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Hydrogenation process of the Gd_3M (M = Ni or Co) intermetallics compound

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Abstract

The reaction of the intermetallic Gd_3M (M = Co or Ni) compounds with hydrogen was studied. The transformation of the crystal structure of the parent Gd_3M sample after subsequent stages of the hydrogenation was investigated by X-ray diffraction. It was found that both intermetallic compounds (Gd_3Ni and Gd_3Co) are thermodynamically unstable during hydrogenation decomposing into the gadolinium hydrides and the transition metal. It is very probable that, in the case of Gd_3Ni, nickel plays the role of a catalyst in the formation of GdH_3 in the low temperature range, whereas in the case of Gd_3Co the transition metal (Co) is rather inactive.

Keywords: Hydrogenation; Structural transformation; Structural instability

1. Introduction

It is known that not only rare earth elements but also many rare earth intermetallic compounds absorb large amounts of hydrogen. The reaction of hydrogen with intermetallic compounds results in crystalline or amorphous solid solutions of hydrogen in the respective compounds or in the formation of hydrides with a fixed chemical composition. In the case of solid solutions, the incorporation of hydrogen atoms into the crystal lattice usually gives rise to an increase of the unit cell volume. Moreover, a charge transfer between hydrogen and other atoms present in the crystal lattice is possible, and very often drastic changes of some physical properties are observed upon hydrogenation. For example, a diamagnet becomes a ferromagnet or a metallic conductor turns into a semiconductor or an insulator [1]. Changes of physical properties of hydrogenated intermetallics of rare earth and d-electron elements when the hydrides have the same crystal structure as the parent intermetallic compounds were recently presented in [2,3]. It should be noted that some intermetallic compounds are unstable during hydrogenation and become amorphous or decompose yielding hydrides of respective metallic elements [4,5]. R_3M compounds are able to absorb up to nine hydrogen atoms per formula unit ($R_3M + xH$; $x \leq 9$) [6]. It was suggested earlier that the hydrogenation under low pressure of hydrogen ($p < 100\,kPa$) and at low temperatures (243–253 K) could lead to the synthesis of the R_3NiH_x hydrides which preserve the crystal structure of the parent compounds [7] but it is very probable that the quality of the previous chemical syntheses and X-ray patterns had not been sufficient. On the other hand it has not been known which products: solid solution or individual hydrides are obtained during reaction of such compounds with hydrogen. The aim of the present investigation was to get insight into the influence of absorbed hydrogen on the phase composition and the transformation of the crystal structures of the parent compounds

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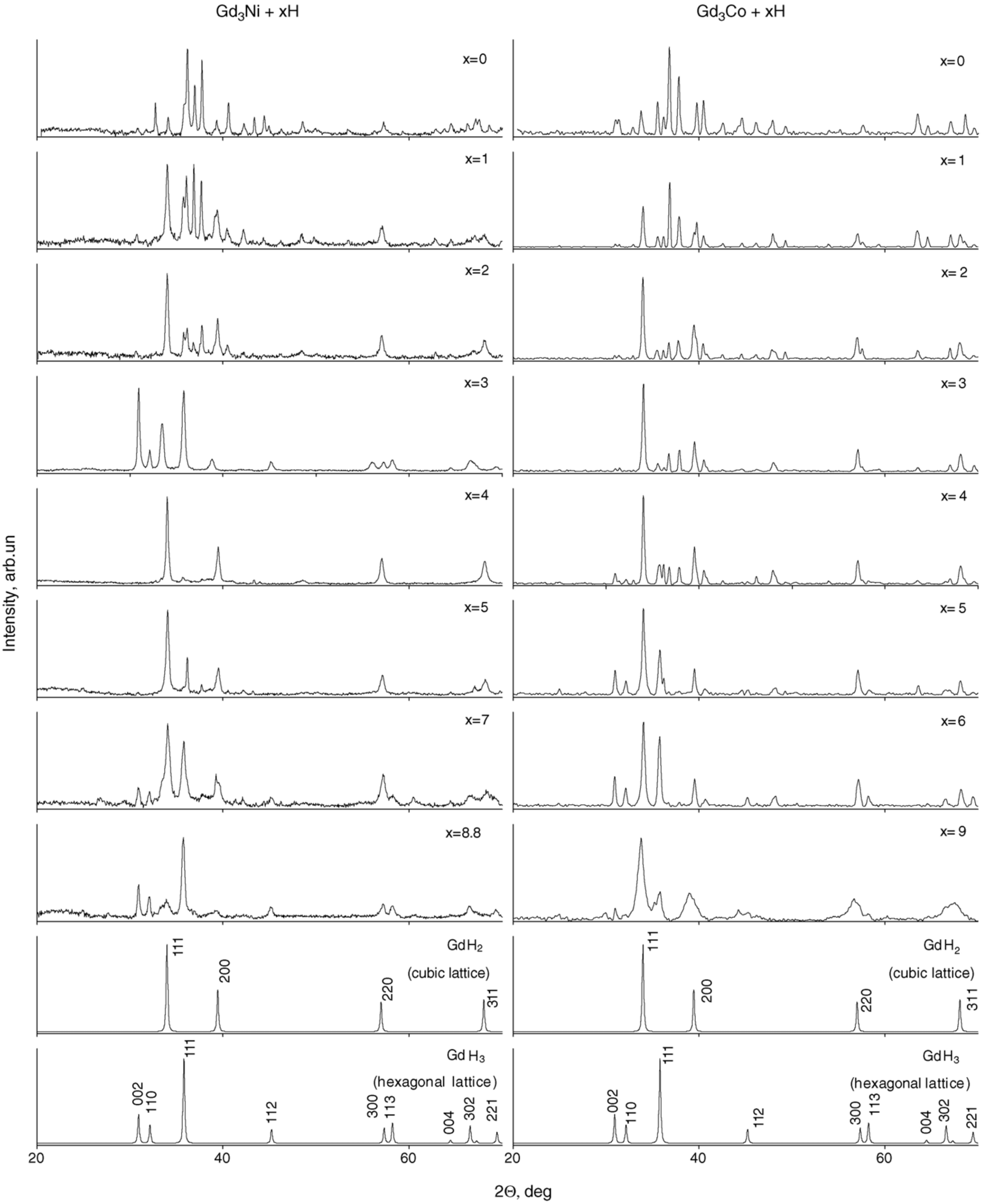

Fig. 1. Diffractograms of Gd_3Ni ($x = 0$) and Gd_3Co ($x = 0$), its products after hydrogenation ($x = 1$–9) and both hydrides of gadolinium.

Gd_3Ni and Gd_3Co during hydrogenation, as a function of its amount.

2. Experimental

The parent Gd_3Ni and Gd_3Co compounds were obtained by melting both metals in a purified argon atmosphere. The purity of gadolinium was 99.9% whereas that of nickel and cobalt was 99.99%. Hydrogen was obtained by thermal decomposition of the $LaNi_5$ hydrogen storage compound. The samples were crushed into powder before hydrogenation and heated in a reaction chamber under vacuum at about 700 K for 2 h. When the sample temperature was lowered to room temperature, hydrogen was put into the reaction chamber in small portions (the initial pressure of hydrogen in the chamber did not exceed 4 kPa) in order to avoid a violent reaction between the powder and the gas. The mass of the Gd_3M sample and the initial pressure of hydrogen balanced such that the concentration of hydrogen (*x*) in the samples ($Gd_3M + x$H) varied gradually from 1 to 9. The samples were then homogenized at room temperature for 60 h and examined using X-ray diffraction with a cobalt radiation source. An additional verification of the elemental composition of each hydride was performed using the Philips SEM 515 and EDAX 9800 electron microscope.

3. Results

Both parent compounds Gd_3M crystallize in an orthorhombic Fe_3C-type crystal structure (*Pnma* space group). The lattice parameters of Gd_3Ni amount to $a = 0.694$ nm, $b = 0.969$ nm and $c = 0.635$ nm, whereas for Gd_3Co $a = 0.705$ nm, $b = 0.950$ nm and $c = 0.631$ nm. An analysis of the X-ray patterns of hydrogenated samples (see Fig. 1) indicates that, in addition to lines (peaks) characteristic of the orthorhombic phase, lines of two other phases may be identified with cubic and hexagonal crystal structures. The lattice parameter of the cubic structure $a = 0.53$–0.55 nm is in good agreement with the value expected of the dihydryde GdH_2, and the lattice parameters of the hexagonal structure ($a = 0.65$ nm, $c = 0.67$ nm) correspond to the lattice parameters of GdH_3 [8]. It is also seen that for the hydrogenated samples with $x \leq 4$ the peak intensity of the Gd_3M phase decreases whereas the peak intensity of the GdH_2 phase increases. In Gd_3Ni which absorbed four hydrogen atoms per formula unit only peaks belonging to the GdH_2 phase are observed while in the case of Gd_3Co some peaks of Gd_3Co are still seen. When more than four hydrogen atoms are absorbed, the lines characteristic of the hexagonal (GdH_3) phase appear, their intensities increasing with increasing *x* with those belonging to the cubic phase decreasing. At the same time in the case of the hydrogenated Gd_3Ni samples, the replacement of GdH_2 by GdH_3 is more evident and, for *x* near 9, practically only peaks of the GdH_3 phase are seen.

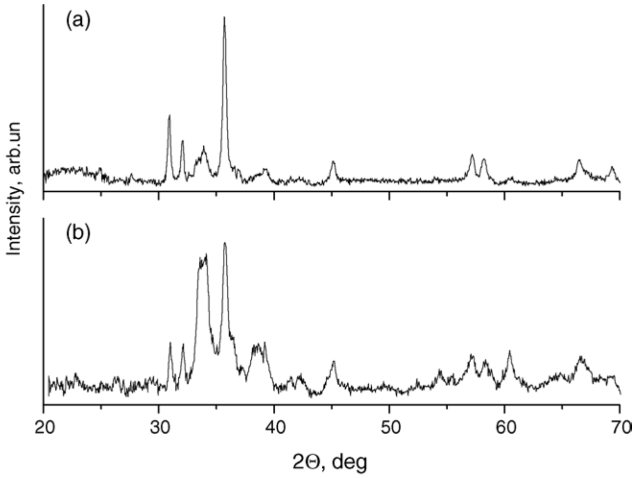

Fig. 2. X-ray diffraction patterns of hydrogenated samples (Gd_3Ni + 8.8 H): (a) obtained at room temperature and homogenized for 60 h; (b) obtained at low temperature (*T* 220 K) without homogenization at room temperature.

In the hydrogenated Gd_3Co samples the formation of GdH3 is more difficult and even for $x = 9$, the GdH_2 and GdH_3 phases coexist. In the X-ray patterns of both hydrogenated compounds two to three very weak additional peaks belonging to an unidentified phase are also visible, but in low intensity does not allow an identification. In addition, no lines of the transition metals (Co or Ni) or of any known crystalline alloys of M (Ni or Co) with gadolinium are observed. Also the elemental analysis showed that nickel and cobalt are distributed unifomly with no visible precipitation. Analyzing these facts one may suppose that nickel and cobalt transform to a dispersed phase not detectable in the reported X-ray investigation. Based on the results described above, we conclude that Gd_3Co and Gd_3Ni decompose during hydrogenation into the pure rare earth hydrides with precipitation of the transition metals (Co or Ni) as dispersed phases. It is widely known that nickel in powder form exhibits catalytic properties, especially in hydrogenation. It is thus possible that Ni plays the role of a catalyst in the formation of GdH_3 at low temperatures; so far this hydride was synthesized at temperatures much higher than room temperature [9,10]. On the other hand cobalt is rather inactive in reactions with hydrogen and this may be the reason of differences between final products after hydrogenation of Gd_3Ni and Gd_3Co; pure GdH_3 or a mixture GdH_2 and GdH_3. In the case of Gd_3Ni some hydrides were synthesized at low temperature ($T \approx 220$ K) and it was found that X-ray patterns were similar to the patterns of samples synthesized at room temperature (see Fig. 2a), however, in the X-ray pattern of this sample (see Fig. 2b) one can find the lines of GdH2 and GdH_3 phases exhibiting significant distortion typical of insufficiently annealed compounds.

4. Conclusions

The presented results point out that Gd_3M (M = Co, Ni) is unstable during hydrogenation, and a direct synthesis of the hydrides Gd_3MH_x is impossible using a standard reaction between gaseous hydrogen and Gd_3M. Thus, it is suggested that the analysis of X-ray patterns of hydrogenated intermetallic compounds should be more accurate and complete to avoid mistakes in the identification of the products. It may be also interesting to confirm the catalytic role of metallic nickel in the formation of other rare earth hydrides.

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