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Hydrogenation process of Gd_3Ni

NATALYA V. TRISTAN[1], TOMASZ PALEWSKI[1*] ,
HENRYK DRULIS[2], LUCYNA FOLCIK[2], SERGEY A. NIKITIN[1, 3]

[1]International Laboratory of High Magnetic Fields and Low Temperature,
95 Gajowicka St, 53-421 Wrocław, Poland

[2]Institute of Low Temperature and Structure Research, 2 Okólna St, 50-950 Wrocław, Poland

[3]Faculty of Physics, Moscow State University, Vorobievy Gory, 119899 Moscow, Russia

Reaction of intermetallic Gd_3Ni with hydrogen and transformation of the crystal structure depending on hydrogen concentration is investigated. It is shown that Gd_3Ni belongs to the group of intermetallic compounds which are thermodynamically unstable during hydrogenation and undergo a decomposition into the rare earth hydride and the transition metal. Nickel plays a role of the catalyst in the reaction and supports the formation of GdH_3 at low temperatures.

Key words: *$(Gd_3Ni)H_x$; hydrogenation; structural transformation; structural instability*

1. Introduction

It is well known that many rare earth intermetallic compounds absorb large amounts of hydrogen. The incorporation of hydrogen into the crystal lattice usually gives rise to an increase of the unit cell volume. Besides, a charge transfer between the hydrogen atom and other atoms in the lattice is possible. Combination of such factors results in drastic changes of the physical properties of the hydrogenated intermetallic compounds. Thus, for example, cases are known where a diamagnet becomes a ferromagnet or an electronic conductor turns into an insulator [1]. All these features make the study of hydride phases very interesting and prospective.

The outcome of the reaction of intermetallic compounds with hydrogen is not always predictable. Usual is the situation when the hydrides have the same crystal structure as the parent intermetallic compounds. On the other hand, in numerous cases the hydrides

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[*]Corresponding author, e-mail: paltom@alpha.mlspmint.pan.wroc.pl.

become amorphous or form new crystal structures. Decomposition of the parent intermetallic compound to components of completely different stoichiometries has also been reported [2, 3].

Compounds of the R_3M stoichiometry, where R is a rare earth atom and M is Ni or Co, are able to absorb up to about 9 hydrogen atoms per formula unit [4]. It was suggested that the hydrogenation under low pressures (< 100 kPa) and at low temperatures (243–253 K) could lead to the synthesis of the R_3NiH_x compounds which preserve the crystal structure of the initial intermetallic compound [5, 6]. Our recent investigations show, however, that the previous chemical syntheses and the analysis of the X-ray patterns have not been accurate enough and, therefore, more precise measurements and analysis should be undertaken.

The purpose of the present work was to investigate the reaction of the intermetallic compound Gd_3Ni with hydrogen and to obtain accurate information on the transformation of the crystal structure in function of the amount of absorbed hydrogen.

2. Experimental

The parent Gd_3Ni compound was obtained by high-frequency melting of the constituent metals in a purified argon atmosphere under the pressure of 1.5 atm followed by cooling at the rate of ~1–2 K/sec. The purities of gadolinium and nickel were 99.9 and 99.99%, respectively. Hydrogen used for the syntheses was obtained by thermal decomposition of a $LaNi_5$ hydrogen storage.

The hydrogenation was performed at room temperature under a low hydrogen pressure. Before hydrogenation, all Gd_3Ni samples were powdered and heated under vacuum at 695 K for 2 h. Hydrogen was let into the working volume at room temperature in small portions ($p \sim 1$–4 kPa) in order to avoid a violent reaction between the powdered sample and the gas. After the whole amount of hydrogen had been absorbed, the samples were homogenized at room temperature for about 60 h. The concentration of the absorbed hydrogen was calculated volumetrically. Some hydride samples were synthesized at low temperature; X-ray diffraction patterns of these samples were similar to the patterns of samples synthesized at room temperature. The former patterns, however, exhibited significant distortions typical of insufficiently annealed compounds.

The X–ray measurements were carried out using a DRON–2 diffractometer with a cobalt radiation source. An additional verification of the elemental composition of each sample was performed using the EDAX 9800 and Philips SEM515 sets.

3. Results and discussion

The X-ray diffraction pattern of the parent powdered Gd_3Ni sample is shown in Fig. 1a. It is a single phase sample crystallizing in an orthorhombic Fe_3C-type structure (the *Pnma* space group) with the lattice parameters a = 0.694 nm, b = 0.969 nm and c = 0.635 nm.

Using the step-by-step hydrogenation procedure, we obtained a number of hydride samples with various compositions $(Gd_3Ni)H_x$, where $0 \le x \le 8.8$. The X-ray diffraction patterns of some of the hydrides obtained are shown in Figs. 1b–f. One can see that insertion of a small amount of hydrogen (Fig. 1b) leads to diminishing of the intensities of the lines corresponding to the Gd_3Ni and to appearance of a few new peaks, their intensities increasing with the hydrogen concentration. When, on average, four hydrogen atoms per formula unit are absorbed by the sample, the initial X-ray pattern of orthorhombic structure totally disappears from the diffractogram and only the lines characteristic of a cubic crystal lattice structure remain (see Fig. 1c). When the hydrogenation process is continued and a larger amount of hydrogen is absorbed, another crystallographic transformation takes place and a few new peaks appear in addition to the peaks of the cubic diffraction pattern (Fig. 1d). Their intensities increase with increasing hydrogen concentration while intensities of the peaks belonging to cubic structure weaken (see Figs. 1e–f).

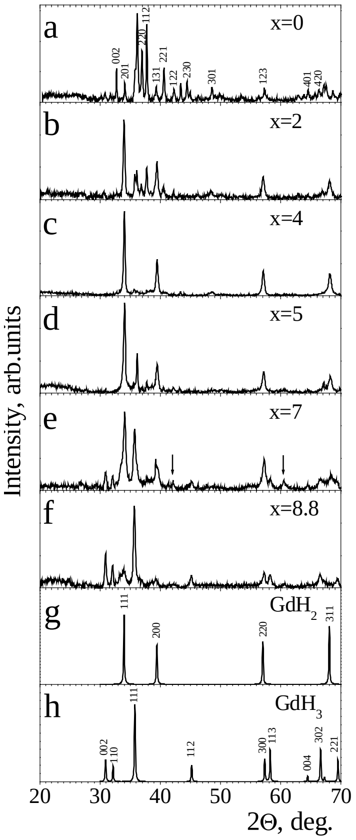

Fig. 1. X-ray diffraction patterns of the parent Gd_3Ni compound (a), of hydrides $(Gd_3Ni)H_x$ with different hydrogen concentrations (b–f) and theoretical X-ray diffraction patterns for GdH_2 (g) and GdH_3 (h). The arrows in Fig. 1e indicate peaks of the "intermediate" phase (see the text for explanation)

Let us focus on some X-ray diffraction patterns obtained. First, the cubic structure, shown in Fig. 1c, has a lattice parameter $a = 0.530$ nm, what is in exact agreement with the value expected of the dihydride GdH_2 [7]. Secondly, the pattern structure shown in Fig. 1f can describe a two-phase equilibrium region. There are ~70% of the hexagonal phase, with the lattice parameters $a = 0.646$ nm and $c = 0.671$ nm, corresponding to GdH_3 [7], and ~25% of cubic $GdH_{2+\delta}$ dihydride phase with the lattice parameter a ranging between ca. 0.530 and ca. 0.550 nm. To support our analysis, theoretical diagrams for both GdH_2 and GdH_3 phases are presented in Figs. 1g, h, respectively.

X-ray diffraction patterns of $(Gd_3Ni)H_x$ compounds with $5 \leq x \leq 7$ (Figs. 1d–e) contain a few peaks which belong to neither parent compound Gd_3Ni nor to GdH_x ($x = 2, 3$) hydrides. A few diffraction peaks belonging to this "intermediate" phase are marked with arrows in Fig. 1e. The low intensity of the peak does not allow us to identify the phase and we could only speculate that it might be a solid solution of hydrogen in

Gd_3Ni or in any of Gd–Ni alloys which possibly could be formed in the process of the decomposition of the parent compound.

Another interesting finding is that the X-ray diffraction patterns do not contain any traces of the diffraction lines corresponding to crystalline nickel nor to any known crystalline alloys of nickel with gadolinium. At the same time, the elemental analysis showed that nickel is distributed uniformly with no visible precipitation. These facts incline us to suppose that nickel transforms to a dispersed phase not detectable in the reported X-ray experiments.

For the sake of completeness, an X-ray diffraction pattern of a sample synthesized at $T = 220$ K with the maximal hydrogen concentration $x = 8.8$, is presented in Fig. 2. One can find that at least three phases, GdH_2, GdH_3 and an unidentified "intermediate" phase, are present in this case. As was already mentioned, the X-ray pattern exhibits significant distortions typical of insufficiently annealed or partially amorphous compounds.

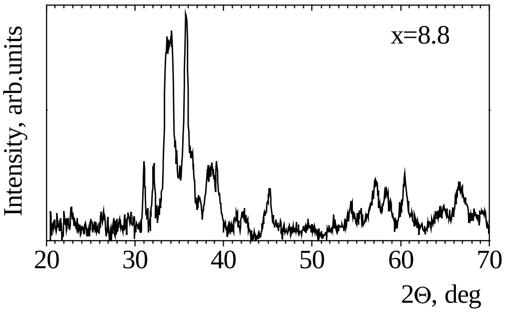

Fig. 2. X-ray diffraction pattern of a $(Gd_3Ni)H_{8.8}$ sample with the highest available hydrogen concentration per formula unit, obtained by hydrogenation at low temperature $T = 220$ K without homogenization at room temperature

Summarizing the results described above, we conclude that Gd_3Ni belongs to the group of intermetallic compounds which are thermodynamically unstable in the hydrogenation process undergoing the decomposition into the pure rare earth hydride phases with precipitation of the transition metal (Ni) as a dispersed phase:

$$\mathrm{Gd_3Ni} + x\mathrm{H} \xrightarrow{x\to 4} \mathrm{GdH_2} + \mathrm{Gd_3Ni}\ \text{(traces)} + \mathrm{Ni}\ \text{(dispersed phase)}$$

$$\xrightarrow{x\to 8.8} \mathrm{GdH_2} + \mathrm{GdH_3} + \mathrm{Ni}\ \text{(dispersed phase)}$$

Considering the observed reaction kinetics, it is obvious that metallic nickel plays the role of a catalyst in the formation of GdH_3 at low temperatures, since usually this hydride can be synthesized only at the temperature higher than room temperature [8, 9].

4. Conclusion

On the basis of the results presented we can state that it is impossible to synthesize the Gd_3Ni hydride in a standard reaction procedure between gaseous hydrogen and Gd_3Ni. Unfortunately, our previous conclusion concerning the crystal structure of hydride samples [5, 6] was based on incorrect interpretation of the X-ray diffraction patterns for $(Gd_3Ni)H_{8.5}$ hydride obtained at low temperature.

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