Journal of Alloys and Compounds 253–254 (1997) 38–40

Synthesis and transformations of hydrides under high quasihydrostatic pressures

V.N. Verbetsky*, E.A. Movlaev

Chemistry Department, Lomonosov Moscow State University, 119899, Moscow, Russia

Abstract

A method of synthesis and investigation of phase transitions of hydrides under high quasihydrostatic pressures (up to 60 kbar in temperature range from ambient to 1400 K) is described. The transformations of alloys with compositions RT_n, R_2T (R–Zr, Ca, Ce, Er; T–Ni, Co) into hydrides have been studied. The formation of new hydrides in the CaH_2–Ni(Co) systems has been found.

Keywords: Hydrides; Phase transitions; Quasihydrostatic pressure

1. Introduction

Metal hydrides are of extreme interest for high pressure chemistry. Their formation is accompanied either by a considerable increase (alkali, alkali-earth metals), or by a decrease of the metal lattice volume (rare-earth and transition metals). Due to this the use of high pressure methods allows to investigate the possibility of obtaining more dense hydride modifications, and of synthesising new metal hydrides. For example, using the high pressure method new phase transitions were found for MgH_2 and $LiAlH_4$ [1–3].

2. Experimental details

For the investigation of solid-phase reactions and the transformations under high pressure a high pressure installation was used. It consisted of a high pressure apparatus, a 60 ton press, a hydraulic system, a system for heating the sample and various measuring devices. The high pressure apparatus consisted of two block-matrixes and a high pressure camera between them. This camera was a container made of lithographic stone with a graphite heater. A sample was placed in the camera together with a thermocouple. To avoid contact of the sample with the graphite heater, the sample was enveloped in NaCl. The hydrides used for the investigations were obtained by the interaction of hydrogen with the corresponding metals and alloys.

3. Results and discussion

Let us consider the transformations, taking place under high pressures for the hydrides of the CrB structure type. Hydrides of compositions $LaNiH_{3.5}$, $CeNiH_{3.7}$, $ErNiH_{3.5}$, $ZrNiH_3$, $ZrCoH_3$ have been investigated. It was found that all the hydrides except $ErNiH_{3.5}$ undergo a disproportionation reaction under heating at high pressure. For the ZrNi and ZrCo hydrides this reaction takes place at rather high temperature and can be described by Eqs. (1) and (2). The conditions for these reactions confirm the high stability of starting compounds, which are rather stable in softer conditions (700 K, $P_{H_2} = 50$ atm or in vacuum) and can undergo multiple absorption–desorption cycling.

$$\mathrm{ZrNi\,(CrB)} \rightarrow \mathrm{ZrNiH_3\,(CrB)} \xrightarrow{>1373\ \mathrm{K},\ 30-47\ \mathrm{kbar}} \mathrm{ZrH_2} + \mathrm{ZrNi_3} + \mathrm{H_2}, \tag{1}$$

$$\mathrm{ZrCo\,(CsCl)} \rightarrow \mathrm{ZrCoH_3\,(CrB)} \xrightarrow{>1273\ \mathrm{K},\ 20-50\ \mathrm{kbar}} \mathrm{ZrH_2} + \mathrm{ZrCo_2} + \mathrm{H_2}. \tag{2}$$

In the case of LaNi and CeNi hydrides the influence of high pressure also increases their thermal stability. If the disproportionation of LnH_3 and $LnNi_5$ in vacuum starts at

---

*Corresponding author.

0925-8388/97/$17.00
PII S0925-8388(96)03077-0

450 K, then under high pressure a more profound decomposition takes place at $T > 900$ K as presented by Eqs. (3) and (4):

$$\text{LaNi (CrB)} \rightarrow \text{LaNiH}_{3.5}\ \text{(CrB)} \xrightarrow{>923\ \text{K},\ 30-40\ \text{kbar}} \text{LaH}_3 + \text{La}_2\text{Ni}_7 + \text{H}_2, \qquad (3)$$

$$\text{CeNi (CrB)} \rightarrow \text{CeNiH}_{3.7}\ \text{(CrB)} \xrightarrow{>973\ \text{K},\ 30-40\ \text{kbar}} \text{CeH}_3 + \text{Ce}_2\text{Ni}_7 + \text{H}_2. \qquad (4)$$

In the case of $\text{ErNiH}_{3.5}$ the following transformation occurred:

$$\text{ErNi (FeB)} \rightarrow \alpha - \text{ErNiH}_{3.5}\ \text{(CrB)} \xrightarrow{>850\ \text{K},\ 40-60\ \text{kbar}} \beta - \text{ErNiH}_{3.5}\ \text{(cubic cell)}. \qquad (5)$$

$$\text{Ti}_4\text{Fe}(\beta - \text{Ti}) \rightarrow \text{Ti}_4\text{FeH}_{8.8}(\text{CaF}_2) \rightarrow \begin{cases} \xrightarrow{650\ \text{K, vacuum}} \text{TiH}_2 + \text{TiFe} \xrightarrow{900-1050\ \text{K, vacuum}} \beta - \text{Ti} + \text{TiFe} \\ \xrightarrow[900\ \text{K, 30kbar}]{} \text{TiH}_2 + \text{Fe} + \text{H}_2 \end{cases} \qquad (7)$$

α-$\text{ErNiH}_{3.5}$ crystallises with the ortho-rhombic structure (Cmcm, $a = 3.652(4)$ Å, $b = 11.19(1)$ Å, $c = 4.587(4)$ Å, $Z = 4$). The X-ray pattern of β-$\text{ErNiH}_{3.5}$ can be satisfactorily indexed as a cubic structure with $a = 9.089(7)$ Å, ($Z = 16$). The cell parameters of this new modification of hydride are linked by simple correlations with cell parameters of rhombic ternary hydride α-$\text{ErNiH}_{3.5}$: $a_\beta = 1/3b_\alpha + 2a_\alpha$; $b_\beta = 2/3b_\alpha - a_\alpha$; $c_\beta = 2c_\alpha$. Thus, although different types of intermetallic compound hydrides of the CrB structure type were studied, only $\text{ErNiH}_{3.5}$ underwent a phase transformation.

The disproportionation reaction is the result of the heating under high pressure of such complex hydrides as $\text{Zr}_2\text{CoH}_{4.8}$ and $\text{Ti}_4\text{FeH}_{8.8}$. In the case of Zr_2Co the reaction can be illustrated by the following scheme:

$$\text{Zr}_2\text{CoH}_{4.8} \xrightarrow{873\ \text{K},\ 35\ \text{kbar}} \text{ZrH}_2 + \text{ZrCoH}_3. \qquad (6)$$

$\text{Zr}_2\text{CoH}_{4.8}$ shows a considerably low stability compared with ZrCoH_3.

The disproportionation of $\text{Ti}_4\text{FeH}_{8.8}$ (a solid solution of iron in titanium hydride) proceeds under high pressure conditions and in vacuum differently (Eq. (7)):

It is clear from these equations that at 900 K under quasihydrostatic pressure the titanium hydride shows rather high thermal stability. It can be anticipated that a further increase in temperature will lead to its decomposition with the formation of TiFe.

The results of the investigation of interactions in the

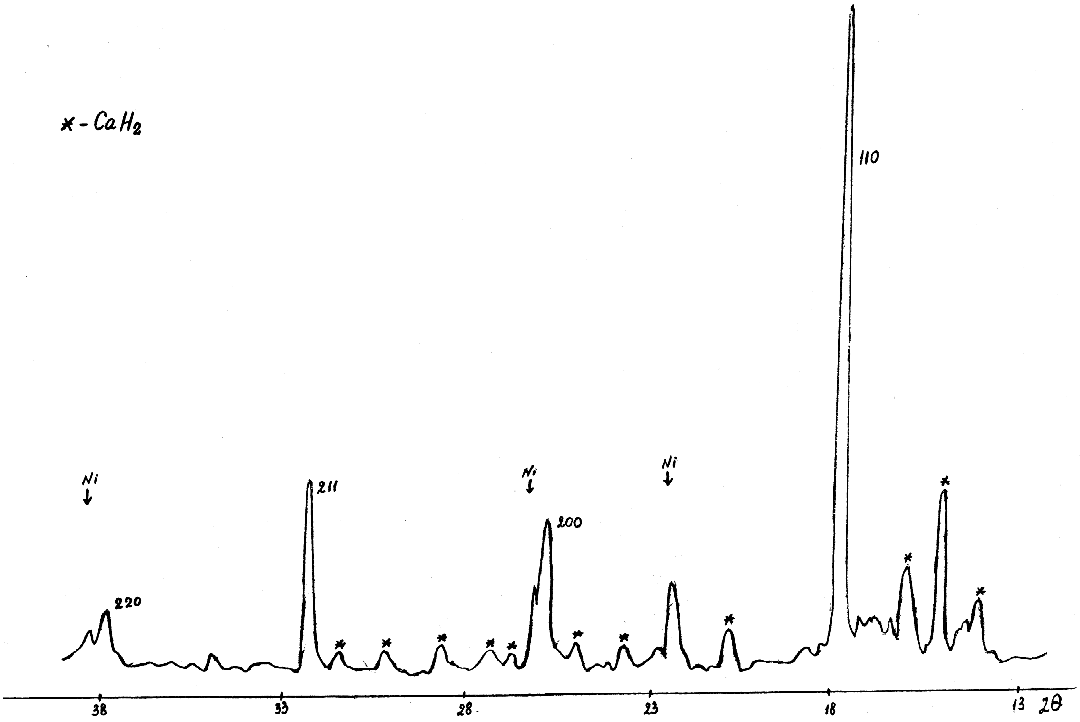

Fig. 1. X-ray diffraction pattern of a CaH_2–Ni sample after high-pressure synthesis (35 kbar, 1220 K, Cu Kα radiation).

CaH_2–Ni system under high pressure show the formation of new ternary hydrides. However, the determination of their compositions (and this is one of the main difficulties for most solid state reactions) is rather perplexing because of the presence of some of the starting substances in the reaction products, apart from new phases. The greatest quantity of a new phase is formed under 40 kbar and 1100 K. It should be mentioned also that the formation of a ternary hydride in the CaH_2–Ni system proceeds with a greater yield compared to the CaH_2–Co system. The X-ray pattern of a new hydride has been indexed as cubic with a cell parameter $a = 3.549 \pm 0.001$ Å in the case of nickel (Fig. 1) and $a = 3.535 \pm 0.002$ Å in the case of cobalt. We also made an X-ray analysis of a ternary hydride, taking as an assumption that its composition is $CaNiH_3$ with a perovskite-like structure. For determination of the calcium and nickel atom positions in the $CaNiH_3$ structure we have calculated the reflex intensities and have taken as a starting point the atom coordinates for the $CaTiO_3$. Calcium cations were at a:(0,0,0) and nickel cations at b:(1/2,1/2,1/2). For such a model the R-factor is:

$$R_i = [\Sigma|I_{\mathrm{obs}} - I_{\mathrm{calc}}|]/\Sigma I_{\mathrm{obs}} = 0.05.$$

While calculating intensities the hydrogen input has not been taken into account. If the hydrogen atoms are placed in the position c:(1/2,1/2,0) the calculated interatomic distances have the following values: $d_{\mathrm{Ca-H}} = 2.5$ Å, $d_{\mathrm{Ni-H}} = 1.78$ Å. These values are quite comparable with analogous distances determined for other hydrides.

Acknowledgments

This work was supported in part by the Russian Foundation for Basic Research, Grant No. 95-03-08787.

References

[1] K.N. Semenenko, V.N. Verbetsky, Ya.A. Kalashnikov, N.V. Timofeeva, M.I. Ioffe, Vestnik MGU, Khimija, 19 (1978) 718.

[2] J.P. Bastide, B. Bonnetot, J.M. Létoffé, P. Claudy, Mater. Res. Bull., 15 (1980) 1215.

[3] B.M. Bulychev and V.N. Verbetsky. Zh. neorganicheskoi khimii, 22 (1977) 2961.