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Interaction of RT_3 (R=Ce, T=Co, Ni, Fe) intermetallic compounds with hydrogen under high pressure

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Abstract

Interaction in $CeCo_3$–H_2, $GdFe_3$–H_2 and $CeNi_2Co$–H_2 systems with hydrogen under pressure to 2000 atm. has been investigated. Intermetallic compounds $CeCo_3$, $GdFe_3$ and $CeNi_2Co$ have $CeNi_3$ or $PuNi_3$ structure type. The maximum compositions of the hydride phases under high pressure $CeCo_3H_{6.1}$, $GdFe_3H_{6.1}$ and $CeNi_2CoH_{5.4}$ have been calculated on the basis of analysis of absorption–desorption isotherms at room temperature. According to X-ray analyses, additional implantation of hydrogen into hydride phases based on $CeCo_3$, $GdFe_3$ and $CeNi_2Co$ under high pressure is accompanied by insignificant increases in their lattice volumes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: High pressure of hydrogen; Hydrides; Pressure-composition

1. Introduction

Intermetallic compounds RT_3 (R=Ce, Gd, T=Co, Ni, Fe) are interesting for the investigation of hydride forming reactions under high pressure. These compounds belong to $PuNi_3$ or $CeNi_3$ structure types, and are able to absorb a considerable amount of hydrogen. The structures of $CeNi_3$ or $PuNi_3$ may be described as fragments of the structures $CaCu_5$ and $MgZn_2$. The distinctive feature of these compounds is that the implantation of hydrogen atoms leads to an increase in their lattice volume.

One of the first works which studied the behavior of compounds under high pressure hydrogen [1], showed that $PrCo_3$ and $ErCo_3$ absorb additionally from 1H/IMC to 1.5H/IMC.

The authors of Ref. [2] studied RT_3 (R=Ce, –Er, T=Ni) compounds under pressure of hydrogen to 2000 atm. For the $CeNi_3$–H_2 system, the maximum amount of hydrogen in the hydride is 5.1 H/IMC. For the $ErNi_3$–H_2 system the maximum amount of hydrogen is 5.2 H/IMC.

The present work continues the investigation previously described. In addition, the results of the study of hydrogen interaction under pressure to 2000 atm. with the intermetallic compounds $CeCo_3$, $GdFe_3$ and $CeNi_2Co$ is presented.

2. Experimental

All alloys were obtained from pure metals by electric melting under an argon atmosphere with sequential quenching for 240 h at 950°C in vacuum. The investigation of the interaction of compounds with hydrogen was conducted on an apparatus under a pressure of hydrogen to 2000 atm. with range of temperatures from -195 to 300°C as described in [3]. Under the first cycle hydrogen was delivered consequently under a small pressure (0.1 atm.). This allowed completion of the formation of hydrides and avoidance of amorphous products. Calculation of amount hydrogen was done using Van der Vaals modified equation for high pressure [4]. The quantity of hydrogen in obtained hydrides was checked by the thermodesorption method. X-ray diffraction (XRD) of alloys and hydrides was conducted at installation Dron-2 (Co, CuKα, Ni filter).

3. Results

Completed X-ray analyses of the investigated alloys showed that the obtained samples of $CeCo_3$, $GdFe_3$ and $CeNi_2Co$ have a single phase and have $PuNi_3$ or $CeNi_3$ structure types. Lattice parameters of these compounds are presented in Table 1 and agree with Refs. [5,6].

The obtained data showed that replacement of one Ni atom in $CeNi_3$ by a Co atom did not change their structure

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Table 1
X-ray diffraction data of compounds and their hydrides

Composition	Type of structure	a (Å)	$\Delta a/a$ (%)	c (Å)	$\Delta c/c$ (%)	V ($Å^3$)	$\Delta V/V$ (%)
$CeCo_3$	$PuNi_3$	4.952±0.002	–	24.80±0.02	–	529.0	–
$CeCo_3H_{4.0}$	$PuNi_3$	4.961±0.001	0.2	32.69±0.01	31.8	697.0	32.1
$CeCo_3H_{6.1}$	$PuNi_3$	5.030±0.003	1.6	32.98±0.02	33.0	723.0	36.8
$ErNi_3$	$PuNi_3$	4.941±0.003	–	24.25±0.02	–	513.2	–
$ErNi_3H_{3.7}$	$PuNi_3$	5.184±0.003	4.8	26.27±0.01	8.4	610.3	19.1
$ErNi_3H_{4.9}$	$PuNi_3$	5.210±0.003	5.4	26.45±0.02	9.1	622.3	21.2
$GdFe_3$	$PuNi_3$	5.166±0.001	–	24.72±0.01	–	570.3	–
$GdFe_3H_{4.0}$	$PuNi_3$	5.382±0.001	4.3	26.88±0.01	8.7	674.3	18.2
$GdFe_3H_{5.0}$	$PuNi_3$	5.501±0.001	6.6	26.66±0.01	7.9	698.8	22.5
$CeNi_3$	$CeNi_3$	4.951±0.002	–	16.49±0.02	–	350.5	–
$CeNi_3H_{3.5}$	$CeNi_3$	4.890±0.001	−1.2	21.78±0.07	32.3	451.6	29.2
$CeNi_3H_{5.1}$	$CeNi_3$	4.902±0.002	−1.0	22.34±0.02	35.5	465.0	32.9
$CeNi_2Co$	$CeNi_3$	4.950±0.002	–	16.46±0.02	–	349.0	–
$CeNi_2CoH_{3.5}$	$CeNi_3$	4.893±0.001	−1.2	21.78±0.07	32.3	451.6	29.2
$CeNi_2CoH_{5.6}$	$CeNi_3$	4.971±0.001	0.4	22.27±0.02	35.3	477.1	36.5

type. So, $CeNi_2Co$ has the same structure $CeNi_3$ type, as $CeNi_3$.

After obtaining hydrides of these compounds under a small pressure (1–3 atm.) the quantity of hydrogen in the hydrides and the obtained X-ray data agree almost completely with Refs. [7–9].

Absorption–desorption isotherms of hydrogen for the investigated compounds at temperatures 20°C, −50°C and −70°C and under pressure to 2000 atm. are presented in Figs. 1–3. The obtained X-ray data of hydrides are presented in Figs. 4–6.

3.1. $CeCo_3$–H_2 system

Analyses of the absorption–desorption isotherms of $CeCo_3$–H_2 system under high pressure shows that over the whole interval of pressure there was equal absorption of hydrogen at room temperatures. There was a change of composition of the hydride phase from $CeCo_3H_{4.5}$ to $CeCo_3H_{6.1}$ with increasing pressure from 40 to 1730 atm. at this temperature. Desorption of hydrogen at room temperature up to 70 atm. leads to the formation of a hydride phase with the composition $CeCo_3H_{4.9}$.

Absorption of hydrogen at low temperature (−70°C) and a pressure of 1730 atm. leads to the formation of a hydride with the composition $CeCo_3H_{6.8}$. At this temperature additional absorption of hydrogen takes place; there is also an increase in the stability of the hydride phase under high pressure. At desorption, a considerable amount of hydrogen exuded out of the hydride at pressure <500 atm. and

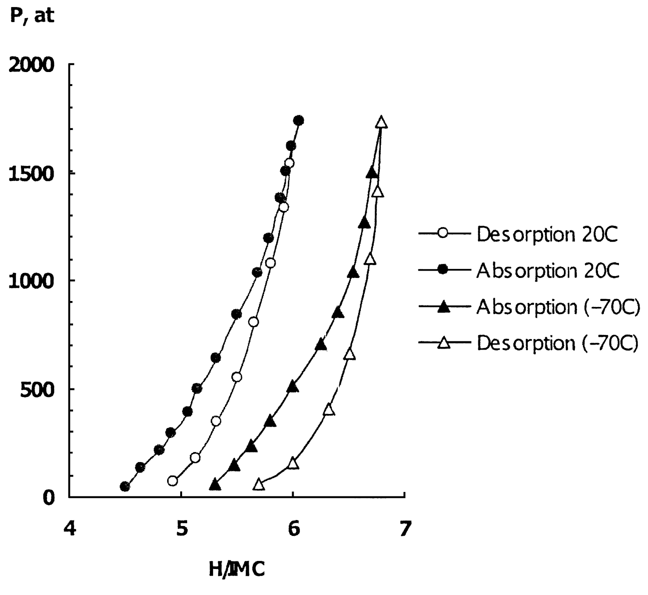

Fig. 1. Absorption–desorption isotherms of hydrogen in the $CeCo_3$–H_2 system.

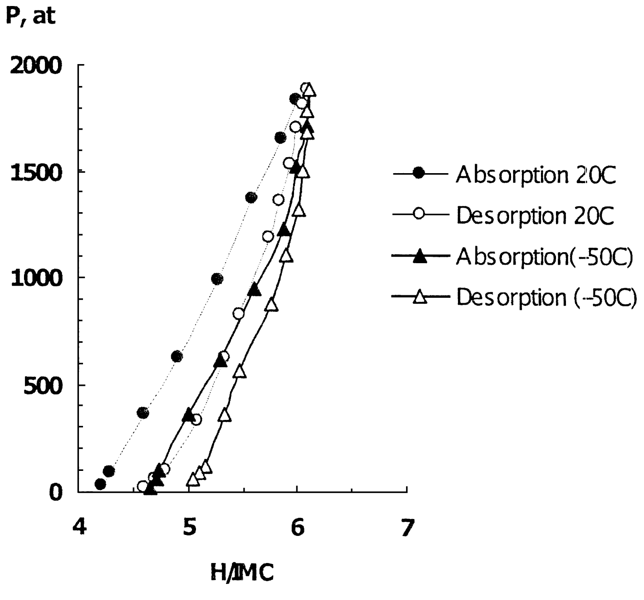

Fig. 2. Absorption–desorption isotherms of hydrogen in the $GdFe_3$–H_2 system.

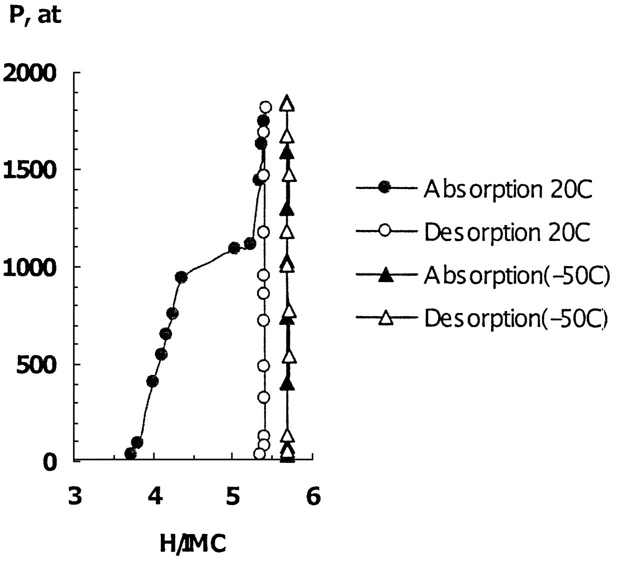

Fig. 3. Absorption–desorption isotherms of hydrogen in the $CeNi_2Co–H_2$ system.

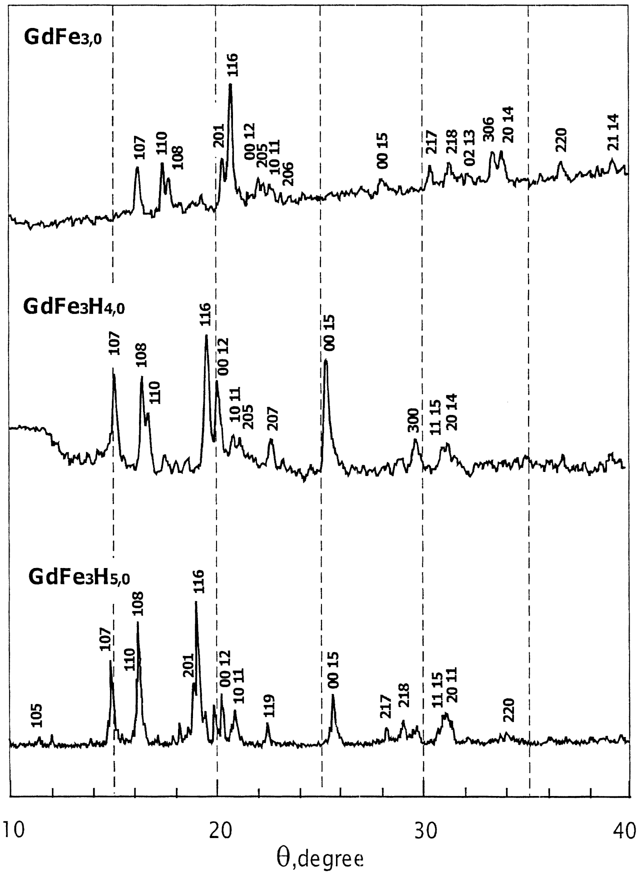

Fig. 4. X-ray diffraction of $GdFe_{3.0}$, $GdFe_3H_{4.0}$ and $GdFe_3H_{5.0}$.

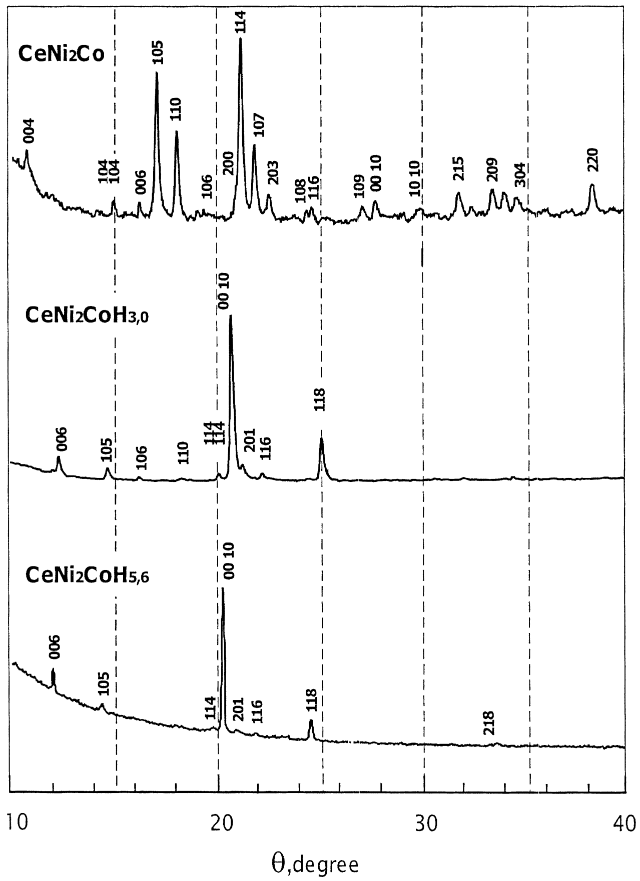

Fig. 5. X-ray diffraction of $CeNi_2Co$, $CeNi_2CoH_{4.0}$ and $CeNi_2CoH_{5.6}$.

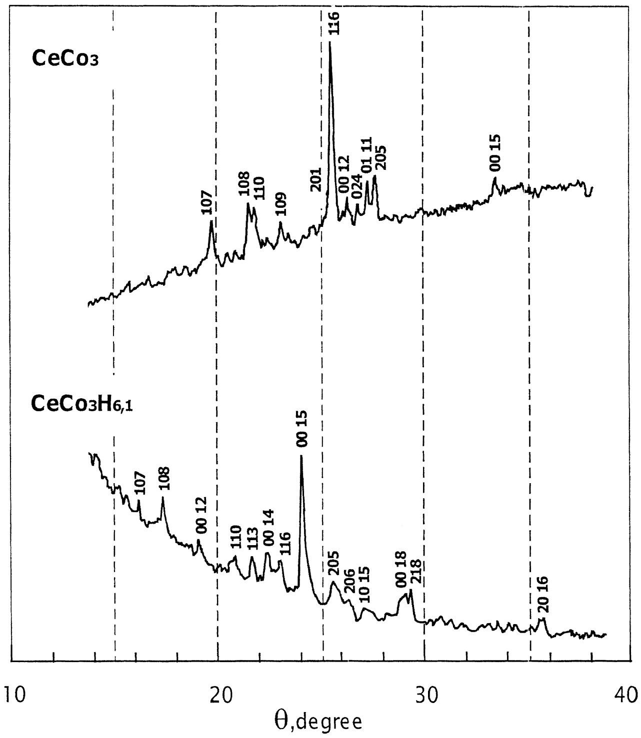

Fig. 6. X-ray diffraction of $CeCo_3$ and $CeCo_3H_{6.1}$.

on decreasing the pressure to atmospheric, the amount of hydrogen in the hydride became equal to the composition $CeCo_3H_{5.7}$. This composition is considerably different to the composition of $CeCo_3H_{4.0}$, which was obtained for the hydride under low pressure.

3.2. $GdFe_3$–H_2 system

Analyses of the absorption–desorption isotherms under high pressure and at room temperatures has shown, that for the $GdFe_3$–H_2 system there is equal absorption of hydrogen from the composition $GdFe_3H_{4.2}$ under a pressure of 30 atm. to the composition $GdFe_3H_{6.1}$ under a pressure of 1891 atm. Desorption of hydrogen up to a pressure of 25 atm. leads to the formation of the hydride phase $GdFe_3H_{6.1}$.

Absorption of hydrogen at low temperatures (−50°C) in the $GdFe_3$–H_2 system does not lead to an increase of the maximum composition of the hydride phase and this composition is $GdFe_3H_{6.1}$ under a pressure of 1886 atm. At 1691–1886 atm. the composition of the hydride phase has hardly changed. At low temperatures and decreasing the pressure to 60 atm. a hydride with the composition $GdFe_3H_{5.1}$ was formed.

3.3. $CeNi_2Co$–H_2 system

There is a plateau in the absorption isotherm at pressures of 947–1116 atm. for the $CeNi_2Co$–H_2 system at room temperature. Absorption of hydrogen proceeded from $CeNi_2CoH_{4.4}$ to $CeNi_2CoH_{5.2}$. A similar process was observed for the $CeNi_3$–H_2 system [1]. For this system absorption of hydrogen was observed from $CeNi_3H_{4.2}$ at a pressure of 650 atm. to $CeNi_3H_{4,9}$ at a pressure of hydrogen 700 atm. The maximum composition was $CeNi_2CoH_{5.4}$ at room temperature and under a pressure of 1810 atm. This absorption was irreversible and a decrease of pressure to 40 atm. did not change the composition of the hydride phase.

Increasing of the pressure of the $CeNi_2Co$–H_2 system at low temperatures (−50°C) was not accompanied by considerable absorption of hydrogen and the maximum composition of the hydride was $CeNi_2CoH_{5.7}$ under a pressure of 1847 atm. The hydride with such a composition, obtained under high pressure and low temperature, was stable enough and did not exude much hydrogen on decreasing the pressure to atmospheric.

4. Discussion

Analyses of the results obtained in Ref. [2], Figs. 4–6 and Table 1, allow the conclusion to be drawn that RT_3 compounds with similar ($PuNi_3$ or $CeNi_3$) structures, display different behaviors under a high pressure of hydrogen.

All intermetallic compounds avoided decomposition during high pressure hydrogen absorption. This is shown in the XRD results (Figs. 4–6) and the additional amounts of hydrogen (Table 1) after absorption under high pressure.

For $CeCo_3$, $GdFe_3$, $ErNi_3$ forming hydrides under low pressure there is a characteristic lattice expansion and formation of stabilized hydride phases at atmospheric pressure. For the $CeCo_3$–H_2 system such an expansion proceeds mainly due to the parameter c ($\Delta c/c$ 31.8%), for $GdFe_3$–H_2 it is due to parameters a ($\Delta a/a$ 4.3%) and c ($\Delta c/c$ 8.7%) and for $ErNi_3$–H_2 also are changed parameters a ($\Delta a/a$ 4.8%) and c ($\Delta c/c$ 8.4%). The increase in volume lattice $\Delta V/V$ for the hydride phase under low pressure for $CeCo_3$–H_2 is 32.1%, for $GdFe_3$–H_2 is 18.2% and for $ErNi_3$–H_2 is 19.1%.

On forming hydride phases at high pressure a further increase in lattice volume lattice was observed. Under such conditions parameters were changed: for $CeCo_3$–H_2 $\Delta a/a=1.6\%$ and $\Delta c/c=33.0\%$; for $GdFe_3$–H_2 $\Delta a/a=6.6\%$ and $\Delta c/c=7.9\%$, and for $ErNi_3$–H_2 $\Delta a/a=5.4\%$ and $\Delta c/c=9.1\%$.

The increase of the lattice volume $\Delta V/V$% for the hydride phases under high pressure was insignificant in comparison with the hydride phases under low pressure and was for $CeCo_3H_{6.1}=4.7\%$, for $GdFe_3H_{5.0}=4.3\%$ and for $ErNi_3H_{4.9}=2.1\%$. As seen from the XRD data (Figs. 4, 6), all hydride phases under high pressure have retained the $PuNi_3$ structure type of the initial compounds.

For $CeNi_3$ and $CeNi_2Co$ on forming hydride phases at low pressure an increase in their lattice volume occurred accompanied by an increase in the c parameter, for $CeNi_3$–H_2 $\Delta c/c=32.3\%$, $\Delta V/V=29.2\%$, and for $CeNi_2Co$–H_2 $\Delta c/c=32.3\%$, $\Delta V/V=29.2\%$. Formation of hydride phases under high pressure was accompanied by changes in their lattice parameters: for $CeNi_3H_{5.1}$ $\Delta a/a=-1.0\%$, $\Delta c/c=35.5\%$, $\Delta V/V=32.9\%$ and for $CeNi_2CoH_{5.6}$ $\Delta a/a=0.4\%$, $\Delta c/c=35.3\%$, $\Delta V/V=36.5\%$. The increase of the lattice volume, $\Delta V/V$, in the hydride phases under high pressure in comparison with hydride phases under low pressure was inconsiderable — for $CeNi_3H_{5.1}=3.7\%$ and for $CeNi_2CoH_{5.6}=7.3\%$. The hydride phases under high pressure $CeNi_3H_{5.1}$ and $CeNi_2CoH_{5.6}$ (Fig. 5) retained the structure type $CeNi_3$ of the initial compounds.

Under high pressure, the difference between $CeNi_3$ and $PuNi_3$ structure types is expressed better. For $CeNi_3$ and $CeNi_2Co$ absorption of hydrogen has saltatory character under high pressure. It is practically irreversible (Fig. 3). Replacement of one Ni atom by Co atom in $CeNi_3$ alloys obstructs the implantation of hydrogen. So, this saltation takes place under higher pressure.

Under normal conditions hydrides of all the studied compounds are stable. This means that the activation energy of hydrogen desorption reaction is high enough. The stability of the hydrides under high pressure shows that hydrogen atoms occupy new type of vacancies. These vacancies are located in the expanded lattice of low pressure hydrides.

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