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THE PHASE DIAGRAM OF THE Ce-H_2 SYSTEM

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ABSTRACT

A peritectic phase diagram has been proposed by Libowitz et al. based on sparse measurements of several authors. On the contrary Toguchi et al. proposed a critical point of the miscibility gap. We have performed P-T-x measurements in the range of 820-1150°C and constructed the Ce-H_2 phase diagram. The location of the phase boundaries have been determined by applying a constant slope criterion $\Delta\log P(H_2)/\Delta\log x_H$ to the P-x curves. The results confirm the peritectic behaviour, but show appreciable differences in the position of the phase boundaries. The peritectic temperature occurs at 1025°C and reflects a substantial increase in the melting point of cerium (795°C) with increasing dissolution of hydrogen (up to ≈40%). Single crystals of $CeH_{2.95}$ have been grown by precipitation from a hydrogen saturated melt above the peritectic point. Optical reemission measurements of $CeH_{2.95}$ show an absorption edge corresponding to a bandgap of $\Delta E = 1.54$ eV.

INTRODUCTION

A recent survey of the literature on rare earth hydrides has shown that the thermodynamic properties are not well known (1). Accurate thermodynamic data is invaluable, however, in the determination of the conditions required for preparation of single crystals of hydride phases. Libowitz et al. (2) first prepared single crystals of a rare earth hydride, CeH_3, by making use of a peritectic phase diagram. This was based on a few sparse data sets from several authors. His phase diagram was partly confirmed by the successful growth of cerium hydride crystals from the melt. More recently, however, Toguchi et al. (3) have reported phase diagrams for a number of rare earth-hydrogen systems including the cerium system. Contrary to the work of Libowitz, they propose a critical point of the miscibility gap between the metal and hydride phases and a eutectoid transformation. This kind of diagram is difficult to understand because the bcc metal phase cannot form solid solutions with the fcc hydride phase above the miscibility gap due to strong mechanical stresses. In case that such a diagram was correct a bcc→fcc phase transition for the hydride must appear, for which there has never been experimental evidence. In order to accurately determine the phase diagram of the cerium-hydrogen system in the range of the proposed peritectic or critical point we have chosen to perform P-x isotherm measurements because of the high sensitivity of this method.

EXPERIMENTAL

The same apparatus was used for measuring P-x isotherms as for the measurement of the La-H_2 phase diagram, the details of which have been described previously (4). The reactor consists of a double-walled horizontal quartz tube capable of $P < 6$ bar and $T < 1150°C$. Hydrogen pressure is monitored continuously with several piezoresistive gauges. The space between the two walls of the reactor was maintained at the same pressure as the actual hydrogen pressure of the inner reaction tube in order to avoid loss of H_2 via diffusion through the inner wall at high temperatures. Reactant hydrogen was purified with a Pd,Ag diffusion apparatus before storing in a thermostatically controlled reservoir (of calibrated volume) and subsequent introduction into the reactor via a saphire UHV high precision dosimeter valve. Charges of cerium metal (5-8g, Rare Earth Products, Ltd., 99.99%) were held in a tungsten boat with a length of the samplewell of 4 cm. Metal charges were mechanically cleaned from the surface layer and introduced into the reactor. All this work has been performed within a train of glove boxes under argon atmosphere gettered by hot cerium turnings (residual O_2,H_2O concentration < 3 ppm at). Reacted samples of cerium hydride were removed from the reactor in the same manner.

RESULTS AND DISCUSSION

Seventeen P-x isotherms for the Ce-H_2 system were measured within the range $820 < T < 1150°C$. Data were plotted both in the form of Sievert's diagram $\log P(H_2)$ vs. $\log x_H$ (see Fig. 1), and also in the form $(\Delta\log P(H_2)/\Delta\log x_H)$ vs. $\log x$. The phase boundaries of two-phase-regions were located at the end of regions of constant and nearly zero slope (i.e. plateaus) in these plots. Based on these data a new phase diagram was constructed and is shown in Figure 2a. For $T < 970°C$ three phase boundaries could be resolved. We attribute the first two of these boundaries to the solidus and liquidus of δ-Ce containing dissolved hydrogen. Above this temperature the central phase boundary (dotted line) disappears and an inflection appears at the remaining two phase boundaries. Another inflection was observed in the two extreme phase boundaries from which a peritectic temperature of 1025°C was determined. Quenching experiments are planned to investigate further this temperature region (970-1025°C). At the peritectic temperature the hydrogen content dissolved in δ-Ce is estimated at ≈ 40 at%H.

The Van't Hoff isochore was plotted for the equilibrium hydrogen pressure at $x_H = 50$ at%H and the following equation resulted from a least squares fit:

$$\log P(H_2)(\text{bar}) = 7.943 \pm 0.200 - (10.734 \pm 0.200)\times 10^3/T(K). \qquad (1)$$

From this equation, thermodynamic functions for the formation of $CeH_{1.5}$ were calculated and are compared with the literature in Table 1.

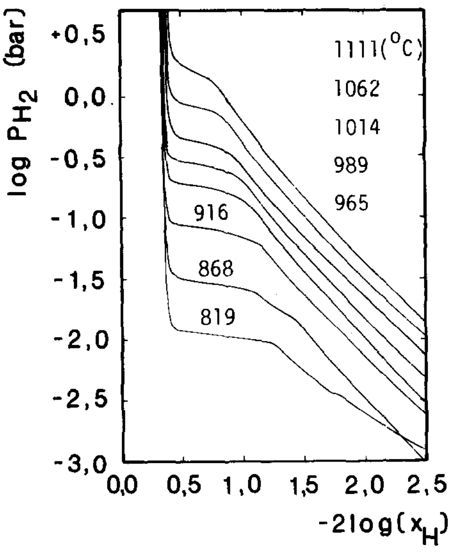

Fig. 1. Typical P-x isotherms of the Ce-H_2 system plotted as a Sievert's diagram.

TABLE 1

ΔH^o_f (kcal/mol H_2)	ΔS^o_f (cal/mol $H_2 \cdot K$)	$\Delta G^o_{f,298}$ (kcal/mol H_2)	Temperature Region (°C)
- 49.1 ± 1	- 36.3 ± 1	- 38.3 ± 1	820 - 1150
- 49.2 ± 1	- 35.4 ± 1	- 38.7 ± 1	600 - 800 (5)

The old phase diagram proposed by Libowitz et al. (2) (see Fig. 2b) was based primarily on the melting curve data of Lynds (6) and to a lesser extent on their own P-T-x measurements in the region $1000 < T < 1050$°C. The boundaries of our new diagram (see Fig. 2a) appear to agree well (within 2%) with the P-T-x data measured by Libowitz et al. (2). However, there is considerable discrepancy in the solidus (data of Lynds (6)) and liquidus for the melting of δ-Ce, which are shifted by ≈10 at%H to higher hydrogen content. In addition, the slope of the boundary marking the complete formation of cerium hydride above the peritectic shows a large difference; the new diagram indicates a tendency to form hydrides of smaller hydrogen content at higher temperatures whereas the old diagram shows an increasing hydrogen content with increasing temperature. This previous boundary was based on the melting curve data of Lynds (6) which may have been subject to a compositional error due to dissociation of the hydride in this T-x region. According to our Van't Hoff data, the equilibrium dissociation

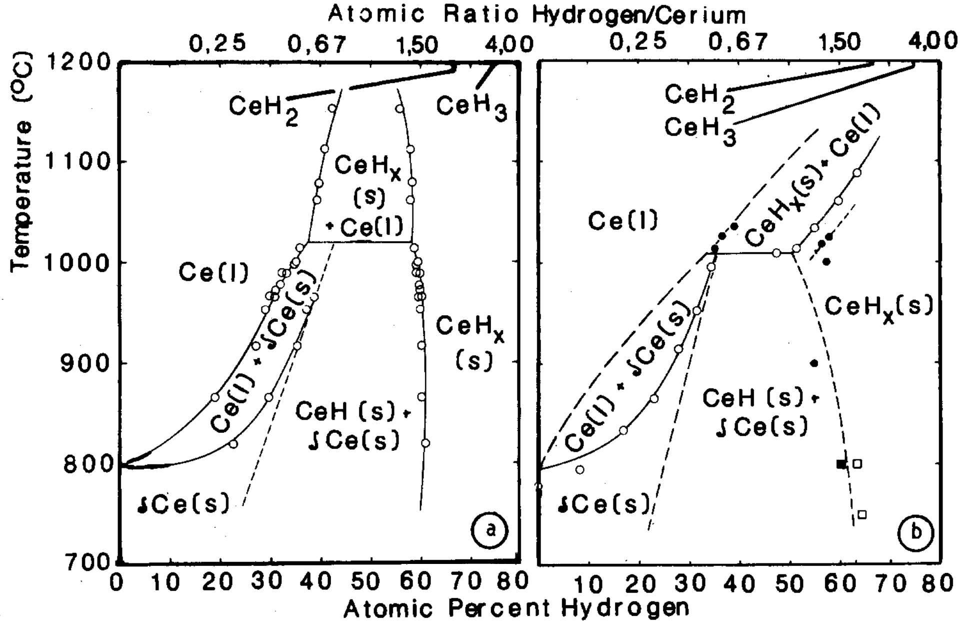

Fig. 2. (a) New T-x phase diagram of the Ce-H_2 system constructed from the data in figure 1. (b) Phase diagram according to Libowitz et al. (2). ●●● P-T-x measurements by the same authors; ○○○ melting curve data of Lynds (6).

pressure of H_2 over $CeH_{1.5}$ at T > 1000°C is greater than 0.3 bar.

Following the method of Libowitz and Pack (2) single crystals of cerium hydride have been prepared by growth from the melt at ≈1030°C followed by slow cooling (40h to room temperature) under a pressure of 4 bar H_2. It was possible to cleave single crystals of dimensions 5x4x3 mm^3. Some were analysed volumetrically (7) yielding a composition of CeHx with $x = 2.95 \pm 0.02$; X-ray analysis gave a cell parameter of 554.08 ± 0.06 pm (cubic fluorite structure). The optical reemission spectrum revealed an absorption edge corresponding to a band gap of 1.54 eV.

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