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The $RENi_4Ga$ (RE = Dy, Ho, Er) Intermetallic Compounds – Crystal Structure and Hydride Properties*

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New ternary rare earth based intermetallic compounds of the composition $RENi_4Ga$ (RE = Dy, Ho, Er) were prepared and studied using X-ray powder diffraction. All compounds were found to be hexagonal and to crystallize in the space group *P*6/*mmm* with the $CaCu_5$ type of structure, *i.e.*, the same symmetry as their prototype binaries $RENi_5$. The interaction with hydrogen was also studied. It was found that all intermetallics react readily and reversibly with hydrogen to form hydrides with hydrogen contents of up to 3.48 hydrogen atoms per alloy formula unit at room temperature. The entropy, the enthalpy and the Gibbs free energy of formation have been extracted from the equilibrium plateau in the pressure composition desorption isotherms. The thermodynamic parameters and the hydrogen capacity of the $RENi_4Ga$–hydrogen systems are compared with the corresponding values for their aluminium analogues and briefly discussed.

Key words: rare earth intermetallics, hydrogen sorption, crystal structure, thermodynamic properties.

INTRODUCTION

The rare earth based intermetallic compounds of the composition $RENi_5$ (RE = rare earth including misch metal) have attracted a great deal of at-

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* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

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tention as possible hydrogen storage materials. This is because many of them react reversibly and absorb large quantities of hydrogen at modest pressure and moderate temperature. For example, the superior representative of the class, $LaNi_5$, forms $LaNi_5H_{6.7}$ at room temperature and under 200 kPa of hydrogen.[1] Substitution of nickel in $RENi_5$ by other metals or metalloids frequently influences the crystal structure of the prototype $RENi_5$ and the thermodynamic properties of the corresponding $RENi_5$–hydrogen system. Some examples are the systems $LaNi_{5-x}Al_x$–hydrogen,[2] $LaNi_{5-x}Sn_x$–hydrogen,[3,4] $CeNi_{5-x}Al_x$–hydrogen,[5] $TbNi_{5-x}Al_x$–hydrogen,[6] $HoNi_{5-x}Al_x$–hydrogen[7] and $NdNi_{5-x}Al_x$–hydrogen.[8]

However, aluminium seems to be the best material for tailoring a metal–hydrogen system for a particular application.[9,10] Accordingly, it was possible to prepare some $LaNi_5$ based compounds that are today commercially used as hydrogen storage materials and as negative electrode in environment friendly rechargeable nickel–metal hydride (Ni/MH) batteries.

Since gallium substituted $RENi_5$ alloys have not been studies so far and gallium and aluminium have similar atomic sizes and configuration of valence electrons, we were interested in performing structural and thermodynamic studies of gallium substituted $RENi_5$ alloys and their hydrides, some results of which have been published elsewhere.[11,12] The results reported here represent the continuation of our systematic study on the structural and hydrogen sorption properties of selected $RENi_5$ compounds where nickel is partially replaced by other metals. The aim is to select potential material for hydrogen storage purposes.

EXPERIMENTAL

The starting materials used in this investigation were supplied by Johnson Matthey, UK (rare earth with purity of 99.9%; gallium with purity of 99.99%) and Carlo Erba, Italy (nickel, 99.5%; main impurity iron). The alloys of the general composition $RENi_4Ga$ (RE = Dy, Ho, Er) were prepared by arc melting under an argon atmosphere. 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 at 1173 K for at least 75 hours.

The X-ray powder diffraction patterns were obtained with a Philips PW 1050 diffractometer equipped with a graphite monochromator and nickel-filtered Cu-Kα radiation. The intensities were calculated using the »Lazy-Pulverix« program.[13]

All alloys were exposed to hydrogen supplied by Jesenice, Slovenia (purity, 99.999%). The pressure composition desorption isotherm (PCDI) 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 15 MPa. Prior to PCDI measurements, the alloys were activated by heating under hydrogen

(700 K, 10 MPa). After cooling, the absorbed hydrogen 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. The PCDI measurements were made on 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 pressure dropped to 10 kPa, when the samples were heated and additional amounts of released hydrogen were measured. The composition was calculated from the pressure–temperature–volume data.

RESULTS AND DISCUSSION

The X-ray powder diffraction data of the $RENi_4Ga$ (RE = Dy, Ho, Er) intermetallic compounds indicated that these single phase materials are of hexagonal symmetry and of the $CaCu_5$ type of structure (space group *P*6/*mmm*). The unit cell parameters for $RENi_4Ga$ are listed in Table I, and the relevant values for the binary $RENi_5$ and the ternary $RENi_4Al$ intermetallic compounds containing the same kind of rare earth metal are also included for comparison.[7,14,15] Figure 1 illustrates the unit cell volume for all three series of compounds. The unit cell parameters of the $RENi_4Ga$ compounds are comparable with those of the aluminium analogues but both series of parameters are expanded in comparison with the corresponding values of the binary compounds. This should be attributed to the size of the

TABLE I

Crystallographic data and hydrogen capacity (n) at room temperature for the $RENi_5$, $RENi_4Ga$ and $RENi_4Al$ (RE = Dy, Ho, Er) compounds

Composition	$\frac{a}{\text{Å}}$	$\frac{c}{\text{Å}}$	$\frac{V}{\text{Å}^3}$	n (H atoms/alloy formula unit)	Ref.
$DyNi_5$	4.869	3.956	81.22	–	14
$DyNi_4Ga$	4.933	4.038	85.10	3.48	
$DyNi_4Al$	4.933	4.037	85.07	3.68	14
$HoNi_5$	4.873	3.963	81.50	–	7
$HoNi_4Ga$	4.931	4.037	85.03	3.19	
$HoNi_4Al$	4.935	4.044	85.29	3.75	7
$ErNi_5$	4.866	3.977	81.55	–	15
$ErNi_4Ga$	4.909	4.032	84.17	3.01	
$ErNi_4Al$	4.910	4.034	84.22	2.63	15

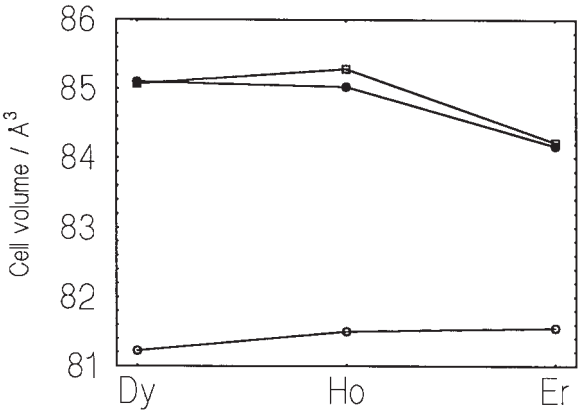

Figure 1. Unit cell volumes for the $RENi_5$ (○), $RENi_4Ga$ (●) and $RENi_4Al$ (□) (RE = Dy, Ho, Er) alloys.

atomic radius of the metals. The atomic radii of gallium (1.41 Å) and aluminium (1.43 Å) are comparable, but larger than the atomic radius of nickel (1.24 Å). One further point. Generally, in none of the three series of compounds the unit cell parameters follow the lanthanide contraction, *i.e.*, a decrease in unit cell parameters with the increasing atomic number of the rare earth metal. In contrast, an increase of cell parameters for binary alloys and a nonlinear decrease of cell parameters for ternary alloys have been observed, whereby $HoNi_4Ga$ exhibits a maximum in the gallium series.

A detailed X-ray intensity analysis was carried out and the atomic coordinates for the $RENi_4Ga$ compounds were determined. Two crystallographically inequivalent nickel sites: exist in the $CaCu_5$ type of structure 2(c) in the basal layer at $z = 0$ (atomic coordinates 1/3, 2/3, 0) of mixed atoms (Ni + RE) and 3(g) in the equatorial layer at $z = 1/2$ (atomic coordinates 1/2, 0, 1/2) containing nickel atoms only. The rare earth atoms occupy the 1(a) sites in the basal layer (atomic coordinates 0, 0, 0). It was found that the replacement of gallium atoms for nickel atoms takes place statistically and preferentially within the equatorial layer only. The unit cell expansion, larger along the *c*-axis than along the *a*-axis, also indicates the substitution of smaller nickel atoms by larger gallium atoms preferentially within the equatorial layer.

In order to determine the thermodynamic characteristics of the $RENi_4Ga$–hydrogen systems, the alloys were exposed to hydrogen gas at different pressures and temperatures. All alloys were easily activated, and were found to absorb large quantities of hydrogen. Hydrogen capacities at room temperature are given in Table I. It should be noted that the corre-

sponding binary compounds $RENi_5$ do not show any significant hydrogen absorption under the experimental conditions applied during the course of our studies (below 700 K; less than 15 MPa).[7,14,15]

Figures 2–4 illustrate the results of the PCDI measurements. The thermodynamic parameters, the entropy and the enthalpy were determined from the equilibrium pressures, at a ratio of 2 hydrogen atoms per alloy for-

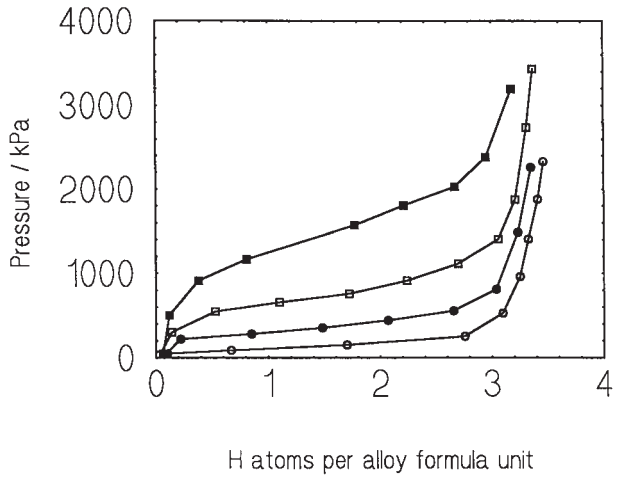

Figure 2. PCDI for the $DyNi_4Ga$–hydrogen system. (○) 255 K, (●) 273 K, (□) 293 K, (■) 313 K.

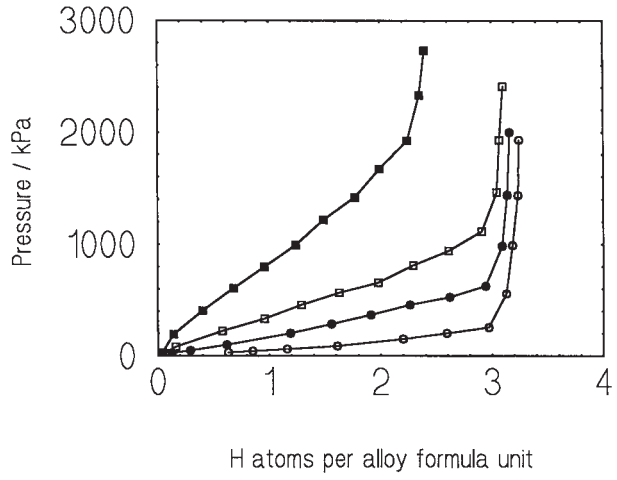

Figure 3. PCDI for the $HoNi_4Ga$–hydrogen system. (○) 255 K, (●) 273 K, (□) 293 K, (■) 313 K.

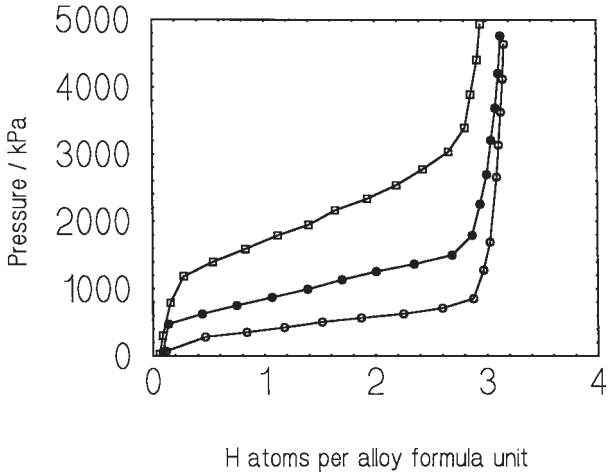

Figure 4. PCDI for the $ErNi_4Ga$–hydrogen system. (○) 255 K, (●) 273 K, (□) 293 K.

mula unit (Table II). The corresponding values were calculated using the least-square fit of the van't Hoff equation $\ln p_{eq} = \Delta H/RT - \Delta S/R$, 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 II. The set of relevant values for the $RENi_4Al$–hydrogen systems is also included in Table I and Table II for comparison.

TABLE II

Thermodynamic parameters and equilibrium pressures for the $RENi_4Ga$–hydrogen and the $RENi_4Al$–hydrogen (RE = Dy, Ho, Er) systems at the ratio of 2 hydrogen atoms per alloy formula unit

System	ΔH kJ (mol H_2)$^{-1}$	ΔS kJ (mol H_2)$^{-1}$ K^{-1}	ΔG kJ (mol H_2)$^{-1}$ at 293 K	P_{eq} kPa at 293 K	Ref.
$DyNi_4Ga$–H_2	–25.64	–105.59	+5.30	847	
$HoNi_4Ga$–H_2	–27.90	–111.41	+4.74	674	
$ErNi_4Ga$–H_2	–23.05	–104.76	+7.64	2390	
$DyNi_4Al$–H_2	–35.38	–116.40	–1.27	58	14
$HoNi_4Al$–H_2	–34.30	–114.73	–0.68	92	7
$ErNi_4Al$–H_2	–32.38	–122.22	+3.43	467	15

The investigated $RENi_4Ga$–hydrogen systems exhibit the following features. Ternary $RENi_4Ga$ compounds react easily with hydrogen to form unstable hydrides at room temperature (p_{eq} > 101.3 kPa). This should be ascribed to the replacement of one nickel atom in $RENi_5$ by gallium, since binary $RENi_5$ compounds are inert to hydrogen up to 700 K and 15 MPa.

The hydrogen capacity of $RENi_4Ga$ decreases (Table I) with the increasing atomic number of the rare earth metal. A maximum hydrogen capacity of 3.48 hydrogen atoms per alloy formula unit at room temperature was observed for $DyNi_4Ga$. The entropy, the enthalpy and the Gibbs free energy of formation increase (with a discrepancy observed for the holmium containing alloy), as does the hydrogen desorption equilibrium pressure, with the increasing atomic number of the rare earth metal.

The results obtained for the $RENi_4Ga$–hydrogen systems were compared with those for the $RENi_4Al$–hydrogen systems (Tables I and II). One can see that the systems with aluminium form more stable hydrides (lower values of ΔH, ΔS, ΔG and desorption equilibrium pressures) but exhibit higher hydrogen capacities than the corresponding systems with gallium. Furthermore, the thermodynamic parameters of gallium and aluminium containing systems generally follow different patterns.

However, to extract a more general conclusion about the thermodynamic behaviour during hydrogenation of these classes of intermetallic compounds, much more relevant data on similar systems should be gathered.

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SAŽETAK

Intermetalni spojevi $RENi_4Ga$ (RE = Dy, Ho, Er) – kristalna struktura i svojstva hidrida

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Priređeni su novi trokomponentni intermetalni spojevi sastava $RENi_4Ga$ (RE = Dy, Ho, Er) i istraženi metodom rentgenske difrakcije na prahu. Nađeno je da su svi spojevi heksagonski i da kristaliziraju u prostornoj skupini *P*6/*mmm* s tipom strukture $CaCu_5$, tj. istom simetrijom kao i njihovi prototipni dvokomponentni spojevi $RENi_5$. Istraživana je i interakcija s vodikom. Nađeno je da svi intermetalici reagiraju lagano i reverzibilno s vodikom i stvaraju hidride koji sadrže do 3,48 vodikovih atoma po formulskoj jedinki slitine na sobnoj temperaturi. Entropija, entalpija i Gibbsova energija stvaranja dobivene su iz vrijednosti ravnotežnih platoa u desorpcijskim izotermama tlak–sastav. Termodinamički parametri i kapacitet vodika u sustavima $RENi_4Ga$–vodik uspoređeni su s odgovarajućim vrijednostima dobivenim za analogne sustave s aluminijem i ukratko prodiskutirani.