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On the structural and thermodynamic properties of the $DyNi_{5-x}Al_x$–hydrogen system

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Abstract. A structural and thermodynamic study of the $DyNi_{5-x}Al_x$–hydrogen system has been performed. It was found that the hexagonal crystal structure of the prototype compound $DyNi_5$ ($CaCu_5$ type; space group, $P6/mmm$) exists up to $DyNi_3Al_2$. Beyond this composition and up to $DyNi_2Al_3$ another related hexagonal structure (YCo_3Ga_2 type; space group, $P6/mmm$) is stable. All alloys have been exposed to hydrogen gas at pressures up to 15 MPa and temperatures between 77 and 700 K. Under these conditions, ternary alloys having the $CaCu_5$ structure react with hydrogen. Their crystal structures remain the same but the hydrogen uptake increases the unit-cell volume by up to 13%. The remaining ternary alloys as well as the binary $DyNi_5$ do not exhibit any significant hydrogen absorption. The pressure–composition isotherms were measured. The entropy and the heat of formation have been extracted for systems that exhibit an equilibrium pressure plateau. It was found that the hydrogen capacity at ambient temperature and the equilibrium pressure decrease with the increasing content of aluminium.

1. Introduction

Many rare-earth-based intermetallics of the general composition AB_5 react reversibly with hydrogen at ambient temperature and modest pressure [1–3]. Among them, the exceptional representatives $LaNi_5$ and the $LaNi_5$-based alloys are even commercially used for hydrogen storage purposes [4] and as negative-electrode material in rechargeable nickel–metal hydride (Ni–MH) batteries [5, 6].

Substitution within the $RENi_5$ stoichiometry (RE ≡ rare earth including mischmetal) has frequently shown that a third component (metal or metalloid) strongly affects the crystal structure and the thermodynamic characteristics of a selected $RENi_5$–hydrogen system. It was reported that the replacement of one nickel atom by gold in $RENi_5$ (RE = Gd to Lu) changes the hexagonal $CaCu_5$ structure into the cubic structure of $MgSnCu_4$ type [7]. It was also reported that in the systems $LaNi_{5-x}Al_x$–hydrogen [8], $LaNi_{5-x}Cu_x$–hydrogen [9], $CeNi_{5-x}Cu_x$–hydrogen [10], $MmNi_{5-x}Al_x$–hydrogen (Mm = mischmetal) [11], $GdNi_{5-x}Al_x$–hydrogen [12] and $ErNi_{5-x}Al_x$–hydrogen [13] the equilibrium pressure and the hydrogen capacity are strongly influenced by partial substitution of nickel by aluminium or copper.

A systematic study on the structural and thermodynamic properties of the system $DyNi_{5-x}Al_x$–hydrogen has not yet been performed. It has only been reported that $DyNi_5$ and $DyNi_4Al$ have a $CaCu_5$ structure type [14] and that $DyNi_4Al$ has been found to absorb about 3.3 hydrogen atoms per formula unit at 4.5 MPa [15].

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2. Experimental details

The materials used in this investigation were dysprosium (purity 99.9%; Johnson Matthey, UK), nickel (purity, 99.5%; Carlo Erba, Italy; containing iron as the main impurity), aluminium (purity 99+%; Ventron, Germany) and hydrogen (purity, 99.999%; Jesenice, Slovenia). Alloys of the composition $DyNi_{5-x}Al_x$ ($x \equiv 0, 0.5, 1, 2, 2.5$ and 3) were prepared in an arc melting furnace under an argon atmosphere. To ensure homogeneity, the alloys were inverted and remelted several times. The weight loss of material was checked and was found to be negligible. All alloys were annealed in vacuum at 1070 K for at least 72 h. In order to prepare a single-phase material, further annealing for 15–18 h at temperatures up to 1300 K was required for $DyNi_3Al_2$, $DyNi_{2.5}Al_{2.5}$ and $DyNi_2Al_3$.

The x-ray powder patterns were obtained with a Philips PW 1050 diffractometer and nickel-filtered Cu Kα radiation. The intensities were calculated using the Lazy Pulverix program [16].

The pressure–composition isotherm (PCI) measurements were carried out in a stainless-steel apparatus that enables work in a temperature range from 77 to 800 K, in vacuum and/or with hydrogen at pressures up to 20 MPa. The temperature was controlled using a thermostat or a cryostat, respectively. Prior to PCI measurements the alloys were activated by heating (up to 700 K) under hydrogen at pressures up to 15 MPa. After cooling, the absorbed gas was removed by heating and evacuating. This procedure was repeated several times and the equilibrium conditions were assumed to be reached when the amount of released hydrogen remained constant. Desorption PCI measurements were made on the activated samples, completely saturated with hydrogen by releasing small quantities of hydrogen from the reactor. The equilibrium pressure was measured after 15 min and the procedure was repeated until the equilibrium pressure dropped to 10 kPa. The samples were then heated and additional amounts of released hydrogen were measured. The hydride composition was calculated from the pressure–temperature–volume data.

3. Results and discussion

X-ray powder diffraction of the $DyNi_{5-x}Al_x$ ($x \equiv 0, 0.5, 1, 1.5, 2, 2.5$ and 3) alloys revealed that these single-phase materials are of the hexagonal symmetry (space group, $P6/mmm$). It was determined that they exhibit either the structure of the $CaCu_5$ type (for $x \leqslant 2$) or of the YCo_3Ga_2 type [17] (for $x > 2$). X-ray patterns of the hydrides of the composition $DyNi_4AlH_{3.66}$, $DyNi_{3.5}Al_{1.5}H_{3.21}$ and $DyNi_3Al_2H_{2.14}$, i.e. those stable at room temperature exhibit the same hexagonal $CaCu_5$ type of structure as do their host alloys. Figure 1 shows the x-ray pattern of $DyNi_4AlH_{3.66}$, i.e. a typical pattern obtained for the hydrides. The unit-cell parameters of the alloys and their hydrides are presented in table 1.

In the prototype $DyNi_5$ structure, two crystallographically inequivalent nickel sites exist: 2c in the basal plane layer of mixed atoms (RE+Ni) and 3g in the layer at $z = 1/2$ containing small atoms only. The YCo_3Ga_2 type can be briefly described as derived from the $CaCu_5$ type by shifting one third of the rare-earth atoms residing in the basal plane along the z axis into the $z = 1/2$ plane; the parameter c remains the same, while the parameter a is increased by a factor of $3^{1/2}$ [12, 17, 18].

A detailed x-ray intensity analysis was carried out and the atomic coordinates of the metallic atoms for both structure types have been determined. The results can be summarized as follows. In the structure of the $CaCu_5$ type the replacement of aluminium atoms for nickel atoms takes place either over the two available crystallographic sites at lower aluminium contents ($x \leqslant 1$) or preferentially within the equatorial layer and proceeds until

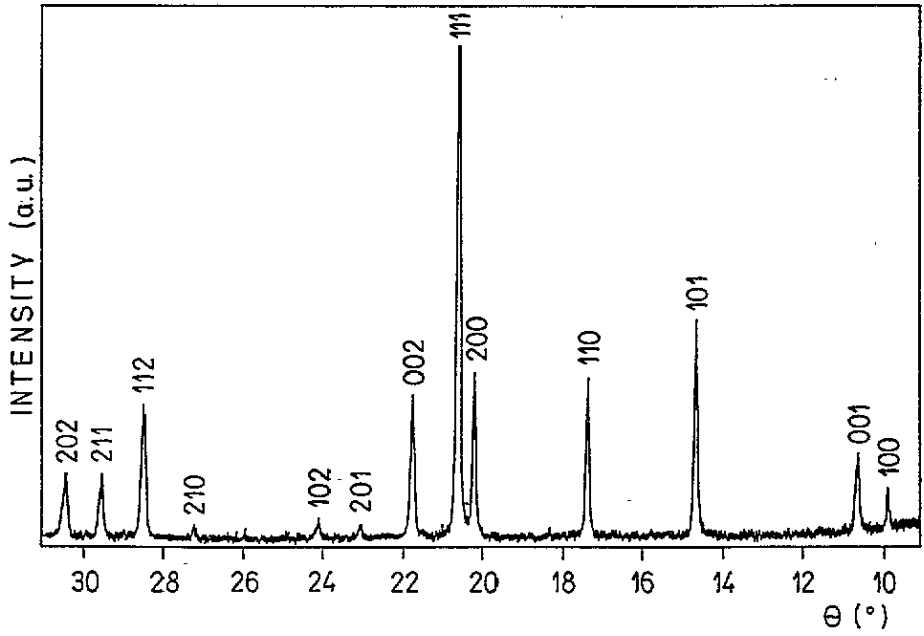

Figure 1. The x-ray pattern of $DyNi_4AlH_{3.66}$.

Table 1. Crystallographic and thermodynamic data for the $DyNi_{5-x}Al_x$–hydrogen system.

Composition	a (Å)	c (Å)	V (Å^3)	ΔH^a (kJ (mol H_2)$^{-1}$ K^{-1})	ΔS^a (J (mol H_2)$^{-1}$ K^{-1})	Reference
$DyNi_5$	4.869	3.956	81.22			
$DyNi_5$	4.869	3.969	81.49			[14]
$DyNi_{4.5}Al_{0.5}$	4.915	4.007	83.83			
$DyNi_{4.5}Al_{0.5}H_{4.27}$				−27.30	−118.89	
$DyNi_4Al$	4.933	4.037	85.07			
$DyNi_4Al$	4.928	4.038	84.93			[15]
$DyNi_4AlH_{3.66}$	5.163	4.167	96.19	−35.38	−116.40	
$DyNi_4AlH_{3.26}$	5.107	4.120	93.06			[15]
$DyNi_{3.5}Al_{1.5}$	4.997	4.060	87.79			
$DyNi_{3.5}Al_{1.5}H_{3.21}$	5.154	4.155	95.58			
$DyNi_3Al_2$	5.035	4.076	89.49			
$DyNi_3Al_2H_{2.14}$	5.151	4.152	95.40			
$DyNi_{2.5}Al_{2.5}$	8.869	4.102	279.42			
$DyNi_2Al_3$	9.026	4.080	287.85			

[a] These data were obtained using a hydrogen-to-alloy formula ratio of 2.

two thirds of the nickel atoms are replaced by aluminium correspondingly; thus we have the formula $DyNi_3Al_2$. The atomic coordinates for the alloys with the YCo_3Ga_2 structure type ($DyNi_{2.5}Al_{2.5}$ and $DyNi_2Al_3$) are given in table 2. In the latter structure an ordering of aluminium atoms within the equatorial layer (3g sites) takes place. The replacement of nickel atoms by aluminium in $DyNi_{2.5}Al_{2.5}$ proceeds in the basal plane (6j sites) only, while in $DyNi_2Al_3$ it takes place in the basal 6j plane and/or the equatorial 6m plane.

In order to determine some thermodynamic properties of the $DyNi_{5-x}Al_x$–hydrogen systems the alloys were exposed to hydrogen gas at different pressures and temperatures.

Table 2. Atomic coordinates for $DyNi_{2.5}Al_{2.5}$ (space group, $P6/mmm$; YCo_3Ga_2 type) and $DyNi_2Al_3$ (space group, $P6/mmm$; YCo_3Ga_2 type).

		Coordinates			
Atom	Position	x	y	z	Occupation
		$DyNi_{2.5}Al_{2.5}$			
Dy	1b	0	0	1/2	1
Dy	2c	1/3	2/3	0	1
Al	6j	0.31	0	0	0.75
Al	3g	1/2	0	1/2	1
Ni	6m	0.185	0.37	1/2	1
Ni	6j	0.31	0	0	0.25
		$DyNi_2Al_3$			
Dy	1b	0	0	1/2	1
Dy	2c	1/3	2/3	0	1
Al	3g	1/2	0	1/2	1
Al	6j	0.31	0	0	0.85
Al	6m	0.185	0.370	1/2	0.15
Ni	6m	0.185	0.370	1/2	0.85
Ni	6j	0.31	0	0	0.15

The alloys $DyNi_{4.5}Al_{0.5}$, $DyNi_4Al$, $DyNi_{3.5}Al_{1.5}$ and $DyNi_3Al_2$ were easily activated while $DyNi_5$, $DyNi_{2.5}Al_{2.5}$ and $DyNi_2Al_3$ do not absorb any significant amount of hydrogen under pressures up to 15 MPa and temperatures up to 700 K.

Figures 2–5 illustrate the results of the PCI measurements. The thermodynamic parameters ΔS and ΔH (table 1) were determined from the equilibrium pressures, at the ratio of two hydrogen atoms per alloy formula unit, for the systems that exhibit a plateau. The corresponding values were calculated using the least-squares fit of the Van't Hoff equation $\ln p_{eq} = \Delta H/RT - \Delta S/R$, where p_{eq} is the plateau pressure, ΔH the reaction enthalpy, R the universal gas constant, T the temperature and ΔS the reaction entropy.

The thermodynamic features of the investigated system are

(i) a decrease in hydrogen desorption equilibrium pressure with increasing content of aluminium.

(ii) a decrease in hydrogen capacity with increasing content of aluminium at ambient temperature,

(iii) a more negative enthalpy with increasing content of aluminium and

(iv) a maximal hydrogen capacity of 4.27 hydrogen atoms per formula unit observed for $DyNi_{4.5}Al_{0.5}$ at ambient temperature.

The behaviour of the 313 K isotherm of the $DyNi_{4.5}Al_{0.5}$–hydrogen system (figure 2) needs some further comments. The possibility of an experimental error was discarded because carefully repeated measurements always led to the same results. A possible explanation for the odd behaviour of this isotherm could be sought in the multiplateau effect similar to those observed in the $LaNi_5$–hydrogen system [19]. However, for a final conclusion, further detailed measurements need to be carried out.

The behaviour of the hydrogen equilibrium pressure and the number of hydrogen atoms

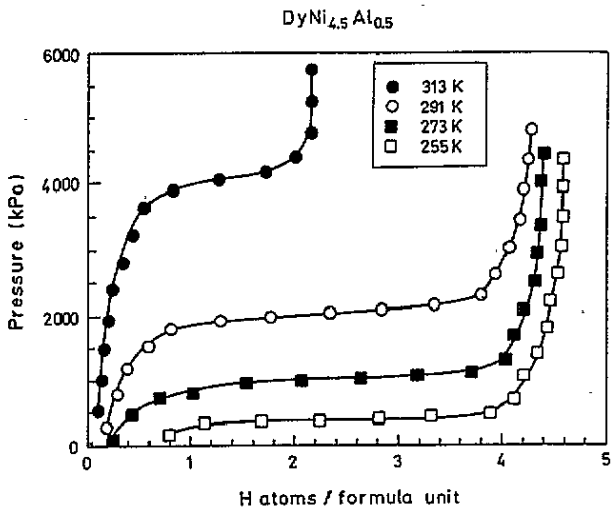

Figure 2. PCI for the $DyNi_{4.5}Al_{0.5}$–hydrogen system.

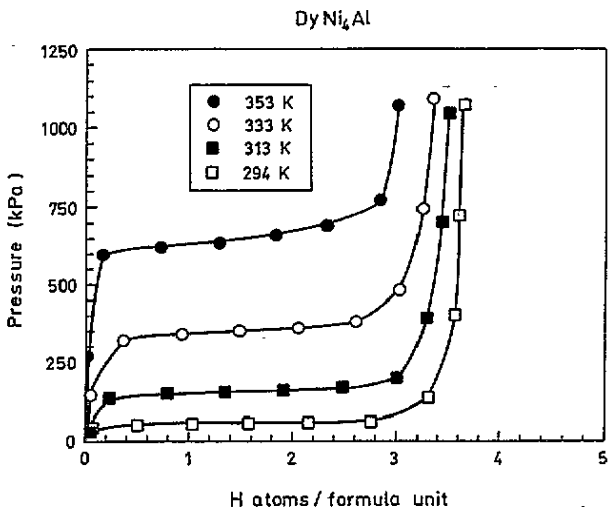

Figure 3. PCI for the $DyNi_4Al$–hydrogen system.

absorbed in the $RENi_{5-x}Al_x$–hydrogen systems have been discussed by Gschneidner *et al* [20]. In their model the hydrogen absorption is assumed to be dominated by two different effects. While the equilibrium pressure depends upon the size of the interstitial holes, the hydrogen capacity depends upon the number of unpaired 3d nickel electrons. This model could be applied to the $DyNi_{5-x}Al_x$–hydrogen system without restrictions. Thus, as aluminium substitution proceeds (the unit cell increases), the equilibrium pressure decreases. In addition the number of electrons in the nickel 3d band becomes increasingly paired (aluminium acts as an electron donor) which decreases the hydrogen capacity.

However, the alloys $DyNi_{2.5}Al_{2.5}$ and $DyNi_2Al_3$ should be regarded as new structures, but at the moment it is not clear how the structural changes (larger unit cell; rare-earth atoms in the interleaving layer) affect their resistivity to hydrogen,

It should be noted that our results obtained for the $DyNi_4Al$–hydrogen system are

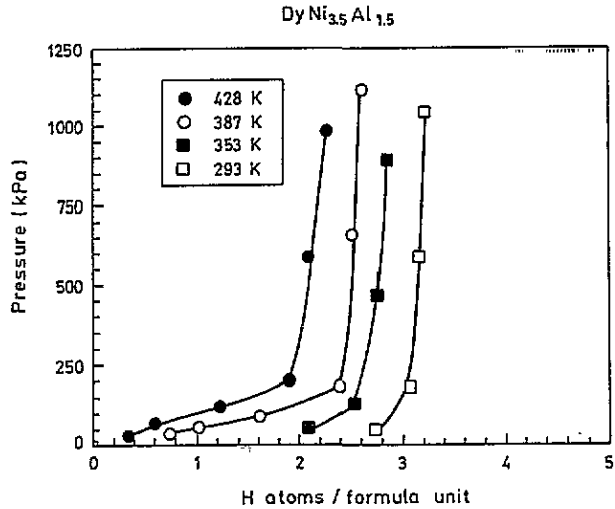

Figure 4. PCI for the $DyNi_{3.5}Al_{1.5}$–hydrogen system.

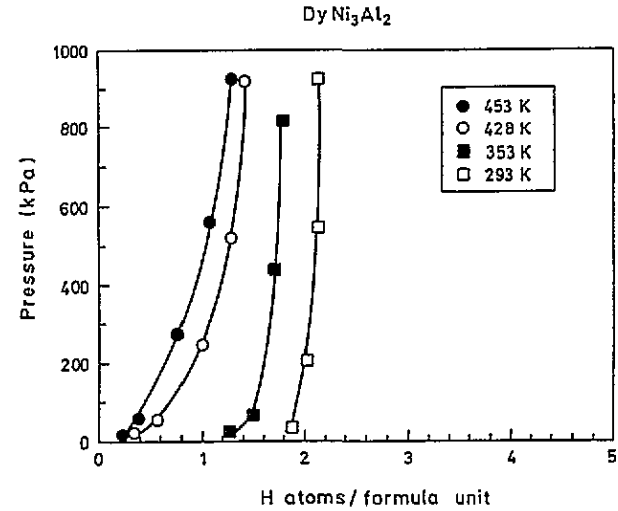

Figure 5. PCI for the $DyNi_3Al_2$–hydrogen system.

in good agreement with the reported data (table 1 [15]) regarding the hydrogen capacity and equilibrium pressure. The results observed for the $DyNi_5$–hydrogen system and the systems with a higher aluminium content are also consistent with the data reported for the related $GdNi_{5-x}Al_x$–hydrogen [12] and $ErNi_{5-x}Al_x$–hydrogen [13] systems, where hydrogen absorption was not observed for the binary alloy nor for the alloys with a higher aluminium content.

4. Conclusion

As a conclusion on the structural and thermodynamic properties of the $DyNi_{5-x}Al_x$–hydrogen system we can say that substitution of aluminium for nickel in the $DyNi_5$ alloy proceeds no further than $DyNi_2Al_3$. The prototype $CaCu_5$ type of structure is preserved at

lower aluminium contents, while at higher aluminium concentrations a larger unit cell of the YCo_3Ga_2 type is stable. The PCI curves indicate that the hydrogen capacity at ambient temperature decreases, the hydrogen equilibrium pressure decreases and the hydride stability increases with increasing aluminium content. Hydrogen uptake increases the unit-cell volume of the host alloy by up to 13%. Binary $DyNi_5$, ternary $DyNi_{2.5}Al_{2.5}$ and $DyNi_2Al_3$ do not absorb any significant amount of hydrogen up to 15 MPa and 700 K.

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