

Hydrogenation and crystal structures of the $\text{Nd}(\text{Ni}_{1-x}\text{Cu}_x)(\text{In}_{1-y}\text{Al}_y)$ intermetallics and their hydrides

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Abstract

The crystal structure of $\text{NdNiInD}_{1.2}$ contains D–D pairs with the shortest known D···D separation of 1.56 Å. This work was aimed on studies of the factors influencing the formation and the length of such a pair. We have studied the NdNiIn-based alloys, in which Ni or In are partially substituted by the chemically related elements, Cu or Al, respectively. Three equiatomic intermetallics, NdNiIn, NdCuIn and NdNiAl, are isostructural and crystallise with the ZrNiAl type of structure. In the $\text{NdNi}_{1-x}\text{Cu}_x\text{In}$ ($x = 0; 0.02; 0.05; 0.25; 0.50; 0.75$ and 1.00) quaternary system a complete solid solubility range has been found. In contrast, in the Al-containing $\text{NdNiIn}_{1-x}\text{Al}_x$ alloys the range of a solid solution is limited to the region $\text{NdNiIn}–\text{NdNiIn}_{0.75}\text{Al}_{0.25}$. The substitutions result in regular changes in V , a , c and c/a of the hexagonal unit cells. Small substitutions by Cu and Al ($x, y \leq 0.05$) do not lead to significant changes in H content and types of the crystal structures formed (PND data). However, a decrease in the stability of the hydrides is observed. In $\text{NdNi}_{1-x}\text{Cu}_x\text{In}$, Cu has a strong preference for the occupation of the $1b$ CuIn_6 trigonal prisms. An increase of the Cu content is accompanied by a decrease of the $\text{D}/\text{Nd}(\text{Ni}_{1-x}\text{Cu}_x)\text{In}$ ratio and a distinct growth of the distance between Ni(Cu) and D (from 1.51 to 1.84 Å). H···H pairing is very sensitive to the content of both Al and Cu. When the level of substitution exceeds $\text{Cu}/\text{Ni}(\text{Al}/\text{In}) > 1/9$, H pairing becomes unstable and H atoms favour other types of ordering in the metal sublattice.

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1. Introduction

The $\text{RNiInD}_{1.2-1.6}$ ($R = \text{La}, \text{Ce}, \text{Nd}$) hydrides formed on the basis of intermetallics crystallising with the ZrNiAl structure type are characterised by a double occupancy by D atoms of the trigonal bipyramids $R_3\text{Ni}_2$. This results in a formation of D···D pairs with uniquely short interatomic distances of 1.56 Å (Nd), 1.61 Å (Ce) and 1.64 Å (La) [1]. Such a feature strongly differentiates the In-containing hydrides from those formed by isostructural Al-containing intermetallics where D

atoms are located in the centres of trigonal bipyramids (e.g. in $\text{TbNiAlD}_{1.1}$ [2]). In the structure of $\text{LaNiInD}_{1.63}$ studied in situ under applied pressure of deuterium gas the other, weakly bound D atoms have been found filling distorted octahedra La_3NiIn_2 [3].

In order to better understand the mechanism of the formation of the $\text{RNiInD}_{1.6-x}$ deuterides, further studies of their structural behaviours as related to the hydrogen absorption–desorption properties, are important. An influence of substitution of the constituent elements, Nd, Ni and In, by chemically related elements is an interesting possibility. In this work we present results of the studies of the influence of substitutions by Cu and Al on the structural

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and hydrogenation characteristics. Two groups of the alloys having stoichiometric compositions $\text{Nd}(\text{Ni}_{1-x}\text{Cu}_x)\text{In}$ and $\text{NdNi}(\text{In}_{1-y}\text{Al}_y)$ were studied.

2. Experimental

The alloys were prepared by arc melting of the mixtures of high purity constituent metals. A slight excess of Nd, 1 at.%, was added to compensate for evaporation during the melting. As-cast alloys were sealed into evacuated quartz tubes and were annealed at 600 °C for 4 weeks in order to improve their homogeneity. After the annealing the alloys were quenched into a mixture of ice and water.

The phase-structural composition of the alloy and their corresponding hydrides was characterised by X-ray powder diffraction (Siemens D5000 diffractometer; Cu $K\alpha_1$ radiation; Bragg–Brentano geometry; position-sensitive detector).

Deuterides were prepared by saturation of the alloys with deuterium gas (99.8% purity) under pressures of 1–5 bar D_2 . Prior to the deuteration the alloys were activated by heating for 1 h at 400 °C in a secondary vacuum ($\sim 10^{-5}$ mbar). Synthesis was normally performed at room temperature. However, materials with higher Cu content close to NdCuIn required much higher deuteration temperatures (annealing in deuterium gas at 400 °C for approximately 2 h followed by cooling in the furnace in D_2 gas to room temperature). Such a process was applied to the alloys with Cu/Ni ratios ≥ 1 . The prepared deuterides were placed into V-cans and sealed under argon gas for the ex situ powder neutron diffraction (PND) experiments.

During the in situ PND studies, the samples were placed into the stainless steel autoclaves (wall thickness 0.25 mm; diameter 6 mm). The alloys were manually ground in the argon filled glove box prior to loading into the autoclave. After that the alloys were activated and charged with deuterium gas at a starting pressure of 10 bar D_2 .

PND data were collected at the R2 reactor at Studsvik Neutron Research Laboratory using SLAD instrument ($\lambda = 1.117$ Å) [4] and the high-resolution diffractometer PND ($\lambda = 1.470$ Å) [5]. The PND instrument uses 35 ^3He counters to measure the intensities in 2θ steps of 0.08° to cover a 2θ range of 4.0 – 137° . The SLAD instrument uses a position-sensitive detector system. The data were fully corrected for multiple scattering and absorption and then normalised to the vanadium standard. During the refinements of the in situ experiments, peaks from the stainless steel tube were excluded from the refinements.

The in situ data were collected at the PND diffractometer at an initial pressure of ~ 10 bar. Then pressure was decreased step-by-step and phase-structural transformations during deuterium desorption were studied. Several sets of data were collected for such samples on the SLAD diffractometer with a high flux neutron beam. When the SLAD measurements revealed modifications of the diffraction pattern, the high quality diffraction data were recollected at PND.

Crystal structure data were derived by Rietveld profile refinements using the GSAS software [6].

Thermal desorption properties were studied by heating the samples at a constant heating rate of 2°min^{-1} . Before the measurements of the low temperature TDS data, a metal jacket pre-cooled to -20 °C was placed on the autoclave.

3. Results and discussion

The compositions of the studied quaternary alloys belong to the quasibinary systems NdNiIn – NdCuIn and NdNiIn – NdNiAl . In case of Ni \rightarrow Cu substitution a continuous solid solution is formed. The ZrNiAl type of structure is preserved for these alloys. In case of In substitution by Al the solubility range is limited to the region NdNiIn – $\text{NdNiIn}_{0.75}\text{Al}_{0.25}$. Regular changes in a , c and V of the hexagonal unit cells take place, dependent on the ratio between Cu and Ni or In and Al.

3.1. $\text{NdNi}_{1-x}\text{Cu}_x\text{In}$ – D_2 system

Eight different $\text{NdNi}_{1-x}\text{Cu}_x\text{In}$ alloys have been studied in this work, with $x = 0, 0.02, 0.05, 0.25, 0.50, 0.75$ and 1.00 . In the ZrNiAl structure type, where both Cu and Ni can occupy the $1b$ and $2c$ sites, these metals complete for the different coordination environment surrounding these two sites. Indeed, $1b$ site is located in the centre of the trigonal prism In_6 while the $2c$ site is co-ordinated by another type of trigonal prism, which is formed by six rare-earth atoms. From the refinements of the PND data it appears that Cu exhibits a strong preference for the occupation of the $1b$ In-formed prisms (Table 1). At the lowest level of Cu substitutions ($\text{Ni}/\text{Cu} \geq 95/5$) it occupies only the $1b$ position. This happens in the structures of β - $\text{NdNi}_{0.98}\text{Cu}_{0.02}\text{InD}_{0.65}$ and γ - $\text{NdNi}_{0.95}\text{Cu}_{0.05}\text{InD}_{1.41}$. An increase of the Cu content is accompanied by a decrease of the $\text{D}/\text{Nd}(\text{Ni}_{1-x}\text{Cu}_x)\text{In}$ ratio and a distinct growth of the distance between Ni(Cu) and D (from 1.51 to 1.84 Å), as derived from the PND data.

In the structures of hydrides with the short $\text{D} \cdots \text{D}$ pairs (D1), formed in the samples with low copper content ($x \leq 0.05$), in addition to the double-occupied Nd_3Ni_2 trigonal bipyramids, the octahedral $\text{Nd}_3\text{Ni}(\text{Cu})_2\text{In}_2$ sites are simultaneously filled by D atoms (D2), leading to the formation of the of the deuteride which is isostructural to the previously studied γ - $\text{LaNiInD}_{1.63}$ [3]. It seems that the filling of

Table 1
Ni/Cu distribution between the $2c$ and $1b$ sites of the $\text{NdNi}_{1-x}\text{Cu}_x\text{In}$ alloys from the PND data

	Ni/Cu ratio	Ni/Cu $2c$	Ni/Cu $1b$
NdNiIn	1/0	1/0	1/0
$\text{NdNi}_{0.75}\text{Cu}_{0.25}\text{In}$	3/1	7/1	1/1
$\text{NdNi}_{0.50}\text{Cu}_{0.50}\text{In}$	1/1	7/4	1/3
NdCuIn	0/1	0/1	0/1

Table 2
Crystallographic characteristics of the NdNi_{1-x}Cu_xIn_{1-y}Al_y-based deuterides

Deuteride	<i>a</i> (Å)	<i>c</i> (Å)	$\Delta a/a$ (%)	$\Delta c/c$ (%)	$\Delta V/V$ (%)	Interatomic distances (Å)		
						Nd–D	Ni–D	D–D
NdNi _{0.98} Cu _{0.02} InD _{1.4}	7.2281(2)	4.5664(3)	–3.8	16.5	7.8			
NdNi _{0.98} Cu _{0.02} InD _{0.65}	7.5961(4)	3.9887(4)	1.1	1.7	4.0	2.32	1.67	
NdNi _{0.95} Cu _{0.05} InD _{1.41}	7.2356(3)	4.5696(3)	–4.2	15.4	5.8	2.34	1.52	1.54
NdNi _{0.95} Cu _{0.05} InD _{0.60}	7.593(7)	4.033(8)	0.8	1.4	3.0	2.25	1.72	
NdNi _{0.75} Cu _{0.25} InD _{0.61}	7.5789(6)	4.0136(4)	0.6	1.9	3.2	2.32	1.67	
NdNi _{0.5} Cu _{0.5} InD _{0.49}	7.569(3)	4.075(2)	0.2	2.9	3.5	2.30	1.84	
NdCuInD _{0.60}	7.440(2)	4.255(1)	–0.3	2.5	1.8	2.28	1.81	
NdNiIn _{0.95} Al _{0.05} D _{1.43} (11 bar)	7.221(1)	4.5789(7)	–3.9	16.6	7.8	2.34	1.52	1.54
NdNiIn _{0.95} Al _{0.05} D _{0.39} (11 bar)	7.620(3)	4.016(2)	1.2	1.3	3.8	2.29	1.69	
NdNiIn _{0.95} Al _{0.05} D _{1.31} (0.12 bar)	7.218(1)	4.5647(8)	–3.9	16.3	7.4	2.35	1.49	1.59
NdNiIn _{0.95} Al _{0.05} D _{0.52} (0.12 bar)	7.600(2)	3.987(1)	1.2	1.6	4.0	2.30	1.71	
NdNiIn _{0.875} Al _{0.125} D _{0.64}	7.6015(5)	3.9600(5)	1.5	1.4	4.5	2.30	1.98	
NdNiIn _{0.75} Al _{0.25} D _{1.2}	7.6144(3)	3.9150(3)	2.5	–0.1	4.5	2.34	1.68	

Interatomic distances (Å) are provided on the basis of the Rietveld refinements of the PND data. D···D distances are given only for the Nd₃[Ni(Cu)1]₂ trigonal bipyramids containing the D···D pairs.

the D2 sites becomes possible only as associated with the formation of short D1···D1 pairs. A possible reason for that is an anisotropic expansion of the unit cell which makes In–D2 distances sufficiently large (In–D2 ≈ 2.28 Å), thus lifting the blocking effect of In on hydrogen insertion into the site. Crystallographic data of the studied deuterides, the volume changes on deuteration, deuterium content in the compounds and the shortest interatomic distances Me–D and D–D derived from the Rietveld refinements of the PND data are shown in Table 2.

After completing the high-resolution neutron powder diffraction study of the γ -NdNi_{0.95}Cu_{0.05}InD_{1.41} deuteride, the autoclave was placed on the SLAD instrument and the deuterium content was reduced in small steps of desorption. Fig. 1 presents the D content in the studied materials versus the applied pressure *P* at 20 °C. The data were collected in situ at different temperatures up to 400 °C. Three stages of the phase-structural transformations have been identified:

- Gradual decrease of D content in the D2 sites.
- Two-phase region where a plateau is observed in the desorption isotherm; decrease in the relative amount of the higher deuteride γ -NdNi(Cu)InD_{1.4-x} and a corresponding increase of the content of the lower deuteride β -NdNi(Cu)InD_{0.67-x}.
- Homogeneity range of the lower β -deuteride; gradual decrease of D content down to 0.33 at.D/f.u. Substantial deuterium evolution from the β -deuteride was observed at relatively high temperature, about 400 °C. The desorption studies indicated a formation of a quite broad homogeneity range of the β -deuteride.

A good agreement between the proposed scheme of phase-structural transformations and the data collected during the Sieverts-type *P*–*C*–*T* measurements of the isotherms of hydrogen desorption [7] is clear.

3.2. NdNiIn_{1-y}Al_y

The hydrogenation behaviour of the Al-containing NdNiIn_{1-y}Al_y alloys is similar to the Cu-substituted ones: short D···D pairs are stable only at a low substitution level ≤5%. Crystallographic data for the NdNiIn_{1-y}Al_y-based deuterides are given in Table 3.

The in situ studies of the NdNiIn_{0.95}Al_{0.05}–D₂ system were performed at D₂ pressures of 11 and 0.12 bar D₂ and revealed the three most important steps of deuterium desorption:

- increase of the relative content of the lower β -deuteride and a corresponding decrease of the content of the higher γ -deuteride in the material (from weight ratio 87:13 to 70:30);

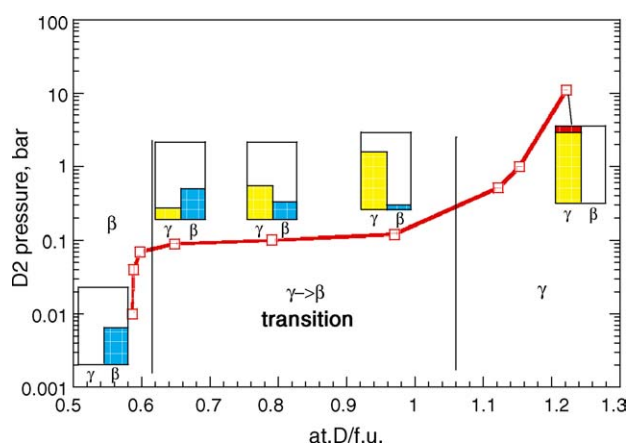


Fig. 1. Deuterium content and ratio between γ - and β -deuterides in the NdNi_{0.95}Cu_{0.05}In–D₂ system derived from the refinements of the powder neutron diffraction data collected at 20 °C at different deuterium pressures. Maximum D content is 1.23 H/f.u. The height of the columns is proportional to the refined D content in the β - and γ -deuterides. The amount of D1 and D2 in the NdNi_{0.95}Cu_{0.05}InD_{1.23} corresponds to the lower and higher segments of the column, respectively.

Table 3
Crystal structure data for the NdNiIn_{1-y}Al_y-based deuterides ($y = 0.05, 0.125, 0.25$)

Experiment	Content of Al (at./f.u.)					
	0.05				0.125	0.25
	In situ (11 bar D ₂)		In situ (0.12 bar D ₂)		Ex situ	Ex situ
	γ	β	γ	β		
D/f.u.	1.43(2)	0.39(4)	1.30(5)	0.52(2)	0.64(3)	1.26(6)
Phase content	86.8(5)	13.2(5)	70.3(8)	29.7(8)	–	–
a (Å)	7.221(1)	7.620(3)	7.218(1)	7.600(2)	7.6015(5)	7.6144(4)
c (Å)	4.5789(7)	4.016(2)	4.5647(8)	3.987(1)	3.9600(5)	3.9150(3)
V (Å ³)	199.4(1)					
x of Nd in 3g	0.6007(9)	0.574(2)	0.603(1)	0.585(2)	0.5915(8)	0.597(1)
x of In(Al) in 3f	0.246(1)	0.270(8)	0.245(2)	0.249(4)	0.250(2)	0.244(2)
z of D1 in 4h	0.326(2)	0.42(–)	0.326(2)	0.43(1)		0.428(1)
n of D1 in 4h	0.89(1)	0.29(3)	0.90(2)	0.39(2)	0.49(1)	
n of D1' in 2d					0.80(1)	
z of D2 in 3g	0.229(7)	–	0.26(1)	–	0.23(1)	
n of D2 in 3g	0.24(2)	–	0.10(2)	–	0.11(2)	
x of D3 in 12l						0.451(1)
y of D3 in 12l						0.246(1)
z of D3 in 12l						0.085(1)
n of D3 in 12l						0.15(1)
R_{wpr}	0.046		0.044		0.050	0.057
R_{pr}	0.036		0.034		0.040	0.044
χ^2	1.57		1.49		2.21	1.98

In the structure of NdNiIn_{1-y}Al_yD_x ($P6\bar{2}m$) atoms occupy the following sites: Nd in 3g ($x0\frac{1}{2}$); Ni1 in 2c ($\frac{1}{3}\frac{2}{3}0$); Ni2 in 1b ($00\frac{1}{2}$); (2.85In + 0.15Al) in 3f ($x00$); D1 in 4h ($\frac{1}{3}\frac{2}{3}z$); D1' in 2d ($\frac{1}{3}\frac{2}{3}\frac{1}{2}$); D2 in 3g; D3 in 12l ($xy z$).

- (b) decrease of the occupation of the D2 octahedral site from 0.24 to 0.10 causing a reduction of the D content in the γ -deuteride from 1.41 to 1.3 at.D/f.u.;
- (c) increase of the D–D separation from 1.54 to 1.59 Å.

Further increase in the amount of Al in the alloy leads to significant changes in structural properties (see Table 3). When the ratio between Al and In increases to 1/7 (NdNiIn_{0.875}Al_{0.125}), in the corresponding deuteride with D content of 0.64 at.D/f.u., deuterium atoms are located in the centres of the trigonal bipyramids Nd₃Ni₁₂ (2d) rather than the constituent Nd₃Ni1 tetrahedra (4h). The second hydrogen site, the Nd₃Ni2(In,Al)₂ octahedron, is also occupied.

Following further increase of the content of Al up to the ratio Al/In = 1/3, the NdNiIn_{0.75}Al_{0.25}D_{1.3} deuteride is formed. In its structure deuterium atoms again occupy the tetrahedra Nd₂Ni1Al (with a maximum, 50%, occupancy) instead of the trigonal bipyramids. However, the second filled by D site changes: the Nd₂Ni1Al tetrahedra are filled instead of the Nd₃Ni₁₂ octahedra. This type of structure is closely related to those observed for the RENiAl-based deuterides (e.g., orthorhombic TbNiAlD_{1.1} [2] and HoNiAlD_{1.2} [8] with ordering of D atoms in the RE₃Ni₂ and RE₂NiAl interstitials).

The study of deuterium desorption from the NdNiIn_{0.95}Al_{0.05}D_{1.41} deuteride showed a clear separation of three desorption events. First peak of deuterium desorption is observed at low temperature (–9 °C) and is attributed to D release from the D2 Nd₃Ni2In₂ site (see Fig. 2). The second peak appears at 90 °C and corresponds to

the decomposition of the deuterium pair inside the trigonal bipyramid Nd₃Ni₁₂. This changes the double D occupancy of the Nd₃Ni₁₂ to the single occupancy of the Nd₃Ni1 tetrahedra. The remaining deuterium is strongly bound to the metal lattice; the vacuum desorption is completed only at 500 °C.

In conclusion, the present study shows a great sensitivity of the H···H pairing in the NdNiIn-based γ -deuteride NdNiInD_{1.4-x} to the content of Al and Cu in the Nd(Ni,Cu)(In,Al) alloys modified by substitution. When the level of substitution is higher than Cu/Ni(Al/In) > 1/9, the pairing becomes unstable and different types of structures of the intermetallic hydrides are formed. The substitutions of

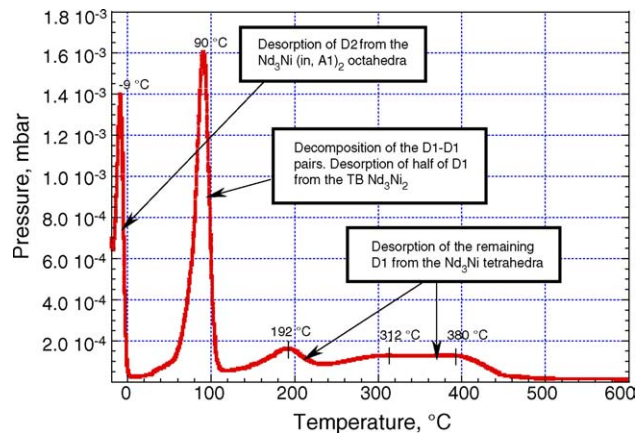


Fig. 2. TDS traces of deuterium desorption from the NdNiIn_{0.95}Al_{0.05}D_{1.41} deuteride.

Nd by heavier rare earth metals will be exercised in order to employ the effect of lanthanide contraction to “compress” the unit cells without significant modifications of the chemistry of the metal–hydrogen interaction, thus creating conditions for further decrease of the length of the H ··· H pair.

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