Hydrogen storage in PrNiIn and related alloys

O Ardelean¹, G Blanita¹, G Filoti² and P Palade²

¹ National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath, 400293 Cluj-Napoca, Romania
² National Institute for R&D of Materials Physics, 105 bis Atomistilor, PO Box MG-7, 077125 Bucuresti, Romania

E-mail: ovidiu.ardelean@itim-cj.ro

Abstract. The effect of partial substitution of Fe for Ni, Sn for In and total substitution of Nd for Pr on hydrogen absorption by PrNiIn type alloys are reported. In these hydrides pairs of H atoms are found at distances of 1.5-1.6 Å, violating the so called “2-Å rule” for metal hydrides. The storage capacity does not increase in the substituted alloys, suggesting that the pair formation is a local phenomenon, which can not lead to high storage capacity.

1. Introduction

For mobile applications to fuel cell powered vehicles, on-board storage materials with hydrogen absorption/desorption capacities of at least 6.5% H are needed. To reach the high volumetric and gravimetric density suitable for mobile applications, most of the research is focused on: high-pressure gas cylinders, liquid hydrogen, physisorbed on a solid surface (e.g. porous metal-organic frameworks, activated carbons), metal hydrides of the metals or intermetallics, complex hydrides of light elements (alanates, boranates) alone or mixed with amides, storage via chemical reactions and some other methods. Despite the research and development of thousands of storage alloys produced now at commercial scale, they are not able to store reversibly more than ~3% H. However, they are still interesting for niche applications (stationary or mobile).

Recently, the NdNiIn type compounds [1-5] attracted interest due to the very short H-H distances of 1.5-1.6 Å observed in their hydrides, violating the so called “2-Å rule” for metal hydrides; the model calculations showed that the interactions is strongly repulsive for such H-H pairs [2]. It might not be inferred straightforwardly that this short local H-H distance might really lead to a high increase in the overall storage capacity but these compounds still deserve attention as storage media. In this work, the characteristics of some RENi₁₋ₓMₓIn₁₋ₓMₓ (RE = Rare Earth) are reported and discussed comparatively with literature data [3].

2. Experimental

Compounds: PrNi₀.₉Fe₀.₁In, PrNiIn₀.₈Sn₀.₂, NdNiIn₀.₈Sn₀.₂ were prepared by arc melting under pure argon. p-c-T isotherms were measured by the volumetric Sieverts’ method. The lattice parameters were calculated with the program Mc Maille and the Mössbauer spectra were obtained using the ⁵⁷Co (in transmission geometry).
3. Results and discussion

PrNi$_{0.9}$Fe$_{0.1}$In, PrNiIn$_{0.8}$Sn$_{0.2}$, NdNiIn$_{0.8}$Sn$_{0.2}$, have been synthesized to determine the effect of substitution on hydride characteristics and especially for the hydrogen atoms pair H–H forming, at unusually short distances.

**PrNi$_{0.9}$Fe$_{0.1}$In**

The Fe substitution for Ni results in the same hexagonal structure of PrNi$_{0.9}$Fe$_{0.1}$In (P-62m – No 189) with a=7.563 Å and c=4.012 Å, a little higher than for the PrNiIn.

Mössbauer spectra, see figure 1, revealed two different sites for the Fe atoms, showing that part of the iron segregates as bcc α-Fe after hydriding. Two hydrides belonging to the same structure were identified: PrNi$_{0.9}$Fe$_{0.1}$InH$_{1.2}$ and PrNi$_{0.9}$Fe$_{0.1}$InH$_{0.6}$ with a = 7.3004 Å, c = 4.5627 Å and respectively a = 7.594 Å, c = 4.074 Å, in agreement with the highly anisotropic expansion characteristic to these compounds [2]. Desorption isotherms for PrNiIn and PrNi$_{0.9}$Fe$_{0.1}$In reported in figure 2, exhibit three regions.

![Mössbauer spectra of hydrided PrNi$_{0.9}$Fe$_{0.1}$In and its components at ambient temperature.](image1)

**Figure 1.**

Desorption isotherms for a) PrNiIn – H$_2$ and b) PrNi$_{0.9}$Fe$_{0.1}$In – H$_2$ systems.

Literature [4] shows that, at room temperature, 1.33 H/mol was achieved at ~1 bar H$_2$ but at higher pressures the composition can reach 1.63 H/mol [5]. The desorption isotherms is composed of 3 regions: 3$^{rd}$ region, hydrogen is desorbed, at high pressure, from octahedral sites Pr$_5$NiIn$_2$, which corresponds to a less stable hydride (high pressure: low ∆H); 2$^{nd}$ region, hydrogen is desorbed from bipiramidal sites Nd$_3$Ni$_2$, which corresponds to H-H pair decomposition; 1$^{st}$ region, at high temperature and low pressure, the rest of the hydrogen from the half-occupied bipiramids is desorbed.
For PrNiIn the second region gives $\Delta H = -34.2$ kJ/mol and $\Delta S = -65.8$ cal/K.mol for the $\beta \rightarrow \gamma$ transformation region corresponding to the decomposition of the H-H pairs, in good agreement with the literature data for LaNiIn (-34.6 kJ/mol and -70.7 cal/K.mol). From the van’t Hoff plots for PrNi$_{0.9}$Fe$_{0.1}$In, $\Delta H = -34.0$ kJ/mol and $\Delta S = -64.4$ cal/K.mol were obtained, showing that at this Fe concentration, the substitution does not influence significantly the H-H interaction.

PrNiIn$_{0.8}$Sn$_{0.2}$

After activation of the material, the total absorption capacity at room temperature corresponds to PrNiIn$_{0.8}$Sn$_{0.2}$H$_{1.33}$.

PrNiIn$_{0.8}$Sn$_{0.2}$ exhibits a single region in the range 0.67-1.2 H/mole. An evaluation of the desorption enthalpy, from the van’t Hoff equation, gives $\approx 5$ kcal/mol H for a less stable hydride, but due to the point scattering, this value is not very accurate.

The lattice parameters for PrNi$_{0.9}$Fe$_{0.1}$InH$_{1.2}$ show anisotropic expansion similar to those reported for PrNiInH$_{1.33}$ [2], characteristic to H-H pairs. However, the Sn substitution for In results in much lower $\Delta c/c$ than 12-16% probably due, either to an instability of the pairs as in NdNiIn$_{0.75}$Al$_{0.25}$ hydride (for Al/In $>1/9$, with H located in other sites) [3] or to formation of other type of hydrides like LaNiSnD$_{2}$ [1].

**Table 1.** Effects of hydrogen on lattice parameters.

|          | a   | c   | c/a   | $\Delta a/a$ (%)* | $\Delta c/c$ (%)* | $\Delta V/V$ (%)* |
|----------|-----|-----|-------|-------------------|--------------------|--------------------|
| PrNiIn   | 7.5410 | 3.9500 | 0.5238 | -                 | -                  | -                  |
| PrNiInH$_{1.33}$ | 7.2600 | 4.5600 | 0.6281 | $-3.73$          | 15.40              | 7.01               |
| PrNi$_{0.9}$Fe$_{0.1}$In | 7.5630 | 4.0120 | 0.5300 | -                | -                  | -                  |
| PrNi$_{0.9}$Fe$_{0.1}$InH$_{1.2}$ | 7.3004 | 4.5627 | 0.6250 | -3.47           | 13.70              | 5.96               |
| NdNiIn$_{0.8}$Sn$_{0.2}$ | 7.4990 | 3.9480 | 0.5265 | -                | -                  | -                  |
| NdNiIn$_{0.8}$Sn$_{0.2}$H$_{x}$ | 7.4320 | 4.2340 | 0.5700 | $-0.90$       | 7.20               | 5.34               |

* Variation of the parameter for hydrogenated alloy compared to the non-hydrogenated alloy

NdNiIn$_{0.8}$Sn$_{0.2}$ was chosen to observe the influence of the lanthanide on the hydride stability. At 3 MPa, it has a NdNiIn$_{0.8}$Sn$_{0.2}$H$_{1.26}$ composition. The desorption isotherms, figure 4, has the same shape as PrNiIn$_{0.8}$Sn$_{0.2}$ suggesting that no H-H pair was formed.

Briefly, it can be said that with Sn ($r_0 = 1.862$ Å) substitution for In ($r_0 = 1.841$ Å), higher atomic radius should lead to a more stable hydride, but the plateau pressure of PrNiIn$_{0.8}$Sn$_{0.2}$ shows the opposite trend, suggesting different types of hydrogen sites accommodating H atoms.
Nd ($r_0 = 1.821 \, \text{Å}$) substitution for Pr ($r_0 = 1.828 \, \text{Å}$) results in a less stable hydride due to the compression of the lattice, as shown by the higher plateau pressure of NdNiIn$_{0.8}$Sn$_{0.2}$ compared to PrNiIn$_{0.8}$Sn$_{0.2}$.

4. Conclusions
The influence of the substitutions in compounds of NdNiIn type hydrides are in agreement with the lattice parameters variations. The enthalpies corresponding to the decomposition of the hydrides prove a repulsive interaction between H-H pairs, in agreement with literature [2-4] and experimental data for other compounds of this type [3]. The substitutions of Fe for Ni or Sn for In do not result in an increase of the H storage capacity: the formation of H-H pairs in this type of hydrides is a characteristic at atomic scale and does not result in materials with high hydrogen storage capacity, suitable for applications.

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