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THERMAL DECOMPOSITION OF HYDROCERUSSITE ($2\ PbCO_3 \cdot Pb(OH)_2$) IN CARBON DIOXIDE ATMOSPHERE (0—50 atm)

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ABSTRACT

The thermal decomposition of hydrocerussite was studied with TG, high-pressure DTA and powder X-ray diffraction techniques in the p_{CO_2} range 0—50 atm. The decomposition process was strongly affected by p_{CO_2}. $PbCO_3$, as a new intermediate, was found at carbon dioxide pressures above 1 atm. The results were different from any of the previous studies. The temperatures of all the endothermic processes increased and the formation temperature of $PbCO_3$ decreased with increasing p_{CO_2}. The results are discussed by referring to the equilibrium phase diagram of the system PbO—CO_2.

INTRODUCTION

The thermal decomposition of hydrocerussite proceeds via dehydration and decarbonation to PbO and many oxycarbonate intermediates appear in this decomposition process. The number and the kind of intermediates involved in the process and their decomposition temperatures are clearly affected by the carbon dioxide pressure, p_{CO_2}.

This paper presents the thermal decomposition of hydrocerussite studied with TG, high-pressure DTA and powder X-ray diffraction techniques in a wide pressure range of carbon dioxide. No worker has studied the effect of carbon dioxide pressure on the thermal decomposition of hydrocerussite systematically.

Pannetier et al. [1] investigated the thermal decomposition of hydrocerussite in a carbon dioxide atmosphere with TG, DTA and powder X-ray diffraction techniques. Dehydration took place at 170°C and an oxycarbonate intermediate, $2\ PbCO_3 \cdot PbO$, was formed. This intermediate decomposed to another intermediate, $PbCO_3 \cdot 2\ PbO$, at 300°C with evolution of carbon dioxide. The final product, PbO, was formed at 420°C.

The TG and DTA studies of Sarig and Kahana [2] in an argon atmosphere showed that hydrocerussite decomposed at 140°C with evolution of water

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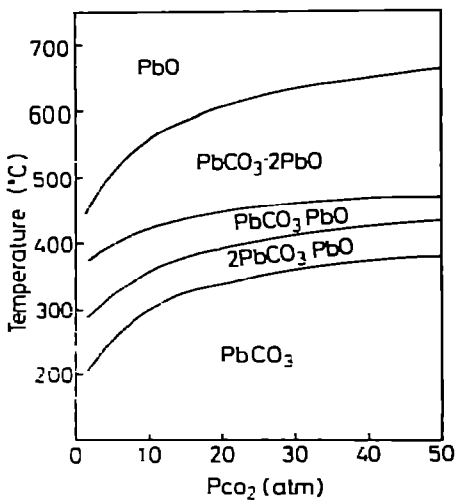

Fig. 1. Phase diagram of the system PbO—CO_2 [4]

vapor to 2 $PbCO_3 \cdot PbO$ which then decomposed to 2 $PbCO_3 \cdot 3\,PbO$ at 240°C with evolution of carbon dioxide and finally to PbO at 320°C, again with evolution of carbon dioxide.

The results of Andreeva and Limar [3] with TG, DTA, IR and powder X-ray diffraction analysis were different from those of the above two studies. No description of the atmosphere was given in their study but it was probably carbon dioxide. They postulated the following process; hydrocerussite decomposed at 240°C to 2 $PbCO_3 \cdot PbO$ which successively decomposed at 348—350°C to $PbCO_3 \cdot PbO$, at 390—400°C to $PbCO_3 \cdot 2\,PbO$ and at 450—470°C to PbO.

In the present study, the thermal decomposition of hydrocerussite is studied in the p_{CO_2} range 0—50 atm. The decomposition process was strongly affected by p_{CO_2} and a new intermediate, $PbCO_3$, was found at $p_{CO_2} > 1$ atm. The results differ from those of the previous studies. The decomposition processes are explained by referring to the equilibrium phase diagram at $p_{CO_2} > 3$ atm. Figure 1 shows the equilibrium diagram of the system PbO—CO_2 [4]. No phase diagram is reported for the system PbO—CO_2—H_2O.

EXPERIMENTAL

Samples

Reagent grade basic lead carbonate (Kanto Chemical Co., Inc., Japan) was used as hydrocerussite. The PbO : CO_2 : H_2O molar ratio (1.00 : 0.70 : 0.28), determined by the compositional analysis, was approximately equal to that of the pure hydrocerussite 2 $PbCO_3 \cdot Pb(OH)_2$ (1.00 : 0.66 : 0.33) and powder X-ray diffraction showed the pattern of hydrocerussite (JCPDS 13-131). The particles were block shaped and the SEM micrograph (Fig. 2) showed them to be larger than 1 μm.

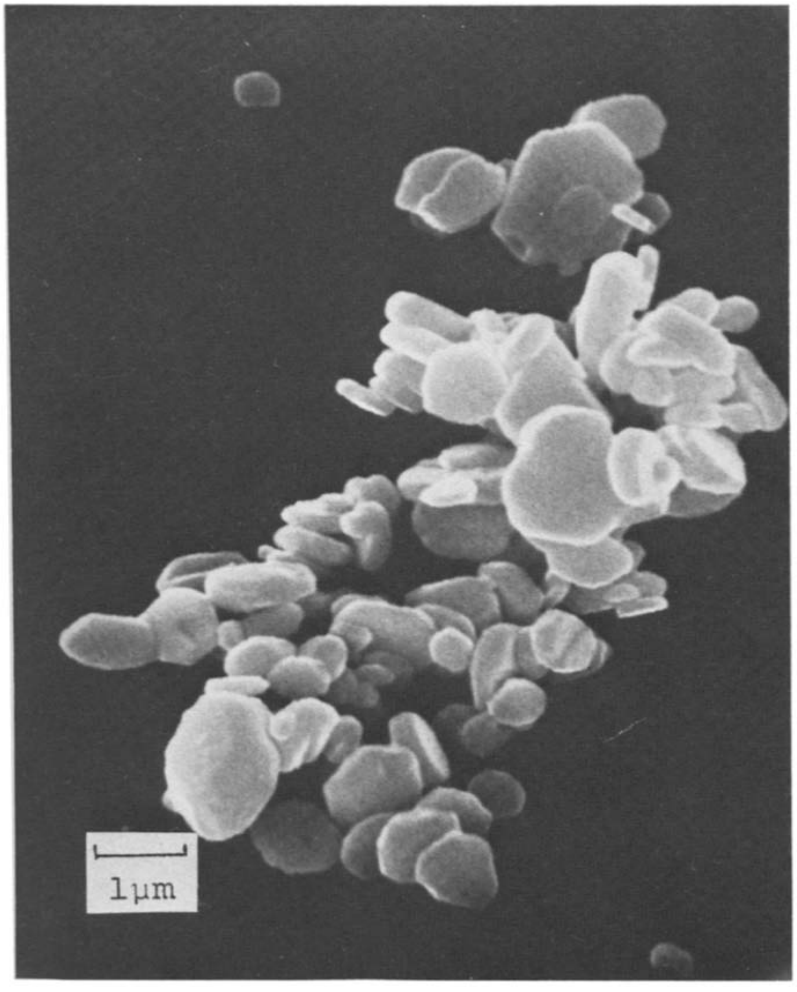

Fig. 2. SEM micrograph of hydrocerussite.

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 [5]. The specimen was heated under various pressures of carbon dioxide ($p_{CO_2} \leqslant$ 50 atm) at a heating rate of ~10°C min^{-1} up to 700°C. The atmosphere in the specimen chamber was changed to pure carbon dioxide by flushing the chamber 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 the gases evolved on thermal decomposition rapidly.

Differential thermal analysis and thermogravimetry

The DTA—TG apparatus (Type M8076, Rigaku Denki Co., Japan) was used in air and a stream 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 specimen were examined by a X-ray diffractometer (APD-10, Philips Co.) with Cu target and monochromator. The specimens at $p_{CO_2} \leqslant 3$ atm were prepared by quenching from various temperatures in air. At $p_{CO_2} > 3$ atm, the specimens were cooled at ~20°C min^{-1} from various temperatures in the high-pressure DTA with the high-pressure carbon dioxide released simultaneously. It was ascertained by high-pressure DTA that no reaction occurred during the cooling process.

RESULTS

A total of over 100 runs were made in the p_{CO_2} range 0—50 atm. Figure 3 shows representative DTA diagrams for the thermal decomposition of hydrocerussite at various carbon dioxide pressures. The strong influence of p_{CO_2} on the thermal decomposition of hydrocerussite is clearly seen. The number of intermediates involved in the decomposition process (endothermic peaks) increased with increasing p_{CO_2}, and at a pressure above approximately 1 atm, $PbCO_3$ was formed (endothermic peak at ~220°C). As described in detail below, with increasing p_{CO_2} the decomposition temperature of each intermediate increased and the formation temperature of $PbCO_3$ decreased. Decomposition of hydrocerussite could be divided into four groups at various

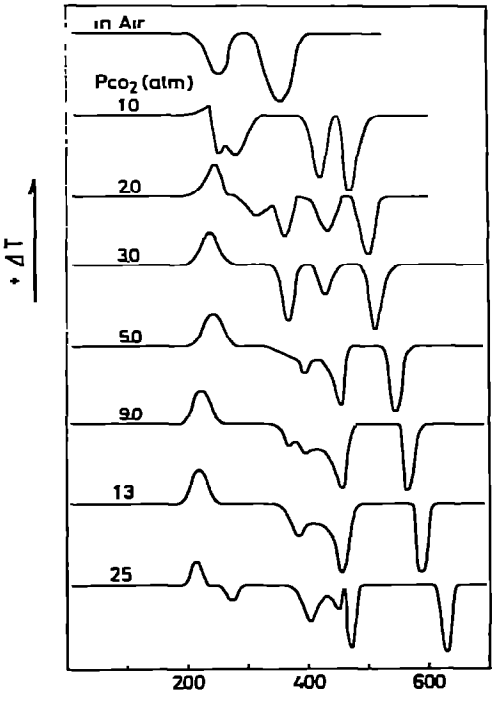

Fig. 3. DTA of hydrocerussite at the carbon dioxide pressures shown.

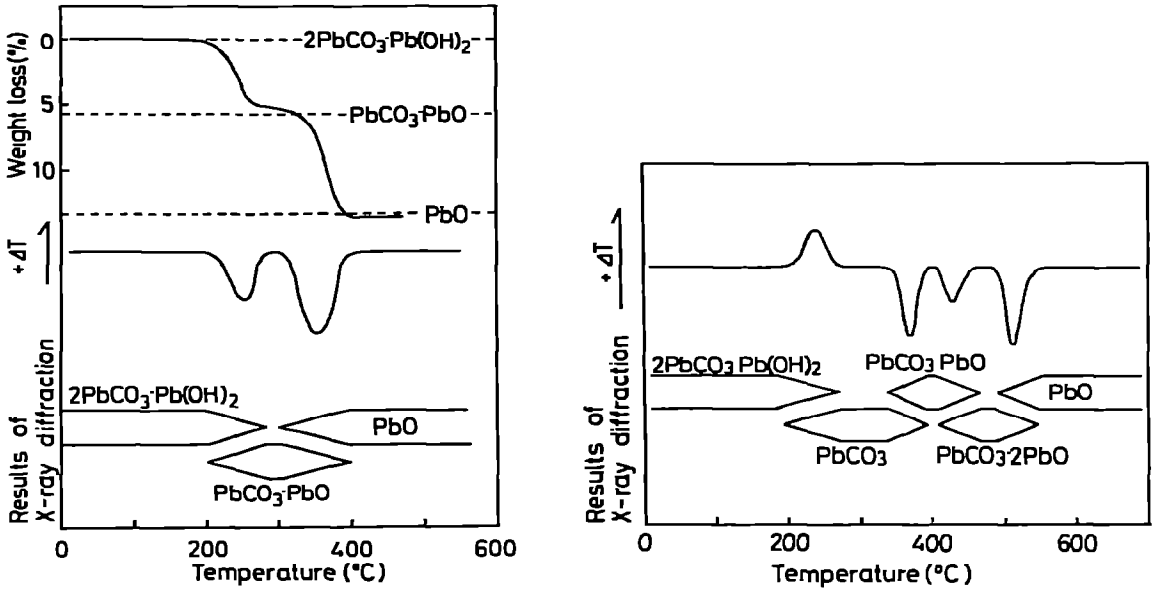

Fig. 4. DTA—TG and the results of X-ray diffraction analysis on the thermal decomposition of hydrocerussite in air. The dotted lines show the calculated weight loss for the formation of each compound. The width of the band in the X-ray diffraction analysis represents the approximate amount of phase present in the specimen.

Fig. 5. DTA and the results of X-ray diffraction analysis on the thermal decomposition of hydrocerussite at p_{CO_2} = 3 atm. The width of the band in the X-ray diffraction analysis represents the approximate amount of phase present in the specimen.

carbon dioxide pressures. Decomposition process belonging to the neighbouring group often occurred simultaneously at the transition region of the groups.

$p_{CO_2} << 1$ atm (in air)

Figure 4 shows the results of TG and DTA, and the phases identified by X-ray diffraction analysis on the specimens quenched from various temperatures. Two endothermic peaks at ~250°C and ~340°C and weight losses at ~200—270°C and ~330—400°C were found in DTA and TG, respectively. The phases identified at various temperatures were 2 $PbCO_3 \cdot Pb(OH)_2$ below ~280°C, $PbCO_3 \cdot PbO$ at ~200—400°C, and PbO above ~300°C.

~1 atm $\leqslant p_{CO_2} <$ ~5 atm

Figure 5 shows the results of the DTA and X-ray diffraction analysis on specimens quenched from various temperatures at a carbon dioxide pressure of 3 atm. One exothermic peak at ~240°C and three endothermic peaks at ~370, ~430 and ~570°C can be seen. The phases identified at various temperatures were 2 $PbCO_3 \cdot Pb(OH)_2$ below ~270°C, $PbCO_3$ at ~200—390°C, $PbCO_3 \cdot PbO$ at ~330—460°C, $PbCO_3 \cdot 2\,PbO$ at ~410—550°C, and PbO

above ~500°C. The exothermic peak obtained by DTA became stronger and moved towards lower temperatures with increasing p_{CO_2}. This exothermic peak was clearly due to the formation of cerussite, $PbCO_3$, from hydrocerussite and carbon dioxide in the atmosphere. With decreasing p_{CO_2}, the fraction of $PbCO_3$ in the quenched specimen decreased. At $p_{CO_2} = 1$ atm, the exothermic peak was very weak and was followed by strong endothermic peaks. The constitution of the specimen quenched immediately after the first endothermic peak was mostly $PbCO_3 \cdot PbO$ with minor amounts of $PbCO_3$ and $PbCO_3 \cdot 2\,PbO$. The endothermic peak which followed immediately after the exothermic peak became weaker and moved towards higher temperatures with the increasing p_{CO_2}.

~5 atm ≤ p_{CO_2} < ~15 atm

Figure 6 shows the results of DTA and X-ray diffraction analysis on the specimens cooled from various temperatures at a carbon dioxide pressure of 9 atm. An exothermic peak at ~220°C and four endothermic peaks at ~370, ~400, ~460 and ~560°C were found. The phases identified by X-ray diffraction analysis were $2\,PbCO_3 \cdot Pb(OH)_2$ below ~260°C, $PbCO_3$ at ~200—450°C, $2\,PbCO_3 \cdot PbO$ at ~340—460°C, $PbCO_3 \cdot PbO$ at ~360—480°C, $PbCO_3 \cdot 2\,PbO$ at ~410—590°C, and PbO above ~550°C. With increasing p_{CO_2}, the peak temperatures of all the endothermic decomposition processes increased and that of the exothermic process decreased. In the temperature range ~350—450°C, three or four intermediates coexisted. At $p_{CO_2} = 5$ and 13 atm in Fig. 3, the number of clear peaks in the DTA apparently decreased; however, the same four intermediates described above were found at various temperatures by X-ray diffraction analysis.

~15 atm < p_{CO_2}

Figure 7 shows the results of DTA and X-ray diffraction analysis on the specimens cooled from various temperatures at a carbon dioxide pressure of 25 atm. The intermediates appearing in this p_{CO_2} region were the same as those found at 5—15 atm. However, the decomposition process was more complicated. A new endothermic peak appeared at the temperature close to the exothermic peak. The endothermic peak was absent at p_{CO_2} < ~15 atm. A significant amount of hydrocerussite starting material, as well as $PbCO_3$ was found in the specimen cooled immediately after the exothermic peak. The specimen cooled immediately after the first endothermic peak contained only $PbCO_3$ according to X-ray diffraction analysis. Apparently, the formation of $PbCO_3$ from the starting material after the exothermic peak and the carbon dioxide in the atmosphere is endothermic under these conditions. The process that followed this endothermic peak at higher temperatures was essentially the same as that found at p_{CO_2} = ~5—15 atm. The phases identified by X-ray diffraction analysis on the cooled specimens were $2\,PbCO_3 \cdot Pb(OH)_2$ below ~290°C, $PbCO_3$ at ~190—430°C, $2\,PbCO_3 \cdot PbO$ at ~370—470°C, $PbCO_3 \cdot PbO$ at ~430—490°C, $PbCO_3 \cdot 2\,PbO$ at ~470—650°C, and PbO above ~620°C.

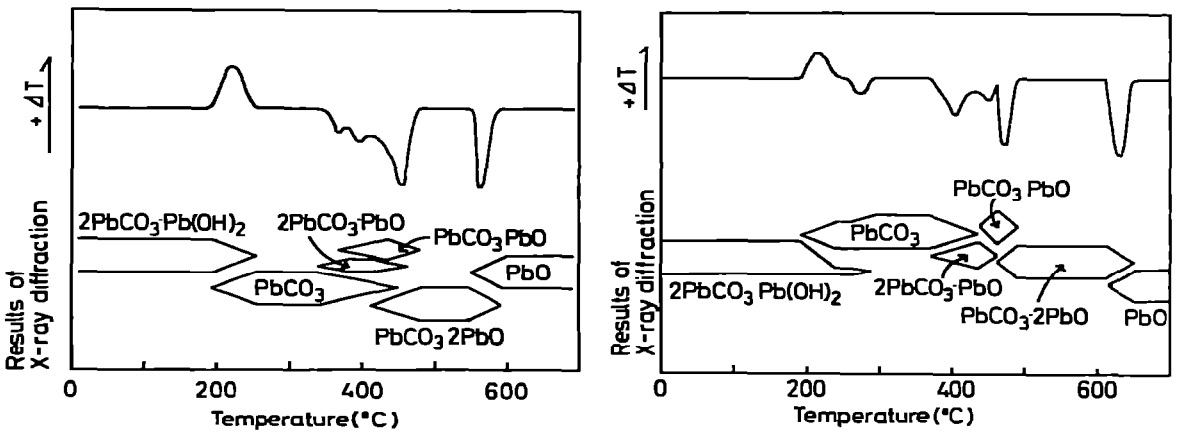

Fig. 6. DTA and the results of X-ray diffraction analysis on the thermal decomposition of hydrocerussite at p_{CO_2} = 9 atm. The width of band in the X-ray diffraction analysis represents the approximate amount of phase present in the specimen.

Fig. 7. DTA and the results of X-ray diffraction analysis on the thermal decomposition of hydrocerussite at p_{CO_2} = 25 atm. The width of band in the X-ray diffraction analysis represents the approximate amount of phase in the specimen.

The peak DTA temperatures at various CO_2 pressures are shown in Fig. 8. With increasing p_{CO_2}, the temperature of all the endothermic peaks increased except for the curious endothermic peak at the $p_{CO_2} > \sim 15$ atm, but that of the exothermic peak decreased. The peak DTA temperature after dehydration lay near the equilibrium phase boundaries of the system PbO—CO_2 (Fig. 1). The peak temperatures were always higher than the temperatures of the equilibrium phase boundaries.

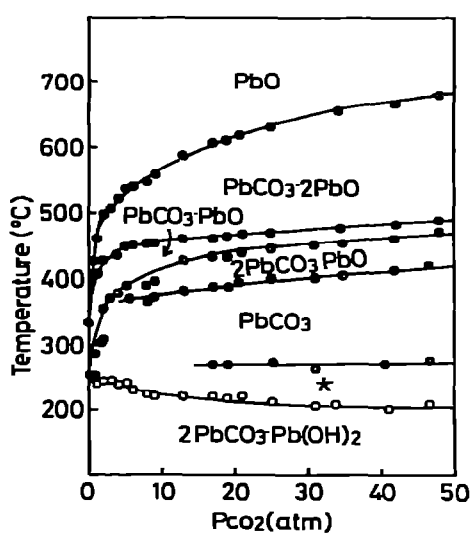

Fig. 8. Effect of p_{CO_2} on the peak temperature of various decomposition processes. The approximately horizontal line starting at $p_{CO_2} = \sim 15$ atm shows the first endothermic peak temperature as shown on the DTA curve at p_{CO_2} = 25 atm in Fig. 3, for example
* The details of this phase will be described in the Discussion.

DISCUSSION

Typical thermal decomposition processes of hydrocerussite at various CO_2 pressures are summarized below.

Process 1 (in air)

$$2\,PbCO_3 \cdot Pb(OH)_2 \xrightarrow[\sim 200^\circ C]{H_2O\uparrow\ CO_2\uparrow} PbCO_3 \cdot PbO \xrightarrow[\sim 300^\circ C]{CO_2\uparrow} PbO$$

Process 2 (p_{CO_2} = 3 atm)

$$2\,PbCO_3 \cdot Pb(OH)_2 \xrightarrow[\sim 200^\circ C]{H_2O\uparrow\ CO_2\uparrow} PbCO_3 \xrightarrow[\sim 330^\circ C]{CO_2\uparrow} PbCO_3 \cdot PbO \xrightarrow[\sim 400^\circ C]{CO_2\uparrow}$$

$$PbCO_3 \cdot 2\,PbO \xrightarrow[\sim 410^\circ C]{CO_2\uparrow} PbO$$

Process 3 (p_{CO_2} = 9 atm)

$$2\,PbO_3 \cdot Pb(OH)_2 \xrightarrow[\sim 190^\circ C]{H_2O\uparrow\ CO_2\uparrow} PbCO_3 \xrightarrow[\sim 340^\circ C]{CO_2\uparrow} 2\,PbCO_3 \cdot PbO \xrightarrow[\sim 360^\circ C]{CO_2\uparrow}$$

$$PbCO_3 \cdot PbO \xrightarrow[\sim 410^\circ C]{CO_2\uparrow} PbCO_3 \cdot 2\,PbO \xrightarrow[\sim 550^\circ C]{CO_2\uparrow} PbO$$

Process 4 (p_{CO_2} = 25 atm)

$$2\,PbCO_3 \cdot Pb(OH)_2 \xrightarrow[\sim 190^\circ C]{H_2O\uparrow\ CO_2\uparrow} * \xrightarrow[\sim 250^\circ C]{CO_2\uparrow} PbCO_3 \xrightarrow[\sim 370^\circ C]{CO_2\uparrow}$$

$$2\,PbCO_3 \cdot PbO \xrightarrow[\sim 420^\circ C]{CO_2\uparrow} PbCO_3 \cdot PbO \xrightarrow[\sim 460^\circ C]{CO_2\uparrow} PbCO_3 \cdot 2\,PbO \xrightarrow[\sim 620^\circ C]{CO_2\uparrow} PbO$$

This study is the first to show the formation of $PbCO_3$.

In air, only one intermediate, $PbCO_3 \cdot PbO$, was involved in the thermal decomposition process. Hydrocerussite decomposed to $PbCO_3 \cdot PbO$ with the simultaneous evolution of carbon dioxide and water vapor. PbO was formed at ~300°C. This result is different from that of Sarig and Kahana [2] who proposed two intermediates, $2\,PbCO_3 \cdot PbO$ and $2\,PbCO_3 \cdot 3\,PbO$, in their thermal decomposition study of hydrocerussite in an argon atmosphere. Detailed discussion is not attempted here since these authors arrived at their conclusion from only the TG study; no X-ray diffraction analysis was made.

The decomposition process 1 is unfavorable at CO_2 pressures above 1 atm. An intermediate $PbCO_3$ appeared at p_{CO_2} = 1 atm. The fraction of hydrocerussite converted to $PbCO_3$ increased with the increasing p_{CO_2} which suggests that $PbCO_3$ is more stable than $PbCO_3 \cdot PbO$ in this p_{CO_2} range at this temperature and that the formation of $PbCO_3$ is governed by the supply of

* The details of this phase are described below.

carbon dioxide from the gas phase. At low p_{CO_2}, the supply of carbon dioxide is insufficient to convert the hydrocerussite completely to $PbCO_3$ and a large proportion of the hydrocerussite was decomposed to $PbCO_3 \cdot PbO$ and $2\,PbCO_3 \cdot PbO$. This decomposition process would probably disappear if the heating rate in the experiment was much lower. It is interesting to note that the decomposition temperature of this process also increased with increasing p_{CO_2}.

$PbCO_3$, $PbCO_3 \cdot PbO$ and small amount of $2\,PbCO_3 \cdot PbO$ apparently coexisted at ~240—320°C at $p_{CO_2} = 1$ atm. All of them decomposed to $PbCO_3 \cdot 2\,PbO$ at ~390°C; apparently, the stability of these intermediates relative to $PbCO_3 \cdot 2\,PbO$ is rather similar. The result presented in Fig. 3 is different from that of Pannetier et al. [1] who studied the thermal decomposition of hydrocerussite under similar conditions. They proposed two intermediates, $2\,PbCO_3 \cdot PbO$ and $PbCO_3 \cdot 2\,PbO$, at ~170—380°C and ~300—470°C, respectively. The presence of $2\,PbCO_3 \cdot PbO$ under these conditions was probably erroneous. In our study, only a small fraction of hydrocerussite was converted to $2\,PbCO_3 \cdot PbO$. A considerable amount of $2\,PbCO_3 \cdot PbO$ was formed only when the p_{CO_2} exceeded 5 atm and its X-ray diffraction pattern agreed with that reported by Grisafe and White [4]. The X-ray diffraction pattern of the intermediate identified as $2\,PbCO_3 \cdot PbO$ by Pannetier et al. differs from those determined by ourselves and by Grisafe and White. We made a reassessment of their X-ray diffraction pattern and found that all the diffraction peaks could be identified successfully provided that the specimen consisted mostly of a mixture of $PbCO_3$ and $PbCO_3 \cdot PbO$, which is in approximate agreement with our result.

The thermal decomposition of hydrocerussite at CO_2 pressures above 3 atm could be explained by reference to the phase diagram of the system PbO—CO_2 extrapolated to low p_{CO_2}. After the hydrocerussite was completely converted to $PbCO_3$ at ~200—280°C, the decomposition behavior which followed was essentially the same as that of $PbCO_3$. The peak temperatures for a given decomposition process lay very close to the corresponding equilibrium phase boundary. The slight difference of temperatures in the DTA peak and the equilibrium boundary is due to the low reaction rate for the process.

The formation mechanism of $PbCO_3$ from hydrocerussite and carbon dioxide in the gas phase is interesting. There are at least two possibilities, (1) H_2O in the hydrocerussite is exchanged directly by the carbon dioxide in the gas phase, and (2) an oxycarbonate intermediate was formed and was immediately converted to $PbCO_3$ by the reaction between this intermediate and the carbon dioxide in the gas phase.

$$2\,PbCO_3 \cdot Pb(OH)_2 \xrightarrow{CO_2\downarrow} 3\,PbCO_3 + H_2O \qquad (1)$$

$$2\,PbCO_3 \cdot Pb(OH)_2 \rightarrow 2\,PbCO_3 \cdot PbO + H_2O \xrightarrow{CO_2\downarrow} 3\,PbCO_3 \qquad (2)$$

In eqn. (2), the oxycarbonate intermediate was tentatively assumed to be $2\,PbCO_3 \cdot PbO$. The direct exchange presented in eqn. (1) is more likely. In the mechanism shown in eqn. (1), the peak temperature of the exothermic

reaction decreased with increasing p_{CO_2} which is in agreement with experiment. In the mechanism shown in eqn. (2), the peak temperature for the intermediate oxycarbonate formation would be independent of p_{CO_2} and an endothermic peak would be expected in the DTA diagram immediately before the exothermic peak, especially at low p_{CO_2}, both of which are in disagreement with the experimental results.

Many intermediates were present in the temperature range ~340—480°C at p_{CO_2} = 9 atm. The coexistence of intermediates could be explained by the low rate of thermal decomposition. Referring to the phase diagram (Fig. 1), these intermediates, $PbCO_3$, 2 $PbCO_3 \cdot PbO$, $PbCO_3 \cdot PbO$ and $PbCO_3 \cdot 2\,PbO$ could exist at p_{CO_2} = 9 atm in the temperature range ~190—450°C, ~340—460°C, ~360—480°C and ~410—590°C, respectively. The intermediate $PbCO_3$ probably began to decompose to 2 $PbCO_3 \cdot PbO$ at ~340°C but with a very low rate. Before all the $PbCO_3$ decomposed to 2 $PbCO_3 \cdot PbO$, the temperature increased and the next oxycarbonate, $PbCO_3 \cdot PbO$, became more stable than 2 $PbCO_3 \cdot PbO$. The considerable fraction of $PbCO_3$ still left in the specimen started to decompose to $PbCO_3 \cdot PbO$ and/or 2 $PbCO_3 \cdot PbO$ and $PbCO_3 \cdot PbO$. At this stage, it cannot be determined whether $PbCO_3$ decomposes to $PbCO_3 \cdot PbO$ directly or through the intermediate 2 $PbCO_3 \cdot PbO$ (or to $PbCO_3 \cdot PbO$ and 2 $PbCO_3 \cdot PbO$ simultaneously). As the temperature was increased further, at ~410—590°C, $PbCO_3 \cdot 2\,PbO$ became the most stable of the various intermediates. The other intermediates then began to decompose to $PbCO_3 \cdot 2\,PbO$. Above ~480°C, this intermediate finally decomposed to PbO. The presence of many intermediates at the transition region of groups can be explained in the same way.

The decomposition behavior at carbon dioxide pressures above ~15 atm (Fig. 7) was puzzling. The phase diagram did not predict the change of decomposition behavior. The low reaction rate is not responsible for this change. The reaction rate generally increased with increasing temperature. The increased reaction temperature at high p_{CO_2} for a given decomposition process should increase the reaction rate and cause the decomposition to occur near the equilibrium condition. The result was tentatively explained by assuming an intermediate which contains more CO_2 (or CO_3) than $PbCO_3$ and forms a dense gas-tight layer on the surface of specimen particles. The exchange reaction of CO_2 and H_2O in the hydrocerussite was inhibited by the low transport rate of gas through this layer. The decomposition of this intermediate at higher temperature results in an endothermic DTA peak and the formation of $PbCO_3$. This explanation is far from complete. Further study is clearly needed to give a more satisfactory explanation.

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