

Thermodynamic characteristics of the Al- and Cu-doped NdNiIn hydrides

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Abstract

The Pressure–Composition–Temperature (P–C–T) relationships in the NdNiIn-based Cu- and Al-containing Nd(Ni_{1-x}Cu_x)(In_{1-y}Al_y)–H systems were measured volumetrically in the temperature range of 298–348 K. The P–C–T diagrams show clear plateau regions indicating a formation of two hydride phases, β- (~0.6 at. H/f.u.) and γ- (1.3–1.5 at. H/f.u.) hydrides. The β-hydride is rather stable and does not decompose at hydrogen pressures above 10⁻³ MPa within the applied range of temperatures. The substitutions cause significant modifications of the P–C–T diagrams. These changes proceed differently for the Cu- and Al-containing systems. The relative partial molar thermodynamic properties for the studied system are: $\Delta H_{\text{H}} = -19.4 \pm 0.6 \text{ kJ (mol}_{\text{H}})^{-1}$, $\Delta S_{\text{H}} = -56.0 \pm 1.4 \text{ J (K} \cdot \text{mol}_{\text{H}})^{-1}$ for NdNiIn–H; $\Delta H_{\text{H}} = -22.6 \pm 1.6 \text{ kJ (mol}_{\text{H}})^{-1}$, $\Delta S_{\text{H}} = -68.8 \pm 3.6 \text{ J (K} \cdot \text{mol}_{\text{H}})^{-1}$ for NdNi_{0.98}Cu_{0.02}In–H; $\Delta H_{\text{H}} = -23.5 \pm 1.3 \text{ kJ (mol}_{\text{H}})^{-1}$, $\Delta S_{\text{H}} = -72.2 \pm 3.1 \text{ J (K} \cdot \text{mol}_{\text{H}})^{-1}$ for NdNiIn_{0.95}Al_{0.05}–H systems.

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1. Introduction

RENiIn (RE=La, Ce, Nd)-based intermetallic hydrides attract significant interest because of their unusual structural properties: their crystal structures contain H atoms with anomalously short (the shortest known for the metal hydrides) H–H distances close to 1.6 Å [1]. Hydrogen atoms occupy with a double occupancy the trigonal bipyramidal sites RE₃Ni₂ which results in a very high local volume density of hydrogen in the metal matrix.

Formation of very short interatomic H–H distances in the RENiInH_{1.2–1.6} systems have been connected to two complementary factors including (a) shielding effect of the significantly contracted on hydrogenation and partially positively charged RE₃ triangle clusters separating partially negatively

charged H–H pairs [1]; formation of the chains H–Ni–H containing strong covalent like Ni–H bonds [2,3]. In addition, indium seems to play an important indirect role in determining the hydrogenation properties of the RENiIn intermetallics [3,4].

Better understanding of the RENiIn–H systems requires careful study of the thermodynamic properties of hydrogen in these systems. This work was devoted to the studies of hydrogen interaction with the NdNiIn-based compounds. Partial substitution of Ni and In in NdNiIn intermetallic compound by chemically related elements Cu and Al has been tried as the way to modify the structural properties of the initial NdNiIn alloy and its corresponding hydrides [5].

The aim of this work was to study the thermodynamic properties of the compounds were the pairing of hydrogen atoms is observed by means of the measurements of the Pressure–Composition–Temperature isotherms. The effect of Ni/Cu and In/Al substitutions have been studied in detail

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focusing on the differences in the thermodynamic behaviour of the chemically modified materials.

2. Experimental

The alloys NdNiIn, NdNi_{0.98}Cu_{0.02}In and NdNiIn_{0.95}Al_{0.05} were prepared by argon arc melting from the mixtures of high purity constituent elements. The alloy samples were annealed in the evacuated sealed quartz ampoules for 4 weeks at 873 K and subsequently quenched into a mixture of ice and water. Powder X-ray diffraction studies performed with Siemens D5000 diffractometer using Cu K α ₁ radiation showed a formation of the purely single phases with the hexagonal ZrNiAl-type structures. Substitutions caused slight variations of the unit cell parameters, NdNiIn: $a = 7.507(3)$ Å, $c = 3.929(2)$ Å; NdNi_{0.98}Cu_{0.02}In: $a = 7.5118(3)$ Å, $c = 3.9201(2)$ Å and NdNiIn_{0.95}Al_{0.05}: $a = 7.5103(4)$ Å, $c = 3.9258(3)$ Å.

Pressure–Composition–Temperature (P–C–T) relationships were determined by a volumetric Sieverts' method. The measurements were made at temperatures between 298 and 348 K and at hydrogen pressures in the range from 10^{−3} to 2.5 MPa. The details of the measurements have been described elsewhere [6].

3. Results and discussion

3.1. P–C–T relationships

3.1.1. NdNiIn–H₂ system

Desorption isotherms were measured at 298, 323 and 348 K and are shown in Fig. 1. The isotherms contain a clear plateau pressure region covering the range between 0.5–0.6 at. H/f.u. (β -phase) and 1.3–1.5 at. H/f.u. (γ -phase). According to the crystal structure studies, the β -hydride is characterised by a single occupancy of the trigonal bipyramidal site with deuterium atoms filling the tetrahedra Nd₃Ni (50% occupancy in maximum) [1]. For the γ -hydride initially deuterium atoms nearly completely occupy the trigonal bipyramidal sites Nd₃Ni₂ (maximum stoichiometric composition NdNiInH(D)_{1.33}) [1]; overstoichiometric hydrogen is filling the Nd₃NiIn₂ octahedra ($\leq 30\%$ occupancy) proving the hydride NdNiInH_{1.6–1.7} [4].

A significant hysteresis is evident for the studied systems. Thus, firstly the hydrides were synthesised at room temperature; then the samples were equilibrated at a set point temperature and the desorption data were collected; finally the sample was cooled down to room temperature where a consecutive charging of the sample with hydrogen has been done.

The stability of the β -hydride is rather high [1]. This hydride does not decompose at pressures and temperatures applied. Thus, the thermodynamic data of the transition β -hydride to α -phase were not measured.

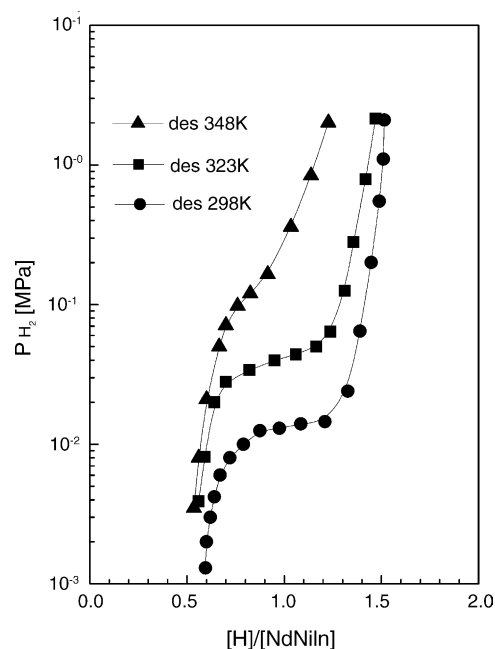


Fig. 1. Hydrogen desorption isotherms for the NdNiIn–H₂ system.

3.1.2. NdNi_{0.98}Cu_{0.02}In–H₂ and NdNiIn_{0.95}Al_{0.05}–H₂ systems

The isotherms for the NdNi_{0.98}Cu_{0.02}In–H₂ and NdNiIn_{0.95}Al_{0.05}–H₂ systems are shown in Figs. 2 and 3, respectively.

Substitution of In by Al significantly modifies the P–C–T diagrams. It leads to noticeable sloping of the plateaux and disappearance of the β – γ transition for the absorption isotherms measured above 323 K within hydrogen pressures applied.

However, this is not the case for the Cu-containing material; its diagrams are very similar to those for the NdNiIn–H₂ system, with no extra inclination of the plateaux observed on doping.

Significant differences in the hysteresis effect during hydrogen absorption and desorption are evident from comparison of the data given in Figs. 2 and 3. This effect, expressed by thermodynamic relation $1/2RT \ln(P^{ab}/P^{des})$, is much stronger [4.1 kJ (mol_H)^{−1}] for the Al-containing hydride compared to the Cu-substituted intermetallic [3.4 kJ (mol_H)^{−1}] at 298 K, where P^{ab} and P^{des} are the plateau pressure for absorption and desorption processes, respectively.

3.2. Thermodynamic properties

Thermodynamic properties were determined by measuring temperature dependence of logarithmic equilibrium pressure versus reciprocal temperature. The calculated values of ΔH_H and ΔS_H in the region of the plateau pressures are summarized in Table 1. For both Al- and Cu- substituted samples the enthalpy values significantly decrease from the values for the NdNiIn–H system, indicating an increase

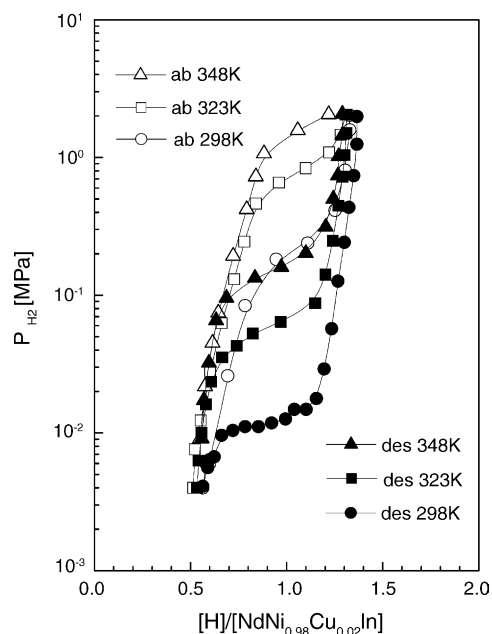


Fig. 2. P–C–T diagram for the NdNi_{0.98}Cu_{0.02}In–H system.

in the stability of the hydrides containing short hydrogen–hydrogen distances. The entropy values in both cases show a profound decrease compared to the NdNiIn–H system. Further systematic studies for the effect of the content and type of the substituting elements on the hydrogenation properties of the intermetallic system are required to understanding better presently reported data and these measurements are in progress for the chemically related compounds.

The relative partial molar enthalpy as a function of H content is shown in Fig. 4. In the plateau regions, with in-

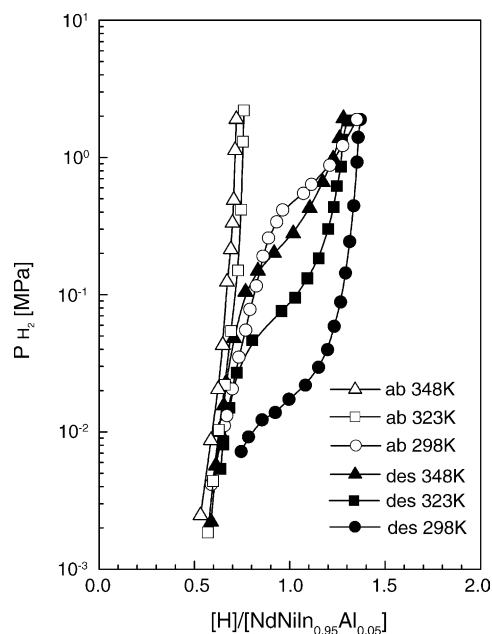


Fig. 3. P–C–T diagram for the NdNiIn_{0.95}Al_{0.05}–H system.

Table 1
Thermodynamic properties of the NdNiIn-based hydrides (desorption process)

| Alloys | ΔH_H (kJ (mol _H) ⁻¹) | ΔS_H (J (K · mol _H) ⁻¹) |
|--|--|---|
| NdNiIn | -19.4 ± 0.6 | -56.0 ± 1.4 |
| NdNi _{0.98} Cu _{0.02} In | -22.6 ± 1.6 | -68.8 ± 3.6 |
| NdNiIn _{0.95} Al _{0.05} | -23.5 ± 1.3 | -72.2 ± 3.1 |

creasing H content, the enthalpy value steadily decreases for all NdNiIn-based systems. The slopes of such dependences, derivative $\partial(\Delta H_H)/\partial(c_H)$ are very similar for all the materials and indicate a significant increase of the exothermic effect of the hydrogenation with increasing H concentration in the plateau regions. The values of such effects are very significant compared to the other metal hydride systems [6]. In contrast, the enthalpy values behave quite differently in the region of high H content $[H]/[f.u.] > 0.9$. For both Cu- and Al- substituted hydrides ΔH_H rapidly increases with increasing H content indicating some destabilisation of the metal hydrides following an introduction of the substituting elements. In contrast, for the non-modified NdNiIn hydride, an unusual decrease of the ΔH_H and corresponding increase of its stability is observed. These observations indicate that a formation of the hydrides containing short H–H separations seems to be very sensitive to the substitutions. Powder neutron diffraction (PND) studies (Riabov et al., this conference [5]) show that substitutions have relatively small effect on the structural characteristics of the Nd₃Ni₂H₂ clusters: H–H pairs slightly shrink [NdNiInD_{1.2}: 1.56 Å; NdNi_{0.95}Cu_{0.05}InD_{1.4} and NdNiIn_{0.95}Al_{0.05}D_{1.4}: 1.54 Å] while keeping the Ni–H distances rather constant, 1.51–1.52 Å. At the same time, PND study shows that occupation of the octahedral sites, Nd₃NiIn₂ for NdNiIn, which

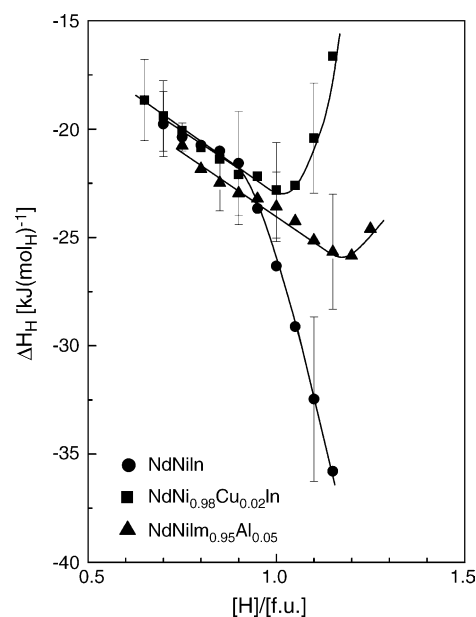


Fig. 4. Changes in the relative partial molar enthalpy during hydrogen desorption as a function of hydrogen content.

transform into the $\text{Nd}_3(\text{Ni,Cu})\text{In}_2$ for the $\text{NdNi}_{0.95}\text{Cu}_{0.05}\text{In}$ alloy and $\text{Nd}_3\text{Ni}(\text{In,Al})_2$ for the $\text{NdNiIn}_{0.95}\text{Al}_{0.05}$, becomes significantly smaller in the modified materials [5]. This suggests that an influence of Cu and Al is in destabilising hydrogen bonds for the D2 atoms occupying the octahedral site, thus eventually leading to the overall destabilisation of the γ -phase. This, in turn, means that pronounced modifications of the electronic structure of the doped materials could be anticipated even at very small content of Al and Cu.

In conclusion, the P–C–T relationships for the Cu- and Al-doped NdNiIn intermetallics–H systems and their thermodynamic properties of hydrogen were determined. Even small substitutions of In by Al and Ni by Cu lead to the noticeable modification of the isotherms and a hysteresis effect. The H–H pairing seems to be stable at relatively low substitution level below 1/10 for both Al/In and Cu/Ni cases.

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