

Available online at www.sciencedirect.com

SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/ijhydene

High-pressure synthesis, crystal structure and cyclability of the Mg_2NiH_4 hydride

R. Martínez-Coronado^{a,*}, M. Retuerto^b, B. Torres^c, M.J. Martínez-Lope^a,
M.T. Fernández-Díaz^d, J.A. Alonso^a

^a Instituto de Ciencia de Materiales de Madrid, C.S.I.C., Cantoblanco, E-28049 Madrid, Spain

^b Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road Piscataway, NJ 08854-808, USA

^c Departamento de Física, Facultad de Ciencias, Universidad de Santiago de Chile and Center for Interdisciplinary Research in Materials, CIMAT, Av. Lib. Bernardo O'Higgins 3363, Santiago, Chile

^d Institut Laue-Langevin, BP156X, Grenoble F-38042, France

ARTICLE INFO

Article history:

Received 10 October 2012

Received in revised form

21 February 2013

Accepted 23 February 2013

Available online 28 March 2013

Keywords:

Mg_2CoH_5

Neutron powder diffraction

High-pressure synthesis

Absorption/desorption

MgH_2

ABSTRACT

We have designed a new synthesis method for the complex Mg_2NiH_4 hydride, based on the direct reaction of simple hydrides under high-pressure and moderate-temperature conditions. A well-crystallized sample was obtained in a piston-cylinder hydrostatic press at moderate pressures of 2 GPa and temperatures around 750 °C from mixtures of MgH_2 and Ni enclosed in gold capsules. X-ray and neutron powder diffraction analysis were used to identify the purity of the samples and provide an accurate description of the crystal structure features. Mg_2NiH_4 hydride shows a monoclinic symmetry with space group $C2/c$ (No. 15). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been carried out to determine the hydrogen desorption temperature, the hydrogen contents and the cyclability of the compound under a hydrogen pressure of 10 atm. These studies reveal two different desorption temperatures that correspond to the loss of the labile hydrogen H3 leading to a stable hexagonal structure (Mg_2NiH_3) followed by the complete hydrogen desorption to give Mg_2Ni . The cyclability of the hydride was studied through 10 cycles at a hydrogen pressure of 10 atm; a slight loss of reversibility was observed due to the progressive oxidation to MgO due to traces of oxygen adsorbed within the DSC chamber.

Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

The utilization of hydrogen as energy vector strongly relies on the development of suitable hydrogen storage materials. Metal hydrides are perhaps the most realistic choice for the storage of hydrogen. For a variety of materials, alloying has been used to improve its hydrogen absorption and desorption characteristics [1–3]. Magnesium-based alloys are very attractive for hydrogen storage due to their large hydrogen

capacity, light weight and low cost. One of the most attractive hydrides is MgH_2 , which presents a high volumetric and gravimetric hydrogen capacity ($\sim 110 \text{ kg (H}_2\text{) m}^{-3}$ and 7.6 wt%, respectively) [4]. Unfortunately, MgH_2 does not desorb hydrogen if the temperature is not raised above 300 °C, and the hydrogenation kinetics is too slow. Many efforts have been done in order to reduce the thermodynamic stability of MgH_2 . Complex hydrides like Mg_2TH_y ($T = \text{Ni, Fe and Co}$) contain mixed ionic-covalent bonding between metal and hydrogen,

* Corresponding author. Tel.: +34 91 334 9000; fax: +34 91 372 0623.

E-mail address: rmartinez@icmm.csic.es (R. Martínez-Coronado).

which may be tuned and facilitate the hydrogenation/dehydrogenation process. In the case of $T = \text{Ni}$, the Mg_2Ni alloy is stable in the Mg – Ni phase diagram, therefore Mg_2NiH_4 can be prepared by mechanical alloying and successive hydrogenation and dehydrogenation [5–8]. This is not the case for $T = \text{Fe}$ and Co , since Mg_2Fe and Mg_2Co are not stable alloys, but the corresponding hydrides could be synthesized by sintering mixtures of fine metal powders at 450–500 °C under H_2 pressure (90 bar).

Actually, Mg_2NiH_4 shows a quite low hydrogen sorption temperature of approximately 200 °C and it is a promising hydrogen storage material, even if its theoretical storage capacity is only 3.6 wt% [9–11]. Rodewald et al. has reviewed recent results on the crystal chemistry, the chemical bonding peculiarities, physical properties, and hydrogenation behavior of intermetallic rare earth-transition metal– Mg compounds [12]. Mg_2NiH_4 has been shown to exist in two crystallographic forms [13]. The low-temperature (LT) phase crystallizes in a monoclinic structure and the high-temperature (HT) phase in a cubic structure. This HT phase has been recently obtained by ball milling methods starting from mixtures of MgH_2 and Ni [14]. The transformations of Mg_2NiH_4 (HT) below 235 °C have been studied by Genossar and Rudman [15], by Darnaudery, Pezat [16] and by Noreous and Werner [17]. Moreover, Martinez [18] observed the formation of two hydrides; whose empirical formulae are Mg_2NiH_4 and $\text{Mg}_2\text{NiH}_{0.3}$, coexisting with unreacted Ni in the ratio 77.9 wt% Mg_2NiH_4 , 14.9 wt% $\text{Mg}_2\text{NiH}_{0.3}$ and 7.2 wt% Ni after the ball-milling reaction.

Solid-state high-pressure synthesis is a powerful and effective technique to explore new compounds in a variety of research fields. In the field of the hydrogen storage materials, this method is being recently used to obtain new hydrides as a different approach from traditional methods [4]. The aim of the present study was to investigate the formation of Mg_2NiH_4 under hydrostatic pressure conditions at moderate temperatures. In this work we describe a comprehensive study of the crystal structure, thermal analysis (TGA) and the thermal effects that occur during the desorption–absorption reaction using differential scanning calorimetry under a hydrogen pressure of 10 atm.

2. Experimental procedure

A polycrystalline sample of Mg_2NiH_4 was prepared from stoichiometric mixtures of MgH_2 and Ni . The reactants were intimately mixed and ground in a glove box under N_2 atmosphere. This mixture was placed into a gold capsule (8 mm diameter, 10 mm length), sealed inside a glove box and then set into a cylindrical graphite heater (10 mm internal diameter). The reaction took place in a piston-cylinder press (Rockland Research Co.), at a moderate reaction pressure (2 GPa) and temperature (750 °C), for short reaction times of 20–30 min. Then, the product was quenched under pressure. The ramp-up for the material synthesis is rather fast, near 150 °C min^{-1} ; we reach 750 °C in approximately 5 min. The ramp-down is a quenching process; in a matter of seconds the sample is quenched from 750 °C down to room temperature. We found these optimal synthesis conditions after performing

several experiments upon different conditions (temperature, starting materials, synthesis time, etc.).

The initial characterization was carried out by X-ray diffraction (XRD) with a Bruker-axs D8 Advanced diffractometer (40 kV, 30 mA), controlled by a DIFFRACT^{PLUS} software, in Bragg-Brentano reflection geometry with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) and a PSD (Position Sensitive Detector). A filter of nickel allows the complete removal of Cu K_β radiation. For the study of the crystal structure, a neutron powder diffraction (NPD) experiment was carried out in the high-resolution powder diffractometer D2B at the Institut Laue-Langevin at Grenoble, with a wavelength of 1.594 Å. The pattern was collected at room temperature. About 0.8 g of sample was contained in a vanadium can, and a time of 3 h was required to collect a full diffraction pattern. The NPD data was analyzed by the Rietveld method [19] with the FULLPROF program [20]. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The following parameters were refined in the final run: scale factor, background coefficients, zero-point error, pseudo-Voigt corrected for asymmetry parameters, positional coordinates and isotropic thermal factors for all the atoms. The coherent scattering lengths for Mg , Ni and H were 5.375, 10.3 and -3.739 fm , respectively.

Thermal analysis was carried out in a Mettler TA3000 system equipped with a TC10 processor unit. Thermogravimetric (TGA) and DSC curves were obtained in a TG50 unit and DSC20 unit, respectively, working at a heating rate of 10 °C min^{-1} , in a reducing $\text{H}_2(5\%)/\text{N}_2(95\%)$ flow of 0.3 L min^{-1} . About 50 mg of sample were used for each experiment. The thermal stability was studied by recording the TGA curve, in order to determine the hydrogen content and the desorption temperature. The quantity of desorbed hydrogen is always calculated from the weight loss between the sample weight at room temperature and the sample weight at the minimum of the peak, corresponding to the highest rate of weight loss. DSC was also used to determine the desorption temperature connected to the thermal dehydrogenation of the sample. We used a H_2/N_2 (5%/95%) flow to avoid oxidation of the samples.

The sample was subjected to successive differential scanning calorimetry (DSC) experiments, in a HP-DSC1 unit from Mettler, under a hydrogen pressure of 10 atm from room temperature to 550 °C with a heating rate of 10 °C min^{-1} , using about 50 mg of sample in each run. The sample was cycled (heating and cooling runs) up to 10 times. Besides, some quenching tests were performed in a N_2 atmosphere in order to reveal some details of the desorption mechanism.

3. Results and discussion

3.1. Crystal structure

The X-ray diffraction patterns of the Mg_2NiH_4 hydride exhibit sharp and well-defined reflections, as shown in Fig. 1. The sample presents a high crystallinity, in contrast with the compounds obtained by the traditional ball-milling method. This novel synthesis method for hydrides presents two main advantages: i) it does not require to deal with high hydrogen pressures, whereas in some ball milling synthesis hydrogen pressures between 1 and 50 bar [21] are often utilized, and ii) a

Download English Version:

<https://daneshyari.com/en/article/1281683>

Download Persian Version:

<https://daneshyari.com/article/1281683>

[Daneshyari.com](https://daneshyari.com)