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Structural and hydrogen sorption properties of $RENi_{5-x}Al_x$ (RE=Gd, Tb, Dy, Ho, Er and Y) alloys

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Abstract

The results of our studies on the crystal structure and hydrogen sorption properties of $RENi_{5-x}Al_x$ (RE=Gd, Tb, Dy, Ho, Er and Y) alloys are reviewed and discussed with respect to the kind of rare earth metal and the aluminium content. In all investigated systems it was found that the binary prototype structure ($CaCu_5$ type) is preserved up to $x=2$. Beyond this composition a transformation into the YCo_3Ga_2 structure type occurs, whereby the latter structure is stable for $x \leq 3$. It was also found that only ternary alloys with the $CaCu_5$ structure react with hydrogen under pressures up to 15 MPa and temperatures between 77 and 700 K to form hydrides. The unit cell parameters of the alloys increase, while the alloy hydrogen capacity and the hydrogen equilibrium pressure decrease, with increasing aluminium content. At a particular Ni/Al ratio the alloy unit cell parameters decrease, as does their hydride stability, while the hydrogen capacity generally decreases with increasing atomic number of the RE. Alloys containing Y fit well into the above trends. However, minor deviations were observed and are indicated.

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1. Introduction

Over the last 30 years, intermetallic compounds of composition AB_5 have received a great deal of attention as possible hydrogen storage materials [1]. This is mainly because of the ability of $LaNi_5$ to absorb up to 6.7 hydrogen atoms per alloy formula unit (f.u.) at modest pressure at room temperature. Substitution of either component by various metals, especially aluminium, was found to have a considerable influence on the structure and hydrogen sorption properties of the prototype alloy [2–5]. In such a way it was possible to tailor materials for particular applications. Therefore, some $LaNi_5$-based hydrogen storage alloys are today widely used as negative electrodes in rechargeable nickel–metal hydride (Ni/MH) batteries. This paper is a review of our results on $RENi_{5-x}Al_x$–hydrogen systems [6–12] with the aim of gaining a better understanding of the role played by a particular component of the alloy in its hydride properties.

2. Experimental

The detailed experimental procedure regarding alloy preparation, structure determination and the measurement of hydrogen sorption properties has been described in detail elsewhere [6–13]. Briefly, alloys of composition $RENi_{5-x}Al_x$ (RE=Gd, Tb, Dy, Ho, Er and Y), $0 \leq x \leq 3$, were prepared from commercial metals by arc melting, followed by annealing at 1100–1150 K for at least 3 days. The binary prototype structure ($CaCu_5$ type) is preserved up to $x=2$. Beyond this composition a transformation into the YCo_3Ga_2 structure type occurs. However, it has been reported that, after prolonged annealing at 1073 and 1273 K, $GdNi_3Al_2$ adopts other structures closely related to the $CaCu_5$ type [14,15]. This suggests that the stability of a particular structural type of $GdNi_3Al_2$ depends greatly on the annealing procedure applied. X-ray powder diffraction (XRD) was used for phase analysis, and structure and unit cell parameter determination. The unit cell parameters for the hydrides stable at room temperature were also determined. Hydride composition and the equilibrium pressure of the alloy–hydrogen system were obtained from

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desorption pressure–composition isotherms (PCI). The thermodynamic properties of the alloy–hydrogen systems were determined for those systems that exhibited well-defined plateau pressures.

3. Results and discussion

XRD of $RENi_{5-x}Al_x$ alloys, $0 \leq x \leq 3$, indicated that these single-phase materials crystallise in the hexagonal structure of space group $P6/mmm$, either of the $CaCu_5$ type (for $x \leq 2$) or of the YCo_3Ga_2 type (for $x > 2$) [16]. The only exemption is the alloy of composition $GdNi_2Al_3$, which crystallises in the $CaCu_5$-type structure. Substitution of aluminium for nickel increases the unit cell parameters (Table 1), with generally a negative (parameter *a*) and a positive (parameter *c*) deviation from Vegard's rule [6–12].

All prepared alloys were exposed to hydrogen gas and it was found that binary $RENi_5$ as well as ternary intermetallic compounds of the YCo_3Ga_2 type do not absorb hydrogen under the experimental conditions applied in this study. Based on results for related $RENi_5$ (RE = Sm, Eu, Gd, Y) alloys [17–20], where high equilibrium pressures were reported, we assume that the binary $RENi_5$ exhibit higher hydrogen absorption pressures than those applied in our study. Ternary alloys of the $CaCu_5$ type (for $x \leq 2$) were easily activated and were found to absorb up to 4.5 ($TbNi_{4.5}Al_{0.5}$) hydrogen atoms per alloy f.u. Hydrides stable at room temperature retained the same crystal structure as the host alloys, whereby hydrogen uptake increases the unit cell volume of the host alloy (Table 1). The enthalpy, entropy change and Gibbs free energy of formation were determined from the plateau equilibrium pressures at a ratio of two hydrogen atoms per alloy f.u. using the least-square fit of the van't Hoff equation. The hydrogen capacity and the equilibrium pressure at room temperature for $RENi_{4.5}Al_{0.5}$ and $RENi_4Al$ alloys (alloys with the highest hydrogen content in a particular $RENi_{5-x}Al_x$–hydrogen system) and the thermodynamic data for the corresponding alloy–hydrogen systems are given in Table 1.

The following features of $RENi_{5-x}Al_x$–hydrogen systems can be summarised. In hydride-forming alloys the hydrogen equilibrium desorption pressure and the hydrogen capacity decrease as the aluminium content increases. This is in agreement with the model proposed by Gschneidner et al. [21] where the equilibrium pressure decreases as the cell volume increases, but the hydrogen capacity decreases as the number of unpaired nickel 3d electrons decreases. Thus, in $RENi_5$, as aluminium is substituted for nickel the cell volume increases and the equilibrium pressure decreases (Fig. 1). At the same time the nickel 3d electrons become increasingly paired (aluminium should be considered as an electron donor into the system), reducing the hydrogen capacity (Fig. 2). However, it is obvious that the model is valid only within

Table 1

Unit cell parameters for $RENi_{4.5}Al_{0.5}$ and $RENi_4Al$ alloys. The hydrogen capacity, the equilibrium pressure, the thermodynamic data and unit cell parameters of hydrides stable at room temperature

Composition	a (Å)	c (Å)	V (Å^3)	p_{eq} (kPa)	n (H atoms/f.u.)	ΔH (kJ (mol H_2)$^{-1}$) at $x=2$	ΔS (J (mol H_2)$^{-1}$ K^{-1}) at $x=2$	ΔG (kJ (mol H_2)$^{-1}$) at $x=2$
$GdNi_{4.5}Al_{0.5}$	4.942	4.009	84.8					
$GdNi_{4.5}Al_{0.5}H_x$	5.195	4.137	96.7	670	3.83	−32.68	−127.54	4.59
$GdNi_4Al$	4.960	4.037	86.0					
$GdNi_4AlH_x$	5.217	4.203	99.1	23.8	3.78	−41.50	−128.95	−3.72
$TbNi_{4.5}Al_{0.5}$	4.925	4.007	84.2					
$TbNi_{4.5}Al_{0.5}H_x$				1029	4.50	−27.29	−112.41	5.35
$TbNi_4Al$	4.935	4.026	84.9					
$TbNi_4AlH_x$	5.163	4.155	95.6	90.6	4.06	−33.88	−113.38	−1.00
$DyNi_{4.5}Al_{0.5}$	4.915	4.007	83.8					
$DyNi_{4.5}Al_{0.5}H_x$				2014	4.27	−27.30	−118.89	7.53
$DyNi_4Al$	4.933	4.037	85.1					
$DyNi_4AlH_x$	5.163	4.167	96.2	58.0	3.66	−35.38	−116.40	−1.27
$HoNi_{4.5}Al_{0.5}$	4.894	4.002	83.0					
$HoNi_{4.5}Al_{0.5}H_x$				4365	2.44	−25.07	−116.40	9.04
$HoNi_4Al$	4.923	4.035	84.7					
$HoNi_4AlH_x$	5.127	4.134	94.1	92.7	3.72	−34.30	−114.73	−0.68
$ErNi_{4.5}Al_{0.5}$	4.890	4.002	82.9					
$ErNi_{4.5}Al_{0.5}H_x$				5530	2.60	−25.43	−120.55	9.89
$ErNi_4Al$	4.910	4.034	84.9					
$ErNi_4AlH_x$	5.120	4.140	94.0	471	2.95	−32.38	−122.22	3.43
$YNi_{4.5}Al_{0.5}$	4.919	4.008	84.0					
$YNi_{4.5}Al_{0.5}H_x$				1870	3.95	−22.42	−100.60	7.06
YNi_4Al	4.941	4.039	85.4					
YNi_4AlH_x	5.143	4.139	94.8	30.4	3.74	−40.85	−129.70	−2.85

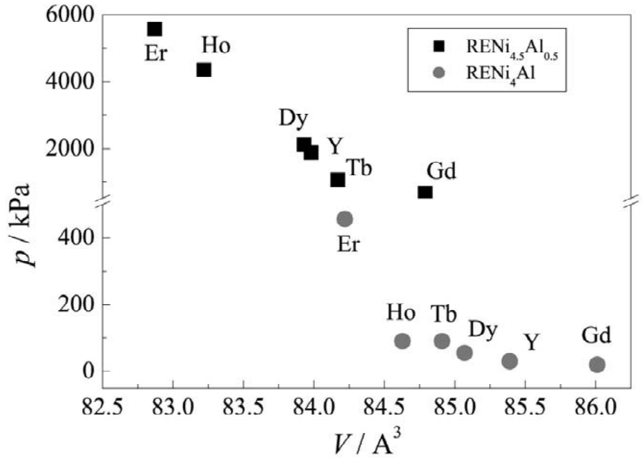

Fig. 1. Desorption equilibrium pressure at room temperature versus unit cell volume for $RENi_{5-x}Al_x$–hydrogen systems ($x=0.5$ and 1; and at two hydrogen atoms/alloy f.u.).

systems containing the same rare earth metal. For example, the unit cell volume of $GdNi_{4.5}Al_{0.5}$ is comparable to those of $TbNi_4Al$ and $HoNi_4Al$, but its hydrogen equilibrium pressure is higher than those of the latter two hydrides. It should be noted that erbium-containing alloys and $HoNi_{4.5}Al_{0.5}$ do not follow the observed hydrogen capacity trend. One further point: the placement of Y-containing alloys with its properties between those of terbium and dysprosium is consistent with its alloying behaviour. Namely, yttrium usually behaves as the lighter members of the heavy rare earth metals. The effects of the kind of rare earth on the hydrogen capacity and the hydrogen equilibrium desorption pressure are shown in Figs. 2 and 3, respectively. Generally, at a particular Ni/Al ratio the equilibrium pressure increases, while the hydrogen capacity decreases with increasing atomic number of the rare earth metal.

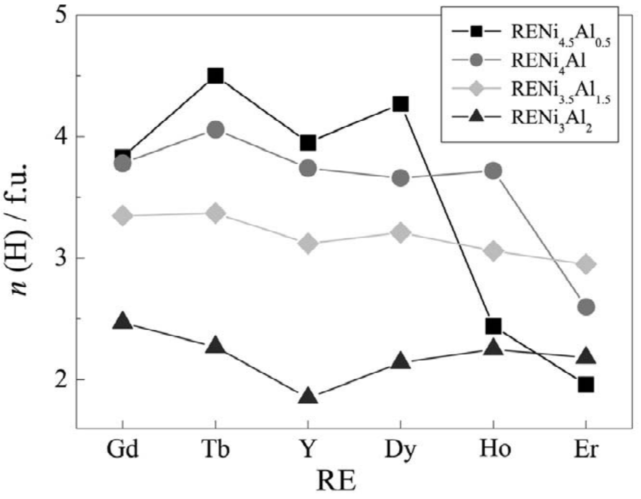

Fig. 2. Hydrogen capacity at room temperature versus rare earth metal for $RENi_{5-x}Al_x$–hydrogen systems ($x=0.5$, 1, 1.5, 2).

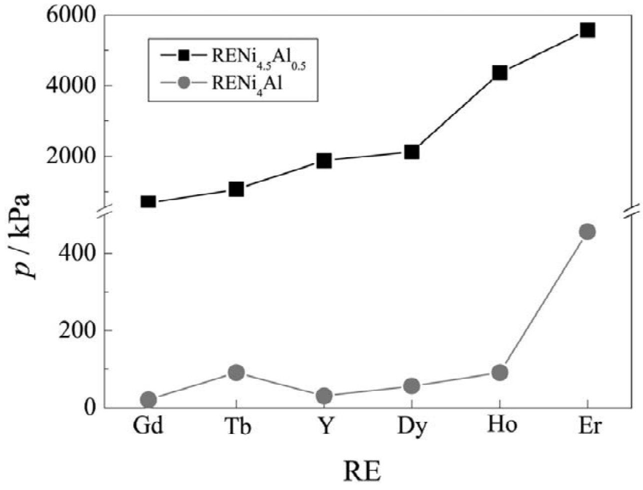

Fig. 3. Plateau pressure (at two hydrogen atoms/alloy f.u.) versus rare earth metal for $RENi_{5-x}Al_x$–hydrogen systems ($x=0.5$ and 1).

The van't Hoff plots, which are indicators of hydride stability, are shown in Fig. 4 for the $RENi_{4.5}Al_{0.5}$–hydrogen and the $RENi_4Al$–hydrogen systems. The rectangular box between 0.1 and 1 MPa and 273 and 373 K indicates systems that could be considered for practical purposes. Also taking into account a hydride capacity of at least 3.5 H atoms per alloy formula unit, the systems $RENi_{4.5}Al_{0.5}$–hydrogen (RE = Gd, Tb) and $RENi_4Al$–hydrogen (RE = Gd, Tb, Y, Dy, Ho) might be selected for possible practical application, whereby the terbium-containing systems exhibit the highest hydrogen capacity.

4. Conclusion

The alloys $RENi_{5-x}Al_x$ (RE = Gd, Tb, Dy, Ho, Er and Y), $0 \leq x \leq 3$, were prepared and their structural and

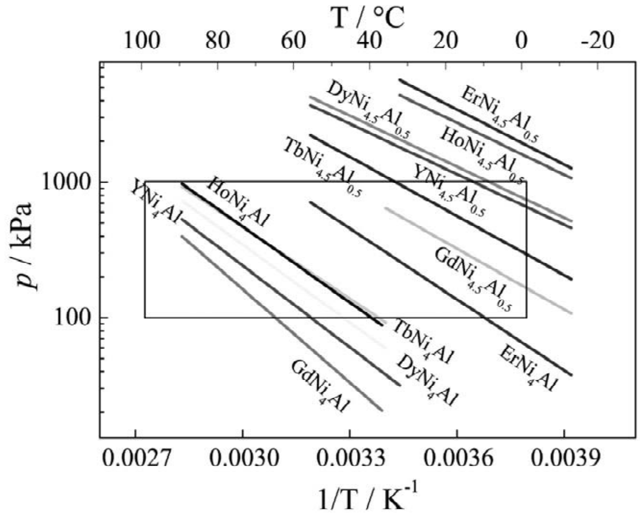

Fig. 4. Van't Hoff plots for $RENi_{5-x}Al_x$–hydrogen systems ($x=0.5$ and 1; and at two hydrogen atoms/alloy f.u.).

hydrogen sorption properties were studied. It was found that only ternary alloys up to $x=2$ which crystallise with the $CaCu_5$ structure type form hydrides under hydrogen pressures up to 15 MPa and between 77 and 700 K. It was also found that the hydrogen equilibrium pressure and hydrogen capacity decrease as the aluminium content increases. Erbium-containing alloys and $HoNi_{4.5}Al_{0.5}$ do not strictly follow the observed hydrogen capacity trend. At a particular Ni/Al ratio the alloy unit cell parameters decrease, the hydrogen equilibrium pressure increases while the hydrogen capacity generally decreases with increasing atomic number of the rare earth metal. Yttrium-containing alloys with their observed hydrogen sorption properties fit well between the hydride properties observed for alloys containing terbium and dysprosium.

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