THERMAL DECOMPOSITION OF SILVER CARBONATE

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Conflicting results have been reported by different workers on the thermal decomposition of silver carbonate, Ag_2CO_3. In the present study, the decomposition mechanism was elucidated by various analytical methods; gas analysis (differential thermal gas analyses) in helium, carbon dioxide and oxygen flows with and without a P_2O_5 trap or a KOH trap, DTA-TG in a carbon dioxide flow and high-temperature X-ray diffraction analysis in a carbon dioxide flow.

The gas evolution at ca. 200°C consisted of carbon dioxide. A simultaneous evolution of carbon dioxide and oxygen occurred at ca. 400°C. Two endothermic peaks (ca. 189 and 197°C) without weight change during the heating in a carbon dioxide atmosphere were due to the phase transition of silver carbonate from the normal via β to α phase. The reverse transition occurred during the cooling.

Introduction

Thermal decomposition of silver carbonate Ag_2CO_3 proceeds via multiple steps. The decomposition process is affected by the preparational conditions of the silver carbonate [1, 2], the dopant (K [3], Cs [3], Ca [4], Sr [4], Ba [3, 5], Y [6, 7] and Gd [7, 8]) and the decomposition atmospheres etc. [7, 9–12]; conflicting results were often reported by different workers. The decomposition steps are divided into two major groups; one at ca. 200° (150–200°) and another at ca. 400° (350–450°) although a few exceptions exist [2].

The result of gas analysis was not reported though the gas analysis is indispensable to understand the decomposition mechanism at ca. 400° where multiple DTA peaks were often observed. It must be examined whether the decarbonation occurs prior to the reduction at ca. 400° or the decarbonation and the reduction occurs simultaneously. In the present study, thermal decomposition of silver carbonate was investigated by differential thermal gas analysis (DTGA).

Van Hattum *et al.* reported a high-temperature phase of Ag_2CO_3 (α-Ag_2CO_3) which was obtained at $210°$ under a carbon dioxide atmosphere (ca. 4.5 atm) [12]. They also reported another high-temperature phase, β-Ag_2CO_3; the diffraction pattern was recorded at $150°$ under a carbon dioxide atmosphere (ca. 4.5 atm) [11]. Reversible endothermic phenomena during the thermal decomposition were reported by Wydeven [9] and Barnes and Stone [2]. In the present study, thermal analyses were focused on the phase transition of silver carbonate at a temperature range (ca. $100-200°$) where no decomposition occurs in a carbon dioxide atmosphere (1 atm). The phase transition of silver carbonate from the normal via β to α phase was detected by high-temperature X-ray diffraction analysis. Two endothermic peaks during the cooling were observed by DTA operated cyclically.

Experimental

Specimen

Reagent grade Ag_2CO_3 (Wako Pure Chemical) was used. The powders (light green aggregation) served for the thermal analysis without grinding.

Differential thermal gas analysis [13]

Gas evolution from the heated specimen was determined by the change in the thermal conductivity of the carrier gas or the reactor gas, The main constituents of the gas evolved from the specimen were assumed to be carbon dioxide, water vapour and oxygen. The arrangement presented in Fig. 1 was used to examine this hypothesis:

1) a helium gas flow with a P_2O_5-trap which removes water vapor,
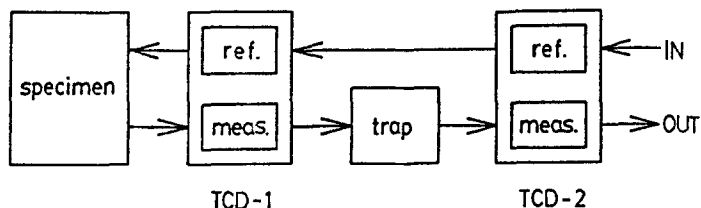

Fig. 1 Arrangement of differential thermal gas analysis.; IN: inlet of the carrier gas (helium) or the reactor gas (carbon dioxide or oxygen), OUT: outlet of the carrier gas or the reactor gas containing the gases evolved from the heated specimen, TCD: thermal conductivity detector, ref: reference cell of TCD, meas.: measurement cell of TCD, and trap: P_2O_5 or KOH

2) a helium gas flow with a KOH trap which removes both water vapour and carbon dioxide,

3) a carbon dioxide flow with a P_2O_5-trap, and

4) an oxygen gas flow with a KOH trap.

DTA-TG

The specimen was heated (ca. 10 deg/min) until ca. 200° in a carbon dioxide flow (60 ml/min) and cooled. The cyclic operation was refrained several times.

High-temperature X-ray diffraction analysis

Rotorflex RU-200 (copper target, 60 kV, 200 mA) equipped with 2311B1 specimen heater (Rigaku) was used. 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 1:

controlled heating (10 deg/min) from room temperature to 210° followed by the uncontrolled cooling to ca. 50° ($2\theta = 32$–35°), and
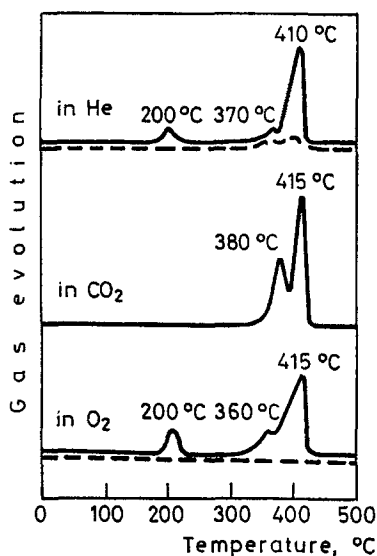

Fig. 2 Differential thermal gas analysis for the thermal decomposition of silver carbonate. Solid line: without a trap (detected by TCD-1) and dotted line: with a KOH trap (detected by TCD-2), heating rate: 10 deg/min

Program 2:

controlled heating (10 deg/min) from room temperature to 50° for the analysis at 50° for 15 minutes, then similarly to 100, 150, 200 and 20° and cooling to 200, 150, 100 and 50° (2θ = 15–60°).

Water vapour was not detected since the result with a P_2O_5 trap (not shown in the figure) was the same as that without the trap.

Results and discussion

Differential thermal gas analysis

The results of DTGA are shown in Fig. 2. The following results were obtained:

1) The gases evolved from the specimen were carbon dioxide and oxygen.
2) Water vapor was not detected.
3) Carbon dioxide was evolved at ca. 200°.
4) Carbon dioxide and oxygen were evolved simultaneously at ca. 400°.

DTA

The results of cyclic-DTA are shown in Fig. 3. The result of the TG was neglected in this figure because no weight change was detected. The endothermic peaks during the heating were attributed to the phase transition from the normal via β to α phase. The exothermic peaks during the cooling were attributed to the reverse transition.
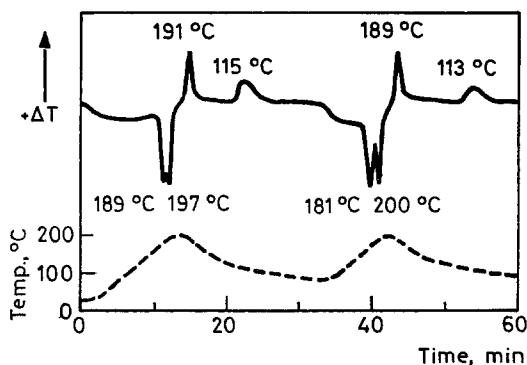

Fig. 3 Cyclic DTA for silver carbonate in a carbon dioxide atmosphere. Specimen weight: 110 mg. Only the first and second cycles are indicated

High-temperature X-ray diffraction analysis

The diffraction patterns for the specimen heated at 10 deg/min are shown in Fig. 4. The peak heights for the typical diffraction of the normal, the β and the α phases are shown in Fig. 5. Thus, the three phases were observed simultaneously at 180–190° during the transition from the normal via β to α phase; β phase was not observed as a single phase.

The thermal expansion of the normal phase is shown in Fig. 6. The expansion coefficients are 1.92×10^{-5} and 5.76×10^{-5}/deg. along a and c-axis, respectively. No 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.
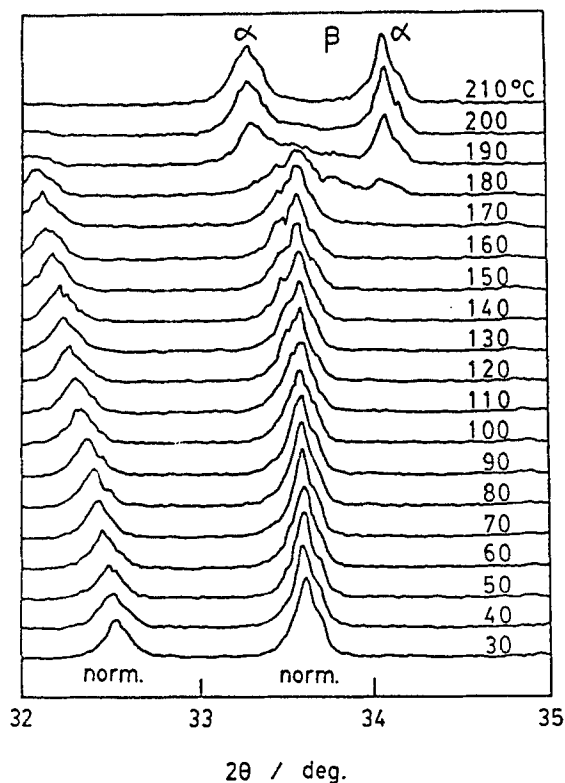

Fig. 4 X-ray diffraction patterns for silver carbonate during the heating.norm., α and β: the normal, α and β phase, respectively, Heating: program 1 (heating rate; 10 deg/min), Atmosphere: carbon dioxide, Target: copper Kα-radiation
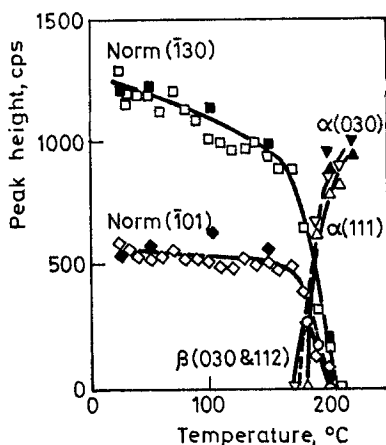
Fig. 5 Height of diffraction peaks for silver carbonate during the heating. , □, Δ, ∇ and ○:
the peaks observed during the heating by the program 1, and ■, ♦, ▲, and ▼: the
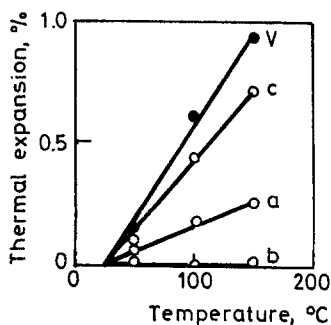peaks observed during the heating by the program 2. Atmosphere: carbon dioxide

Fig. 6 Thermal expansion for the normal silver carbonate during the heating. a, b and c: linear
expansion along the a, b and c-axis, respectively, and V: volumetric expansion. Heating:
program 2, Atmosphere: carbon dioxide.

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Zusammenfassung — Die von verschiedenen Autoren veröffentlichten Resultate über die thermische Zersetzung von Silbercarbonat, Ag_2CO_3, sind widersprüchlich. In der vorliegenden Arbeit wurde der Zersetzungsmechanismus mittels unterschiedlicher analytischer Methoden aufgeklärt: Differenzthermische Gasanalytik in strömendem Helium, Kohlendioxid sowie Sauerstoff mit und ohne eine P_2O_5-Falle oder eine KOH-Falle, DTA-TG in strömendem CO_2 und Hochtemperatur-Röntgendiffraktion in strömendem CO_2.

Die Gasentwicklung bei ca. 200°C bestand aus CO_2. Eine simultane Evolution von CO_2 und O_2 wurde bei ca. 400°C beobachtet. Zwei endotherme Maxima (ca. 189 und 197°C) ohne Gewichtsänderung beim Aufheizen in CO_2 Atmosphäre wurden auf die Phasenumwandlung des Silbercarbonats von der normalen via β- zur α-Phase zurückgeführt. Der umgekehrte Prozess lief während des Kühlvorgangs ab.