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THE PHASE DIAGRAM $PdCl_2$–$CdCl_2$

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ABSTRACT

The melting points of $PdCl_2$ and $CdCl_2$ have been determined by DTA in a sealed crucible, to avoid any decomposition of the samples. The phase diagram $PdCl_2$–$CdCl_2$ was determined; it shows an eutectic at 45% of $PdCl_2$ (melting point 483°C).

INTRODUCTION

The study of the phase diagram $PdCl_2$–$CdCl_2$ has been undertaken within the framework of the synthesis of the boracite $Pd_3B_7O_{13}Cl$. This synthesis was proved impossible from Bi_2O_3 and $PdCl_2$. The only way was to use the mixture Bi_2O_3–$PdCl_2$–$CdCl_2$. To our knowledge, the phase diagram $PdCl_2$–$CdCl_2$ has not been studied, so that no data were available on the liquidus and the Ostwald–Miers domains, and on the solubility of the two chlorides in the solid state. Moreover the melting points of these two compounds published in the literature [1] are rather scattered, due to the decomposition of the chlorides near the melting temperature. We have then used sealed crucibles to avoid any decomposition.

EXPERIMENTAL

$PdCl_2$ (Fluka, purum) and $CdCl_2$ (Merck, zur Synthese) were dried thoroughly at 120°C under vacuum (less than 0.1 Torr) for 12 h. In the case of $CdCl_2$, a heating rate of 0.5°C min^{-1} was used from 25 to 120°C to avoid the partial hydrolysis of the compound. The platinum crucibles were filled with ca. 50 mg in a dried glove box and sealed with the technique described before [2]. DTA was performed at 4°C min^{-1}, using a Mettler TA1 and a Mettler TA2000 apparatus.

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TABLE 1

Phase transitions of $PdCl_2$ and $CdCl_2$

Compound	Transition	T (°C)	ΔH (kJ mol^{-1})
$PdCl_2$	$\gamma \rightarrow \alpha$	402	10.5
	$\alpha \rightarrow \beta$	487	1.7
	$\beta \rightarrow$ liq	677	21.9
$CdCl_2$	sol → liq	567	46.6

RESULTS AND DISCUSSION

Pure $PdCl_2$ and $CdCl_2$

Three modifications of $PdCl_2$ have been described [3]; the temperature and the ΔH of the transitions are indicated in Table 1. The temperature of the irreversible transition $\gamma \rightarrow \alpha$ is in good agreement with that found by Soulen and Chappell [4]. The $\alpha \rightarrow \beta$ transition at 487°C presents a very small ΔH; it is reversible with a delay of ca. 22°C. In the literature [3] a small endothermic effect has been described at temperatures between 504 and 525°C. The melting point of $PdCl_2$ (677°C) is in good agreement with the value determined by Puche [5]. This author has found a ΔH of 21.9 kJ mol^{-1} by the difference between the heat of dissociation in the liquid and the solid state. The value found in this work by DSC measurement is 40.5 kJ mol^{-1}.

Figure 1 shows the evolution of DTA curves for dry $CdCl_2$ carried out in an open crucible; a small peak appears at 554°C as early as the second

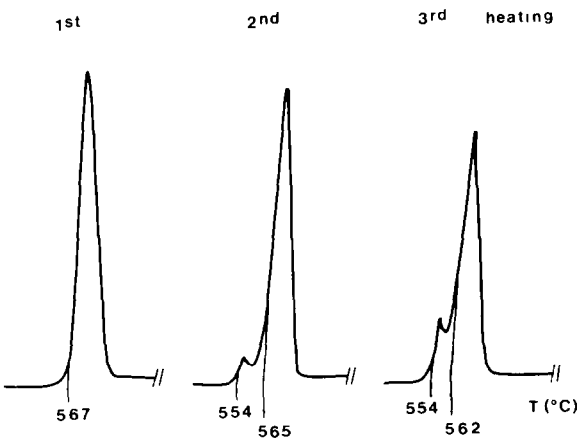

Fig. 1. DTA curves of dry $CdCl_2$ in an open crucible. Sample mass, ca. 50 mg; heating rate, 4°C min^{-1}; atmosphere, N_2, 5 l h^{-1}.

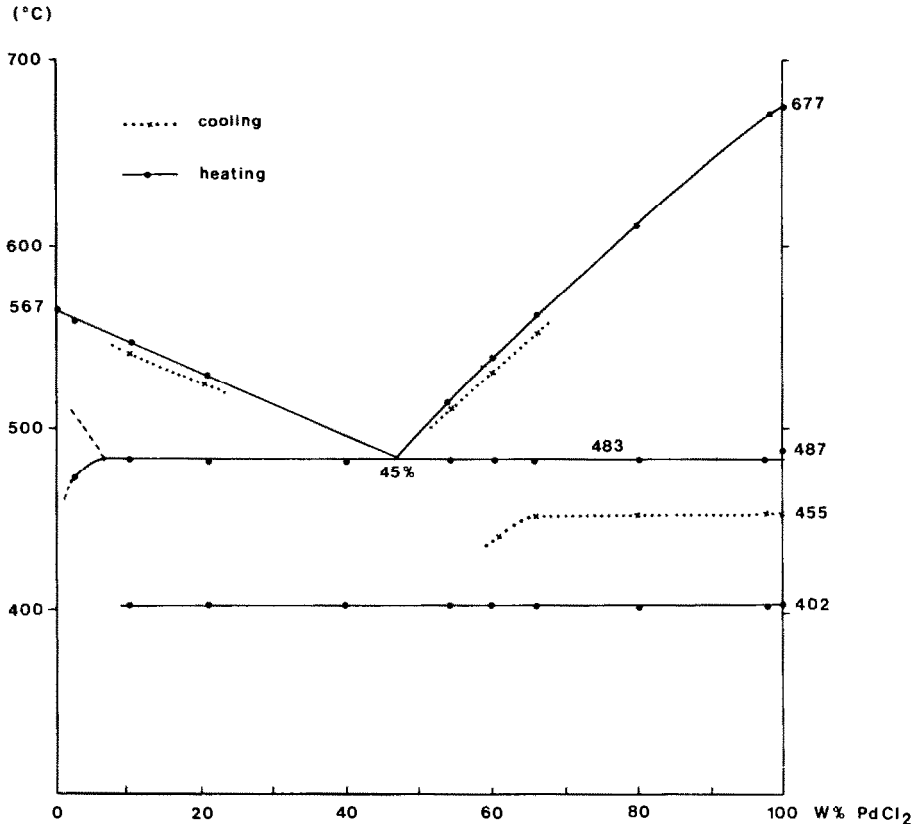

Fig. 2. Phase diagram $PdCl_2$–$CdCl_2$.

heating, and the melting point is progressively lowered. If the DTA is performed with dry $CdCl_2$ in a sealed crucible, one obtains a single peak at 567°C even after several cycles; however if the product is not dried as indicated above, one obtains a single peak at 557°C in a sealed crucible. These results show that it is very important to avoid the hydrolysis and the decomposition of $CdCl_2$ according to the reactions:

$$CdCl_2 + 2H_2O \rightarrow CdO + 2HCl \text{ and/or } CdCl_2 \rightarrow Cd + Cl_2$$

by the use of thoroughly dried $CdCl_2$ in a sealed platinum crucible.

Phase diagram

Figure 2 shows the phase diagram obtained by DTA. An eutectic is formed at 45% of $PdCl_2$ (melting point = 483°C). $PdCl_2$ seems very slightly soluble in $CdCl_2$ (< 1% at 400°C), when $CdCl_2$ is insoluble in $PdCl_2$.

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