Scientific paper

Crystal Structure snd Hydrogen Sorption Properties of the $YNi_{5-X}Ga_X$ Alloys

Antun Drašner and Želimir Blažina*

Laboratory for Solid State Chemistry, Department of Materials Chemistry, Ruđer Bošković Institute,
PO Box 1016, 10001 Zagreb, Croatia

** Corresponding author: E-mail: blazina@irb.hr*
Phone: +385 1 4561 111; Fax: +385 1 4680 098

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Dedicated to the memory of Professor Ljubo Golič

Abstract

Alloys of the general composition $YNi_{5-x}Ga_x$ were prepared and studied by X-ray powder diffraction. It was found that in the $YNi_{5-x}Ga_x$ system the single phase region exists up to the composition YNi_2Ga_3. The hexagonal structure of the prototype compound YNi_5 ($CaCu_5$ type, space group P6/mmm) is preserved in all alloys for $x < 2$. Within the composition region YNi_3Ga_2 – YNi_2Ga_3 the existing single phase alloys crystallize also in the hexagonal symmetry with the same space group P6/mmm, but with a larger unit cell of the YCo_3Ga_2 type. All single phase alloys have been exposed to hydrogen gas, whereby binary YNi_5, and ternary alloys with the YCo_3Ga_2 type of structure do not show any significant hydrogen absorption up to 5 MPa of hydrogen. All ternary alloys having the $CaCu_5$ structure react readily with hydrogen. The pressure composition desorption isotherms for the corresponding alloy-hydrogen systems were determined and it was found that the equilibrium pressure and the hydrogen capacity decrease with the increased gallium content. The change of entropy, the change of enthalpy and the change of the Gibbs free energy of formation for the alloy-hydrogen systems have also been extracted from the pressure composition desorption isotherms. The relevant thermodynamic parameters confirmed that the stability of the hydride increases with the increased amount of gallium.

Keywords: Yttrium-nickel-gallium alloys; crystal structure; hydrogen sorption

1. Introduction

Since hydrogen was assigned as a promising fuel source for the future, considerable interest has been raised for both fundamental and practical research of intermetallic compounds. This is because many intermetallic compounds absorb large amounts of hydrogen and are therefore considered as potential materials for hydrogen storage purposes.

Among different intermetallic compounds, those of the general composition AB_5 play an important role and therefore have been extensively investigated. Primarily, this is due to the ability that $LaNi_5$ absorbs large amounts of hydrogen (up to 6.7 hydrogen atoms per formula unit), and exhibits at moderate pressures and at room temperature a wide equilibrium plateau[1]. At present some of the LaNi5-based compounds are commercially traded as hydride-forming alloys with a wide variety of applications including fuel cells and negative electrode materials for rechargeable nickel-metal hydride (Ni/MH) batteries.

The effect of replacement of either components in selected RET_5 compounds (RE = rare earth metal, T = transition 3d metal) has frequently shown that the substituent strongly affects the crystal structure of the prototype compound and the thermodynamic characteristics of the corresponding RET_5– hydrogen system. Some typical examples can be found for the alloys of the composition $RENi_{5-x}Al_x$[2–4], where the stability of a particular crystal structure type is composition dependent, while the equilibrium pressure, as well as the hydrogen capacity of the $RENi_{5-x}Al_x$ – hydrogen system, is generally drastically reduced with the increased aluminium content. Some other examples of influence of substitution on the structural, hydrogen sorption and magnetic properties of AB_5 compounds can be found in the systems

$RECo_{5-x}Ga_x$[5], $CeNi_{5-x}Ga_x$[6,7], $CeNi_{5-x}Cu_x$[8], $LaNi_{5-x}Sn_x$[9], $MmNi_{5-x}Sn_x$ (Mm = mishmetal)[10] $DyNi_{5-x}Al_x$[11] and $DyNi_{5-x}Ga_x$[12].

The results on the crystal structure and hydrogen sorption properties of the $YNi_{5-x}Ga_x$ alloys reported here represent the continuation of our systematic studies on structural and hydrogen sorption properties of selected $RENi_5$ compounds where nickel has partially been replaced by other metals or metalloids. To the best of our knowledge a systematic study of the $YNi_{5-x}Ga_x$ –hydrogen system has not been performed so far. The only published data for this system report on the $CaCu_5$ type of structure for YNi_5[13] and for YNi_4Ga[14], and on hydrogen sorption properties for YNi_4Ga[14]. There are also some data on absorption of about 4 H atoms per YNi_5 formula unit at pressures above 30 MPa[1,15,16] as well as on absorption of 4.4 H atoms at 1.2MPa[17].

2. Experimental

The starting materials used in this investigation were supplied by Johnson Matthey, UK (yttrium and nickel of 3N purity; gallium 5N purity) and Messer Croatia Gas, Croatia (hydrogen of 99.999% purity). Sample alloys of the weight of about 2.0 g were prepared by argon arc melting. To ensure homogeneity the alloys were turned upside down and remelted several times. The weight loss of the material was checked and was found to be negligible. Therefore it is assumed that the starting composition of the alloys is preserved. Good single phase alloys were obtained after annealing in vacuum at 1123 K for 7 days.

The X-ray powder diffraction patterns were obtained on a Philips PW 1880 diffractometer using monochromated Cu K_α radiation. The line positions were corrected using silicon powder (5N purity, Johnson Matthey, UK) as an internal standard. The intensities were calculated with the "Lazy Pulverix" program[18].

The pressure-composition isotherm (PCI) desorption measurements were carried out in a stainless-steel apparatus of a Sieverts type in a temperature range from 253 K to 400 K and with hydrogen gas at pressures up to 3.5 MPa. The apparatus has been described in details elsewhere[19]. Prior to PCI measurements the alloys were activated by heating under hydrogen (700 K, 5 MPa). It was assumed that the activation process has been completed when the repeated amount of released hydrogen remained constant. Desorption measurements were made on alloys completely saturated with hydrogen by releasing small amounts of the gas. The equilibrium pressure was measured after 15 min, assuming that then the equilibrium was reached. The hydride composition was calculated from the pressure-volume-temperature data, and the thermodynamic data of the alloy-hydrogen system were extracted from the PCI data applying the Van't Hoff equation.

3. Results and Discussion

3. 1. Structure

Alloys of the composition $YNi_{5-x}Ga_x$ (x = 0.5, 0.75, 1.25, 1.5, 2, 2.5 and 3) were prepared and their phase equilibrium was studied. The corresponding data for the alloys with x = 0 and x = 1 which have been published elsewhere[14] are here also included for comparison. The X-ray powder diffraction data revealed that all these single phase materials are of the hexagonal symmetry but adopt different structure types. All alloys with x <2 are of the $CaCu_5$ type (space group P6/mmm), but the alloys with x ≥ 2 crystallize with a larger unit cell of the YCo_3Ga_2 type (space group P6/mmm) [20]. This is true for both as-cast and annealed alloys. These two structure types are closely related (Table 1). Briefly, in the $CaCu_5$ type there exist two layers of atoms. The basal layer at z = 0 contains nickel atoms (2*c* sites) and rare earth atoms (1*a* sites), while the equatorial layer at z = 1/2 contains nickel atoms only (3*g* sites). The YCo_3Ga_2 type can be regarded as being derived from the $CaCu_5$ type by shifting one third of the rare earth

Table 1. Atomic coordinates for various $YNi_{5-x}Ga_x$ alloys

Atom	Position	Coordinates			Occupation
		x	y	z	
YNi_5					
(Space group P6/mmm,$CaCu_5$ type)					
Y	1(a)	0	0	0	1
Ni	2(c)	1/3	2/3	0	1
Ni	3(g)	1/2	0	1/2	1
YNi_3Ga_2					
(Space group P6/mmm, YCo_3Ga_2 type)					
Y	1(b)	0	0	1/2	1
Y	2(c)	1/3	2/3	0	1
Ni	6(m)	0.175	0.35	1/2	0.33
Ni	3(g)	1/2	0	1/2	0.33
Ga	6(m)	0.175	0.35	1/2	0.67
Ga	3(g)	1/2	0	1/2	0.67
Ni	6(j)	0.31	0	0	1
$YNi_{2.5}Ga_{2.5}$					
(Space group P6/mmm, YCo_3Ga_2 type)					
Y	1(b)	0	0	1/2	1
Y	2(c)	1/3	2/3	0	1
Ni	6(m)	0.183	0.366	1/2	0.25
Ni	3(g)	1/2	0	1/2	1
Ga	6(m)	0.183	0.366	1/2	0.75
Ni	6(j)	0.33	0	0	0.5
Ga	6(j)	0.33	0	0	0.5
YNi_2Ga_3					
(space group P6/mmm, YCo_3Ga_2 type)					
Y	1(b)	0	0	1/2	1
Y	2(c)	1/3	2/3	0	1
Ga	6(m)	0.184	0.368	1/2	1
Ga	3(g)	1/2	0	1/2	1
Ni	6(j)	0.31	0	0	

Table 2. Unit cell parameters and cell volumes for the $YNi_{5-x}Al_x$ alloys

Composition	*a* (±0.002 Å)	*c* (±0.001 Å)	c/a	*V* (±0.004 Å^3)	Literature
YNi_5	4.892	3.975	0.813	82.38	[14]
YNi_5	4.891	3.961	0.810	82.06	[13]
$YNi_{4.5}Ga_{0.5}$	4.907	4.012	0.818	83.66	
$YNi_{4.25}Ga_{0.75}$	4.914	4.036	0.821	84.40	
YNi_4Ga	4.924	4.039	0.820	84.90	[14]
$YNi_{3.75}Ga_{1.25}$	4.935	4.044	0.819	85.29	
$YNi_{3.5}Ga_{1.5}$	4.984	4.046	0.812	87.04	
YNi_3Ga_2	8.680	4.130	0.475	269.47	
$YNi_{2.5}Ga_{2.5}$	8.845	4.076	0.461	276.15	
Ni_2Ga_3	8.778	4.143	0.472	276.45	

atoms from the basal plane along the z-axis into the equatorial plane (1*b* sites), whereby the parameter *a* is increased by a factor of √3, while the parameter *c* is increased up to 2.5%. The mutual structure relationship of these crystal structures has been discussed in details elsewhere[3, 20–22]. The unit cell parameters and cell volumes for all alloys are given in Table 2. It can be seen that they increase with the increasing content of gallium. This should be ascribed to the larger atomic radius of Ga (1.41 Å) compared to that of Ni (1.24 Å).

A detailed intensity analysis was carried out. For the alloys of the CaCu5 type of structure it was determined that gallium atoms replace nickel atoms within both available nickel sites (3*g* and 2*c* sites; Table 1).

For the alloys with the larger unit cell of the YCo_3Ga_2 type substitution of gallium for nickel atoms (Table 1) takes place either preferentially within the equatorial layer (YNi_3Ga_2, YNi_2Ga_3) or within 6*m* and 6*j* nickel sites at both layers ($YNi_{2.5}Ga_{2.5}$). The atomic arrangement of gallium (nickel) atoms over these two layers can probably explain the rather odd values of cell parameters at the composition $YNi_{2.5}Ga_{2.5}$. Namely, partial moving of larger gallium (compared to nickel) atoms from the equatorial into the basal plane at this particular composition is related with an increase of parameter *a* and a decrease of parameter *c*. At higher gallium content (composition YNi_2Ga_3) the removing of gallium atoms into the equatorial layer only, reflects again in decrease (increase) of parameters *a* (*c*), respectively.

3. 2. Hydride Properties

In order to determine the thermodynamic properties of the $YNi_{5-x}Ga_x$ – hydrogen systems single phase alloys were crushed and pulverized into powder which was then exposed to hydrogen gas at different pressures and temperatures.

Ternary alloys with the $CaCu_5$ structure and with $0.5 \le x < 2$ were easily activated. However, up to 700 K and up to 5 MPa of hydrogen binary YNi_5 and ternary alloys with $2 \le x \le 3$ are inert to hydrogen. Fig. 1 illustrates the results of the desorption PCI measurements. The results for YNi4Ga which have been published elsewhere[14] are also here included for comparison reasons. The maximum hydrogen capacity for the alloys which absorb hydrogen was extracted from the PCI data and it was found that they absorb up to 3.9 hydrogen atoms per alloy formula unit ($YNi_{4.5}Ga_{0.5}$ at 253 K).

The change of entropy, *ΔS*, and the change of enthalpy, *ΔH*, have been calculated for the metal-hydrogen systems at the ratio of 2 hydrogen atoms per alloy formula unit. A least-square fit of the Van't Hoff equation $\ln p_{eq} = \Delta H/RT - \Delta S/R$, where p_{eq} is the plateau pressure, *R* the universal gas constant equal to 8.314 J/K mol, and *T* the temperature, was applied. The change of the Gibbs free energy of formation at room temperature (*ΔG*) was calculated according to $\Delta G = \Delta H - T\Delta S$. The corresponding values for the change of entropy, the change of enthalpy and the change of the Gibbs free energy of formation are summarized in Table 3.

Table 3. The thermodynamic parameters *ΔH*, *ΔS* and *ΔG* for the $YNi_{5-x}Ga_x$ – hydrogen system at 2 H atoms / alloy formula unit

Composition	*ΔH* (kJ/mol H_2)	*ΔS* (J/mol H_2)	*ΔG* (kJ/mol H_2) (at 293 K)
$YNi_{4.5}Ga_{0.5}$	23.98	−109.73	+8.171
$YNi_{4.25}Ga_{0.75}$	−29.46	−122.20	+6.339
YNi_4Ga	−30.76	−113.90	+2.613
$YNi_{3.75}Ga_{1.25}$	−30.19	−100.59	−0.723
$YNi_{3.5}Ga_{1.5}$	−26.35	−86.46	−1.021

A brief analysis of the relevant data permits us to extract the following features of the $YNi_{5-x}Ga_x$ – hydrogen system. The alloys of the $CaCu_5$ structure within the $YNi_{4.5}Ga_{0.5}$ and $YNi_{3.5}Ga_{1.5}$ composition region react easily with hydrogen. With the increasing gallium content the hydrogen equilibrium pressure decreases as does the hydrogen capacity. The change of the Gibbs free energy of formation (Table 3) decreases as the gallium content in the alloys increases. This indicates that the relative stability of the alloy-hydrogen systems increases with the increasing content of gallium since it is known that the reaction is

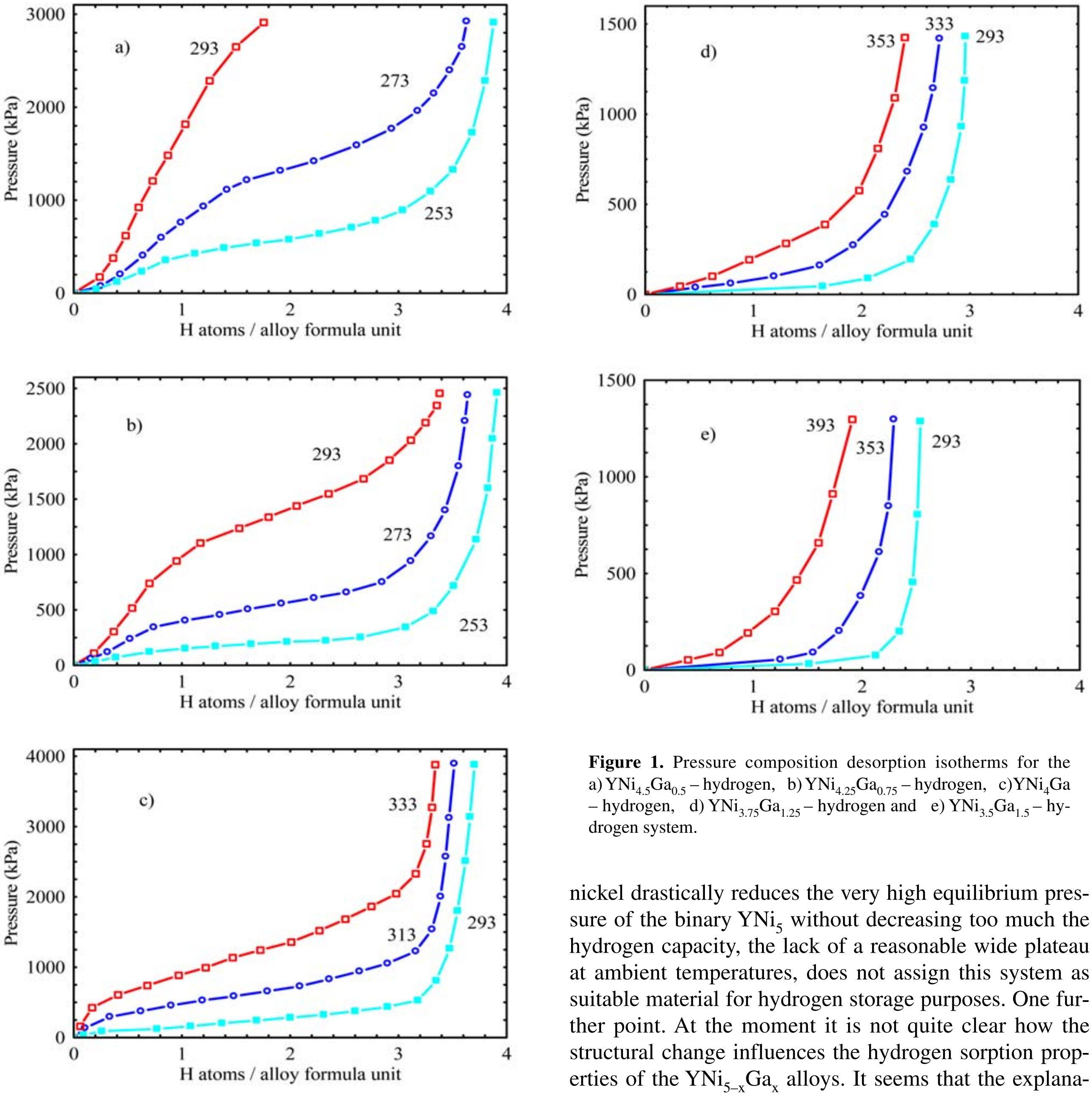

Figure 1. Pressure composition desorption isotherms for the a) $YNi_{4.5}Ga_{0.5}$ – hydrogen, b) $YNi_{4.25}Ga_{0.75}$ – hydrogen, c) YNi_4Ga – hydrogen, d) $YNi_{3.75}Ga_{1.25}$ – hydrogen and e) $YNi_{3.5}Ga_{1.5}$ – hydrogen system.

spontaneous in the direction of decreasing free energy. The above is in good agreement with the observed trend of the equilibrium pressure (Fig. 1), which also can be regarded as the measure of the stability of the corresponding alloy-hydrogen system.

Binary YNi_5 and ternary alloys with 2≤ x ≤ 3, i.e., those with the larger unit cell of the YCo_3Ga_2 type, are inert to hydrogen up to 700 K and 5 MPa. Since binary YNi_5 does not absorb hydrogen under the above mentioned condition, but ternary alloys with small amounts of gallium do, it can be assumed that YNi_5 absorbs hydrogen at very high pressures, i.e., that the data from refs.[1, 15, 16] are the accurate ones. However, although gallium substitution for nickel drastically reduces the very high equilibrium pressure of the binary YNi_5 without decreasing too much the hydrogen capacity, the lack of a reasonable wide plateau at ambient temperatures, does not assign this system as suitable material for hydrogen storage purposes. One further point. At the moment it is not quite clear how the structural change influences the hydrogen sorption properties of the $YNi_{5-x}Ga_x$ alloys. It seems that the explanation should be in tetrahedra which are built up of different kind of atoms in the larger unit cell than those in the smaller cell and are more distorted in the former case. However, for an even general conclusion much more relevant studies must be performed.

4. Conclusion

The structural study of the $YNi_{5-x}Ga_x$ alloys revealed their single phase nature up to the composition YNi_2Ga_3. All single phase alloys are of the hexagonal symmetry, but depending on the gallium content they crystallize with the $CaCu_5$ or the YCo_3Ga_2 type of structure. Both structures are closely related, whereby the smaller cell of the $CaCu_5$ type is stabilized at lower gallium contents, while the larger cell of the YCo_3Ga_2 is stable at higher gallium contents. Only alloys of the $CaCu_5$ type of structure and within the composition range $YNi_{4.5}Ga_{0.5}$ and $YNi_{3.5}$ $Ga_{1.5}$ react readily and reversibly with hydrogen. The hydrogen capacity and the equilibrium pressure decreases with the increased content of gallium. This behavior is consistent with other related $RENi_{5-x}Ga_x$ systems.

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6. References

1. J. H. N. van Voucht, F. A. Kuijpers and H. C. A. M. Bruning, *Philips Res. Rep.* **1970**, 25, 133–139.
2. M. H. Mendelsohn, D. M. Gruen and A. E. Dwight, Nature **1977**, *269,* 45–47.
3. T. Takeshita, S. K. Malik and W. E. Wallace, *J. Solid State Chem.* **1978**, *23*, 271–274.
4. B. Šorgić, A. Drašner and Ž. Blažina, *J. Alloys Comp.* **1996**, *232*, 79–83.
5. Ch. Routsi, J. Alloys Comp. **1998**, 27, 275–277.
6. J. Tang, L. Li, C. J. O'Connor and Y. S. Lee, *J. Alloys Comp.* **1994**, *207/208*, 241–244.
7. H. Flandorfer, P. Rogl, K. Hiebl, E. Bauer, A. Lindbaum, E. Gratz, C. Godart, D. Gignoux and D. Schmitt, *Phys. Rev. B* **1994**, *50,* 15527–15541.
8. A. T. Pedziwiatr, F. Pourarian and W. E. Wallace, *J. Appl. Phys*. **1984**, *55*, 1987–1989.
9. J. M. Hughes, J. S. Cantrell and R. C. Bowman, Jr, Int. *J. Hydrogen Energy* **1997**, *22,* 347–349.
10. V. Iosub, M. Latroche, J. M. Joubert, A. Percheron-Guegan, Int. *J. Hydrogen Energy* **2006**, *31,* 101–108.
11. G. I.Miletic, Ž. Blažina, *J. Magn. Magn. Mater.* ***2004**, 268, 205–211.*
12. *G. I. Miletić, A. Drašner and Ž. Blažina, J. Alloys* Comp. **2000**, *296,* 170–174.
13. A. E. Dwight, *Trans Am. Soc. Metals* **1961**, *53,* 479–500.
14. Ž. Blažina, B. Šorgić and A. Drašner, *J. Mater. Sci. Lett.* **1998**, *17*, 1585–1587.
15. T. Takeshita, K. A. Gschneidner, Jr., D. K.Thome and O. D. McMasters, *Phys. Rev.B, 21* (1980) 5636–5641
16. T. Takeshita, K. A. Gschneidner, Jr., J. F. Lakner, *J. Less-Common Met.* **1981**, *78*, 43–47.
17. R. H. van Essen and K. H. J. Buschow, *J. Less-Common Met., 70* (1980) 189–198
18. K. Yvon, W. Jeitschko and E. Parthé, *J. Appl. Crystallogr.* **1977**, *10*, 73–74.
19. A. Drašner and Ž. Blažina, J. Less-Common Met. **1990**, *163*, 151–157.
20. M. A. Fremy, D. Gignoux, J. M. Moreau, D. Paccard and I. Paccard, *J. Less-Common Met.* **1985**, *106,* 251–255.
21. Ch. D. Routsi, Y. K. Yakinthos and E. Ressouche, *J. Alloys Comp*. **1997**, *256*, 61–64.
22. P. Schobinger-Papamantellos, D. P. Middleton and K. H. J. Buschow, *J. Alloys Comp.* **1994**, *206,* 189–193.

Povzetek

Pripravili smo zlitine s splošno sestavo $YNi_{5-x}Ga_x$ in jih preiskali s praškovno rentgensko difrakcijo. Ugotovili smo, da v sistemu $YNi_{5-x}Ga_x$ obstoja le ena faza do sestave YNi_2Ga_3. Heksagonalna struktura prototipne spojine YNi_5 ($CaCu_5$ tip, prostorska skupina P6/mmm) se ohrani v vseh zlitinah za x < 2. Znotraj področja sestave YNi_3Ga_2 – YNi_2Ga_3 kristalizirajo obstoječe enofazne zlitine s heksagonalno simetrijo in z isto prostorsko skupino P6/mmm vendar z večjo osnovno celico tipa YCo_3Ga_2. Binarne YNi_5 in ternarne zlitine strukturnega tipa YCo_3Ga_2 ne absorbirajo znatnih množin vodika do 5 MPa. Vse ternarne zlitine strukturnega tipa $CaCu_5$ pa z vodikom reagirajo. Določili smo desorpcijske izoterme vodika v odvisnosti od sestave zlitine in tlaka vodika in ugotovili, da se ravnotežni tlak in absorpcijska kapaciteta znižujeta pri povečani vsebnosti galija. Iz desorpcijskih izoterm smo določili tudi spremembe entropije in entalpije ter spremembe Gibbsove proste energije nastanka sistema zlitina-vodik. Termodinamski parametri so potrdili, da se stabilnost hidrida povečuje z višjo vsebnostjo galija.