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Hydrogen Absorption in RNi_4Al (R = Rare Earth) Ternary Compounds*

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Hydrogen absorption in a series of eleven rare earth ternary intermetallic compounds, RNi_4Al (where R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm) has been studied. All these compounds are found to crystallize in the hexagonal $CaCu_5$-type structure and absorb a large quantity of hydrogen at moderate pressure and ambient temperature. In terms of equilibrium pressure, the hydrides of these ternaries are more stable than those of corresponding binary, RNi_5, compounds. This is consistent with previous observations on the $Th(Ni, Al)_5$ ternary system.

Introduction

Many rare earth, yttrium, and thorium intermetallic compounds have been shown to absorb a large quantity of hydrogen (*1*). The typical compound, $LaNi_5$, absorbs hydrogen to form $LaNi_5H_{6.7}$, which has a proton density ($\sim 6.2 \times 10^{22}$ protons/cm^3) (*2*) about 50% greater than that of liquid hydrogen. We have been studying the effects of substituting transition metals by Ag, Al, etc., in RCu_5, RCo_5, and RNi_5 compounds as regard their structural and magnetic properties (*3*). In this work we report the hydrogen absorption characteristics of aluminum substituted RNi_4Al compounds. The RNi_4Al systems are found to crystallize in the hexagonal $CaCu_5$-type structure and absorb a substantial amount of hydrogen. The original crystal structure is maintained with merely the expansion of the unit cell after absorbing hydrogen. The hydrides of these ternary compounds are seen to be more stable than those of corresponding binaries in terms of their equilibrium pressures. This is consistent with our previous observation on $Th(Ni,Al)_5$ ternaries, where $ThNi_5$ does not absorb hydrogen, but $ThNi_4Al$ is seen to absorb hydrogen (*4*).

Experimental

The intermetallic compounds used were prepared by the same procedure as described in previous communications (*3*, *4*). The purities of the starting materials were as follows: rare earth, 99.9%; Ni, 99.999%; and Al, 99.999%. After several meltings of metals in the cold boat, the formation of intermetallic compounds in the $CaCu_5$ structure was established by their X-ray powder diffraction patterns. These alloys were hydrided without further heat treatments. The hydriding apparatus was the one used in the previous work (*4*). The hydrogen gas was obtained from Air Products and Chemicals Inc. and was used as received. Its stated purity was 99.999%. X-Ray powder diffraction patterns were obtained by Picker X-ray diffractometer with Cu$K\alpha$ radiation.

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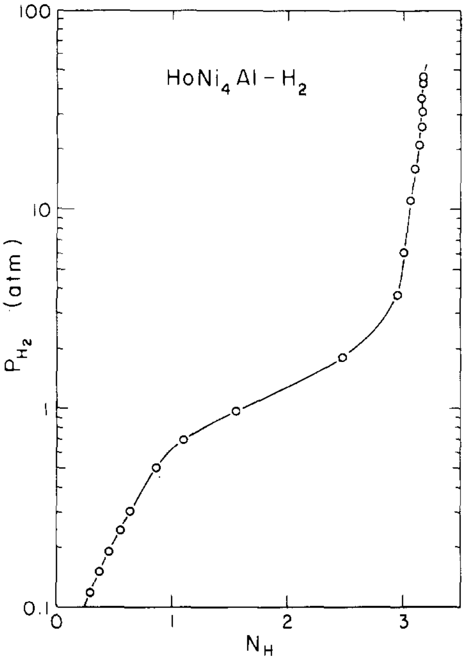

FIG. 1. Desorption isotherm curve of $HoNi_4Al$ at 24°C, where N_H is the number of hydrogen atoms per formula unit of the intermetallic compound.

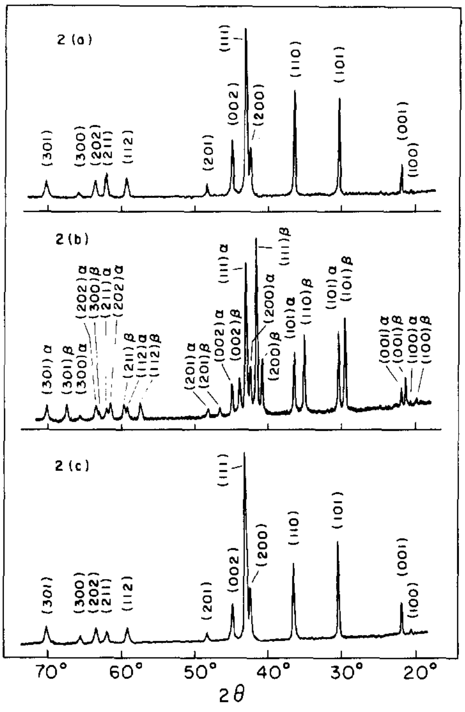

FIG. 2. Powder X-ray diffraction patterns of (a) original $HoNi_4Al$, (b) hydride $HoNi_4AlH_{1.8}$ (Miller indices with α are for the solid solution and those with β for the β-phase hydride), and (c) $HoNi_4Al$ after complete removal of hydrogen.

The lattice constants of the compounds were obtained by using the least-squares-fit program.

Results and Discussion

All the compounds studied are found to absorb hydrogen at 100 atm and room temperature. The pressure–composition isotherm of desorption for $HoNi_4Al$ at 24°C is shown in Fig. 1. In this figure, a well-defined plateau is not seen, suggesting that this temperature may be above the critical temperature. However, the X-ray powder diffraction patterns of $HoNi_4AlH_{1.8}$ showed two sets of diffraction peaks, which are shown in Fig. 2. Each set of peaks can be indexed as the hexagonal $CaCu_5$-type compounds and only one set of peaks with the smaller lattice parameters were obtained after removing all hydrogen from the sample. The hydride of larger lattice constants is designated as a β-phase hydride and the one with smaller lattice parameter is defined as an α-phase hydride, the later of which is a solid solution of hydrogen in metal. Similar behavior is seen in the other heavy rare earth systems. If the critical temperature of $HoNi_4Al$ hydride is below 24°C, one expects a single phase (solid solution) and one set of X-ray powder diffraction peaks for $HoNi_4AlH_{1.8}$ (*6*). Since there are two phases in this composition as seen in X-ray patterns, it is reasonable to assume that these ternary compounds form β-phase hydrides at 24°C. The origin(s) of the slope in the pressure–composition isotherm curves in the two phase region is not understood clearly. It is possible that the desorption kinetics is very slow and that equilibrium was not reached experimentally, although more than 24 hr elapsed between experimental points. In some cases it is known that compounds with local composition variation have sluggish pressure–

TABLE I

CRYSTALLOGRAPHIC AND HYDROGEN ABSORPTION DATA OF RNi$_4$Al COMPOUNDS

Compound	a (Å)	c (Å)	V (Å)^3	$\Delta V/H^a$	P_{eq} (atm)^b
$LaNi_4Al$	5.066	4.070	90.55		
$LaNi_4AlH_{4.3}$	5.319	4.235	103.76	3.0_7	$<10^{-3}$
$CeNi_4Al$	4.943	4.085	86.47		
$CeNi_4AlH_{3.7}$	5.227	4.186	99.05	3.4_0	$<10^{-3}$
$PrNi_4Al$	5.023	4.064	88.80		
$PrNi_4AlH_{3.7}$	5.254	4.203	100.48	3.1_6	$<10^{-2}$
$NdNi_4Al$	5.004	4.067	88.19		
$NdNi_4AlH_{4.0}$	5.229	4.183	99.05	2.7_2	$<10^{-2}$
$SmNi_4Al$	4.980	4.050	86.98		
$SmNi_4AlH_{3.6}$	5.193	4.155	97.04	2.7_9	$<10^{-1}$
$GdNi_4Al$	4.969	4.048	85.95		
$GdNi_4AlH_{3.5}$	5.169	4.142	95.84	2.8_3	$<10^{-1}$
$TbNi_4Al$	4.941	4.037	85.35		
$TbNi_4AlH_{3.2}$	5.134	4.131	94.30	2.8_0	<1
$DyNi_4Al$	4.928	4.038	84.93		
$DyNi_4AlH_x{}^c$	5.107	4.120	93.06	(2.4_9)	<1
$HoNi_4Al$	4.919	4.037	84.59		
$HoNi_4AlH_x{}^c$	5.105	4.128	93.17	(2.5_6)	~ 1
$ErNi_4Al$	4.910	4.033	84.20		
$ErNi_4AlH_x{}^c$	5.096	4.122	92.70	(2.8_3)	~ 1
$TmNi_4Al$	4.900	4.026	83.71		
$TmNi_4AlH_x{}^c$	5.078	4.121	92.03	(2.8_4)	~ 1

[a] Volume expansion (Å^3) per hydrogen atom.

[b] The precise values were not determined (see text).

[c] Hydrogen contents in these compounds are not known. These are estimated by using the hydrogen contents at 45 atm, where $x = 3.26, 3.35, 3.00$, and 2.93 for Dy, Ho, Er, and Tm compounds, respectively.

composition isotherm curves (*7*). It is therefore likely that the slopes of the curves of these ternaries are due to local composition fluctuation.

The hydrogen contents in β-phase hydrides and crystallographic data on RNi$_4$Al compounds are given in Table I. The numbers of hydrogen atoms absorbed per formula unit of intermetallic compounds are between ~3 and 4 ($TmNi_4AlH_{2.9}$ to $LaNi_4AlH_{4.3}$). $LaNi_5$ absorbs hydrogen to form $LaNi_5H_{6.7}$ and the aluminum-substituted ternary $LaNi_4Al$ makes $LaNi_4AlH_{4.3}$. However, the equilibrium pressure of $LaNi_5$–H_2 is 2.5 atm and that of $LaNi_4Al$–H_2 is below 10^{-3} atm at room temperature. Similarly, $SmNi_5$ has a plateau pressure of >60 atm and $SmNi_4Al$ has this parameter <1 atm at room temperature (*2*). This tendency is general for all the compounds studied and shows that the aluminum substitution stabilizes the β-phase hydrides. This is in agreement with previous results on $Th(Ni,Al)_5$ (*4*).

The unit cell volumes of the compounds RNi$_4$Al and their β-phase hydrides RNi$_4$AlH$_x$ are shown in Fig. 3. The unit cell volumes of hypothetical β-phase hydrides, RNi$_4$AlH$_{3.5}$, are also included in the same figure in order to make a comparison of volume expansions in β-phase hydrides of the same hydrogen content. This hydrogen content (RNi$_4$AlH$_{3.5}$) was chosen for comparison, because this is close to

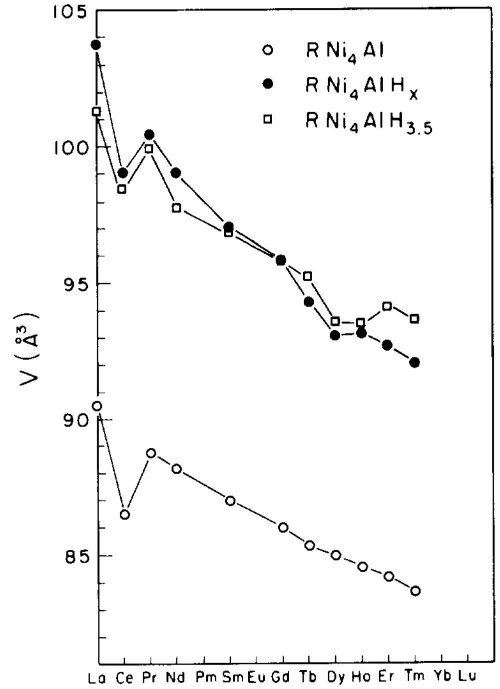

FIG. 3. Unit cell volumes of $R\mathrm{Ni_4Al}$, $R\mathrm{Ni_4AlH}_x$, and $R\mathrm{Ni_4AlH_{3.5}}$.

the average value in the actual hydrides. (The compound $\mathrm{GdNi_4Al}$ forms the β-phase hydride of this composition, i.e., $\mathrm{GdNi_4AlH_{3.5}}$.) The unit cell volume of each $R\mathrm{Ni_4Al}$ was obtained by a linear extrapolation using the value of $\Delta V/H$ for the corresponding hydride, $R\mathrm{Ni_4AlH}_x$, either by subtracting a necessary amount of volume from the unit cell volume of $R\mathrm{Ni_4Al}_x$ ($x > 3.5$) or by adding it to that of $R\mathrm{Ni_4Al}_x$ ($x < 3.5$). It is seen that the unit cell volume of $\mathrm{CeNi_4Al}$ is smaller than that expected from the lanthanide contraction. This is believed to be due to the tetravalency of cerium in this compound as is also the case in $\mathrm{CeNi_5}$ (*8*). It is interesting to note that the unit cell volumes of $\mathrm{CeNi_4AlH_{3.7}}$ and $\mathrm{NdNi_4AlH_{4.0}}$ are comparable while $\mathrm{CeNi_4Al}$ has a much smaller unit cell volume than $\mathrm{NdNi_4Al}$. (In the case of hypothetical hydrides $\mathrm{CeNi_4AlH_{3.5}}$ and $\mathrm{NdNi_4AlH_{3.5}}$, the unit cell volume of the former is even larger than that of the latter.) It appears, therefore, that the hydrogen absorption changes the effective valency of cerium in $\mathrm{CeNi_4AlH_{3.7}}$. Since the unit cell volume of $\mathrm{CeNi_4AlH_{3.7}}$ is still smaller than that of $\mathrm{PrNi_4AlH_{3.7}}$, cerium seems to have an effective valence between 3 and 4 in $\mathrm{CeNi_4AlH_{3.7}}$.

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