

A preliminary study of some “pseudo-AB₂” compounds: RENi₄Mg with RE = La, Ce and Gd. Structural and hydrogen sorption properties

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Abstract

The compounds RENi₄Mg have been elaborated by mechanical alloying (MA) and a subsequent heat treatment at 600 °C for 1 h. The lattice parameters are in good agreement with those already reported: 7.165 Å for LaNi₄Mg, 7.030 Å for CeNi₄Mg and 7.038 Å for GdNi₄Mg. The hydrogen sorption behaviors are strongly influenced by the rare earth used: for La compound, hydrogen absorption leads to a structural change and no desorption can be observed, for Ce compound, no reaction towards hydrogen can be noticed and for Gd compound, hydrogen can be absorbed and desorbed reversibly at room temperature. Moreover, for GdNi₄Mg, no structural change is reported after hydrogenation and only a slight volume expansion can be noticed (e.g. 5%). The MA process has also been used successfully for the elaboration of GdNi_{4-x}Al_xMg up to $x = 1$. In these substituted compounds, hydrogen can also be absorbed and desorbed reversibly at room temperature.

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1. Introduction

Hydrogen is an ideal non-polluting vector of energy for the future. However, the widespread of hydrogen is closely associated with the methods of both its storage and its mass production. Among the various ways envisaged for storage, the reversible bonding of hydrogen with some metals and alloys, forming hydrides, is of special interest [1]. Recently, substantial research has been done in two main directions:

- (i) Relationship between hydrogen sorption properties (especially the thermodynamic properties) and the crystallographic structure. The most usual compounds studied are the AB₅- and AB₂-type compounds [2,3].
- (ii) Improvements of the kinetic behavior of magnesium-based mixtures by mechanical grinding and addition of various

elements or compounds [4,5]. According to its 7.6 wt% absorption capacity, magnesium is a very attractive material for hydrogen storage in the form of MgH₂. However, the poor reaction kinetics as well as the temperature of use are drawbacks that have to be solved. As previously mentioned the use of ball milling and the addition of various elements or compounds [6,7] can help the kinetics but the thermodynamics (so the temperature of use) remain unchanged.

Our study deals with the preparation of intermetallics containing magnesium. The basic cubic AB₂ structure was used as the starting structure. In such structure the crystallographic site occupied by A element can be disorderly (AuBe₅ structure type, known as C15) or orderly (MgCu₄Sn structure type, known as C15b) occupied by rare earth and magnesium (to lighten the sample and to improve the sorption properties). For the synthesis, both solid-state reaction and mechanical alloying have been used. The preliminary results will be discussed not only in terms of phase composition but also in terms of hydrogen sorption properties (maximum capacity and reversibility

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at room temperature). Finally, the structural evolution of the compounds with the partial replacement of Ni by Al will be discussed.

2. Experimental details

Pure elemental powders of Mg, RE (i.e. La, Ce, Gd), Ni and Al (purity > 99.5%) were mixed in an argon dry box (with appropriated stoichiometry) (i) pressed into pellets and heat treated at 600 °C for 48 h under 0.5 MPa Ar for the solid-state reaction method or (ii) put in a stainless steel container hermetically closed and ball milled with a Fritsch P5 equipment with a plateau rotation speed of 250 RPM for the ball milling process. The milling was performed for 2 h in continuous and rest for 30 min to decrease the temperature of the vial and then milled again until the total milling time was achieved.

The chemical composition and homogeneity of the products were checked by electron microprobe analysis (EPMA) with a CAMECA SX-100 instrument. The quantitative determination was performed on the basis of intensity measurements of Mg $K\alpha_1$, RE $L\alpha$, Ni $K\alpha_1$ and Al $K\alpha_1$ X-ray emission lines using $RENi_5$, $MgNi_2$ and $RENiAl$ as reference compounds. The structural changes of the products were analyzed by X-ray powder diffraction using a Philips PW 1050 diffractometer with $Cu-K\alpha$ radiation ($\lambda = 0.15405$ nm). In order to determine the intermetallic and the hydride structure, the Rietveld method for refinement was applied, the diffraction patterns being analyzed by a whole pattern fitting procedure using the program FULLPROF [8].

Hydrogen sorption properties were investigated with the use of an automatic Sievert-type volumetric apparatus (HERA, Hydrogen Storage System, Québec, Canada) in the temperature range between room temperature and 573 K. Hydriding experiments were carried out up to $P = 4$ MPa while desorption proceeded at $P = 0.03$ MPa. A detailed description of the volumetric method for hydrogen sorption measurements is given in [9].

3. Results and discussion

Some authors already published works on “pseudo- AB_2 ” compounds (so-called because it derives from the parent

structure AB_2 as shown in Fig. 1). For example, Guénée et al. [10,11] reported works on $LaNi_4Mg$ and $NdNi_4Mg$ and Orimo et al. [12–14] published works on YNi_4Mg and $CaNi_4Mg$. The structural analysis is essentially based on the disorder between RE (or Ca) and Mg on both 4a and 4c sites. It is even sometimes claimed [12–14] that the order/disorder can strongly influence the H_2 sorption properties. It has also been shown by Wang et al. that the RE could have an influence on the electrode performance of $RENi_4Mg$ compounds [15].

3.1. Synthesis of $RENi_4Mg$ by solid-state reaction and ball milling

The powders of rare earth (La, Gd and Ce), Ni and Mg were manually milled, pressed into pellets and then heated at 600 °C under Ar for 48 h. As an example, the result of the Rietveld refinements for $LaNi_4Mg$ is presented in Fig. 2 and Table 1. The results were in good agreement with the literature ($a = 7.165$ Å). For the three studied compounds impurities (e.g. Mg_2Ni , Ni for RE = La and mainly RE_2Ni_2Mg and RE oxides for RE = Gd and Ce) were always found and the relative amount of impurities was sometimes even higher than 25 wt%. The same type of results was obtained for both $CeNi_4Mg$ and $GdNi_4Mg$ ($a = 7.030$ and 7.038 Å, respectively). However, it has not been possible to synthesize a pure compound by the solid-state reaction process.

For the ball milling process, the initial powder mixtures have been ball milled for 114 h by step of 6 h. The XRD results are presented in Fig. 3. After the first 6 h, some new peaks appeared and could not be indexed with the initial powder peaks. However, the three peaks could be indexed on the basis of the $RENi_4Mg$ compounds even if some others were missing. Continuing the milling allowed to get a more amorphous compound. After approximately 60 h of milling the product was almost completely amorphous and further milling did not lead to more modifications. From Fig. 3, it clearly appears that the compounds could be formed during the first 6 h. Then, it was of interest to look closely at these first 6 h. Fig. 4 presents the XRD patterns of the powder milled for 2, 4 and 6 h. After 2 h, the milled powder is almost completely amorphous. After 4 h, the peaks related to $RENi_4Mg$ appear and a better crystallinity

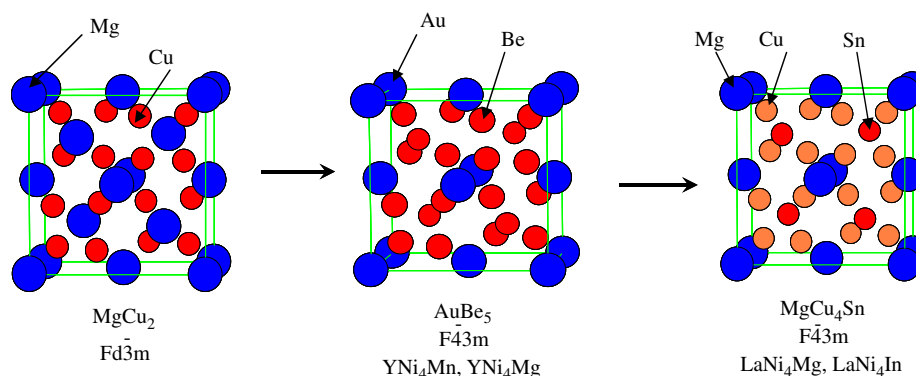


Fig. 1. Relationship between cubic AB_2 structure type and the related $AuBe_5$ and $MgCu_4Sn$ (so-called “pseudo- AB_2 ”). The space group change will induce new diffraction peaks for the $h00$ with $h = 2n$ and $hk0$ with $h + k = 2n$.

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