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Mechanochemical synthesis of nanostructured chemical hydrides in hydrogen alloying mills

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Abstract

Mechanical alloying of magnesium metal powders with hydrogen in specialized hydrogen ball mills can be used as a direct route for mechanochemical synthesis of emerging chemical hydrides and hydride mixtures for advanced solid-state hydrogen storage. In the 2Mg–Fe system, we have successfully synthesized the ternary complex hydride Mg_2FeH_6 in a mixture with nanometric Fe particles. The mixture of complex magnesium-iron hydride and nano-iron released 3–4 wt.%H_2 in a thermally programmed desorption experiment at the range 285–295 °C. Milling of the Mg–2Al powder mixture revealed a strong competition between formation of the Al(Mg) solid solution and the β-MgH_2 hydride. The former decomposes upon longer milling as the Mg atoms react with hydrogen to form the hydride phase, and drive the Al out of the solid solution. The mixture of magnesium dihydride and nano-aluminum released 2.1 wt.%H_2 in the temperature range 329–340 °C in the differential scanning calorimetry experiment. The formation of MgH_2 was suppressed in the Mg–B system; instead, a hydrogenated amorphous phase $(Mg,B)H_x$, was formed in a mixture with nanometric MgB_2. Annealing of the hydrogen-stabilized amorphous mixture produced crystalline MgB_2.

Keywords: Hydrogen storage materials; Nanostructures; Amorphous materials; Magnesium diboride; High-energy ball milling; Mechanochemical synthesis; X-ray diffraction; Differential scanning calorimetry

1. Introduction

Mg metal exhibits a high-storage capacity by weight (7.6 wt.%H_2) in MgH_2 hydride and has been considered a candidate for solid-state hydrogen storage in fuel cell for cars. However, its high-thermodynamic stability, high-desorption temperature, low-plateau pressure, and slow sorption kinetics preclude its use. Nanocrystalline MgH_2, prepared in laboratory high-energy ball mills shows improved kinetics of sorption–desorption, yet the storage of hydrogen in magnesium metal still needs development of new compositions and processes. Several studies on hydrogenation of Mg–Fe mixtures have been reported, all of them targeting the synthesis of Mg complex hexahydroferrate, Mg_2FeH_6 (containing 5.5 wt.%H_2). This hydride has usually been synthesized by mechanical activation of powders followed by sintering in a hydrogen atmosphere [1,2], and in a single process by reactive mechanical alloying under hydrogen at room temperature [3,4]. However, the yield of these reactions must still be improved. Magnesium tetrahydroaluminate, $Mg(AlH_4)_2$ contains 9.3 wt.%H_2. However, little is known about this alanate and its synthesis has been conducted via an indirect reaction in organic solvents, from which it crystallizes as an impure compound [5].

We have recently reported on the use of a controlled reactive mechanical alloying (CRMA) route towards development of hydrogen storage media based on Mg–Fe [6] and Mg–Al [7] systems. In the present work, we recapitulate our findings with these two systems, and add new results on another Mg–B system.

2. Experimental

2.1. Mechanical milling in hydrogen alloying mill

The reagent grade (Alfa Aesar) fine elemental powders of Mg with purity better than 99.8% were used for preparation of a stoichiometric 2Mg–Fe mixture for reactive mechanical alloying with hydrogen to form Mg_2FeH_6 complex hydride. The cast Mg–2Al alloy from an experimental foundry (CANMET, Ottawa) was crushed and used for milling with intent to form $Mg(AlH_4)_2$ alanate. Mechanical milling was carried out in a Uni-Ball Mill 5 (A.O.C. Sci. Eng. Pty, Australia) using a controlled energy impact mode [6,7] under 3200 impacts per minute, in

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the mill cylinder rotating at 200 rpm with four hardened steel balls. The ball-to-powder ratio was as 40:1 and the milling time varied from 1 to 300 h. The pressure of the H_2 gas was adjusted sequentially during the milling to maintain a pressure of 880 kPa, after the hydrogen was absorbed in the powders. Small powder samples were collected at various times of milling for microstructural XRD and thermal DSC analysis. The processing details for milling Mg–2Fe and 2Mg–Al powders were given in our previous publications [6,7].

2.2. Materials characterization

The crystalline structure of as-milled and reference powders were characterized by Rigaku Rotaflex D/Max B rotating anode powder diffractometer using Cu $K\alpha_1$ radiation ($\lambda = 0.15406$ nm). The separation of crystallite size and strain was obtained from broadening of Bragg peaks using Cauchy/Gaussian approximation and the linear regression plots as described in our previous studies [6,7]. The standard reference material, LaB_6 (National Institute of Standards and Technology NIST-SRM # 660) was used for subtracting the instrumental broadening of the Bragg peaks.

The thermal behaviour of the powders was studied by differential scanning calorimetry (DSC) using a ∼20 mg powder sample, a heating rate of 4 °C/min and an argon flow rate of 16 ml/min. The enthalpy change of desorption, ΔH, was calculated from the endothermic peak area. The yield of reactions was estimated assuming that the enthalpy formation of β-MgH_2 and Mg_2FeH_6 is $\Delta H_f = 74$ and 77.4 kJ/mol H_2, respectively [8].

3. Results

3.1. Hydrogen alloying in Mg–Fe system: direct synthesis of ternary Mg_2FeH_6

Nanostructured ternary complex hydride, Mg_2FeH_6 was synthesized after more than 100 h of reactive milling of the 2Mg–Fe powder mixture under 880 kPa of H_2 (Fig. 1). The 'hydrogen alloying' reaction yielded ∼60% of the ternary complex metal hydride. The hydride was in a mixture with a nanometric phase of α-Fe, with a grain size of ∼17 nm, the latter being uniformly distributed in the hydride matrix, as shown in Fig. 1, obtained with field-emission transmission electron microscope (FE TEM). In a thermally programmed desorption (TPD) experiment, reported in [6], 3–4 wt.%H_2 was desorbed in less than 20 min at 285–295 °C temperature range, without use of additional catalyst.

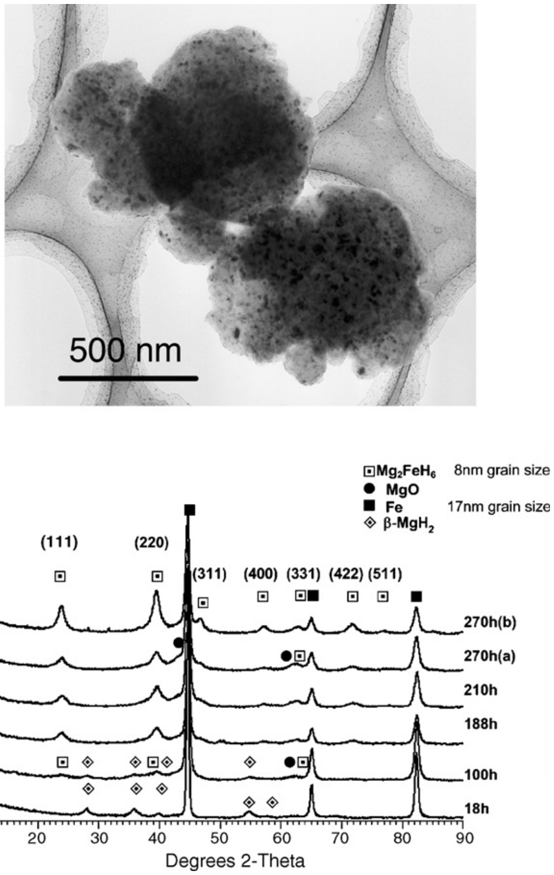

Fig. 1. Development of the nanostructure in the 2Mg–Fe powder milled with hydrogen; XRD patterns (bottom; replotted from [6]), and direct imaging of structure in FE TEM (top); the latter shows Fe nanoparticles in a hydride matrix.

3.2. Hydrogen alloying in a Mg–Al system: formation of Al(Mg) solid solution

The FCC cubic solid solution of Mg in Al, Al(Mg), is the only product of the reaction up to 10 h of milling (Fig. 2). The cast Mg–2Al alloy exhibited a microstructure consisting of Al dendrites in the Al_3Mg_2 intermetallic matrix. Upon relatively short milling, the Mg released from the intermetallic compound dissolves in Al. This induces nanostructure formation in Al(Mg) solid solution in the early stages of the milling, which is seen as a large broadening of XRD lines in the pattern for 10 h milling, Fig. 2. With increasing milling time, upon hydrogenation, the Al(Mg) extended solid solution disproportionates with the formation of β-MgH_2 and Al phases. This is reflected in a change of the lattice parameter a from 0.4038 ± 0.0016, through 0.4114 ± 0.0014, to 0.4034 ± 0.0015 nm for powders milled for 1, 10 and 200 h, respectively (Table 1). Quantification of those effects for various scenarios used in mechanochemical synthesis of hydrides and hydride mixtures in this system can be found in our previous report [7].

The hydrogenated Mg–2Al powder, when milled for 100 h, yields approximately 2.1 wt.%H released in the DSC experiment (estimated from endothermic signal) in the temperature range of 329–340 °C. This hydrogen was stored in a nanometric

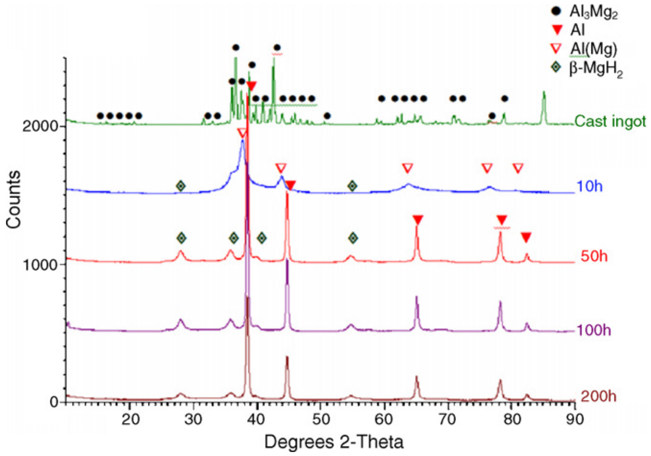

Fig. 2. Development of the nanostructure in the Mg–2Al powder milled with hydrogen, as revealed by XRD (replotted from [7]).

Table 1
Al grain size, lattice parameter *a*, strain, and H desorbed from Mg–2Al powder mixture

Milling time (h)	Grain size (nm)	*a* (nm)	Strain	H_2 (wt.%)
10	7[a]	0.4114 ± 0.0014[a]	$0\,(10^{-3})$	0.0
50	73	0.4036 ± 0.0015	1.1×10^{-3}	1.9
100	77	0.4035 ± 0.0014	1.1×10^{-3}	2.1
200	50	0.4034 ± 0.0015	1.4×10^{-3}	2.0

The *a* for Al metal in unmilled powder was 0.4038 ± 0.0016.
[a] Solid solution.

magnesium dihydride/Al metal mixture. No formation of ternary hydride $Mg(AlH_4)_2$ was observed.

3.3. Hydrogen alloying in Mg–B system: formation of amorphous Mg–B–H phase

Amorphous boron batches were mixed with elemental Mg in the atomic ratio 1:2 with the intent to mechanically synthesize the $Mg(BH_4)_2$ complex hydride, however, no formation of this ternary, complex hydride was observed. The reaction product after short time milling of powders was a mixture of MgH_2 and MgO (the latter forming during manipulation in the X-ray diffractometer). However, the XRD pattern at the bottom of Fig. 3, for the powders milled for 200 h, demonstrates absence of the MgH_2 phase. Instead, the peaks rising above the background can be attributed to MgB_2. The prominent feature is the broad background, which rises between 25° and 45° and is centered roughly at $2\theta \sim 35°$. The annealing of this powder in the DSC produced a single endothermic heat event at 358 °C. We are inclined to attribute it to the hydrogen evolution. The XRD pattern for the annealed powder is shown in Fig. 3 (top pattern). The pattern exhibits strong peaks from the MgB_2 phase, and the elevated background disappears. Therefore, the XRD pattern in Fig. 3 can be understood if assuming further MgB_2 phase forms during the decomposition of the amorphous phase containing hydrogen. Since the enthalpy of decomposition of the amorphous phase is unknown, we are not able to evaluate the amount of hydrogen released from this phase using DSC.

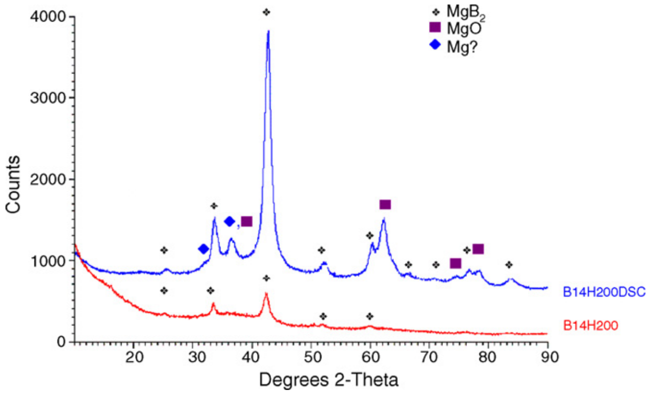

Fig. 3. XRD patterns of Mg–2B powders milled with hydrogen as-milled (bottom) and the annealed (top) powders.

4. Discussion

Several concurrent mechanisms may occur during milling: (i) reaction of hydrogen with milled Mg to form the most stable phase of MgH_2; (ii) dissolution of the alloying atoms of the second metal into the crystalline lattice of host metal that lowers the strength of the Mg–H bond, destabilizes the MgH_2, thus promoting the formation of a ternary complex hydride; (iii) enhanced interdiffusion of the atoms of Mg and the second metal that leads to the formation of an extended nanocrystalline solid solution, followed by disproportionation of the solid-state solution that is driven by its reaction with the hydrogen; this results in the formation of a nanometric mixture of MgH_2 with the second metal; (iv) mixing of elements in an amorphous phase containing hydrogen and formation of 'amorphous hydride phase', am-Mg(M)H_x. The 'alloying' of MgH_2 and the mixing of elements can be effectively promoted by proliferation of microdefects in ball-milled powders.

In this study, we observed all the mechanisms described above. The formation of Mg_2FeH_6 complex hydride in the 2Mg–Fe system (Fig. 1) can be explained by the enthalpy of formation of the ternary hydride that differs only slightly from that for MgH_2 [8]. On the other hand, the observed disproportionation of Mg–2Al alloys can be explained by a relatively high-thermodynamic stability of MgH_2 compared to that of Mg–Al–H, compounds [9], combined with a relatively low stability of $Mg(AlH_4)_2$ complex hydride. Finally, the ultimate mixing of elements was observed in the Mg–B–H system. Apparently, the metastable amorphous phase is the preferred phase when compared to the unstable $Mg(BH)_2$ complex and the stable magnesium dihydride.

5. Conclusions

Mechanical alloying of magnesium metal powders with hydrogen in specialized hydrogen ball mills can provide a direct route for mechanochemical synthesis of complex chemical (complex) hydrides and hydrides mixtures for advanced solid-state hydrogen storage. Chemical (complex) hydride mixed with crystalline extended solid solutions, metal nanoparticles, and amorphous phases can be produced depending on chemical composition and process conditions.

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