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### Journal of Alloys and Compounds

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# Enhanced dehydriding thermodynamics and kinetics in Mg(In)–MgF<sub>2</sub> composite directly synthesized by plasma milling



ALLOYS AND COMPOUNDS

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### ARTICLE INFO

Article history: Received 23 August 2013 Received in revised form 4 October 2013 Accepted 4 October 2013 Available online 16 October 2013

Keywords: Hydrogen storage Magnesium alloys Thermodynamics Kinetics

### ABSTRACT

The reversible formation of Mg(In) solid solution provides a new way to tune the dehydriding thermodynamics of MgH<sub>2</sub>. However, the preparation of this solid solution is quite difficult and its dehydriding kinetics is rather sluggish. This work offers a novel technique, plasma milling (P-milling), to solve the two problems simultaneously. The efficiency of the synthesis of Mg(In) solid solution, with a hydrogen capacity of up to 5.16 wt.%, is improved significantly. Meanwhile, the kinetics is also modified by the catalyzing effect of *in situ* synthesized MgF<sub>2</sub>.

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### 1. Introduction

Hydrogen storage systems have been considered as potential solutions for the dwindling fossil fuel resources and growing environmental problems [1,2]. Among them, MgH<sub>2</sub> has shown promise as an energy carrier medium due to its high hydrogen content (7.6 wt.%) and low cost [3,4]. However, its on-board applications are obstructed by sluggish desorption kinetics and high thermodynamic stability ( $\Delta H$  = 75 kJ/mol H<sub>2</sub>). The dehydrogenation of MgH<sub>2</sub> requires a high temperature (>350 °C), and the hydrogenation of Mg without catalysts is very difficult which generally needs a temperature higher than 300 °C and pressure more than 20 bar [5].

During the past decades, considerable efforts have been devoted to destabilizing Mg-based systems, aiming either at improving the kinetic properties or decreasing the reaction enthalpy change. Different approaches have been explored, which have mainly involved alloying [6,7], nanostructuring [8,9], doping with catalytic additives [10–15] or surface modification [16–18]. Of these strategies, doping with F-containing species led to superior catalysis through improving both the hydrogen absorption and desorption kinetics of MgH<sub>2</sub> [19–22]. Park et al. [22] reported that MgH<sub>2</sub> catalyzed with NbF<sub>5</sub> could release 5 wt.% H<sub>2</sub> after being exposed to air for even as long as 24 h because the addition of NbF<sub>5</sub> could form protective layers on the surfaces of MgH<sub>2</sub> particles, which contributed to the mitigation of degradation in the dehydrogenation behavior of air-exposed MgH<sub>2</sub>. Meanwhile, surface treatment with fluoride resulted in the formation of magnesium fluoride (MgF<sub>2</sub>) on the particle surface of Mg-based alloys, which also effectively improved their surface activity and promoted the hydriding kinetics under conditions of low temperature and pressure [16–18]. Although the hydrogenation and dehydrogenation kinetics of these F-containing Mg-based alloys have been dramatically improved, their high thermodynamic stabilities remain almost unchanged, and a low dehydrogenation pressure at ambient temperature is required for their hydrogen desorption.

In recent works, it has been found that the desorption enthalpy change of MgH<sub>2</sub> could be substantially altered by reversibly forming an Mg(In) or Mg(In, Y) solid solution during dehydrogenation [23,24], but the kinetic properties of these solid solution systems were rather sluggish. The dehydrogenation activation energy of Mg(In) solid solution was even as high as 161 kJ/mol. Thus, improving its kinetic properties would be significantly beneficial for making use of this thermodynamic tuning effect. Zhou et al. [5] found that adding the Ti intermetallic alloys as catalysts could significantly improve both dehydrogenation and hydrogenation kinetics of MgH<sub>2</sub>, especially for TiMn<sub>2</sub>-doped Mg system, which demonstrated extraordinary hydrogen storage properties at room temperature and 1 bar hydrogen pressure. Subsequently, they used this catalyst to catalyze the dehydriding kinetics of Mg(In) solid

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 $<sup>0925\</sup>text{-}8388/\$$  - see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jallcom.2013.10.029

solution, and found that this thermodynamic destabilized Mg-0.1In alloy showed excellent dehydrogenation kinetics: this catalyzed alloy began to dehydrogenate at approximately 100 °C and was fully dehydrogenated at 150 °C within 3 h [25], which realized the thermodynamic and kinetic destabilization of MgH<sub>2</sub> simultaneously. Additionally, as Zhong's report [23], the synthesis of Mg(In) solid solution requires the combination of prolonged sintering and ball milling due to the quite different atomic radii between the soft metal In (1.93 Å) and Mg (1.73 Å) [23]. Through the above analysis, it would be very valuable to find a simple way to synthesize Mg(In) solid solution and to combine it with the effective catalyst doping.

In previous works [26,27], dielectric barrier discharge plasmaassisted milling (P-milling), a new material processing method, has been reported. It showed much higher mechanical alloying efficiency, and may thus provide a new means of synthesizing Mg-based alloys. In this work, P-milling has been used to synthesize Mg(In) solid solution. On the other hand, polytetrafluoroethylene has been deployed in the milling process in a certain way to realize the *in situ* formation of MgF<sub>2</sub> catalyst in Mg(In) solid solution. By this new method, the effective synthesis of Mg(In) solid solution and catalyst doping have been achieved simultaneously. The Mg(In)–MgF<sub>2</sub> composite exhibited greatly improved hydrogen desorption thermodynamics and kinetics. The present work provides a new strategy for simultaneous tuning of the thermodynamics and kinetics of Mg-based hydrogen storage alloys.

#### 2. Experimental details

Mg and ln powders (both with a purity of 99.9%, 200 mesh) were mixed in a molar ratio of 95:5. This powder mixture was loaded together with steel balls into a cylindrical stainless steel vial filled with high purity argon (0.1 MPa), and the ball-to-powder weight ratio was chosen as 30:1. The vial was vibrated for 2 h at a double amplitude of 10 mm and a frequency of 25 Hz. The dielectric barrier discharge plasma was generated by high-voltage (24 kV) alternating current at a frequency of 12 kHz. Polytetrafluoroethylene was introduced to induce the *in situ* formation of MgF<sub>2</sub> catalyst. Before milling, all sample handlings were performed in a glovebox with a moisture content of less than 3 ppm and an oxygen content of less than 5 ppm.

The microstructures of all of the samples were characterized by X-ray diffraction analysis (XRD, Philips X'pert-MPD) using Cu K $\alpha$  radiation ( $\lambda$  = 0.15406 nm). Lattice constants were calculated from the XRD data by the Rietveld model employing highscore software. As the lattice parameter was the only variable during the transformation between Mg and Mg(In) solid solution, here we only considered the refinement information of Mg in the XRD profile. Before the measurements, a high purity (99.9999%) silicon wafer was used to calibrate the instrumental zeroshift. Scanning electron microscopy (SEM) was carried out on a Philips XL-30 FEG equipped with an EDX accessory. Differential scanning calorimetric (DSC) analysis was performed using a NETZSCH STA409PC at a heating rate of 2 K/min. The hydrogen desorption properties were evaluated using a Sieverts-type automatic gas reaction controller (Pct Pro2000). Samples of about 0.3 g were used for these measurements, and the reaction cell was inductively heated with an accuracy of ±1 K.

### 3. Results and discussion

### 3.1. Phase transition of the Mg–In–F system during hydrogenation and dehydrogenation

Fig. 1 shows the XRD patterns of the Mg–In–F system at different stages. The diffraction peaks of the In phase could be clearly identified in the initial powder mixture (Fig. 1a), and it should be noted that no F was present in the sample before milling. Fig. 1b shows the XRD pattern of Mg–In powder after P-milling for 2 h. It can be observed that the In peaks disappeared and peaks attributable to Mg<sub>5</sub>In<sub>2</sub> and Mg<sub>2</sub>In developed. Lattice constant calculations showed that those of Mg decreased slightly from a = 0.32098(6) nm, c = 0.52016(0) nm in the initial powder mixture to a = 0.32091(1) nm, c = 0.52099(5) nm in the P-milled product, which indicated that part of the In had dissolved in the Mg to form



**Fig. 1.** XRD patterns for Mg–In–F system at different stages: (a) the mixture of the Mg and In, (b) P-milling for 2 h, (c) the first hydrogenated sample, (d) the first dehydrogenated sample, (e) hydrogenated product after 10 hydrogenation/dehydrogenation cycles, and (f) dehydrogenated product after 10 cycles.

Mg(In) solid solution, besides the formation of  $Mg_5In_2$  and  $Mg_2In$ . This outcome was consistent with the results of Zhong et al. [23] and Busk [28], who also noted that the incorporation of In led to a decrease in the lattice constants of the host Mg. More importantly, as initially designed, MgF<sub>2</sub> was formed due to the reaction between Mg and polytetrafluoroethylene under the influence of the plasma-assisted ball milling process. The amount of MgF<sub>2</sub> was approximately 12.9 wt.%, as determined from an XRD profile refinement. Fig. 1c shows the XRD pattern of P-milled Mg-In-F powder after the first hydrogenation at 623 K. Compared with the pattern of the P-milled product, the diffraction peaks of Mg(In) solid solution, Mg<sub>5</sub>In<sub>2</sub> and Mg<sub>2</sub>In disappeared, while peaks due to MgH<sub>2</sub> and MgIn ( $\beta''$ ) phase with L1<sub>0</sub>-structure appeared. It could be concluded that Mg(In) solid solution, Mg<sub>5</sub>In<sub>2</sub>, and Mg<sub>2</sub>In phases were transformed into  $MgH_2$  and  $\beta''$ , while the  $MgF_2$  phase remained unchanged. Fig. 1d shows the XRD pattern of the dehydrogenated sample. After dehydrogenation, the  $\beta''$  phase had disappeared and no In-containing phases had emerged. Meanwhile, calculation showed that the lattice constants of the Mg phase further decreased to a = 0.32071(7) nm, c = 0.52099(4) nm, which suggested that an Mg(In) solid solution with an increased solubility of In had been recovered through reaction of the  $\beta''$  phase and MgH<sub>2</sub>. MgF<sub>2</sub> was stable even when the operation temperature was above 1573 K [29,30]. Fig. 2 shows SEM images of the Mg(In)-MgF<sub>2</sub> composite. The morphology of this composite was largely composed of flocculent structures. Very fine MgF<sub>2</sub> particles  $(\sim 300 \text{ nm})$  were separated out along the bulk Mg(In). Fig. 3 shows the element mapping of this Mg(In)-MgF<sub>2</sub> particle. The mapping results showed that MgF<sub>2</sub> was uniformly dispersed in the Mg(In)–MgF<sub>2</sub> composite, and its grain size was 38.6 nm, as calculated from the XRD data by the Rietveld method. These results showed that the P-milling method yielded an Mg(In) solid solution with an in situ synthesized MgF2 phase homogeneously distributed



Fig. 2. SEM images of (a) Mg(In)-MgF<sub>2</sub> composite and (b) its partial enlargement.



Fig. 3. (a) The mapping results of the Mg(In)-MgF<sub>2</sub> composite, and the element distribution of (b) Mg, (c) F, (d) In, respectively.

within it. Fig. 1e and f show the XRD patterns for the hydrogenation and dehydrogenation products of the Mg–In–F system after ten hydrogenation/dehydrogenation cycles at 623 K, respectively. These patterns confirmed that the products after ten cycles were stable and identical to those from the first hydrogenation/dehydrogenation.

Based on the above structural analysis, an alloy containing Mg(In) solid solution, Mg<sub>5</sub>In<sub>2</sub>, Mg<sub>2</sub>In and MgF<sub>2</sub> was obtained after P-milling, then transformed into MgH<sub>2</sub>,  $\beta''$ , and MgF<sub>2</sub> phases after hydrogenation, and finally reverted to Mg(In)–MgF<sub>2</sub> composite following dehydrogenation. The reaction mechanism can be expressed as follows:P-milling:

 $Mg+In+(C_2F_4)_n \rightarrow Mg(In)+Mg_5In_2+Mg_2In+MgF_2$ 

1st hydrogenation:

 $Mg(In) + Mg_5In_2 + Mg_2In + H_2 \rightarrow MgH_2 + \beta''$ 

Following hyd./dehyd. cycles:

 $Mg(In) + H_2 \leftrightarrow MgH_2 + \beta''$ 

To further reveal the reaction temperature and mechanism, DSC curves of the hydrogenated product and pure MgH<sub>2</sub> were measured, and the results are shown in Fig. 4. The endothermic peak of the hydrogenated product of Mg(In)–MgF<sub>2</sub> composite was obviously broader than that for pure Mg, suggesting an overlap of multi-step reactions upon dehydrogenation, i.e., decomposition of MgH<sub>2</sub> and dissolution of the  $\beta''$  phase in Mg to form Mg(In) solid solution. This result is consistent with the results of Zhong et al. [23] and Luo et al. [24], who found the endothermic peaks of both Mg(In) binary and Mg(In, Y) ternary solid solutions to be broader than that of pure Mg. Furthermore, the hydrogenated Mg(In)–MgF<sub>2</sub> composite showed a decrease in the decomposition temperature compared with pure MgH<sub>2</sub>, indicating tuning of the dehydriding thermodynamics and kinetics of MgH<sub>2</sub>.

## 3.2. Dehydriding thermodynamic properties of $Mg(In)-MgF_2$ composite

Fig. 5a shows the pressure-composition isotherm (PCI) curves for hydrogen desorption from the  $Mg(In)-MgF_2$  composite and pure  $MgH_2$ . It is impressive that the decomposition equilibrium



**Fig. 4.** DSC curves for (a) Pure  $MgH_2$ , (b) hydrogenated  $Mg(In)-MgF_2$  composite, (c) hydrogenated Mg(In) solid solution [23] and (d) hydrogenated Mg(In, Y) solid solution [24], with a heating rate of 2 K/min.



Fig. 5. (a) PCI curves for the hydrogen desorption of the  $Mg(In)-MgF_2$  composite and pure  $MgH_2$ , (b) Van't Hoff plots of the  $Mg(In)-MgF_2$  composite, pure  $MgH_2$ , Mg(In) [23] and Mg(In, Y) [24] solid solutions.

pressures of this system were much higher than that of pure MgH<sub>2</sub> at the same temperature, which confirmed the thermodynamic destabilization indicated by the DSC analysis. Based on the PCI data, Van't Hoff plots for this sample and MgH<sub>2</sub> were obtained, and the results are shown in Fig. 5b. Van't Hoff plots from refes [23,24] are also presented for comparison. The  $\Delta H$  for the dehydrogenation of the hydrogenated Mg(In)–MgF<sub>2</sub> composite was calculated as 69.2 kJ/mol H<sub>2</sub>, which is comparable to the experimental (68.1 kJ/mol H<sub>2</sub>) and calculated (67.8 kJ/mol H<sub>2</sub>) values obtained by Zhong et al. [23]. Although the experimental value for MgH<sub>2</sub> (79.1 kJ/mol H<sub>2</sub>) slightly deviated from the standard value (75 kJ/mol H<sub>2</sub>) due to experimental error or a different type of Mg pow-

der, the Mg(In)–MgF<sub>2</sub> composite had a much lower  $\Delta H$  than that of pure Mg. According to the above results, the improved thermodynamics and related mechanism of the present Mg-In system incorporating MgF<sub>2</sub> should be the same as those for the Mg(In) solid solution reported by Zhong et al. [23]. The incorporation of MgF<sub>2</sub> had no influence on the dehydriding thermodynamics. In addition, we would like to point out that the system still had a high hydrogen storage capacity of 5.16 wt.% at 609 K.

### 3.3. Dehydriding kinetic properties of Mg(In)–MgF<sub>2</sub> composite

In addition to the above thermodynamic tuning, the kinetics was also greatly improved in the present work. Fig. 6a displays the hydrogen desorption curves for the hydrogenated Mg(In)–MgF<sub>2</sub> composite compared with that for pure MgH<sub>2</sub>. At 623 K, the composite could release the stored hydrogen in less than 30 min, whereas for MgH<sub>2</sub> the dehydrogenation process was incomplete even after 120 min. The activation energy for the dehydrogenation process of Mg(In)–MgF<sub>2</sub> was obtained by fitting the isothermal dehydriding curves at different temperatures using the Johanson–Mehl–AvramiKolmogorov (JMAK) equation [31–33]:

$$\ln[-\ln(1-\alpha)] = \eta \ln t + \eta \ln k \tag{1}$$

where  $\alpha$  is the reaction fraction, *k* is the rate constant, and  $\eta$  is the Avrami exponent. The hydrogen desorption fraction ranging from 0.2–0.5 was adopted to fit the kinetic curves. The Avrami exponent  $\eta$  was in the range 1.10 to 2.41, implying that the dehydrogenation reaction for the sample followed a diffusion-controlled mechanism [31,32,34]. The values of *k* were applied to calculate the dehydrogenation activation energy according to the Arrhenius equation. As shown in Fig. 6b (1),  $E_a$  for the dehydrogenation was calculated to be 127.7 kJ/mol, much lower than the values for pure MgH<sub>2</sub> (~160 kJ/mol) [35-38], Mg(In) binary (161 kJ/mol) [23], and Mg(In, Y) ternary solid solution (147.41 kJ/mol) [24]. To further verify the reaction mechanism and the obtained dehydrogenation activation energy, the observed dehydrogenation rate curves were also fitted using the rate equations proposed by Li et al. [39]. As shown in Fig. 6b (2), the activation energy fitted by the Jander diffusion model was 125.7 kJ/mol, in good agreement with the result from the JMAK model. This also provides strong evidence that the rate-limiting step of the desorption process follows the diffusion-controlled mechanism as proposed by the JMAK model.



**Fig. 6.** (a) Dehydriding kinetic curves for the hydrogenated  $Mg(In)-MgF_2$  composite, (b): (1) and (2) are the Arrhenius plots fitted by the JMAK model and the Jander diffusion model, respectively.

As is well known, the poor dehydriding kinetics arises from the poor permeability of the  $MgH_2$  layer to H atoms. By P-milling,  $MgF_2$  particulates were formed *in situ* and dispersed homogeneously in the Mg–In–F system (Fig. 3). Upon hydrogenation, some cracks were produced along the interfaces of  $MgH_2$  and  $MgF_2$ , thus providing channels for hydrogen diffusion in the dehydriding process [16–18]. More importantly, these  $MgF_2$  particulates, which exhibit an extremely high affinity for H-uptake, expedite hydrogen diffusion to the surface of the hydride [16–18], thus decreasing the energy barrier for decomposition. That is to say, they are responsible for the improvement of the dehydrogenation kinetics. We would like to emphasize that this effect of the  $MgF_2$  was enhanced by its dispersed distribution that resulted from its *in situ* formation.

### 4. Conclusions

In summary, P-milling of an Mg–In–F system has been shown to simultaneously accomplish efficient synthesis of Mg(In) solid solution and *in situ* generation of the catalyst MgF<sub>2</sub> as a dispersed dopant. The time required for the synthesis process of Mg(In) solid solution was decreased to 2 h due to the effect of the plasma. The dehydrogenation activation energy ( $E_a$ ) of Mg(In) solid solution was reduced to 127.7 kJ/mol because of the catalytic effect of the *in situ* formed MgF<sub>2</sub>, and so the addition of other catalysts was unnecessary. At the same time, the system maintained a high hydrogen storage capacity of 5.16 wt.% at 609 K and the thermodynamic destabilization was the same as that obtained in the Mg-In system.

### Acknowledgements

This work was financially supported by the Ministry of Science and Technology of China (No. 2010CB631302), the National Natural Science Foundation of China (Nos. U1201241, 51271078 and 50925102) and KLGHEI (KLB11003).

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