ELSEVIER

Journal of Alloys and Compounds 463 (2008) 539–545

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Influence of particle size on electrochemical and gas-phase hydrogen storage in nanocrystalline Mg

O. Friedrichs[a,b,*], L. Kolodziejczyk[a], J.C. Sánchez-López[a], A. Fernández[a], L. Lyubenova[c], D. Zander[c], U. Köster[c], K.F. Aguey-Zinsou[d], T. Klassen[d], R. Bormann[d]

[a] *Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Avda. Américo Vespucio 49, 41092 Seville, Spain*
[b] *EMPA Materials Sciences and Technology, Department of Environment, Energy and Mobility, Div. "Hydrogen and Energy", Überlandstrasse 129, CH-8600 Dübendorf, Switzerland*
[c] *Department of Biochemical and Chemical Engineering, University of Dortmund, D-44221 Dortmund, Germany*
[d] *Institute for Materials Research, GKSS Research Centre, Max-Planck-Street 1, 21502 Geesthacht, Germany*

Received 3 June 2007; received in revised form 21 September 2007; accepted 21 September 2007
Available online 29 September 2007

Abstract

Nanocrystalline Mg powders of different particle size were obtained by inert gas evaporation and studied during electrochemical and gas-phase hydrogen cycling processes. The samples were compared to dehydrided samples obtained by mechanical milling of MgH_2 with and without 2 mol% Nb_2O_5 as catalyst. The hydrogen overpotential of the pure Mg, which is a measure of the hydrogen evolution at the electrode surface, was observed to be reduced with smaller particle sizes reaching values comparable to samples with Nb_2O_5 additive. On the other hand gas-phase charging experiments showed the capacity loss with smaller particle sizes due to oxidation effects. These oxidation effects are different depending on the synthesis method used and showed a major influence on the hydrogen sorption kinetics.

Keywords: Hydrogen storage; Metal hydrides; Nanocrystalline magnesium hydride; Electrochemical; Gas-phase; Kinetics

1. Introduction

Magnesium as a light, abundant and cheap metal with high hydrogen capacity of 7.6 wt.% is a very attractive material for hydrogen storage. Hydrogen charging can hereby be performed from the gas-phase [1] or in solution by electrochemical methods [2,3]. The disadvantage of using Mg in the gas-phase however lies in the slow sorption kinetics and the high thermodynamic stability of the MgH_2, which demand high temperatures (>300 °C). In the case of the electrochemical hydrogenation the corrosion behavior of Mg in electrolytes reduces the hydrogen capacity and kinetics as well as the cycle stability.

By using nanocrystalline MgH_2 obtained by mechanical milling [4–6] with transition metal oxides as milling additives [7–11] big improvements of the sorption kinetics have been achieved for the sorption kinetics. Nb_2O_5 has been shown to behave as one of the best additives [12,13] for hydrogenation in the gas-phase at the present time, and has been demonstrated to catalyze significantly also the electrochemical charging process as reported in [14]. The mechanism however is not yet understood. One of many possible explanations for the sorption improvement is the particle size reduction and formation of MgH_2 nanoparticles due to the Nb_2O_5 [15,16]. The milling additive helps to break the MgH_2 particles and avoids its agglomeration leading to cold welding during the milling process.

The aim of the present work was to investigate the influence of the Mg particle size on the hydrogen sorption mechanisms by electrochemical and gas-phase methods. Therefore samples of variable size prepared by inert gas evaporation technique (IGE), which consist of ultrafine Mg nanoparticles, were compared to samples synthesized by high energy ball milling (BM) with and

---

* Corresponding author at: EMPA Materials Sciences and Technology, Department of Environment, Energy and Mobility, Div. "Hydrogen and Energy", Überlandstrasse 129, CH-8600 Dübendorf, Switzerland. Tel.: +41 823 4153; fax: +41 823 4022.

E-mail address: oliver.friedrichs@empa.ch (O. Friedrichs).

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.09.085

Table 1
Overview of samples analyzed in the presented work

Sample type	Label	Preparation method	Analysis
Commercial (Mg rod)	Mg bulk	–	PM
BM	BM-Mg	BM of MgH_2 + dehydrogenation	PM
	BM-Mg/Nb_2O_5	BM of MgH_2/Nb_2O_5 + dehydrogenation	PM
	BM-MgH_2	BM of MgH_2	XRD
IGE	IGE700-Mg	IGE of Mg at 700 °C	TEM, HS, PM
	IGE900-Mg	IGE of Mg at 900 °C	TEM, HS, PM
	IGE700-MgH_2	IGE of Mg at 700 °C + hydridation	XRD
	IGE900-MgH_2	IGE of Mg at 900 °C + hydridation	XRD

BM: ball milling; IGE: inert gas evaporation; PM: polarization measurements; HS: hydrogen sorption measurements; XRD: X-ray diffraction; TEM: transmission electron microscopy.

without Nb_2O_5 as milling additive with respect to their electrochemical properties and their gas-phase sorption behavior.

2. Experimental

2.1. Sample preparation

The samples studied in this paper were prepared by two different methods, the inert gas evaporation and the high energy ball milling. An overview of the samples and the corresponding analysis methods is presented in Table 1.

The IGE method was performed by thermal evaporation of Mg (supplied by Aldrich with purity >99.98%) in a He gas atmosphere of 3 Torr and by collecting the powder (IGE-Mg) on a nitrogen-cooled container and subsequent transfer of the sample in He to the glove box as described in [17].

The milling was done under argon atmosphere (<10 ppm water and oxygen) with a Fritsch P5 planetary mill applying 100 g Cr-hardened balls as milling tools within a 300 ml stainless steel vial. MgH_2 (purchased from Goldschmidt AG with purity >95% (rest being Mg)) was milled for 20 h (BM-MgH_2) and additional milled for 100 h with Nb_2O_5 additive (BM-Mg/Nb_2O_5, 2 mol% Nb_2O_5, supplied by Sigma–Aldrich with purity >99.99%). The ball to powder ratio was 10/1.

For the electrochemical experiments the BM-MgH_2 samples were first dehydrogenated at 300 °C. The obtained BM-Mg or the as-produced IGE-Mg is then compacted with 5 wt.% graphite and 5 wt.% PTFE to a pressed pellet electrode suitable for electrochemical hydrogenation (compaction pressure of 6.2 N/mm^2). Thereby the polymer (PTFE) was chosen to increase the void fraction for hydrogen transport and the graphite to enhance conductivity, which results in higher capacity and improved hydrogen kinetics as shown in [18]. The electrode preparation was performed inside the glove box under pure Ar atmosphere. Since the preparation by IGE is very complex and the yield of sample is very low only the electrochemical characterization of the IGE700-Mg sample by potentiodynamic polarization was done up to now. For comparison the obtained results are compared to a bulk Mg rod.

2.2. Sample characterization

The microstructural characterization was carried out by X-ray diffraction (XRD) with a Bruker D8 advance X-ray diffractometer using Cu Kα radiation in conventional Bragg–Brentano configuration and by transmission electron microscopy (TEM) and electron diffraction (ED) in a Philips CM200 with 200 kV electron acceleration voltage and a point-to-point resolution of 0.24 nm. For the TEM analysis the nanocrystalline Mg powder was dispersed in toluene as protective agent against oxidation before introduction in the pre-vacuum chamber of the microscope [19].

The potentiodynamic polarization curves were obtained using a FAS1 potentiostat (Gamry Instruments) with a voltage scan rate of 1 mV/s. For all measurements a three-electrode electrochemical cell was used with an Hg/HgO reference electrode and a platinum counter electrode. All the potential values are reported with respect to the Hg/HgO reference electrode. The electrochemical tests using the DC (potentiodynamic polarization) technique were carried out in a de-aerated, not stirred, 6 M KOH electrolyte at 25 °C. The samples were embedded in a thermoplastic resin to provide electrical isolation. Sample surfaces were ground with a 1200 grid SiC-emery paper and ethanol.

The kinetic sorption measurements from the gas-phase were carried out by a volumetric Sievert apparatus designed by HERA Hydrogen Storage Systems [20]. The measurements consisting of hydrogen absorption and desorption cycles were performed at 300 °C and 1 MPa of hydrogen pressure for absorption and 0.1 kPa of hydrogen pressure for desorption. Therefore the samples of about 100 mg were loaded into a reactor under argon atmosphere and transferred to the Sievert apparatus without air exposure.

3. Results and discussion

3.1. Microstructural characterization of IGE samples by TEM

Compared to samples prepared by high energy milling, with particle sizes ranging from about 0.1 μm to 1 μm [19], the magnesium synthesized by IGE displays a different microstructure that consists of isolated particles of variable size and shapes depending on the evaporation temperature. At 700 °C (IGE700-Mg), the particles are almost spherical, single-crystal and well dispersed with an average diameter of about 35 ± 8 nm (see Fig. 1a).

Fig. 1b shows the analysis of Mg powder prepared by inert gas evaporation at a higher synthesis temperature of 900 °C (IGE900-Mg). Here the spherical particles (from the synthesis at 700 °C) are replaced by platelets or particles with isometric shapes of hexagonal symmetry as schematically illustrated in Fig. 1c. The particle size distribution of Fig. 1b shows the variation of hexagonal diameter and width of these particles. The comparison of the particle size histograms for both samples illustrates the increase in particle size and dispersion with the increment in synthesis temperature. In other words, the particle size distribution is less homogeneous and the mean value increases substantially with the increment of evaporation temperature during the gas-phase condensation. A characteristic selected area electron diffraction pattern (SAED) is represented in Fig. 1d. The rings observed in the SAED can be assigned to polycrystalline magnesium metal together with a magnesium oxide phase. This latter phase is constituted by smaller nanocrystalline grains than the pure magnesium metal as can be concluded by the presence of diffuse diffraction rings of MgO appearing in the diffraction pattern.