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THERMAL DECOMPOSITION OF SILVER CARBONATE. PART III. HIGH TEMPERATURE X-RAY DIFFRACTION ANALYSIS

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ABSTRACT

The thermal change of silver carbonate at < 220 ° C in a carbon dioxide atmosphere was investigated by high temperature X-ray diffraction analysis. Phase transition from the normal via the β to the α phase was observed during the heating; the reverse phase transition was observed during the cooling. The phase transition proposed in our previous papers was corroborated by the present work. Thermal expansion coefficients of the normal phase were 1.92×10^{-5}, 0.00×10^{-5} and 5.76×10^{-5} °C^{-1} along the *a*-, *b*- and *c*-axes, respectively.

INTRODUCTION

Van Hattum et al. have reported on the high temperature phase of Ag_2CO_3, α-Ag_2CO_3 (hexagonal, $a_0 = 0.9094$ nm and $c_0 = 0.3329$ nm), which was obtained at 210 ° C under a carbon dioxide atmosphere (4.5 MPa, i.e. ~ 4.5 atm.) [1]. They also reported another high temperature phase, β-Ag_2CO_3 (hexagonal, $a_0 = 0.9180$ nm and $c_0 = 0.6485$ nm); the diffraction pattern was recorded at 150 ° C under a carbon dioxide atmosphere (~ 4.5 atm.) [2].

Reversible endothermic phenomena during the thermal decomposition were reported by Wydeven [3], Barnes and Stone [4] and by the present authors [5]. Wydeven detected none of the high temperature phases using a high temperature Debye–Scherrer X-ray powder photograph method in a carbon dioxide atmosphere [3]. The present authors detected none of the high temperature phases for the specimens quenched from the DTA [5].

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Recently, the present authors [6] detected two endothermic peaks without weight change at around 200 °C during heating in a carbon dioxide atmosphere (1 atm.); two exothermic peaks were observed during the cooling. The peaks during the heating were tentatively attributed to the phase transition from the normal [7] via the β to the α phase, and vice versa during cooling.

This hypothesis has been confirmed in the present work by high temperature X-ray diffraction analysis in a carbon dioxide atmosphere.

EXPERIMENTAL

Specimen

Silver carbonate Ag_2CO_3 was used as reported elsewhere [5,6]. The X-ray diffraction pattern of the normal Ag_2CO_3 [7] was found; no other phases were detected.

High temperature X-ray diffraction analysis

The high temperature X-ray diffraction was investigated using a Rotorflex RU-200 (copper target, 60 kV, 200 mA) equipped with a 2311B1 specimen heater (Rigaku Co. Ltd., Japan). The specimen powders were mounted on a platinum container and heated with a platinum heater in a carbon dioxide flow (1 atm.). The following heating/cooling programs were executed: program I, controlled heating (10 °C min^{-1}) from room temperature to 210 °C followed by uncontrolled cooling to ~ 50 °C ($2\theta = 32$–35 deg.); and program II, controlled heating (10 °C min^{-1}) from room temperature to 50 °C for the analysis at 50 °C for 15 min, then similarly to 100, 150, 200 and 220 °C and subsequent uncontrolled cooling to 200, 150, 100 and 50 °C ($2\theta = 15$–60 deg.). The lattice constants of Ag_2CO_3 (normal phase) were determined from 25–27 diffractions at 25, 50, 100 and 150 °C heated according to program II. No internal standard was used for the calibration of the diffraction angles. The lattice constants at 25 °C ($a_0 = 0.485(7)$ nm, $b_0 = 0.955(6)$ nm, $c_0 = 0.326(0)$ nm and $\beta = 92.0(3)$) agreed with the reported values ($a_0 = 0.48510(7)$ nm, $b_0 = 0.95544(2)$ nm, $c_0 = 0.32533(6)$ nm and $\beta = 91.96(2)$ [7]) within the maximum error of 0.2% (c_0).

RESULTS AND DISCUSSION

Heating process

The X-ray diffraction patterns for the specimen heated at 10 °C min^{-1} (program I) are shown in Fig. 1. The $(\bar{1}01)$ diffraction peak of normal

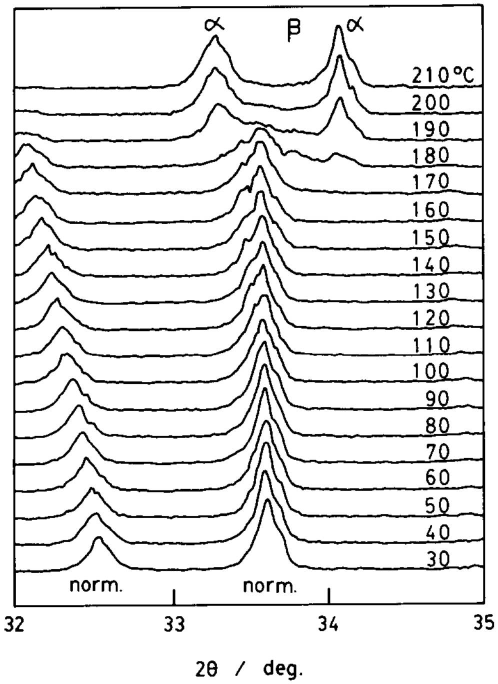

Fig. 1. X-ray diffraction patterns for Ag_2CO_3 during heating. Heating, program I (heating rate, 10 °C min^{-1}); atmosphere, carbon dioxide; target, copper; and norm., α and β, the normal, α and β phases, respectively.

Ag_2CO_3 ($2\theta = 32–32.6$ deg.) remarkably shifted to lower angles during heating while the ($\bar{1}30$) diffraction peak (33.6 deg.) was virtually unchanged until ~ 170 °C.

A very weak diffraction peak at ~ 33.8 deg. was observed in the specimen heated at 180–190 °C. The peak was assigned to β-Ag_2CO_3, a duplication of the (030) and the (112) diffraction. A couple of diffraction peaks (~ 33.3 and ~ 34.1 deg.) appeared at ~ 190 °C; these peaks were assigned to the (111) and (030) diffraction peaks of α-Ag_2CO_3, respectively. Thus, the transition from the normal via the β to the α phase was clearly observed.

The interplanar distances (*d*-values) during the heating are indicated in Fig. 2. In this figure, the data obtained by heating program II are also plotted and are basically consistent with the data obtained by heating program I. The reported values for the normal [7], α [1] and β [2] phases are also plotted. Thermal expansion of the normal phases was clearly observed along the $\langle\bar{1}01\rangle$ direction. The (111) diffraction peak of Ag_2O [8] was detected at 220 °C (program II); a slight decarbonation had occurred.

The peak heights for a typical diffraction of the normal, α and β phases are shown in Fig. 3. Thus, the three phases were observed simultaneously at 180–190 °C during the transition from the normal via the β to the α phase; the β phase was not observed as a single phase.

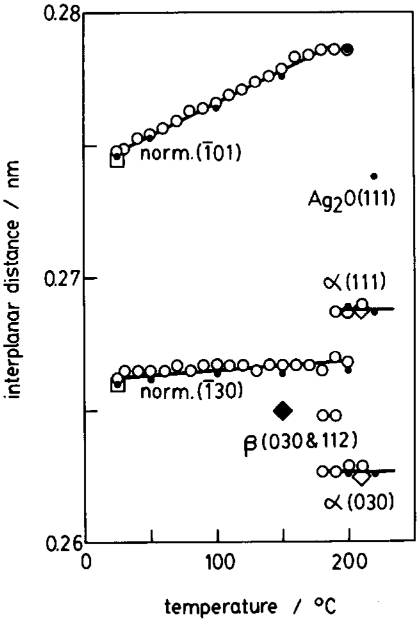

Fig. 2. Interplanar distances for Ag_2CO_3 during heating: atmosphere, carbon dioxide; norm., α and β, the normal, α and β phases, respectively; ○ and ●, the observed values heated according to programs I and II, respectively; and □, ◇ and ◆, the reported values for the normal [7], α [1] and β [2] phases, respectively.

The thermal expansion calculated from the data obtained by program II is shown in Fig. 4. Thermal expansion coefficients were 1.92×10^{-5}, 0.00×10^{-5} and 5.76×10^{-5} $°C^{-1}$ along the *a*-, *b*- and *c*-axes, respectively. No thermal expansion was observed along the *b*-axis. The expansion along the *c*-axis is approximately three times as much as that along the *a*-axis; that is, thermal expansion occurred approximately along the ⟨103⟩ direction.

Van Hattum et al. [2] reported that the β phase could only be formed by cooling from the structure-related α phase; their diffraction pattern was recorded at 150 °C under a high pressure atmosphere of carbon dioxide (~ 4.5 atm.). However, in the present study, a small amount of β phase was detected at 180–190 °C when heated by program I at a lower pressure (1 atm) of carbon dioxide. During the cooling process, the β phase was more clearly observed at 164 and 200 °C in the specimens cooled by programs I and II, respectively, to room temperature. The present results seem to support the proposition in our previous paper [6] that the β phase is not a process-dependent intermediate but a temperature-dependent equilibrium phase.

The density of silver carbonate determined from the lattice constants is shown in Fig. 5. The reported values for the α and β phases are plotted in this figure. It is clear that the density changes drastically from the normal to the β phase. The change from the β to the α phase is less drastic.

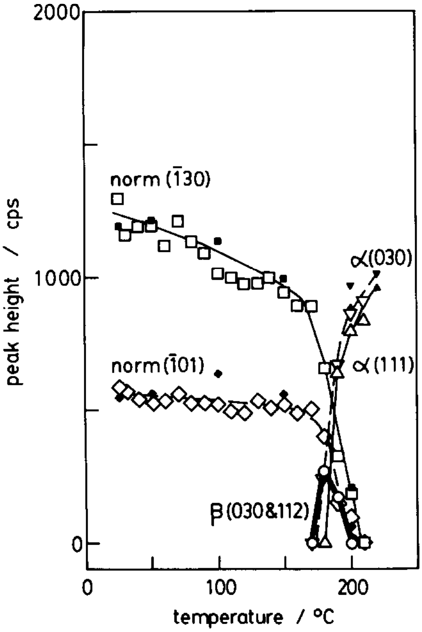

Fig. 3. Height of the diffraction peaks for Ag_2CO_3 during heating: atmosphere, carbon dioxide; ———, the normal phase; - - - - - -, the α phase; ———, the β phase. □ and ■, ◇ and ◆, the two strongest peaks ((1̄30) and (1̄01)) for the normal phase observed during heating according to programs I and II, respectively; ▽ and ▼, △ and ▲, the two strongest peaks ((111) and (030)) for the α phase during heating according to programs I and II, respectively; and ○, the strongest peak ((030) and (112)) for the β phase during heating according to program I.

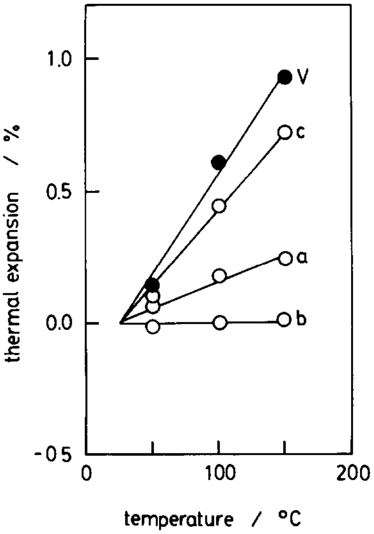

Fig. 4. Thermal expansion for normal Ag_2CO_3 during heating: heating, program II; atmosphere, carbon dioxide; a, b and c, linear expansion along the *a*-, *b*- and *c*-axes, respectively; and V, volumetric expansion.

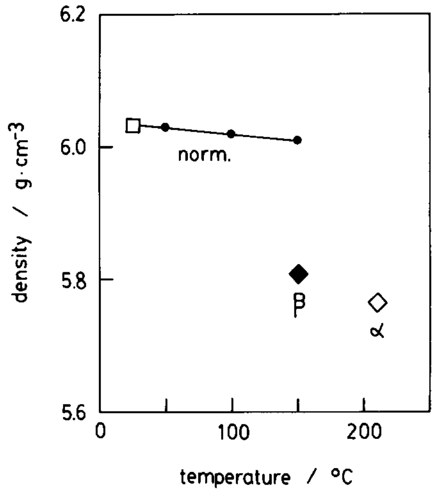

Fig. 5. Density for the various phases of Ag_2CO_3: norm., α and β, the normal, α and β phases, respectively; ●, estimated from the reported density (6.084 g cm^{-3} [7]) at room temperature and the observed values during heating (program II) in a carbon dioxide atmosphere and; □, ◇ and ◆, the reported values for the normal [7], α [1] and β [2] phases, respectively.

Cooling process

The X-ray diffraction patterns, the interplanar distances and the peak heights for the specimen during the cooling process are shown in Figs. 6, 7 and 8, respectively. Transitions from the α via the β to the normal phase seemed to occur during the cooling although multiple phases coexisted. The (111) diffraction peak of Ag_2O observed at 220 °C in heating program II disappeared during the cooling process; this suggests that carbonation of the oxide occurred. The peak height of the α phase decreased gradually and disappeared at 164 °C. The β phase (the (030) and (112) diffraction) appeared at 184 or 200 °C when cooled by programs I or II, respectively. The highest peak was obtained from the specimens heated at 164 and 150 °C by programs I and II, respectively. A very weak peak at 32.8 deg. appeared at 164 °C; the peak was too weak to indicate in Fig. 6. This was assigned to the (121) diffraction peak of the β phase whose relative intensity, as reported by van Hattum et al. [2], was 4%. This peak was preserved until 38 °C; the interplanar distance and the peak height remained approximately unchanged during the cooling. The ($\bar{1}01$) diffraction peak of the normal phase appeared at 146 °C. The ($\bar{1}30$) diffraction peak of the normal phase appeared at 99 and 100 °C by programs I and II, respectively. The peak heights of the normal phase increased during cooling. The peaks at ~ 33.0–34.2 deg. (interplanar distances 0.262–0.267 nm) at ~ 150–30 °C are difficult to assign as small peaks were duplicated. The peak splitting of the β

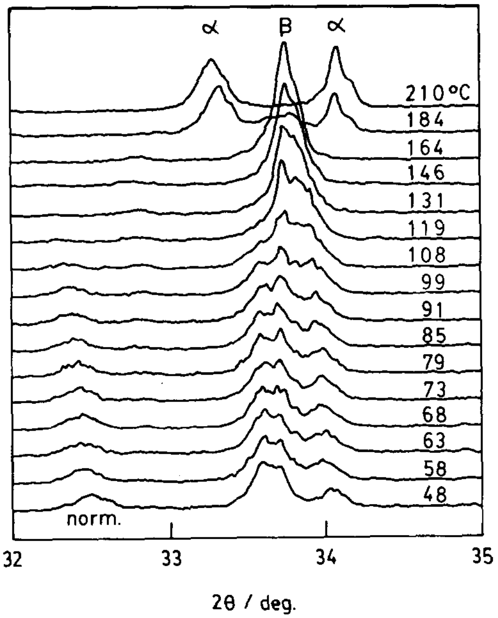

Fig. 6. X-ray diffraction patterns for Ag_2CO_3 during cooling. Cooling, program I (uncontrolled cooling); atmosphere, carbon dioxide; target, copper; and norm., α and β, the normal, α and β phases, respectively.

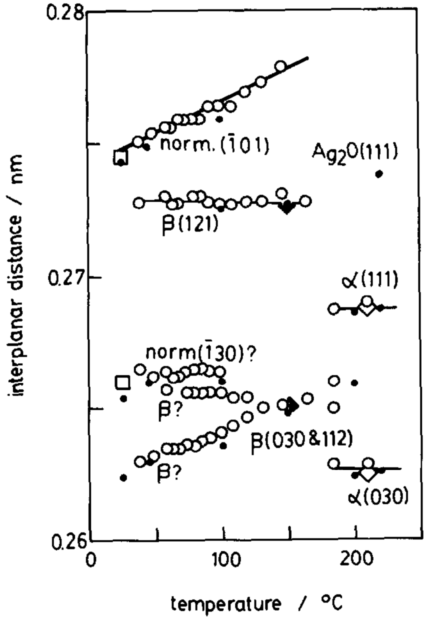

Fig. 7. Interplanar distances for Ag_2CO_3 during the cooling. The diffraction indices are indicated in parentheses: atmosphere, carbon dioxide; norm., α and β, the normal, α and β phases, respectively; ○ and ●, the observed values during cooling according to programs I and II, respectively; and □, ◇ and ◆, the reported values for the normal [7], α [1] and β [2] phases, respectively.

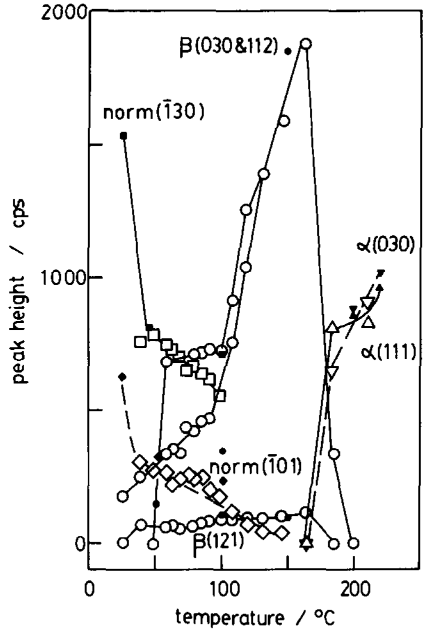

Fig. 8. Height of the diffraction peaks for Ag_2CO_3 during cooling: atmosphere, carbon dioxide; □ and ■, ◇ and ◆, the two strongest peaks ($(\bar{1}30)$ and $(\bar{1}01)$) for the normal phase observed during cooling according to programs I and II, respectively; △ and ▲, ▽ and ▼ the two strongest peaks ((111) and (030)) for the α phase during cooling according to programs I and II, respectively; and ○ and ●, the two strongest peaks ((030) and (112, and (121)) for the β phase during cooling according to programs I and II respectively.

(112) and (030) diffractions seemed to occur under ~ 130 °C, i.e. the lower symmetry of the crystal may appear.

CONCLUSIONS

Silver carbonate changed from the normal via the β to the α phase when heated at < 220 °C in a carbon dioxide atmosphere; the reverse transition occurred during cooling. The phase transition proposed in our previous papers was corroborated by the present work. The thermal expansion of the normal phase was measured.

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