

The crystal structure and some thermodynamic properties of the $TbNi_{5-x}Al_x$ - hydrogen system

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 3099

(<http://iopscience.iop.org/0953-8984/9/15/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 08:28

Please note that [terms and conditions apply](#).

The crystal structure and some thermodynamic properties of the $\text{TbNi}_{5-x}\text{Al}_x$ -hydrogen system

Ž Blažina, B Šorgić and A Drašner

Laboratory for Solid State Chemistry, Institute Ruder Bošković, PO Box 1016, 10001 Zagreb, Croatia

Received 26 November 1996, in final form 27 January 1997

Abstract. A structural study of the $\text{TbNi}_{5-x}\text{Al}_x$ alloys revealed that nickel in TbNi_5 can be replaced by aluminium up to the composition TbNi_2Al_3 . However, the hexagonal crystal structure of the binary compound (CaCu₅ type, space group $P6/mmm$) exists only up to TbNi_3Al_2 , while beyond this composition another hexagonal structure (YCo₃Ga₂ type, space group $P6/mmm$) is stable. All of the single-phase alloys have been exposed to hydrogen gas at pressures up to 15 MPa and temperatures between 77 K and 700 K. It was found that under the above conditions only ternary alloys having the CaCu₅ structure react with hydrogen, whereby the hydrogen uptake increases the unit-cell volume by up to 12.5%. It was also found that the hydrogen equilibrium pressures decrease with the increasing content of aluminium as does the hydrogen capacity at room temperature. Binary TbNi_5 , and the ternary alloys crystallizing with the YCo₃Ga₂ type of structure, do not show any significant hydrogen absorption. The entropy, the enthalpy, and the Gibbs free energy of formation have been extracted for the systems that exhibit an equilibrium plateau in the pressure–composition isotherms.

1. Introduction

It is well known that the LaNi_5 -based alloys are commercially used for hydrogen-storage purposes [1]. TiNi_2 -based [2] and LaNi_5 -based alloys [3, 4] are also used as negative-electrode material in rechargeable nickel–metal hydride (Ni/MH) batteries. Most intermetallics react reversibly with hydrogen under the influence of temperature. However, LaNi_5 reacts reversibly at room temperature, and under 200 kPa of hydrogen, forms $\text{LaNi}_5\text{H}_{6.7}$ [5].

It is also known that substitution within the RENi_5 stoichiometry ($\text{RE} \equiv$ rare earth including misch metal) strongly affects the crystal structure and the thermodynamic characteristics of a selected RENi_5 -hydrogen system. However, the role of aluminium as a substituent seems to be the most promising feature as regards tailoring the metal–hydrogen system for a particular application [6, 7].

A systematic study on the structural and thermodynamic properties of the $\text{RENi}_{5-x}\text{Al}_x$ -hydrogen systems has been performed so far only for the systems containing La [6, 7], Gd [8], Dy [9], Er [10], and Mm ($\text{Mm} \equiv$ misch metal) [11]. As rare-earth metals often exhibit different structural properties when alloyed with the same kinds of transition metal, and their corresponding hydrides have various thermodynamic characteristics, the interest was in expanding the investigations on the $\text{TbNi}_{5-x}\text{Al}_x$ -hydrogen system too. The economic feasibility of its practical usage is however rather doubtful, because terbium is one of the less abundant and more expensive rare-earth metals.

The only published data on this system relate to the CaCu_5 structure type of TbNi_5 [12] and TbNi_4Al [13], and to absorption of 3.2 hydrogen atoms per formula unit at 100 kPa for TbNi_4Al [13].

2. Experimental details

The materials used in this investigation were terbium (99.9%; Johnson–Matthey, UK), nickel (99.5%; Carlo Erba, Italy; main impurity: iron), aluminium (99+%; Ventron, Germany), and hydrogen (99.999%; Jesenice, Slovenia). A series of alloys of the composition $\text{TbNi}_{5-x}\text{Al}_x$ were prepared under argon in an arc-melting furnace. To ensure homogeneity the alloys were inverted and remelted several times. The weight loss of the material was checked and was found to be negligible. Good single-phase material was obtained after annealing in vacuum (96 h at 1120 K for $x \equiv 0, 0.5, 1$; 216 h at 1120 K for $x \equiv 1.5, 2$; and 408 h at 1100 K for $x \equiv 2.5, 3$).

The x-ray powder patterns were obtained with a Philips PW 1050 diffractometer and nickel-filtered $\text{Cu K}\alpha$ radiation. The intensities were calculated using the ‘Lazy Pulverix’ program [14].

The pressure–composition isotherm (PCI) measurements were carried out in a stainless-steel apparatus that enables investigations to be carried out over a temperature range from 77 to 800 K, in vacuum and/or with hydrogen at pressures up to 20 MPa. The apparatus, the activation process, and the hydrogen desorption measurement procedure have been described elsewhere [10, 15].

Table 1. Atomic coordinates for TbNi_5 , $\text{TbNi}_{2.5}\text{Al}_{2.5}$, and TbNi_2Al_3

Atom	Position	Coordinates			Occupation
		x	y	z	
TbNi_5 (space group $P6/mmm$, CaCu_5 type)					
Tb	1a	0	0	0	1
Ni	2c	1/3	2/3	0	1
Ni	3g	1/2	0	1/2	1
$\text{TbNi}_{2.5}\text{Al}_{2.5}$ (space group $P6/mmm$, YCo_3Ga_2 type).					
Tb	1b	0	0	1/2	1
Tb	2c	1/3	2/3	0	1
Al	3g	1/2	0	1/2	1
Al	6j	0.31	0	0	0.75
Ni	6m	0.185	0.37	1/2	1
Ni	6j	0.31	0	0	0.25
TbNi_2Al_3 (space group $P6/mmm$, YCo_3Ga_2 type).					
Tb	1b	0	0	1/2	1
Tb	2c	1/3	2/3	0	1
Al	3g	1/2	0	1/2	1
Al	6j	0.29	0	0	1
Ni	6m	0.185	0.370	1/2	1

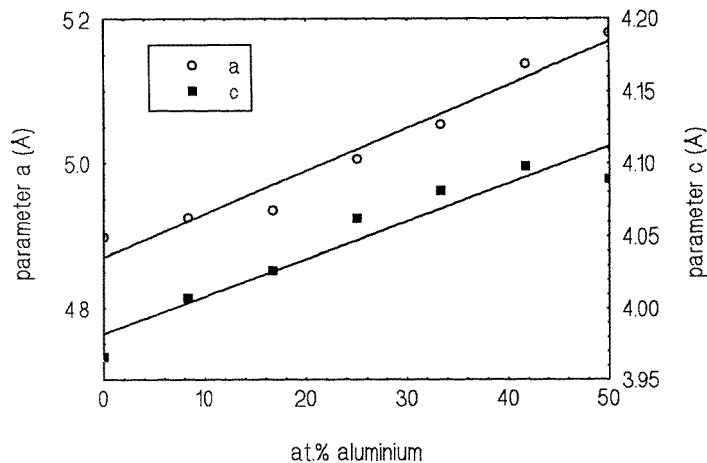


Figure 1. The variation of the unit-cell parameters in the $\text{TbNi}_{5-x}\text{Al}_x$ alloys (the parameter a_L of the larger unit cell is normalized to $a = a_L/\sqrt{3}$).

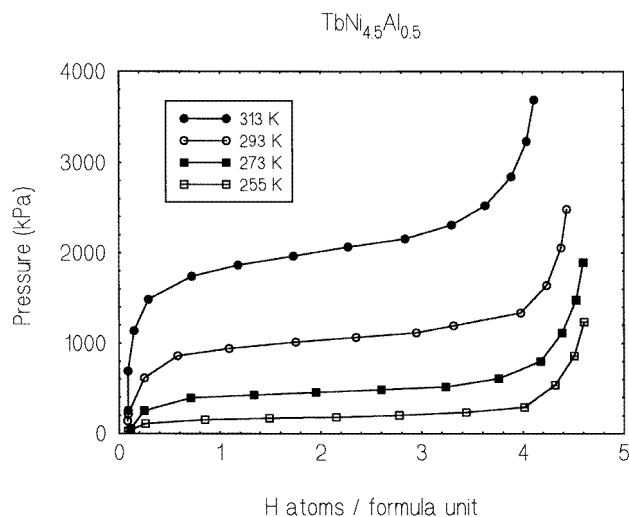


Figure 2. PCI for the $\text{TbNi}_{4.5}\text{Al}_{0.5}$ -hydrogen system.

3. Results and discussion

3.1. Crystal structure

X-ray powder diffraction of the $\text{TbNi}_{5-x}\text{Al}_x$ ($x \equiv 0, 0.5, 1, 1.5, 2, 2.5$ and 3) alloys indicated that these single-phase materials are of hexagonal symmetry (space group $P6/mmm$). They exhibit structure of either the CaCu_5 type (for $x \leq 2$) or the YCo_3Ga_2 type [16] (for $x > 2$). These two types of structure are closely related (table 1). In the CaCu_5 type of structure there exist two layers of atoms: the basal layer ($z = 0$) containing nickel ($2c$ sites) and terbium atoms ($1a$ sites); and the equatorial layer ($z = 1/2$) containing nickel atoms only ($3g$ sites). The YCo_3Ga_2 type of structure can be briefly described as being derived from the

Table 2. Crystallographic data for the TbNi_{5-x}Al_x alloys and their hydrides.

Composition	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	<i>V</i> _{hydride} / <i>V</i> _{alloy}	Reference
TbNi ₅	4.898	3.966	82.40		
TbNi ₅	4.894	3.966	82.26		[12]
TbNi _{4.5} Al _{0.5}	4.925	4.007	84.17		
TbNi ₄ Al	4.935	4.026	84.91		
TbNi ₄ Al	4.941	4.037	85.35		[13]
TbNi ₄ AlH _{4.06}	5.163	4.155	95.55	1.125	
TbNi ₄ AlH _{3.2}	5.134	4.131	94.30	1.105	[13]
TbNi _{3.5} Al _{1.5}	5.006	4.062	88.16		
TbNi _{3.5} Al _{1.5} H _{3.37}	5.171	4.151	96.12	1.090	
TbNi ₃ Al ₂	5.054	4.081	90.27		
TbNi ₃ Al ₂ H _{2.27}	5.172	4.157	94.37	1.045	
TbNi _{2.5} Al _{2.5}	8.898	4.098	280.99		
TbNi ₂ Al ₃	8.972	4.089	285.05		

CaCu₅ type by shifting one third of the terbium atoms from the basal plane along the *z*-axis into the equatorial plane, whereby the parameter *c* remains the same, while the parameter *a* is increased by a factor of 3^{1/2} [9, 16, 17].

The x-ray patterns of the hydrides stable at room temperature exhibit the same hexagonal CaCu₅ type of structure as do their host alloys, but the unit-cell volume has increased, depending on the composition, up to 12.5%. The unit-cell parameters and the cell volumes of the alloys and their hydrides are given in table 2. The unit-cell parameters expand linearly with the increasing amount of aluminium (figure 1) since the atomic radius of Al (1.43 Å) is larger than that of Ni (1.24 Å). The values of the parameter *a* of the larger unit cell are comparable with the corresponding values for the smaller unit cell provided that they are normalized by division by a factor of 3^{1/2}.

A detailed x-ray intensity analysis was carried out, and the atomic coordinates of the metallic atoms for both structure types have been determined. In the structure of the CaCu₅ type, the replacement of nickel atoms by aluminium atoms takes place either over the two available crystallographic sites at lower aluminium contents (*x* ≤ 1.5) or preferentially within the equatorial layer (*x* ≡ 2).

The atomic coordinates for the alloys with the YCo₃Ga₂ structure type (TbNi_{2.5}Al_{2.5} and TbNi₂Al₃) are given in table 1. In this structure an ordering of aluminium atoms within the equatorial layer (3g sites) takes place. The replacement of nickel atoms by aluminium proceeds in the basal plane (6j sites) only, until all nickel atoms are replaced by aluminium; thus we have the formula TbNi₂Al₃.

3.2. Thermodynamic properties

In order to determine some thermodynamic properties of the TbNi_{5-x}Al_x-hydrogen systems the alloys were exposed to hydrogen at different pressures and temperatures. It was found that ternary alloys with the CaCu₅ structure (TbNi_{4.5}Al_{0.5}, TbNi₄Al, TbNi_{3.5}Al_{1.5}, and

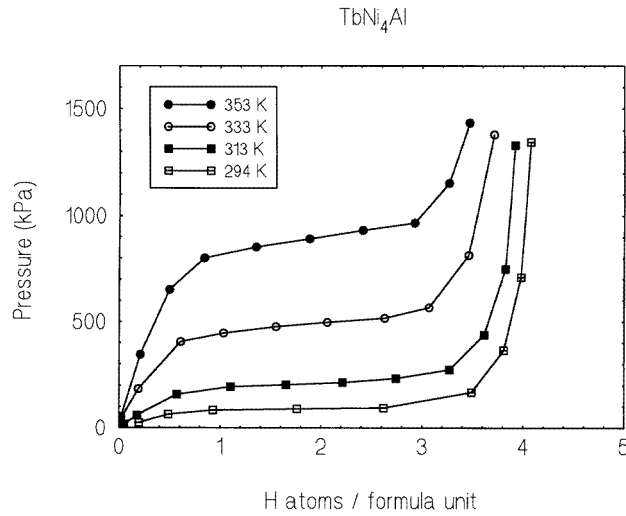


Figure 3. PCI for the $TbNi_4Al$ -hydrogen system.

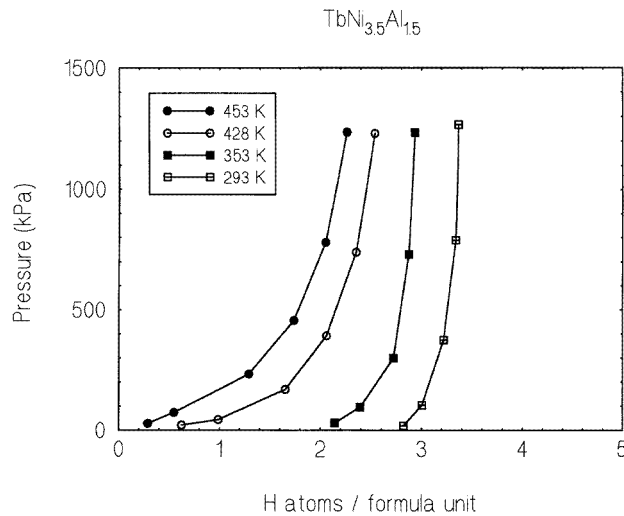


Figure 4. PCI for the $TbNi_{3.5}Al_{1.5}$ -hydrogen system.

$TbNi_3Al_2$) were easily activated, while binary $TbNi_5$ and ternary alloys with the YCo_3Ga_2 structure ($TbNi_{2.5}Al_{2.5}$ and $TbNi_2Al_3$) 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 3) were determined from the equilibrium pressures, at the ratios of 1.5 and 2 hydrogen atoms per alloy formula unit, for the systems that exhibit plateaux. The corresponding values were calculated using the least-square fit of the Van't Hoff equation

$$\ln p_{eq} = \Delta H/RT - \Delta S/R$$

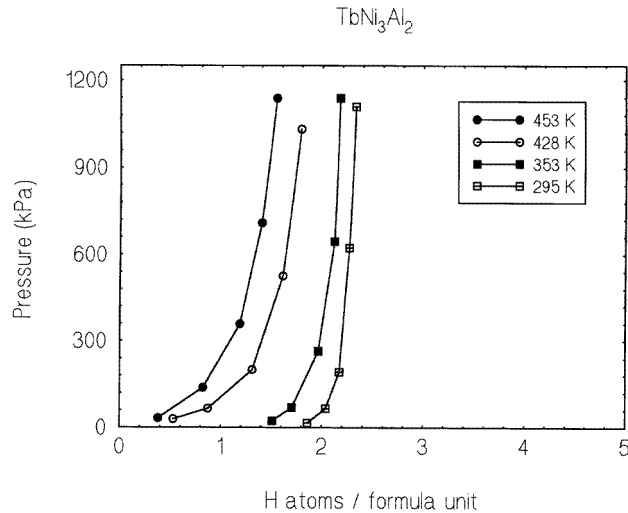


Figure 5. PCI for the TbNi_3Al_2 -hydrogen system.

Table 3. Thermodynamic data for the $\text{TbNi}_{5-x}\text{Al}_x$ -hydrogen system.

Composition	x	ΔH (kJ (mol H_2) $^{-1}$)	ΔS (J (mol H_2) $^{-1}\text{K}^{-1}$)	ΔG at 293 K (kJ (mol H_2) $^{-1}$)
$\text{TbNi}_{4.5}\text{Al}_{0.5}\text{H}_x$	1.5	-27.29	-111.41	5.35
	2.5	-27.24	-112.24	5.65
$\text{TbNi}_4\text{AlH}_x$	1.5	-33.88	-113.38	-0.66
	2.5	-33.47	-113.38	-0.25

where p_{eq} = plateau pressure, ΔH = reaction enthalpy, R = universal gas constant, T = temperature, and ΔS = reaction entropy. The Gibbs free energy of formation (ΔG) was calculated according to $\Delta G = \Delta H - T \Delta S$, and the corresponding values for room temperature are also included in table 3.

A brief analysis of the relevant data permits us to extract some thermodynamic features of the system investigated. The hydrogen desorption equilibrium pressure and hydrogen capacity at room temperature decrease with the increasing content of aluminium. The enthalpy and the entropy become more negative, while the free energy of formation decreases with the increasing content of aluminium. A maximum hydrogen capacity at room temperature of 4.5 hydrogen atoms per alloy formula unit was observed for $\text{TbNi}_{4.5}\text{Al}_{0.5}$.

The behaviour of the hydrogen equilibrium pressure and the hydrogen capacity of the $\text{RENi}_{5-x}\text{Al}_x$ -hydrogen systems has been discussed by Gschneidner *et al* [18]. In their model the hydrogen absorption process 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 electrons of nickel. It seems that this model can be applied to the $\text{TbNi}_{5-x}\text{Al}_x$ -hydrogen system without restrictions. Thus, as aluminium substitution proceeds (the unit cell increases), the equilibrium pressure decreases. In addition, the electrons in the nickel 3d band become increasingly paired up (aluminium acts as electron donor), which decreases the hydrogen capacity.

In this scheme the alloys TbNi_{2.5}Al_{2.5} and TbNi₂Al₃ 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 hydrogen absorption properties.

It should also be noted that our results obtained for the TbNi₄Al-hydrogen system are in good agreement with the reported data (table 1, reference [13]) on the hydrogen capacity and equilibrium pressure. The results observed for the TbNi₅-hydrogen system and for the systems with the higher aluminium content are also consistent with data reported for the related RENi_{5-x}Al_x-hydrogen (RE ≡ Gd, Dy, Er) systems [8–10], where hydrogen absorption was observed neither for the binary alloys nor for the alloys with the larger unit cells.

4. Conclusion

A structural study of the TbNi_{5-x}Al_x-hydrogen system indicated that substitution of aluminium for nickel in TbNi₅ proceeds no further than the composition TbNi₂Al₃. The structure of the prototype binary compound (of CaCu₅ type) is preserved at lower aluminium contents ($x \leq 2$), while at higher aluminium concentrations ($x > 2$) a larger unit cell of the YCo₃Ga₂ type is stable. The thermodynamic properties extracted from the PCI curves indicate that the hydrogen capacity decreases, as does the hydrogen equilibrium pressure, while the hydride stability increases with increasing aluminium content. Hydrogen uptake increases the unit-cell volume of the host alloy up to 12.5%. Binary TbNi₅, ternary TbNi_{2.5}Al_{2.5}, and TbNi₂Al₃ do not absorb any significant amount of hydrogen up to 15 MPa and 700 K.

References

- [1] Houston E L and Sandrock G D 1980 *J. Less-Common Met.* **74** 435
- [2] Sakai T, Ishikawa H, Miyamura H, Yamada S and Iwasaki T 1991 *J. Electrochem. Soc.* **138** 908
- [3] Notten P H L, Einerhand R E F and Daams J L C 1994 *J. Alloys Compounds* **210** 221
- [4] Wada M 1994 *Sci. Technol. Japan* **51** 54
- [5] van Vucht J H N, Kuijpers F A and Bruning H C A M 1970 *Philips Res. Rep.* **25** 133
- [6] Dwight A E 1975 *J. Less-Common Met.* **43** 117
- [7] Mendelsohn M H, Gruen D M and Dwight A E 1977 *Nature* **269** 45
- [8] Šorgić B, Drašner A and Blažina Ž 1995 *J. Alloys Compounds* **221** 169
- [9] Šorgić B, Drašner A and Blažina Ž 1995 *J. Phys.: Condens. Matter* **7** 7209
- [10] Šorgić B, Drašner A and Blažina Ž 1996 *J. Alloys Compounds* **232** 79
- [11] Rai K N, Rani R, Srikanth V and Kumar J 1986 *J. Less-Common Met.* **118** 285
- [12] Haszko S E 1960 *Trans. Metall. Soc. AIME* **218** 763
- [13] Takeshita T, Malik S K and Wallace W E 1978 *J. Solid State Chem.* **23** 271
- [14] Yvon K, Jeitschko W and Parth S E 1977 *J. Appl. Crystallogr.* **10** 73
- [15] Drašner A and Blažina Ž 1990 *J. Less-Common Met.* **163** 151
- [16] Fremy M A, Gignoux D, Moreau J M, Paccard D and Paccard I 1985 *J. Less-Common Met.* **106** 251
- [17] Schobinger-Papamantellos P, Middleton D P and Buschow K H J 1994 *J. Alloys Compounds* **206** 189
- [18] Gschneidner K A, Takeshita T, Chung Y and McMasters O D 1982 *J. Phys. F: Met. Phys.* **12** L1