Journal of Alloys and Compounds 530 (2012) 111–115

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Hydrogen sorption kinetics of magnesium hydride enhanced by the addition of Zr_8Ni_{21} alloy

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ARTICLE INFO

Article history:
Received 1 March 2012
Received in revised form 21 March 2012
Accepted 22 March 2012
Available online 30 March 2012

Keywords:
Hydrogen storage
Magnesium hydride
Zirconium-nickel alloy
Ball milling
Kinetic behaviour

ABSTRACT

Hydrogen absorption and desorption kinetics, and thermodynamics of MgH_2 ball milled with addition of the Zr_8Ni_{21} alloy have been studied. Different additive amounts were used from 3 to 12.5 wt%. The highest reversible capacity of 6.5 wt% of hydrogen was found for the samples with 3 and 5 wt% of additive. The best reaction kinetics was found with 10 wt% of additive: 5.9 wt% H_2 was desorbed in 4 min at 300 °C and 0.1 bar of hydrogen pressure. Regardless of the different storage capacities, all the samples were almost fully hydrided in 1 min using a hydrogen pressure of 10 bar at 250 and 300 °C. The enthalpy of formation of magnesium hydride was not affected by the presence of the additive.

1. Introduction

Magnesium hydride is one of the most studied materials for hydrogen storage in solid state. It is characterized by high gravimetric capacity and good reversibility of the hydrogen absorption/desorption (a/d) process, but has the handicap of a too high desorption temperature (around 300 °C, due to the rather high value of the formation enthalpy, 76 kJ/mol) and a sluggish hydrogen a/d kinetics. It is also abundant, cheap and environment friendly. While it is very difficult to modify the thermodynamics, it has been shown that the comminution of the hydride particles by high energy milling along with the use of additives like metal oxides [1,2] or transition metals [3–6] significantly improves the a/d kinetics.

Recently, attention has been paid to the study of catalytic properties of multicomponent alloys composed by transition metals [7–10]. Dehouche et al. observed that MgH_2 ball-milled with some Zr–Ni alloys exhibited an improved a/d kinetics, which also depended on the stoichiometry of the alloy [11]. More precisely, the eutectoid composition $Zr_{36}Ni_{64}$ formed by the two crystalline phases Zr_7Ni_{10} and Zr_8Ni_{21} [12] showed a faster kinetics than Zr_7Ni_{10} and Zr_9Ni_{11}. This motivated the question about the influence of the Zr_8Ni_{21} phase on the a/d kinetics. In a study of hydride-forming alloys in nickel-metal batteries Ruiz et al. observed that Zr_8Ni_{21} had a better charge/discharge performance than Zr_7Ni_{10} and Zr_9Ni_{11} [13].

On the basis of the previous considerations, we have studied MgH_2 powders ball milled with Zr_8Ni_{21}, analyzing the corresponding activation process and a/d hydrogen kinetic and thermodynamic properties.

2. Materials and methods

The Zr_8Ni_{21} alloy was prepared by arc-melting the elements Zr and Ni under Ar atmosphere inside a water cooled copper crucible in order to avoid contamination. The purities were 99.9% for Zr and Ni, and 99.999% for Ar. A reduction of contamination from the furnace atmosphere was obtained by melting a sacrificial button before Zr and Ni melting. The arc was established by a torch with tungsten tip. The additive was remelted three times to ensure homogeneity. Then, it was wrapped in a Ta foil which is a getter of oxygen and annealed for 30 days at 1000 °C inside an evacuated quartz capsule. Thereafter, several cycles of heating and cooling from ambient temperature to 250 °C at 15 bar of hydrogen were performed on the alloy to make it brittle and so facilitate its reduction into small pieces by crushing.

MgH_2 powder, supplied by Goldschmidt (95% MgH_2 + 5% Mg), was ball milled under Ar atmosphere with the amounts indicated below the obtained Zr_8Ni_{21} grains for 20 h in a hardened steel vial using a SPEX-8000 shaker mill with a ball to powder ratio 10:1. Five different MgH_2–x wt% Zr_8Ni_{21} compounds, with $x = 12.5$, 10, 7.5, 5, 3, labelled 12.5 cat, . . ., 3 cat, respectively, were synthesized. Sample handling was carried out inside a M-Braun glove box filled with Ar (contamination levels lower than 1 ppm for oxygen and 0.1 ppm for water).

The hydrogen a/d process was studied by means of a Sievert's type apparatus supplied by Advanced Materials Co. Before each a/d measurement the samples were dehydrided for 1 h at 250 °C and 4×10^{-4} bar. The kinetic data were obtained by

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http://dx.doi.org/10.1016/j.jallcom.2012.03.100

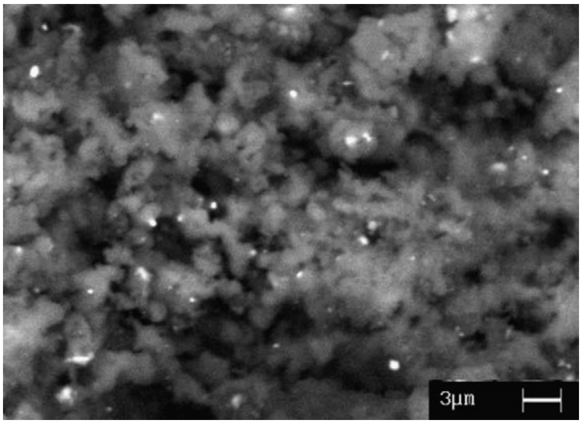

Fig. 1. SEM image of MgH_2–10 wt% Zr_8Ni_{21} obtained with backscattered electrons. The white spots correspond to the additive particles and the grey regions to the MgH_2 matrix.

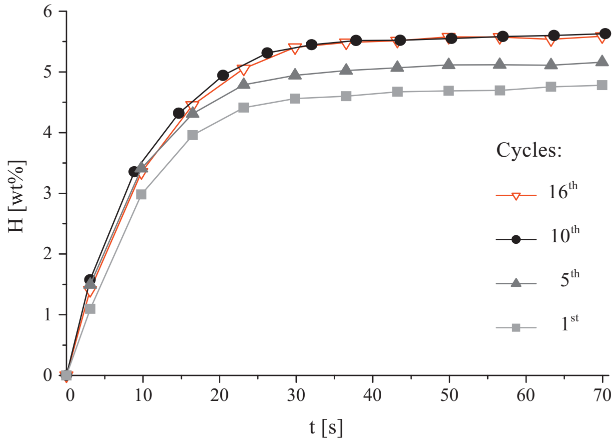

Fig. 2. Absorption curves at 250 °C and 10 bar for the sample MgH_2–10 wt% Zr_8Ni_{21}.

measuring the hydrogen pressure in calibrated reservoirs connected to the sample chamber by valves. In the absorption experiments, the pressure in a small reservoir was set at 10 bar before valve opening. In the desorption experiments, the hydrided sample was connected to an evacuated larger reservoir. Due to the gaseous hydrogen present in the sample holder, there was a rise in the reservoir pressure of approximately 0.1 bar immediately after the valve opening. We took this value as the output pressure during desorption. Powder X-ray diffraction (XRD) patterns were measured by a Philips PW 1820/00 diffractometer using the Cu-Kα radiation. The samples were placed into the sample holder and covered with an 8 μm kapton foil inside the glove box in order to avoid air contamination. A blank measurement performed on only kapton foils showed two broad diffraction peaks below 20° that did not interfere with the patterns of the phases under analysis. Scanning electron microscopy (SEM) observations were performed by using a Cambridge Stereoscan 440 SEM equipped with Philips PV5800 EDS.

3. Results and discussion

The catalyzed hydride powders obtained after 20 h milling display a homogeneous distribution of the additive particles, which can be well distinguished from the MgH_2 in the SEM image of sample 10 cat reported in Fig. 1. The white spots, with size not exceeding 1 μm, are due to the elastic collisions of backscattered electrons with the heavy nuclei of zirconium, while the grey weak region is due to the light nuclei of magnesium hydride.

3.1. Activation of samples

Ten cycles of hydrogen a/d at 250 °C were performed for the activation of all samples and an extra cycle at 300 °C in the special case of sample 3 cat. The result of the activation cycles was a stabilized absorption kinetics. In Fig. 2 are shown the absorption curves for the 1st, 5th, and 10th cycles of sample 10 cat at 250 °C and 10 bar. The hydrogen absorbed within 1 min was 4.8, 5.2 and 5.7 wt%, respectively, which is an increment of 19% after 10 cycles. This can be due to the mechanical stress produced by expansion and contraction during cycling that may comminute the magnesium particles by cracking and change their surface extension and characteristics. This transformation may allow hydrogen to react with material that was previously inaccessible. Dehouche et al. suggested that in their Zr–Ni doped compounds rougher surfaces may be due to the formation of nanochannels that facilitate the hydrogen access to the particle bulk [11]. The improvement continues up to 10 cycles and then a steady state is reached, as seen with subsequent cycles from the 10th to 16th. The need of a/d cycles to reach the optimal sorption properties has been reported for other Mg-based hydrides (e.g. the Mg + Mg_2Ni composite [5]).

The milling and activation processes also introduce changes in the crystalline structure and chemical composition. In Fig. 3, the XRD patterns of an as-milled (bottom) and an activated (top) hydrided sample are shown. The broad peaks of the as milled sample are due to the reduced size of the grains, the lattice strain and the structural defects produced by high energy milling. There is a major contribution of β–MgH_2 and a lower one of γ–MgH_2: the former is the equilibrium phase of magnesium hydride, the latter is a high pressure metastable phase typically generated by milling. The pattern exhibits low intensity peaks of pure Mg, present in the commercial magnesium hydride, and also a peak of Mg_2Ni. The Mg_2Ni may be originated by a mechanically driven solid-state displacement reaction, where Ni moves from the Zr_8Ni_{21} additive into MgH_2. The Mg_2Ni formation was also found by other authors in similar experiments [5,11]. Little contributions of MgO by air contamination during material handling, milling process or X-ray measurements cannot be ruled out.

After activation with hydrogen a/d cycles, the diffraction peaks of a hydrided sample are sharper, this fact being due to the relaxation of strain and reduction of structural defects. The disappearance of γ-MgH_2 peaks testifies that magnesium hydride relaxed completely to the β-phase. The increment in Mg_2Ni intensity and formation of Mg_2NiH_4 indicate that Ni continues reacting with Mg during a/d cycling. The peak of ZrH_2, not observed in the as-milled sample, may be produced by the remaining Zr after the mentioned Mg–Ni reaction, the possibility of which is also suggested by the experiments of Ebrahimi-Purkani and Kashani-Bozorg on ball-milled Mg and Ni [14]. Their differential scanning

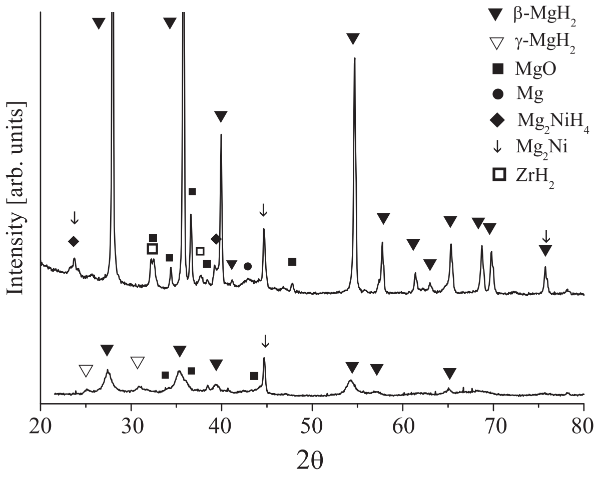

Fig. 3. Diffraction patterns of MgH_2–10 wt% Zr_8Ni_{21} as-milled (bottom) and hydrided after cycling (top).