Thermochimica Acta, 143 (1989) 319–324
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF SILVER CARBONATE. PART II. CYCLIC DIFFERENTIAL THERMAL ANALYSIS

YUTAKA SAWADA *

Department of Industrial Chemistry, Faculty of Engineering, Tokyo Institute of Polytechnics, Iiyama, Atsugi-shi, Kanagawa 243-02 (Japan)

NOBUYASU MIZUTANI and MASANORI KATO

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

(Received 20 September 1988)

ABSTRACT

The thermal decomposition of silver carbonate Ag_2CO_3 was studied by DTA–TG and DSC–TG, heated and cooled cyclically in the temperature range 100–200 ° C in a carbon dioxide atmosphere (1 atm). No weight change was observed. Two endothermic peaks during the heating and two exothermic peaks during the cooling were observed. These peaks were attributed to phase transitions from the normal via the β to the α phase during the heating, and the reverse phase transitions during the cooling. The results support the mechanism proposed in our previous paper in which the thermal decomposition in a carbon dioxide atmosphere proceeds via the high temperature phase of silver carbonate.

INTRODUCTION

Van Hattum et al. have recorded the X-ray diffraction pattern of two high temperature phases of silver carbonate, the α-Ag_2CO_3 at 210 ° C and the β-Ag_2CO_3 at 150 ° C, under a high pressure atmosphere (~ 4.5 atm) of carbon dioxide [1,2].

Wydeven [3], Barnes and Stone [4] and the present authors [5] investigated the thermal decomposition of silver carbonate and reported reversible endothermic phenomena which were not fully clarified.

In the present study, thermal analyses were focused on the thermal behaviour of silver carbonate in the temperature range ~ 100–200 ° C, where the carbonates are stable in a carbon dioxide atmosphere (1 atm). Two endothermic peaks during the heating and two exothermic peaks during the cooling were observed by DTA and DSC, operated cyclically. The two

---

* Author to whom all correspondence should be addressed.

0040-6031/89/$03.50

peaks during the heating were attributed to the phase transition of silver carbonate from the normal via the β to the α phase [1,2,6]. The present results support the mechanism proposed in our previous paper [5], in which the thermal decomposition from the normal carbonate to the oxide or the metal in a carbon dioxide atmosphere proceeds via the high temperature phase of the carbonate.

EXPERIMENTAL

Specimen

The silver carbonate Ag_2CO_3 used was as reported elsewhere [5]. The X-ray diffraction pattern showed that of normal Ag_2CO_3 [6]; no other phase was detected.

Thermal analyses

A DTA–TG and a DSC–TG instrument (Rigaku–Denki Co. Ltd., Japan) was used in a carbon dioxide flow (flow rate, 60 ml min^{-1}). The heating was stopped at ~ 200 °C in order to prevent the decomposition at the higher temperature determined from our previous work [5]. The heating rate was ~ 10 °C min^{-1} for the DTA–TG and ~ 5 °C min^{-1} for the DSC–TG, respectively, until ~ 180 °C beyond which the heating rate was gradually decreased. Subsequently, the specimen was cooled without using the temperature controller; the cooling rate decreased gradually. The cyclic operation (heating and cooling between ~ 100 and 200 °C) was repeated several times.

RESULTS

DTA

The result of cyclic DTA (the first and the second cycles) is shown in Fig. 1. The TG result was not included in this figure because there was no weight change. During the first heating, a split endothermic peak was observed (189 and 197 °C). Two exothermic peaks (191 and 115 °C) were observed during the subsequent cooling. The result of the second cycle was similar to that of the first cycle except that the two endothermic peaks (181 and 200 °C) were clearly separated.

The endothermic peaks during the heating were tentatively attributed to the phase transition from the normal via β to the α phase, and the exothermic peaks during the cooling were attributed to the reverse phase transition. The phase transition is expected to occur slowly as the peak

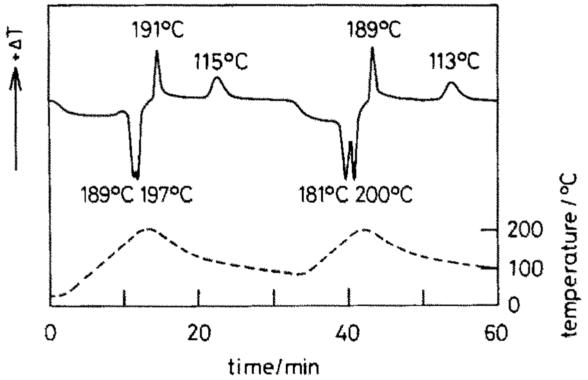

Fig. 1. Cyclic DTA for Ag_2CO_3 in a carbon atmosphere, specimen weight, 110 mg. Only the first and the second cycles are indicated: solid line, DSC; dotted line, temperature.

temperature during cooling is lower than the corresponding peak temperature during heating. An extremely broad peak at low temperatures during the cooling supports this hypothesis.

DSC

The result of cyclic DSC–TG (the first cycle) is shown in Fig. 2; weight change (not included in the figure) was not observed. The heats (absolute values) corresponding to the DSC peaks were tentatively estimated; ~ 0.8, 0.4 and 0.6 kcal mol^{-1} for the heat corresponding to the transition from the normal to the β phase, the reverse transition and their average, respectively, and ~ 0.2, 0.6 and 0.4 kcal mol^{-1} for the heat corresponding to the transition from the β to the α phase, the reverse transition and their average, respectively. Thus, the tentatively estimated values differed remarkably depending on the direction of the transition; these differences were larger than the possible error of ~ 12% which is mainly attributed to

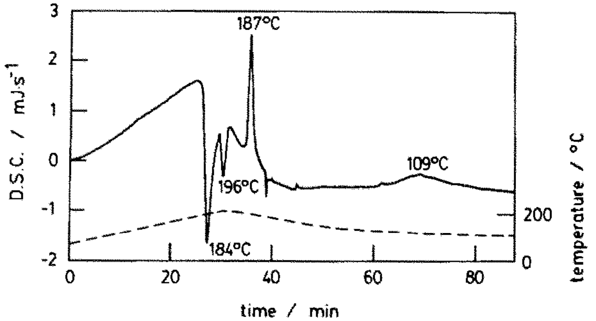

Fig. 2. Cyclic DSC for Ag_2CO_3 in a carbon dioxide atmosphere, specimen weight, 20.9 mg. Only the first cycle is indicated: solid line, DSC; dotted line, temperature.

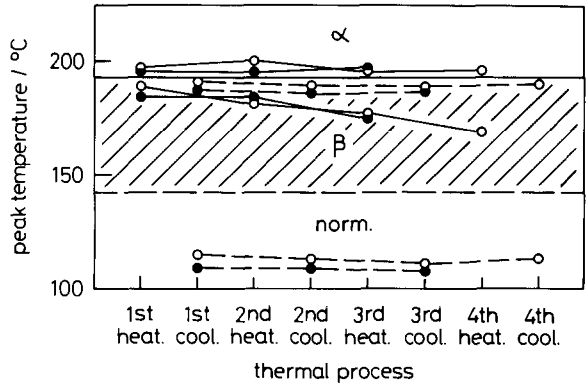

Fig. 3. Peak temperatures of cyclic DTA and DSC for Ag_2CO_3 in a carbon dioxide atmosphere: solid line, endothermic peak during the heating measured by DTA (○) and DSC (●); dotted line, exothermic peak during the cooling measured by DTA (○) and DSC (●). The DTA and DSC cycles were repeated 4 and 3 times respectively. Expected phase relations are tentatively indicated in this figure: normal, α and β.

the method of baseline subtraction of the duplicated endothermic peaks. The averaged values (~ 0.6 and 0.4 kcal mol^{-1}) agreed approximately with those reported by Wydeven [3] (0.73 and 0.47 kcal mol^{-1}, respectively) with a deviation of ~ 0.1 kcal mol^{-1}.

Small DSC peaks shown in Fig. 2 were observed reproducibly during the repeated cycles; the assignment of these peaks was impossible in the present study.

Peak temperatures

The peak temperatures of the DTA and the DSC are shown in Fig. 3. The peak temperature of the first endothermic peak decreased gradually during the repeated cycles.

DISCUSSION

Van Hattum et al. reported that the β phase could only be achieved on cooling from the α phase [2]. However, in the present study, two endothermic peaks suggest the occurrence of the β phase during the heating. This further suggests that the β phase is not a process-dependent intermediate phase but a temperature-dependent equilibrium phase.

Expected phase relations are tentatively indicated in Fig. 3 wherein higher pressures of carbon dioxide will be necessary, of course, for the α phase to be stable at temperatures higher than ~ 200 °C. The equilibrium temperatures were estimated from the present results; the transition temperature between the α and β phase (193 ° C) was approximated by the average of the minimum peak temperature of the corresponding endothermic phenomenon and the maximum peak temperature of the corresponding exothermic phenomenon. The transition temperature between the normal and the β phase (142 ° C) was similarly approximated although considerable error was expected because a lower transition rate was expected at the lower temperature.

Only one endothermic peak was observed at 194 ° C in our previous study [5] when heated at 10 ° C min^{-1} in a carbon dioxide atmosphere (1 atm). The different result obtained in the present work can be explained by the heating rate; in the previous case, the two transitions occurred almost simultaneously. In the present case, the actual heating rate at ~ 190 ° C was much lower, as shown in Figs. 1 and 2, so that the endothermic peaks were separated.

The peak temperature of the first endothermic peak gradually decreased during the repeated cycles. This can be attributed to the crystal growth of the specimen which enhances the rate of transition.

The values tentatively estimated as the heat of transition differ remarkably depending on the direction of the transition. This suggests that the transition proceeded incompletely because of the slow transition. It should be noted that the total heat corresponding to the two endothermic phenomena was approximately equal to that corresponding to the two exothermic phenomena i.e. ~ 1 kcal mol^{-1}. This seems to explain the reproducibility during the repeated cycles. Detailed investigation will be necessary for complete clarification of this.

CONCLUSIONS

The thermal changes of silver carbonate were investigated by a cyclic DTA–TG and DSC–TG at ~ 100–200 ° C in a carbon dioxide atmosphere (1 atm). No weight change was observed. Two endothermic peaks during the heating and two exothermic peaks during the cooling were observed. These peaks were attributed to transitions from the normal via the β to the α phase during the heating, and vice versa during the cooling.

ACKNOWLEDGEMENTS

The authors thank Prof. K. Manabe and Mr. M. Ogawa of Tokyo Institute of Polytechnics for the thermal analyses.

REFERENCES

1 Van Hattum et al., Joint Committee on Powder Diffraction Standards 31–1237.
2 Van Hattum et al., Joint Committee on Powder Diffraction Standards 31–1236.
3 T. Wydeven, Aust. J. Chem., 20 (1967) 2751.
4 P.A. Barnes and F.S. Stone, Thermochim. Acta, 4 (1972) 105.
5 Y. Sawada, N. Watanabe, H. Henmi, N. Mizutani and M. Kato, Thermochim. Acta, in press.
6 Joint Committee on Powder Diffraction Standards 26–339.