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HYDROGEN INTERACTION WITH RNi$_3$ TYPE INTERMETALLIC COMPOUNDS AT HIGH GASEOUS PRESSURE

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Abstract—Pressure–composition isotherms for CeNi$_3$–H$_2$, CeNi$_{2.2}$Mn$_{0.8}$–H$_2$ and ErNi$_3$–H$_2$ systems were measured at pressures up to 2000 atm and at temperatures from $-78°C$ to $23°C$. New hydride phases RNi$_3$H$_{5.5-5.6}$ were synthesized and characterized by X-ray diffraction. Thermodynamic parameters of formation–decomposition reactions at low temperature for intermediate ErNi$_3$H$_4$ phase were calculated as $\Delta H = 23.8$ kJ mol^{-1} and $\Delta S = 103$ J K^{-1} mol^{-1}. The phenomenon of irreversible hydrogen absorption at high pressure was found for all studied systems. Thermal desorption peculiarities for CeNi$_3$H$_x$ and ErNi$_3$H$_x$ hydrides were determined. Copyright © 1996 International Association for Hydrogen Energy

INTRODUCTION

RT$_3$ (R = rare earth, T = Ni, Co) intermetallic compounds as a matrix for hydrogen rich hydride phases have been the object of many experimental [1–5] and theoretical [6, 7] investigations. The structure of these compounds (PuNi$_3$ and CeNi$_3$ types) represents a combination of CaCu$_5$ and MgZn$_2$-type fragments and allows calculation of a limiting hydrogen composition. Takeshita *et al.* [6] have determined a maximum hydride stoichiometry of RT$_3$H$_6$. This value has been defined more accurately by Yartis' [7]. His analysis, based on available data from neutron diffraction studies of CeNi$_3$ and HoNi$_3$ deuterides, has given a limiting composition of $5\frac{2}{3}$ H atoms per formula unit. Moreover, Yartis' has considered that hydrogen intercalation in RT$_3$ provoked an anisotropic extension of the intermetallic matrix and, therefore, the change of different interstitial sites parameters was not identical. Due to the phenomenon some tetrahedral and octrahedral sites interdicted for hydrogen atoms in the initial intermetallic compound became available after preliminary hydrogen intercalation.

In this case the use of high hydrogen pressure can be very effective in achieving the predicted compositions. The results reported here concern hydrogen interaction at pressures up to 2000 atm with CeNi$_3$, CeNi$_{2.2}$Mn$_{0.8}$ and ErNi$_3$ intermetallic compounds for which previous workers have reported compositions less than 3.5 H/RT$_3$, i.e. only 60% of the theoretically calculated maximum.

EXPERIMENTAL DETAILS

The alloys were prepared from pure metals by arc melting under an inert atmosphere. The excess of the metals were 2% for Er and 3% for Ce. CeNi$_3$ and CeNi$_{2.2}$Mn$_{0.8}$ samples were annealed in vacuum at 750°C for 170 h and ErNi$_3$ at 1000°C for 100 h.

Hydrogen interaction with the intermetallic compounds was studied on the high pressure apparatus with the following parameters: a working pressure up to 2000 atm, working temperature from $-195°C$ to $300°C$. A schematic diagram of the apparatus and the experimental method were described in previous paper [8].

The calculations were performed by using the modified Van der Waals equation of state for hydrogen at high pressure proposed in [9].

The hydrogen content of the hydride samples was checked after the experiments by means of the high temperature vacuum extraction method.

X-ray studies of the initial alloys and their hydrides were carried out using a DRON-2 powder X-ray diffractometer (Cu K$_\alpha$ radiation, Ni-filter, Si-standard).

RESULTS AND DISCUSSION

Characteristics of the synthesized alloys are presented in Table 1. All of the obtained X-ray patterns correspond to single-phase samples and the calculated parameters are in good correlation with available literature data. The CeNi$_{2.2}$Mn$_{0.8}$ alloy has slightly higher cell volume than CeNi$_3$ due to the different radii of Ni and the substituted Mn atoms.

Hydrogen interaction with CeNi$_3$ and CeNi$_{2.2}$Mn$_{0.8}$

Some regularities of hydrogen absorption and desorption in the studied systems can be noted.

Table 1. X-Ray data for initial intermetallic compounds

Composition	Structure type	a (Å)	c (Å)	V (Å³)
$CeNi_3$	$CeNi_3$	4.980 ± 0.001	16.57 ± 0.01	356
$CeNi_{2.2}Mn_{0.8}$	$CeNi_3$	5.037 ± 0.001	16.46 ± 0.01	362
$ErNi_3$	$PuNi_3$	4.943 ± 0.001	24.24 ± 0.01	513

First, hydrogenation at low pressure (30–40 atm) and at room temperature led to a different hydride phase formation for $CeNi_3$ and Mn-substituted compounds. Hydrogen contents under these conditions were 3.3 and 4.7 H/RT_3 correspondingly (see Figs 1 and 2). Increase of the cell volume and interatomic distances by means of
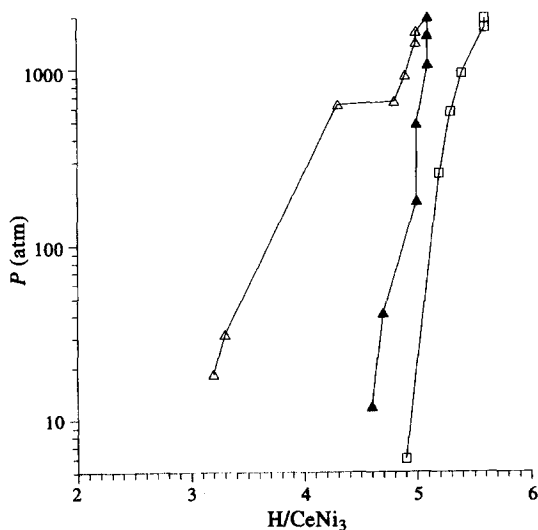

Fig. 1. P–C isotherms for $CeNi_3$–H_2 system, △ absorption, 20°C; ▲ desorption, 20°C; ☐ absorption, −78°C.

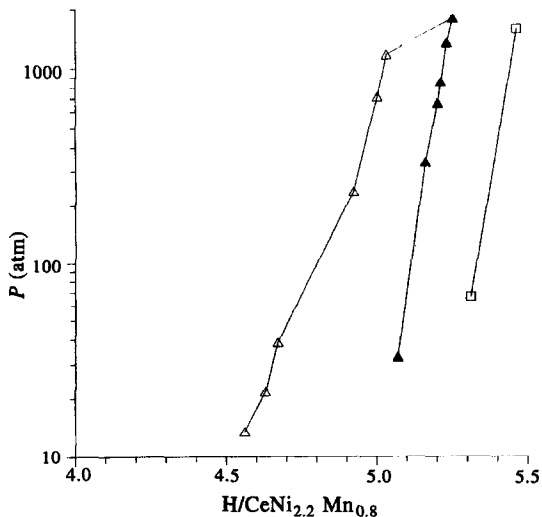Fig. 2. P–C isotherms for $CeNi_{2.2}Mn_{0.8}$–H_2 system, △ absorption, 20°C; ▲ desorption, 20°C; ☐ absorption, −78°C.

Ni substitution, as had been predicted, facilitated the filling of interstitial sites by hydrogen atoms.

Second, the pressure rise up to 2000 atm provoked additional hydrogen absorption. The maximum compositions achieved at room temperature were 5.1–5.3 H/RT_3 for both compounds. It is necessary to note that this additional absorption was not reversible: changes of the hydrogen content in hydrides under pressure decrease from 2000 to 10 atm were less than 0.5 H/RT_3. Furthermore, any characteristic regions present in the absorption isotherms (at 700–800 atm for $CeNi_3$ and at 1500–2000 atm for $CeNi_{2.2}Mn_{0.8}$) could not be detected in the desorption isotherms.

Third, an experimental temperature decrease to −78°C did not lead to any changes in interaction character, except a small increase in the hydrogen capacity. A similar effect of low temperature on hydrogen absorption by intermetallic compounds has been found for many metal–hydride systems.

X-ray investigation of the synthesized $CeNi_3H_{4.2}$ and $CeNi_{2.2}Mn_{0.8}H_{4.9}$ high pressure hydride phases showed that both of them were slightly crystallized: X-ray patterns were characterized by the presence of few broad reflections. These patterns did not let us conclude that the detected reflections corresponded to any possible product of the decomposition of initial compounds (cerium hydride and nickel or binary Ce–Ni compounds). So, the obtained hydrides were probably individual phases. However, we failed to identify them because of significant distortion of the crystalline lattice.

Hydrogen interaction with ErNi₃

Interaction in the $ErNi_3$–H_2 system differed significantly from that described previously for the Ce-based systems. In the low pressure range two plateaus have been found. One of them, with equilibrium pressure close to 1.3 atm at room temperature (Fig. 3) correspond to a dihydride phase that was in good correlation with the experimental data in [1] where the existence of another plateau had been proposed for the $ErNi_3$–H_2 system. We succeeded in detecting this plateau characteristic for the reversible transition from the dihydride to the tetrahydride phase, but only at a lower temperature: between −25°C and −50°C (Fig. 3). In addition to that, the plateau length decreased with the temperature rise, that evidently indicated an approach to a critical point for this phase transition. The phenomenon could cause an absence of the corresponding plateau on the room temperature isotherms.
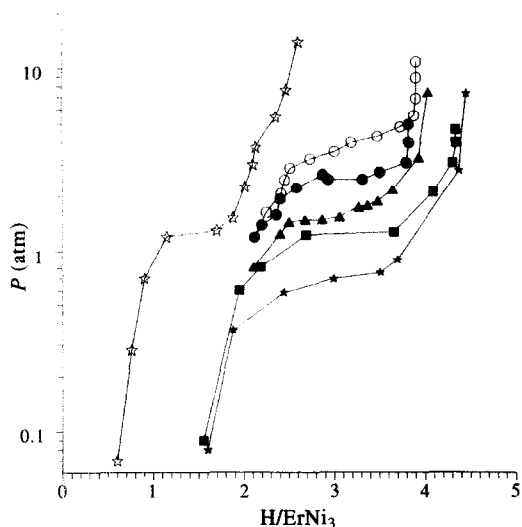
According to the determined dependence $\lg P =$

Fig. 3. P–C isotherms for ErNi₃–H₂ system at low pressure, ☆ desorption, 23°C; ○ absorption, −25°C; ● desorption, −25°C; ▲ desorption, −35°C; ■ desorption, −40°C; ★ desorption, 50°C.

Fig. 5. P–C isotherms for ErNi₃–H₂ system at high pressure, $T = 23°C$ △ absorption, 1st cycle; ▲ desorption, 1st cycle; □ absorption 2nd cycle; ■ desorption, 2nd cycle.

$f(1/T)$ (Fig. 4), thermodynamic parameters of the ErNi₃H₄ → ErNi₃H₂ phase transition were calculated as $\Delta H = 23.8 \pm 0.5\ kJ\ mol^{-1}$ and $\Delta S = 103 \pm 2\ J\ K^{-1}\ mol^{-1}$. It should be mentioned that this reaction possessed a noticeable hysteresis: at −25°C the absorption equilibrium pressure exceeded the desorption value for 40%.

With the experimental pressure rise up to 2000 atm the hydrogen content of the hydride increased up to 5.2 (at 23°C) and 5.65 (at −50°C) H/RT₃. At the same time, hydrogen absorption ceased to be completely reversible. It can be seen in Figs 5 and 6 that after the pressure decreased the differences in hydride composition was only 0.5 H/RT₃.
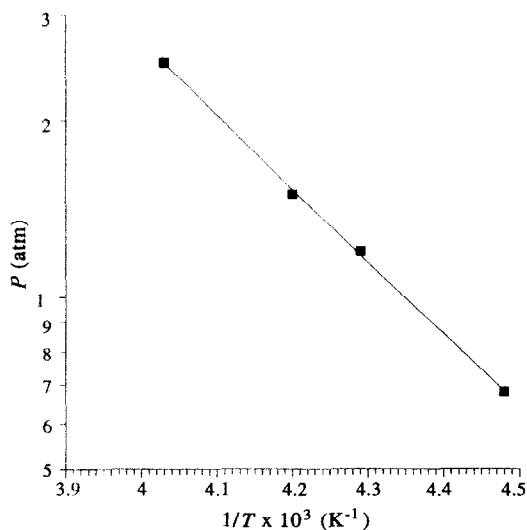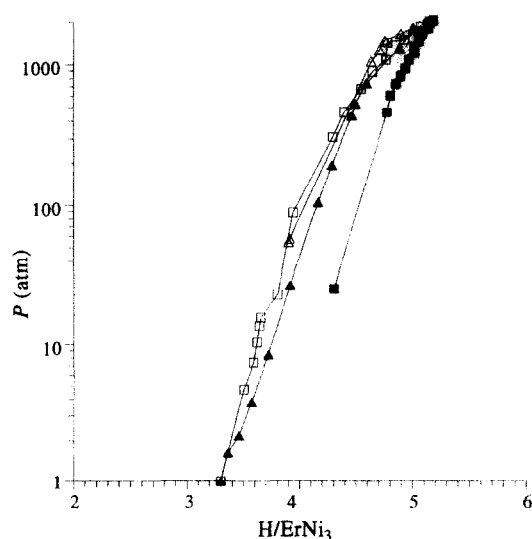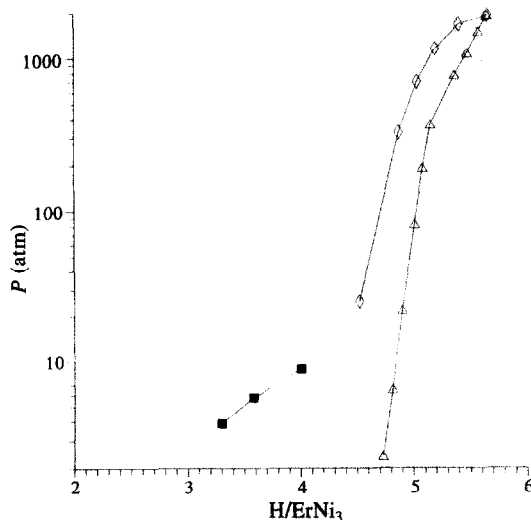
Fig. 6. P–C isotherms for ErNi₃–H₂ system at high pressure, $T = -50°C$, ◇ absorption; △ desorption; ■ desorption, $T = 23°C$.

Comparison of the ErNi₃Hₓ hydride samples after low-pressure and high-pressure cycling showed that the remaining hydrogen content was close to 1 and 3 H/RT₃, correspondingly. The first value correlated with the literature data [1] and the latter was connected with the irreversibility of the absorption reaction at high pressure.

Thermal desorption study of hydride phases

The quantity of hydrogen desorbed in vacuum while heating CeNi₃H₃.₆, CeNi₂.₂Mn₀.₈H₄.₅ and ErNi₃H₃.₁ hydride samples was recorded as a function of temperature. An analysis of these data and the results of the

Fig. 4. Van't Hoff plots for ErNi₃–H₂ system.

Table 2. Characteristics of hydride phases in the $ErNi_3$ H_2 system

T (°C)	H/ErNi₃	a (Å)	c (Å)	V (Å³)	ΔV (%)
23	1.1	4.971 ± 0.003	24.28 ± 0.01	519.7	1.3
23	2.8	5.058 ± 0.006	25.93 ± 0.04	574.5	10.7
140*	2.2	4.96 ± 0.01	25.2 ± 0.1	536.6	4.4
260*	0.9	4.912 ± 0.002	24.84 ± 0.03	519.1	1.2
800*	0	4.945 ± 0.002	24.24 ± 0.01	513.2	—

* Products of thermal desorption.

Table 3. Characteristics of hydride phases in the $CeNi_3–H_2$ system

T (°C)	H/CeNi₃	Composition	a (Å)	c (Å)
23	4.2	X˙	—	—
320*	1.2	X˙	—	—
		CeH₃	5.56 ± 0.03	
500*	0.9	CeH₃	5.53 ± 0.01	
		CeNi₅	4.88 ± 0.02	4.02 ± 0.01
900*	0	CeH₃	4.966 ± 0.001	16.49 ± 0.01

X˙ Unknown phase.
* Products of thermal desorption.

step-by-step X-ray study of hydrides during the thermal description (Tables 2 and 3) allowed us to conclude that Er- and Ce-based systems had different decomposition mechanisms. In the case of $ErNi_3H_x$ no structural changes were detected during desorption: hydrogen extraction led to a gradual decrease of the phase parameters. Hydrogen desorption from the cerium containing samples also resulted in the initial intermetallic compounds at 900°C; however, in the intermediate stage (320–500°C) the decomposition products CeH_x and $CeNi_5$ were fixed.

CONCLUSIONS

This study disclosed the following trends:

(1) For all $CeNi_3$, $CeNi_{2.2}Mn_{0.8}$ and $ErNi_3$ samples the hydride phases with hydrogen content close to 5.7 H/RT_3 were synthesized at about 2000 atm. This confirms the predictions of Yartis' [7] about limiting composition for both $CeNi_3$ and $PuNi_3$ type intermetallic hydrides.

(2) The effect of nickel substitution by manganese in $CeNi_3$ was noticeable only at low pressures (30–50 atm) when the larger cell parameters of the Mn-containing alloy led to higher hydrogen absorption capacity. The maximum hydrogen content achieved at high pressure did not depend on the alloy composition.

(3) The formation of high pressure hydride phases was a partially an irreversible reaction. This phenomenon was more pronounced for Ce-based compounds that correlated with a more anisotropic character of the lattice distortion. As a result, at the same hydride composition

the local extension of the $CeNi_3$ cell was more significant, and provoked an excess of elasticity limit for some Me–Me bonds. The results of the X-ray investigations led to the same conclusions.

(4) The existence of a new intermediate tetrahydride phase in the $ErNi_3–H_2$ system at low temperature was detected. Approximation of the measured thermodynamic parameters for this phase to room temperature and the character of the plateau length change with temperature led to the conclusion that its critical point was below 23°C.

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