

The equilibrium between Ag_2CO_3 and Ag_2O plus CO_2 calculated from the thermochemical data [10,11] is shown in Fig. 5 as a function of the partial pressure of carbon dioxide (P_{CO_2}) and temperature (T). In this figure, the broken lines A and B indicate the approximate phase boundaries for silver carbonate (normal, β and α phases), the precise phase boundaries being unknown at present. The results of DTA in carbon dioxide can be explained by this figure as follows.

The phase transition of silver carbonate from the normal via the β to the α phase was detected as two endothermic peaks when a small specimen (21

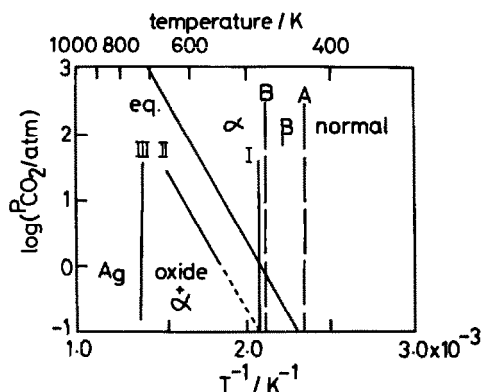


Fig. 5. Equilibrium between silver carbonate and silver oxide plus carbon dioxide as a function of the partial pressure of carbon dioxide and temperature: P_{CO_2} , partial pressure of carbon dioxide; α , β and normal, the phases of silver carbonate (Ag_2CO_3); oxide, Ag_2O ; Ag, metallic silver; line eq., equilibrium between Ag_2CO_3 and Ag_2O plus CO_2 calculated from the thermochemical data [10,11]; line I, the temperature of the first endothermic peak which was attributed to the phase transition of silver carbonate from the normal phase via the β -phase to the α -phase; solid line II, the temperature of the second endothermic peak which was attributed to the decarbonation of the surface of the specimen; line III, the temperature of the third endothermic peak which was attributed to the decarbonation of the interior and the reduction of both the surface and the interior; line A, boundary between the normal and β phases of silver carbonate; and line B, boundary between the β and α phases of silver carbonate.

mg) was heated slowly (5°C min^{-1}) [2]. When heated at approximately $10^\circ\text{C min}^{-1}$, the two endothermic peaks combined to form one endothermic peak at approximately 200°C (the solid line I in Fig. 5) which is called "the first endothermic peak" in the present paper. This peak temperature is independent of the partial pressure of carbon dioxide.

The decarbonation took place at a temperature higher than that expected from the equilibrium condition (the solid line "eq."). The endothermic peak (the solid line II) corresponding to the decarbonation is called "the second endothermic peak" in the present paper. This peak temperature was dependent on the partial pressure of carbon dioxide; line II is approximately parallel to line "eq." in this figure. Line II intersects line I when the partial pressure of carbon dioxide is lower than approximately 0.1 atm, which may correspond to the so-called self-generated atmosphere of carbon dioxide during decomposition in a static air atmosphere reported in our previous paper [1]. The decarbonation was limited to the surface of the specimen.

The decarbonation of the interior and the reduction of the oxide (Ag_2O) on the surface and in the interior resulted in the formation of metallic silver. These two endothermic reactions took place simultaneously, so that only one endothermic peak was observed. This is indicated by the solid line III, which is called "the third endothermic peak" in the present paper. Line III, when extrapolated, intersects line II at approximately 100 atm. The following

tentative hypotheses are proposed to explain why the peak temperature of the third peak was independent of the partial pressure of carbon dioxide although the decarbonation occurred.

(1) The silver layer on the surface of the specimen prevents the transport of carbon dioxide and oxygen which restricts the decarbonation and reduction of the interior, because a volumetric increase (27%) [12] occurs during the reduction of Ag_2O to metallic silver. The silver layer is destroyed at a certain critical temperature which is determined not by chemical factors but by thermodynamic factors, such as the sintering of metallic silver, the thermal expansion, the phase transition etc.

(2) Similar examples are shown in Fig. 6 where the decarbonation temperatures of some basic carbonates are independent of the partial pressure of carbon dioxide. These examples may be explained by a common mecha-

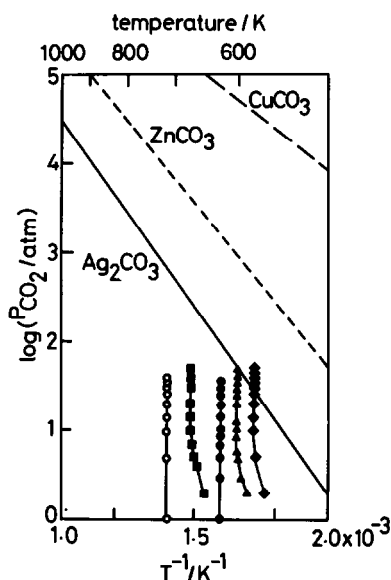


Fig. 6. Equilibrium between carbonates and their corresponding oxides plus carbon dioxide as a function of partial pressure of carbon dioxide and the temperature for silver, zinc and copper: P_{CO_2} , partial pressure of carbon dioxide; solid line, equilibrium between Ag_2CO_3 and Ag_2O plus CO_2 calculated from the thermochemical data [10,11]; broken lines, equilibrium between ZnCO_3 and ZnO plus CO_2 and between CuCO_3 and Cu_2O plus CO_2 calculated from the thermochemical data [10,11]; \circ , the temperature of the third endothermic peak for the thermal decomposition of silver carbonate, Ag_2CO_3 (decarbonation and reduction); \blacksquare , the temperature of the endothermic peak for the thermal decomposition of natural malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (decarbonation and dehydration); \bullet , the temperature of the endothermic peak for the thermal decomposition of natural azurite, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (decarbonation and reduction); \blacktriangle , the temperature of the endothermic peak for the thermal decomposition of synthesized malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (decarbonation and dehydration); and \blacklozenge , the temperature of the endothermic peak for the thermal decomposition of synthesized basic zinc carbonate, $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ (decarbonation and dehydration).

nism, for example, the size effect of the crystal: natural azurite seems to have the largest particle size.

(3) The decarbonation may be affected by the reduction. The reduction should be affected by the partial pressure of oxygen which may be independent of the partial pressure of carbon dioxide.

CONCLUSIONS

The thermal decomposition of silver carbonate was investigated by DTA under a high pressure atmosphere of carbon dioxide (1–40 atm). Three endothermic peaks were observed. The temperature of the first peak (approximately 200°C) was independent of the partial pressure of carbon dioxide. This endothermic phenomenon was attributed to the transition of silver carbonate from the normal phase via the β to the α phase. The temperature of the second peak (200–400°C) depends on the partial pressure of carbon dioxide. This endothermic phenomenon was attributed to decarbonation on the surface of the specimen. The temperature of the third peak (approximately 400°C) was independent of the partial pressure of carbon dioxide although decarbonation and reduction occurred simultaneously to form metallic silver. A mechanism for this endothermic phenomenon was proposed.

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