INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 37 (2012) 10724–10732

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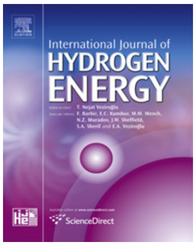

Mg_3Cd: A model alloy for studying the destabilization of magnesium hydride

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ARTICLE INFO

Article history:
Received 31 January 2012
Received in revised form
3 April 2012
Accepted 12 April 2012
Available online 17 May 2012

Keywords:
Magnesium alloys
Hydrogen storage properties
Hydride destabilization
High energy ball milling
Thermodynamics of alloys

ABSTRACT

We prepared an ordered Mg_3Cd alloy by high energy ball milling of elemental powders. The synthesized alloy exhibited good hydrogenation kinetics and reversibly absorbed about 2.8 wt. % of hydrogen. The temperature dependence of hydrogenation kinetics of the alloy measured in the range of temperatures covering the order-disorder phase transformations in the Mg_3Cd and MgCd phases did not exhibit any anomalies and could be fitted with a single Arrhenius line. The measured apparent activation energy (69 ± 2 kJ/mol) hinted that hydrogenation process was controlled by diffusion of Cd in metallic phase. The pressure-composition isotherms exhibited negligible pressure hysteresis and sloping pressure plateau. Based on microstructural evidence obtained with the aid of X-ray diffraction and scanning electron microscopy, we built a thermodynamic model predicting the plateau hydrogen pressure for partially hydrogenated alloy. The predictions of the model were in a good agreement with the experimental data. Finally, we discussed the origins and the growth mechanisms of Cd whiskers observed in the alloys after full hydrogenation cycle.

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1. Introduction

A great deal of attention in the field of mobile hydrogen storage was paid to Mg-based alloys because of their low cost, low density and high gravimetric hydrogen storage capacity (up to 7.6 wt% in pure Mg). However, very slow hydrogenation and dehydrogenation kinetics along with low desorption pressures at the temperatures of interest (100–200 °C) make their application in automobile industry highly problematic. Numerous attempts to improve the hydrogen storage performance of pure Mg and Mg-based alloys by refinement of microstructure down to the nanometric level (mainly by high energy ball milling (HEBM)) combined with alloying with catalytic additions [1–5] were made. It was found that many catalytic additives to pure Mg (Ni, Ti, Fe, Pd, V, Nb_2O_5, CeO_2 and Mn) improve its hydrogenation kinetics significantly, provided that both Mg and an additive, or at least the additive, are present in the nanopowder form [3,4]. Additive atoms play the role of a catalyst assisting the dissociation of H_2 molecules on the surface and lowering the strength of Mg–H bonds [5]. However, all these attempts led to improvement of hydrogenation kinetics only and failed to change significantly the thermodynamics of Mg–H interaction. High enthalpy of formation of MgH_2 hydride makes the technical solutions for the rapid hydrogenation of large quantities of Mg problematic, since large amounts of heat released during hydride formation should be dissipated in a short time.

A promising approach to changing the thermodynamics of Mg–H interaction is thermodynamic destabilization of

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URL: http://materials.technion.ac.il/eugen-rabkin-metals-interfaces-diffusion/

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doi:10.1016/j.ijhydene.2012.04.065

hydride through the alloy or compound formation [1,6]. The high enthalpy of the direct dehydrogenation reaction

$$AH_2 \rightarrow A + H_2$$

can be significantly reduced by formation of AB_x compound or solid solution, provided that its formation from the mixture of A and xB is exothermic. The possibility of increasing the equilibrium hydrogen desorption pressure using Mg hydride destabilization has been demonstrated for Si, Ge, Cu, Ni, Al, Zn, Nb, Fe and Ta additions [7–11].

Cadmium is the only element exhibiting unlimited solubility in Mg in the solid state. Below 253 °C an ordered MgCd α'' phase is formed from the disordered Mg–Cd solid solution. Mg-rich alloys can form another α''' ordered phase, which forms according to the peritectoid reaction at 206 °C [12]. The formation enthalpies of the MgCd and Mg_3Cd phases are in the range of 5–7 kJ/mol [13,14] and, therefore, these phases can lower the formation/decomposition enthalpy of Mg hydride, provided that Mg liberated during hydride decomposition is swiftly absorbed in one of the ordered Mg–Cd phases.

Moreover, the Mg–Cd system is the only Mg-based system exhibiting order-disorder transformation in the temperature range relevant for the hydrogenation reaction. Previous studies of hydrogen diffusion in metals undergoing "paramagnetic-ferromagnetic" [15,16] or "order-disorder" [17] transformation demonstrated that an abrupt change of hydrogen diffusivity occurs in the vicinity of transformation temperature. Generally, the atomic structure of the alloy undergoing order-disorder transformation becomes highly dynamic, with the correlation length of heterophase fluctuations diverging at the transformation temperature [18]. The literature data demonstrate that such destabilization of the lattice may both accelerate and slow down atomic diffusion processes [19–21]. The acceleration of hydrogen diffusion either in the metallic or in the hydride phases may facilitate the absorption and desorption of hydrogen. Therefore, the Mg–Cd alloys represent a convenient model system for studying both the possibility of thermodynamic destabilization of magnesium hydride, and the effect of order-disorder transformation on the hydrogenation kinetics.

The first hydrogenation study of the Mg–Cd system was performed by Douglass [22]. The Mg-1 at.% Cd alloy synthesized in his work absorbed 5 wt. % of hydrogen in 24 h at 400 °C. The hydrogen desorption kinetics was very slow and the Mg–Cd system has been forgotten for the following 25 years.

Later, Liang and Schulz performed a more detailed study of the hydrogenation kinetics and thermodynamics of Mg with 5, 10 and 20 at. % of Cd [23]. The alloys were prepared by HEBM technique in the planetary ball mill. It was found that binary Mg–Cd alloy cannot be activated for hydrogen absorption even after annealing at 350 °C for 24 h under the hydrogen pressure of 1.5 MPa. Therefore, 2.5 at.% of V and 2 wt.% of C were added to the alloy for catalytic activation. These quaternary alloys exhibited fast hydrogen absorption/desorption kinetics and sloping pressure plateau in the "pressure-composition-temperature" (PCT) diagrams (i.e. the plateau pressure increased with increasing hydrogen content). However, increasing Cd contents compromised the maximal hydrogen storage capacity of the studied alloys. Moreover, the minimal temperature employed by Liang and Schulz was 280 °C, which is still above the highest order-disorder transformation temperature in the Mg–Cd system. Though the ordered MgCd and Mg_3Cd phases were detected in the X-ray diffraction (XRD) studies of the investigated alloys after hydrogen desorption, they most probably nucleated during cooling. The PCT diagrams determined by Liang and Schulz exhibited significant pressure hysteresis and this is why the thermodynamic parameters of hydrogenation reaction were not determined in their work.

The objective of this work was twofold: First, to determine the thermodynamic parameters of the hydrogenation reaction of the ordered Mg_3Cd alloy and to compare the obtained results with the prediction of a simple thermochemical model of hydride destabilization, and, second, to study the effect of order-disorder transformation in this alloy on the kinetics of hydrogenation.

2. Experimental

The Mg–25 at.% Cd alloy was prepared from a mixture of pure Mg and Cd by the HEBM technique. The Mg chips were produced by lathe machining from as-cast Mg sample of technical purity (99.5 wt.%, supplied by Dead Sea Magnesium Ltd., Israel). The Cd chips were produced from as-cast Cd granules (supplied by BDH Chemicals Ltd., UK, with Pb and Zn as major impurities with 0.02 and 0.01 wt.% content, respectively) by filing with a rasp. The Mg and Cd chips were first processed separately by HEBM (in Pulverisette-7 planetary ball mill of Fritsch GmbH) for 4 h. The ball to powder ratio was 25:1, and the HEBM was performed in hexane, to avoid the oxidation and agglomeration of the powders. Afterwards, the powders were blended and HEBM processed together for additional 10 h (in hexane).

The apparatus for measuring the Mg–Cd powders interaction with hydrogen was a closed volume Sieverts' system with computerized data acquisition set-up controlled by LABView software. The powder samples of about 1 g in weight were placed in stainless steel reactor with internal volume of 16.0 cm^3. The reactor was heated by an external resistance furnace that maintained a constant temperature with the accuracy of 0.5 °C. The mass ratio of the sample and the hot reactor was approximately 1:200. The temperature of the powder sample was determined by an embedded chromel–alumel thermocouple with the accuracy of 0.5 °C.

Desorption of hydrogen in the evacuated volume (initial residual pressure of about 10 mTorr) was studied by measuring the changes in gas pressure. For determining the apparent activation energy for hydrogen absorption, the fraction of absorbed hydrogen, α, was determined from the change of hydrogen pressure in the reactor during hydrogen absorption. The kinetic constant, k, was determined under the assumption of a first order hydrogenation reaction employing the following relationship: $kt = -\ln(1-\alpha)$, where t is the

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