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THERMAL DECOMPOSITION OF CERUSSITE ($PbCO_3$) IN CARBON DIOXIDE ATMOSPHERE (0—50 ATM)

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ABSTRACT

The thermal decomposition of cerussite, $PbCO_3$, was studied over a wide range of CO_2 pressures (0—50 atm) using high pressure DTA and X-ray powder diffraction.

At low CO_2 pressures (<1 atm), cerussite decomposed to PbO via only one intermediate, $PbCO_3 \cdot 2\,PbO$, but at medium pressures (~1 atm), two intermediates, $PbCO_3 \cdot PbO$ and $PbCO_3 \cdot 2\,PbO$, were formed. At high pressures (>4 atm), cerussite decomposed to PbO via three intermediates, $2\,PbCO_3 \cdot PbO$ and those given above.

As the pressure of CO_2 increased, the temperatures at which the DTA peaks appeared increased, the number of intermediates also increasing. The thermal behaviour is discussed on the basis of the phase diagram of the PbO—CO_2 system and also on the temperature-dependence of the decomposition rate.

INTRODUCTION

Past studies on the thermal decomposition of cerussite have shown that the decomposition process is very complicated and that the intermediates appearing during the decomposition process are strongly affected by the experimental conditions, particularly the pressure of carbon dioxide (p_{CO_2}).

The thermal decomposition of cerussite over a wide range of p_{CO_2} is discussed in this paper. Previous studies using dynamic analytical instruments have been confined to low p_{CO_2}; static studies only have been reported at high p_{CO_2}.

Grisafe and White [1], who used high-pressure hydrothermal apparatus, have reported the phase diagram of the PbO—CO_2 system in the pressure range 15—1400 atm. Four intermediate oxycarbonates, $2\,PbCO_3 \cdot PbO$, $PbCO_3 \cdot PbO$, $PbCO_3 \cdot 2\,PbO$ and $4\,PbCO_3 \cdot 3\,PbO$, are present in their phase diagram. Of these, $4\,PbCO_3 \cdot 3\,PbO$ is stable only above 300 atm and the other three intermediates are stable below 200 atm. No phase diagram for pressures below 15 atm has been reported.

Ball and Casson [2] have studied the effect of p_{CO_2} (0—1 atm) on the thermal decomposition of cerussite using thermogravimetry and X-ray diffrac-

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tion. The decomposition occurring under 0.08 atm of carbon dioxide is reported to be as follows: cerussite decomposed successively to $PbCO_3 \cdot PbO$ at ~300°C, to $PbCO_3 \cdot 2\,PbO$ at ~360°C and to PbO at ~430°C. It was found that the decomposition temperature increased with increasing p_{CO_2} and that at very low p_{CO_2} cerussite decomposed directly to $PbCO_3 \cdot 2\,PbO$. The intermediate, $PbCO_3 \cdot 2\,PbO$, was not found, suggesting that either it is not present, or that it is so unstable that it cannot be detected with the instrument employed. Several other workers [3—5] have reported similar results.

Warne and Bayliss [6] studied the effects of some controllable variables on the thermal decomposition of cerussite. These included dilution with inert materials, composition of furnace atmosphere, heating rate, uniformity and sizing of particles. All these factors were found to affect the decomposition behavior.

Komoda et al. [7] studied the thermal decomposition of cerussite under isothermal conditions using thermogravimetry. The important effect of sample preparation on decomposition behavior was demonstrated. The cerussite precipitated at 70°C from an aqueous solution of lead acetate and ammonium carbonate decomposed to $PbCO_3 \cdot 2\,PbO$ in a nitrogen atmosphere, while $PbCO_3 \cdot PbO$ was formed from the cerussite precipitated at 15°C. The thermal behavior of $2\,PbCO_3 \cdot PbO$ is also interesting since this phase has not been found in the thermal decomposition of cerussite though it appeared in an equilibrium study of the phase diagram.

In the present work, the thermal decomposition of cerussite was studied over a wide range of p_{CO_2} (0—50 atm) using DTA—TG, high-pressure DTA and X-ray powder diffraction. The only variable in the experimental conditions was p_{CO_2}.

EXPERIMENTAL

Samples

Reagent-grade normal lead carbonate (Merck, West Germany) was used as cerussite. The $PbO : CO_2 : H_2O$ molar ratio (1.00 : 1.02 : 0.04) obtained from compositional analysis was approximately equal to that of the pure cerussite, $PbCO_3$ (1.00 : 1.00 : 0.00). The powder diffraction pattern was that of cerussite (JCPDS 5-0417). A trace of basic lead carbonate was also present. The particles were block-shaped and the SEM micrograph (Fig. 1) showed them to be greater than 1 μm in diameter.

High-pressure differential thermal analysis

The decomposition process was studied in detail using a high-pressure DTA apparatus which was newly designed and constructed by the authors [8]. The specimen was heated under various pressures of carbon dioxide ($p_{CO_2} < 50$) at a rate of ~10°C min^{-1} to 700°C. The atmosphere in the specimen chamber was changed to pure carbon dioxide by flushing the chamber

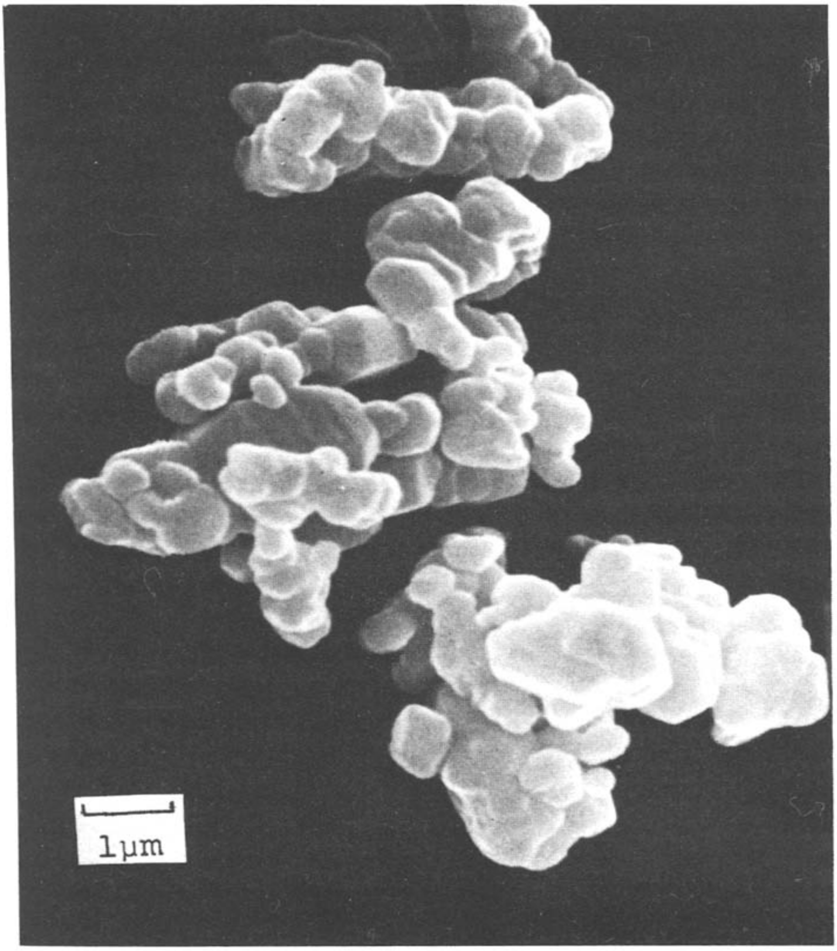


Fig. 1. SEM micrograph of cerussite.

with the gas three times before the experiment was carried out. Carbon dioxide was then passed through this chamber (100 ml min^{-1}) to remove gases evolved on thermal decomposition.

Differential thermal analysis and thermogravimetry

The DTA—TG apparatus (type M8076, Rigaku Denki Co., Japan) was used in air and under a flow of carbon dioxide (p_{CO_2} = 1 atm, flow rate, 60 ml min^{-1}); the heating rate was ~10°C min^{-1}.

X-ray powder diffraction

The structural changes in the specimens quenched from various temperatures were examined using a powder X-ray diffractometer (APD-10, Philips Co.) with Cu target and monochromator.

RESULTS

DTA curves at various p_{CO_2} are shown in Fig. 2. The curves at p_{CO_2} below 1 atm were recorded with commercial apparatus and those at p_{CO_2} above 1 atm were recorded with high-pressure equipment constructed by the authors. No abrupt change in the decomposition behavior was found on passing through $p_{CO_2} = 1$ atm, suggesting that instrumental effects were negligible at $p_{CO_2} = 1$ atm.

The thermal decomposition of cerussite was strongly affected by p_{CO_2}. The temperatures at which the cerussite and oxycarbonate intermediate decomposed increased with increasing p_{CO_2}. The number of oxycarbonate intermediates increased with increasing p_{CO_2}. The decomposition behavior of cerussite can be classified into three types, which depend on the p_{CO_2}.

Decomposition at low p_{CO_2} ($p_{CO_2} < 1$ atm)

The results of DTA and TG in air are shown in Fig. 3. Only one intermediate, $PbCO_3 \cdot 2\,PbO$, was found under these conditions. Cerussite decomposed to $PbCO_3 \cdot 2\,PbO$ at ~200°C, then to PbO at ~310°C. This result was supported by X-ray diffraction analysis of the specimens quenched from various temperatures in air.

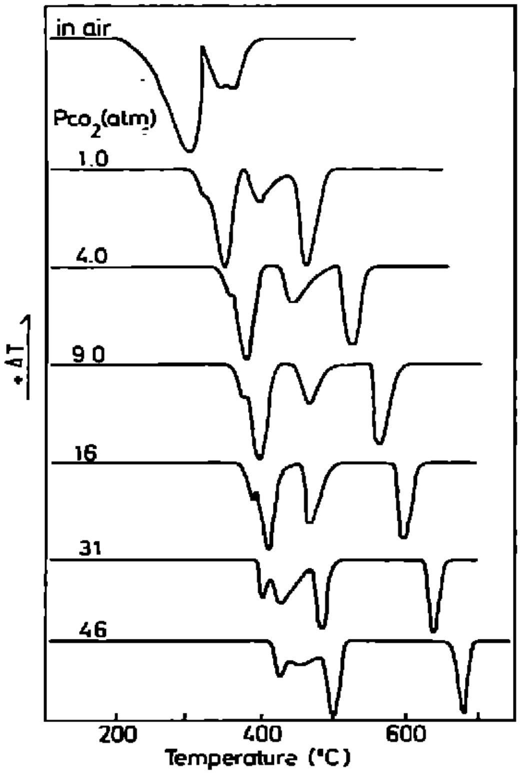
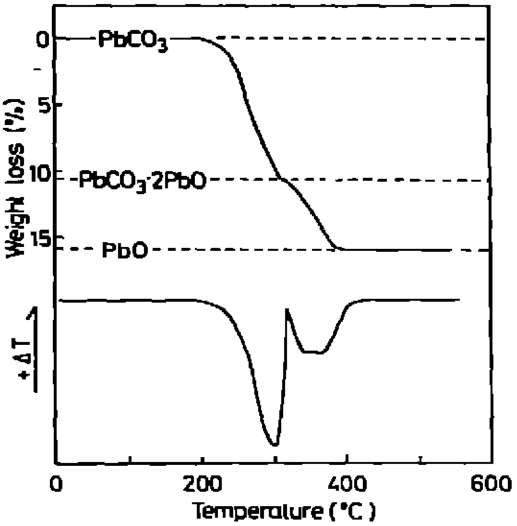


Fig. 2. DTA of cerussite, $PbCO_3$, at various p_{CO_2}.



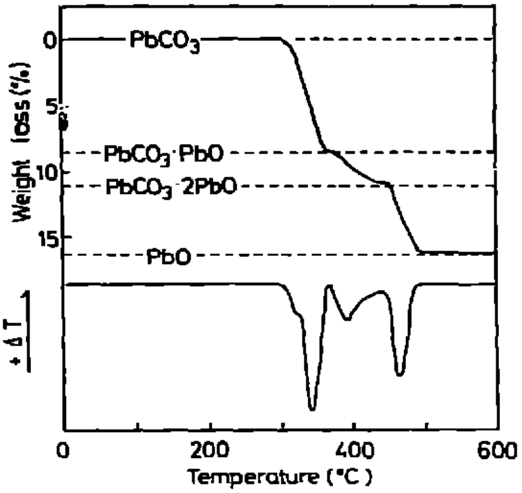
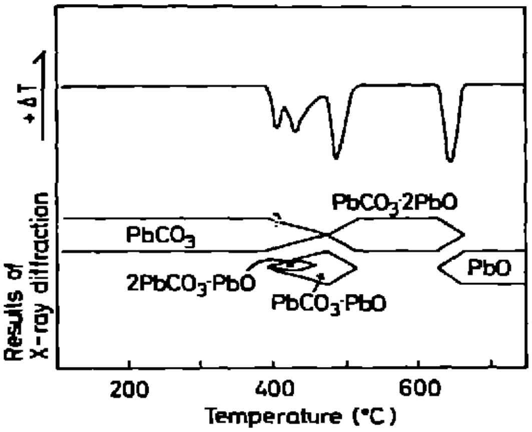


Fig. 3. DTA—TG of cerussite, $PbCO_3$, in air. The dotted lines show the weight loss calculated for the formation of each compound.

Fig. 4. DTA—TG of cerussite, $PbCO_3$, in CO_2 (p_{CO_2} = 1 atm). The dotted lines show the weight loss calculated for the formation of each compound.



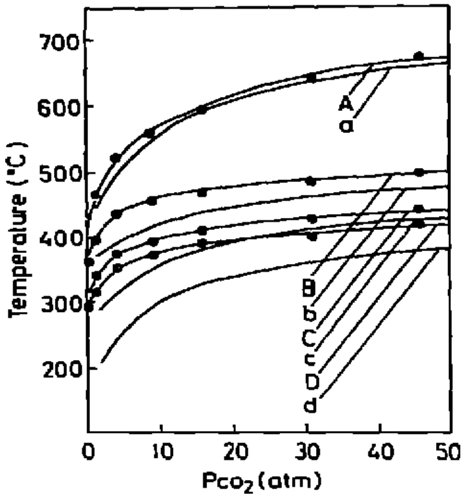


Fig. 5. Thermal decomposition of cerussite, $PbCO_3$, at p_{CO_2} = 31 atm, determined by DTA and X-ray powder diffraction. The width of the bands in the X-ray diffraction results represents the approximate amount of each phase present in the quenched specimens.

Fig. 6. Effect of p_{CO_2} on DTA peak temperature for cerussite, $PbCO_3$. ●, DTA peak temperature. Lines represented by capital letters show experimental results for various decomposition processes and those represented by small letters their corresponding phase boundaries (Grisafe and White [1]):

A, a: $PbCO_3 \cdot 2\,PbO \rightarrow 3\,PbO + CO_2$;
B, b: $3\,(PbCO_3 \cdot PbO) \rightarrow 2\,(PbCO_3 \cdot 2\,PbO) + CO_2$;
C, c: $2\,(2\,PbCO_3 \cdot PbO) \rightarrow 3\,(PbCO_3 \cdot PbO) + CO_2$;
D, d: $3\,PbCO_3 \rightarrow 2\,PbCO_3 \cdot PbO + CO_2$.

Decomposition at medium p_{CO_2} ($p_{CO_2} \sim 1$ atm)

The results of DTA and TG at $p_{CO_2} = 1$ atm are shown in Fig. 4. Two intermediates, $PbCO_3 \cdot PbO$ and $PbCO_3 \cdot 2\,PbO$, were found. Cerussite decomposed to $PbCO_3 \cdot PbO$ at ~300°C; this then decomposed to $PbCO_3 \cdot 2\,PbO$ at ~370°C and to PbO at ~440°C.

Decomposition at high pressure ($p_{CO_2} > 4$ atm)

The results of DTA and X-ray powder diffraction at $p_{CO_2} = 31$ atm are shown in Fig. 5. There were three intermediates, $2\,PbCO_3 \cdot PbO$, $PbCO_3 \cdot PbO$ and $PbCO_3 \cdot 2\,PbO$. A trace of $2\,PbCO_3 \cdot PbO$ was found by X-ray diffraction at $p_{CO_2} = 4$ atm. This intermediate, was not found at lower values of p_{CO_2}. In this p_{CO_2} range, cerussite decomposed to $2\,PbCO_3 \cdot PbO$ which then decomposed successively to $PbCO_3 \cdot PbO$, $PbCO_3 \cdot 2\,PbO$ and PbO.

The effect of p_{CO_2} on the DTA peak temperatures for cerussite, $PbCO_3$, is shown in Fig. 6. All the peak temperatures increased with increasing p_{CO_2}. The peak temperatures were located approximately on the phase boundaries of the PbO—CO_2 system reported by Grisafe and White [1]. The line connecting the peak temperatures for the reaction $PbCO_3 \cdot 2\,PbO \rightarrow 3\,PbO + CO_2$ was very close to the phase boundary of $PbCO_3 \cdot 2\,PbO$ and PbO.

DISCUSSION

Under low pressures of carbon dioxide, the thermal decomposition of cerussite proceeds as follows

$$PbCO_3 \xrightarrow[\sim 200^\circ C]{CO_2\uparrow} PbCO_3 \cdot 2\,PbO \xrightarrow[\sim 310^\circ C]{CO_2\uparrow} PbO$$

This result is consistent with that of Ball and Casson [2] obtained under nitrogen.

At $p_{CO_2} \sim 1$ atm, the thermal decomposition of cerussite proceeds as follows

$$PbCO_3 \xrightarrow[\sim 300^\circ C]{CO_2\uparrow} PbCO_3 \cdot PbO \xrightarrow[\sim 370^\circ C]{CO_2\uparrow} PbCO_3 \cdot 2\,PbO \xrightarrow[\sim 440^\circ C]{CO_2\uparrow} PbO$$

This result is also consistent with those of Ball and Casson [2], Pannetier et al. [3] and Peretti [4], obtained under carbon dioxide.

The thermal decomposition of cerussite has not been studied at values of p_{CO_2} above 1 atm. We found an intermediate, $2\,PbCO_3 \cdot PbO$, at a high p_{CO_2}. This oxycarbonate was found at carbon dioxide pressures down to 4 atm. Grisafe and White [1] demonstrated the presence of oxycarbonate with this formula at values of p_{CO_2} above 15 atm in their high-pressure hydrothermal study; the stability of this compound at $p_{CO_2} = 4$ atm was not reported. However, an extrapolation of their results suggests that the oxycarbonate is stable at this pressure. The result shows that the thermal decomposition of cerussite at high pressures of carbon dioxide proceeds as follows

$$PbCO_3 \xrightarrow{CO_2\uparrow} 2\ PbCO_3 \cdot PbO \xrightarrow{CO_2\uparrow} PbCO_3 \cdot PbO \xrightarrow{CO_2\uparrow} PbCO_3 \cdot 2\ PbO \xrightarrow{CO_2\uparrow} PbO$$

The good agreement of the peak temperature (for the reaction $PbCO_3 \cdot 2\ PbO \rightarrow 3\ PbO + CO_2$) with the equilibrium decomposition temperature suggests that this reaction proceeds very close to the equilibrium condition, since the decomposition rate probably increases at high temperatures. The decomposition temperature is the highest of the various intermediates. The peak temperatures of the other reactions are noticeably higher than the equilibrium decomposition temperatures. The differences in temperature are probably due to the low rates of reaction at low temperatures. The increasing similarity between the high-pressure DTA decomposition temperature and the equilibrium decomposition temperature with increasing p_{CO_2} (or decomposition temperature) supports this explanation.

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