

Structural and hydrogen storage capacity evolution of Mg_2FeH_6 hydride synthesized by reactive mechanical alloying^①

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Abstract: Mg-based metal hydrides are promising as hydrogen storage materials for fuel cell application. In this work, Mg_2FeH_6 complex hydride phase was synthesized by controlled reactive ball milling of 2Mg-Fe (atomic ratio) powder mixture in H_2 . Mg_2FeH_6 is confirmed to be formed via the following three stages: formation of MgH_2 via the reaction of Mg with H_2 , incubation stage and formation of Mg_2FeH_6 by reaction of fully refined MgH_2 and Fe. The incubation stage is characterized by no traces of Mg or hydride crystalline phase by XRD. On the other hand, Mg is observed uniformly distributed in the milled powder by SEM-EDS. Also, almost the same amount of H_2 as the first stage is detected stored in the powders of the second stage by DSC and TGA.

Key words: hydrogen storage materials; hydride; fuel cell; mechanical alloying; solid state synthesis

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1 INTRODUCTION

The interest in fuel cell as an alternative to internal combustion engines is growing rapidly with the increasing concern with environmental issues such as reducing vehicle emissions. An important project for fuel cell strategy is how to store the fuel (hydrogen in most cases). Usually, there are three kinds of hydrogen storage means, i. e. in liquid form, in gas form and in metal hydride. Compared with other two methods, metal hydride has the pronounced features of safety and high volumetric storage capacity^[1].

For mobile and energy storage applications, high gravimetric and volumetric densities are two essential requirements for the potential hydrogen storage materials. It is revealed that metallic hydride Mg_2FeH_6 has the highest volumetric hydrogen density of 150 kg/m³ and high theoretical gravimetric density of 5.47%, which can fit for the corresponding demands proposed by International Energy Agency^[2].

Mg_2FeH_6 were prepared by sintering Mg and Fe in high H_2 pressure and high temperature^[3,4]. Synthesis of Mg_2FeH_6 directly by mechanical alloying/ball milling was realized by Huot et al in 1998^[5]. From then on, a few papers were published but the yield ratios of Mg_2FeH_6 in these work were not high^[5-7]. In these papers, different milling apparatus, such as spex mill, planetary ball mill, were applied in which movements of the balls are chaos and

not controllable. Controlled Reactive Mechanical Alloying (CRMA), differing from the above mentioned ball mills, can control the ball in the milling vials to move along specific trajectory only in "shearing mode" or in "impact mode" by using strong outer magnet. It is a new effective means for refinement of grain size and synthesis of metastable phases^[8,9].

The synthesis mechanism of Mg_2FeH_6 is not clear until now. Didisheim J J et al and Bogdanovic et al^[10] stated it is produced directly from the reaction of Mg, Fe, and H_2 . Gennari et al^[6] studied the microstructural evolution during milling of Mg-Fe powders in H_2 using XRD and SEM and reported that Mg_2FeH_6 is actually formed through the reaction between MgH_2 and Fe. In this paper, we used XRD, SEM-EDS, together with H_2 pressure monitor, DSC and TGA measurement to quantitatively investigate the forming process of Mg_2FeH_6 .

2 EXPERIMENTAL

The starting powder Mg (< 45 μ m, 99.8% purity, Alfa Corp.) and Fe (< 10 μ m, 99.9% purity, Alfa Corp.) were prepared with the stoichiometric ratio of 2:1 and subsequently mechanically alloyed in 750 kPa of H_2 in a Union Ball Mill 5 model ball mill using "impact 1" mode. At regular intervals, powder samples (designated as 2 MFH powders) were taken out in a glove bag, which was evacuated and purged

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with high purity of helium for 4 times.

Phase structures of the milled powder were recorded by X-ray diffraction (XRD) (Simens D500 diffractometers with $\text{CuK}\alpha$ radiation); the software TRACESTM v. 6. 5. 1 was used for determination phase features and for calculation of FWHM (full-widths at half maximum) of the milled powders. Refinement of the grain size was calculated using Scherry's equation. Morphology, particle size of the powders and Mg detection were measured by scanning electron microscopy (SEM) (LEO 1530). Thermogravimetric analysis (TGA) (TA Instrument 2100) and differential scanning calorimetry (DSC) (Netzsch 404C) were applied to determine hydrogen desorption properties of the synthesized powders; the heating rate for TGA is 20 °C/min under the protection of helium gas with the flow rate of 130 mL/min; whereas, for DSC measurement, the heating rate is 4 °C/min and the flow rate of argon is 16 mL/min.

3 RESULTS

3.1 H₂ pressure variation as a function of milling time

During ball milling, H₂ pressure in the vial was measured and the vial was backfilled to the starting pressure of 750 kPa if there is any pressure drop. The H₂ pressure variation as a function of milling time for 2 MFH powder was plotted in Fig. 1. Three stages of H₂ pressure variation can be found. In the first stage (0 - 170 h), H₂ pressure drops dramatically with milling in H₂. It can be seen from Fig. 1 that the H₂ pressure drops in the first 4 h and 18 h are 50 kPa and 630 kPa, respectively. This reduction of H₂ pressure comes from formation of MgH₂ by the reaction of Mg with H₂ (see Fig. 2). In stage 2 (170 - 210 h), H₂ pressure keeps constant which indicates no further reaction between Mg and H₂ takes place. It is interesting to see that after this stage (stage 3, 210 - 270 h), there is another small decrease of H₂ pressure as shown in Fig. 1.

3.2 Microstructural evolution during milling (XRD measurement)

The XRD patterns of the milled mixture of Fe and Mg powders after different time spans are plotted in Fig. 2. After 18 h of milling, MgH₂ (JCPDS12-0697) is formed with broad peak (The grain size is calculated to be 7.1 nm), while peaks of Mg (JCPDS35-0821) and Fe (JCPDS06-0696) remain. After 100 h, the MgH₂ peaks are broadened and Mg peaks disappear. From H₂ pressure monitor, it is impossible for all the Mg to react with H₂ to form MgH₂ (Fig. 1). The Mg must exist in a state uneasy to be detected by XRD (e. g. noncrystallite). The powder milled for 188 h has the same phase features as that

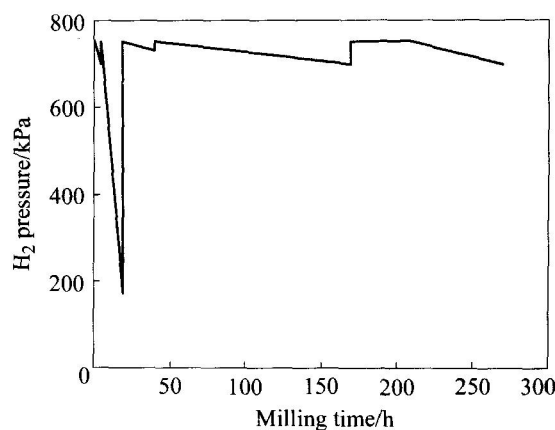


Fig. 1 H₂ pressure in milling vial as a function of milling time (after each measurement, under vial was backfilled to 750 kPa under H₂ pressure)

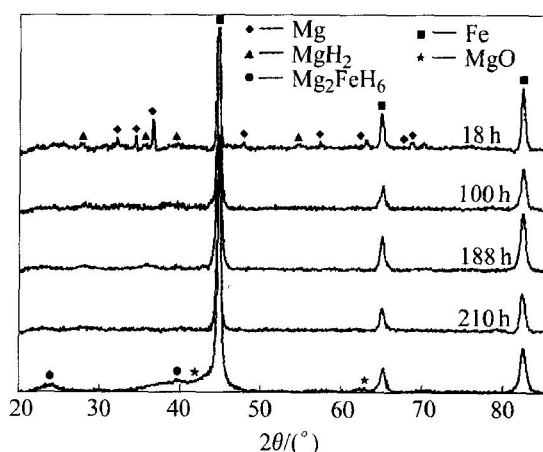


Fig. 2 XRD patterns of milled 2MFH powders after different time spans

milled for 100 h but with more broadened peaks for Fe and MgH₂. Strangely enough, with the milling time being 210 h, XRD pattern only shows peaks of Fe. Trace of neither Mg nor MgH₂ crystallite was detected in XRD pattern. Apparently, Mg element should stay in the mixture because after 270 h of milling, the ternary phase Mg₂FeH₆ (JCPDS38-0843) was formed.

The grain size of Fe as a function of milling time is plotted in Fig. 3. Fig. 3 clearly shows that the grain size of Fe decreases progressively to 32 nm after 270 h of milling.

3.3 SEM-EDS measurements

SEM micrographs of the starting and milled powder are shown in Fig. 4. The particle size of starting Mg and Fe are measured to be around 5 - 30 μm and 0.5 - 5 μm, respectively. With milling going on, the particle size of most Fe and Mg decrease to 200 - 300 nm after milled for 188 h. These results indicate that not only grain size but also particle size of Fe decreases with milling.

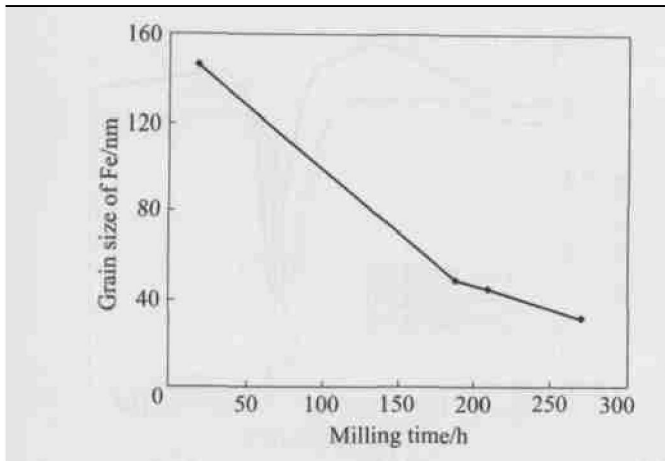


Fig. 3 Grain size of Fe as a function of milling time

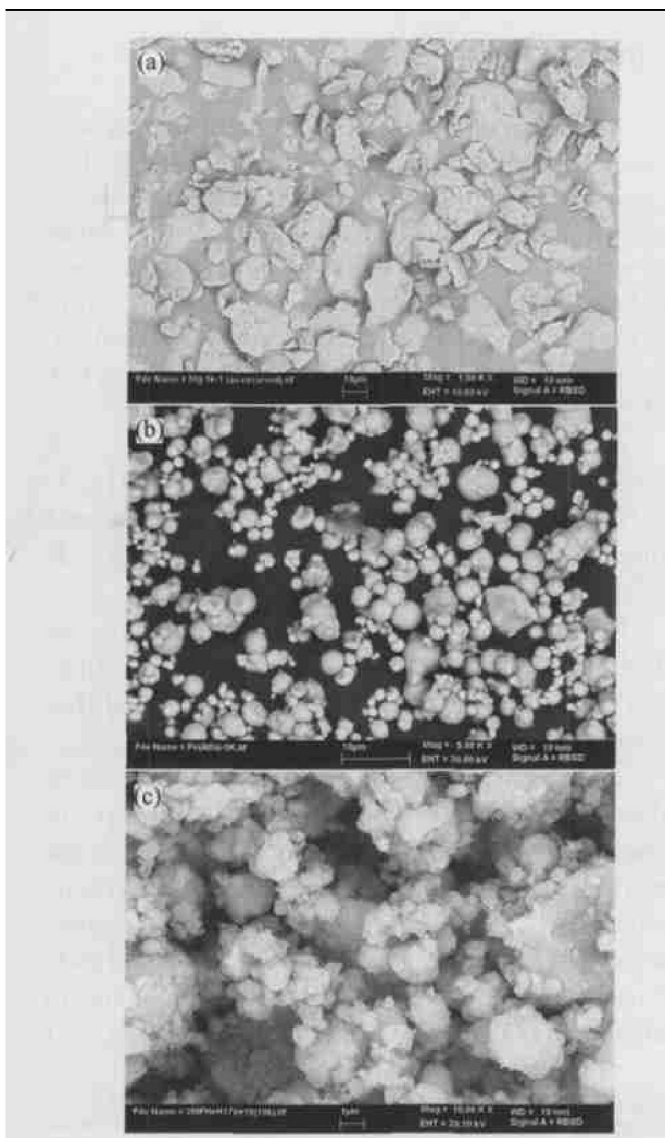


Fig. 4 SEM images of starting powders and milled powder

(a) —Starting Mg powder; (b) —Starting Fe powder;
(c) —Mg-Fe powder milled for 188 h

As stated before, XRD curve of the powder milled for 210 h in Fig. 2 does not show any trace of Mg-related crystalline phase. We did EDS of this

powder (Fig. 5). The EDS curve unambiguously shows the existence of Mg element. Fig. 6 shows the distribution of Mg and Fe in the powder. It can be seen that Mg and Fe elements are quite uniformly distributed in the powder.

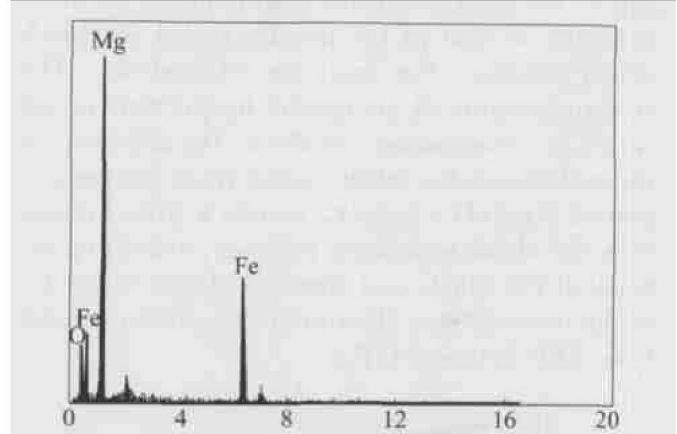


Fig. 5 EDS spectra of 2MFH powder milled for 210 h showing existence of Mg element

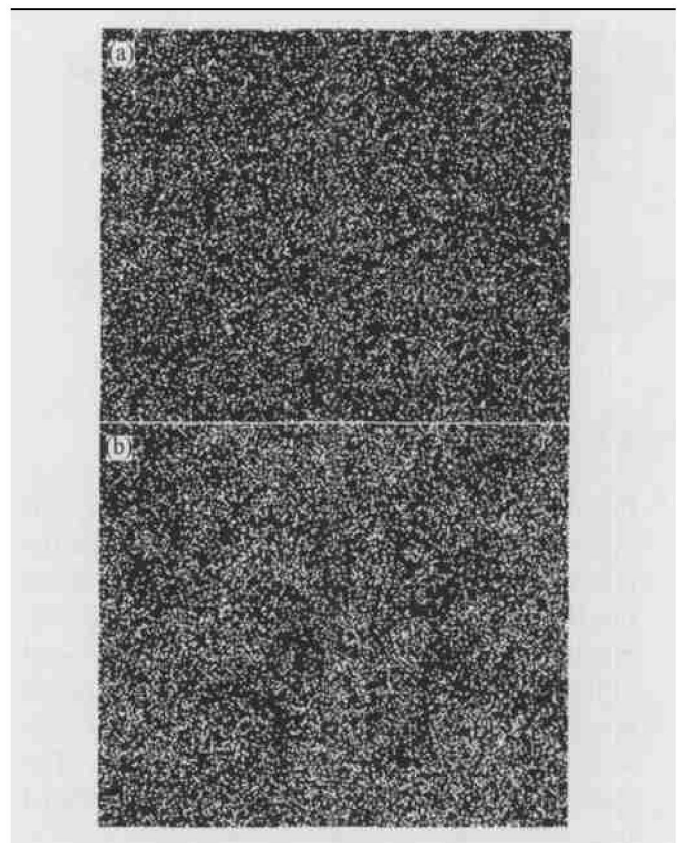


Fig. 6 Picture mapping of 2MFH powder milled for 210 h showing Mg element is uniformly distributed in powder
(a) —Fe element; (b) —Mg element

3.4 TGA measurement

The mass variation as a function of temperature for 2MFH powders is depicted in Fig. 7. As an example, the mass loss of the sample after milled in H_2 for 188 h is 2.14% indicating about 57% of Mg reacts with H_2 to form MgH_2 . This mass loss keeps almost constant after further 22 h (2MFH 210 h) of

milling. It is interesting if we compare TGA result with XRD pattern of the sample milled for 210 h. XRD pattern in Fig. 2 did not show any crystalline hydride phase whereas in Fig. 7, the mass loss of the powder milled for 210 h is similar to that of the powder milled for 188 h which indicates the existence of hydride. The structure feature of the powder in this time period is still in investigation. At 270 h, the mass loss of the milled sample, which comes from the desorption of Mg₂FeH₆ (Fig. 2), is only a little bit less than the above-mentioned powders, indicating almost all the MgH₂ was transferred into Mg₂FeH₆ at the interval from 210 h to 270 h as demonstrated from XRD patterns in Fig. 2.

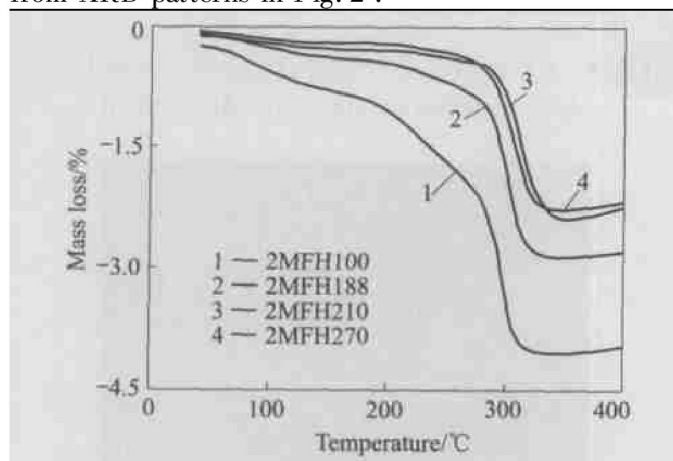


Fig. 7 TGA curves of 2MFH powders

3.5 DSC measurement

DSC curves for 2MFH powders are shown in Fig. 8. The calculations from the measured DSC curves are listed in Table 1. It can be seen that the peak temperatures are around 290–310 °C, while the H₂ release temperature span are 260–370 °C. Similar desorption temperature areas are also found in the previous literatures^[6, 11]. For Mg₂FeH₆, the desorption peak temperature is 300 °C, which is also similar to the result observed in Ref. [6]. The yield of Mg₂FeH₆ after 270 h of milling, calculated from endothermic peak area of DSC trace, is 33% assuming the formation enthalpy of Mg₂FeH₆ is 77.4 kJ/mol^[10].

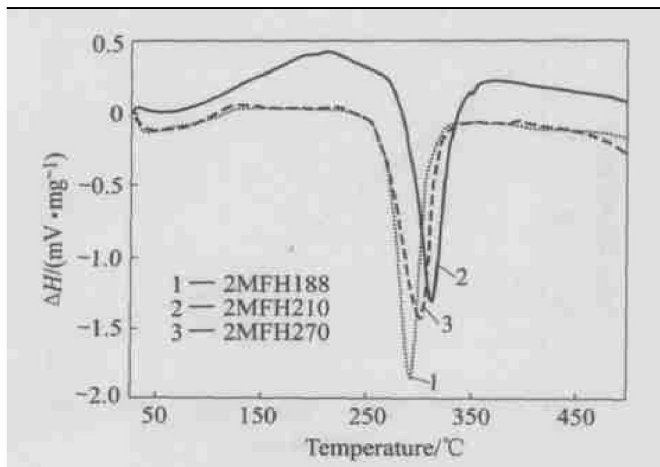


Fig. 8 DSC curves of 2MFH powders

4 DISCUSSION

At the beginning of ball milling of the Mg and Fe powders in H₂, MgH₂ is formed (Fig. 2). The amount of formed MgH₂ can be measured or calculated by three ways: H₂ pressure drop, TGA mass loss curve and DSC curve. Assuming H₂ fits ideal gas behavior, we can calculate the hydrogen storage capacity and the reaction ratio of Mg based on



and

$$pV = mRT/M \quad (2)$$

where *p* is the total pressure reduction of H₂, *V* the free volume of the vial, *m* and *M* the mass and molar mass of H₂, *T* the temperature (298 K), *R* the constant (8.314 J·mol⁻¹·K⁻¹).

H₂ storage capacity of the powder can also be calculated from DSC curves, assuming the enthalpy of desorption for MgH₂ is 74 kJ·mol⁻¹ and that for Mg₂FeH₆ is 77.4 kJ/mol^[10].

TGA is of course the most distinct means of determining the H₂ storage capacity (However, in some other systems, TGA curve may not show the exact number due to the oxidation of some particular powders). The H₂ storage amount of the powders milled for different time periods were calculated using the above-stated methods and listed in Table 2. The data in Table 2 demonstrate that

Table 1 DSC calculation of milled 2MFH powders

Sample No.	Milling time/h	<i>t</i> _{on} / °C	<i>t</i> _{end} / °C	<i>t</i> _{peak} / °C	Δ <i>H</i> / (J·K ⁻¹)	<i>w</i> (MgH ₂) / %	<i>w</i> (Mg ₂ FeH ₆) / %	<i>w</i> (Mg reacted) / %
2MFH188	188	269.4	306.6	291.6	674.8	24.01	no	49.20
2MFH ₂ 10	210	282.4	369.6	311.7	736.2	26.19 ^a	no	53.70
2MFH270	270	265.3	317.0	300.7	706.4	–	33.00	31.50

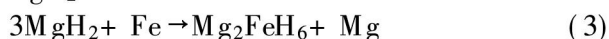
a—Assuming endothermic enthalpy of DSC is from released MgH₂

Table 2 Comparison of hydrogen storage capacity of 2MFH powder using different methods

Material	Hydrogen storage capacity/ %		
	by Δp_{H_2}	by TGA	by DSC
2MFH188	2.56	2.14	1.84
2MFH210	2.56	1.97	2.01
2MFH270	2.73	1.95	1.93

these three methods fit each other well in this experiment. So they are all useful means for determining the actual H₂ storage percentage in this powder mixture.

The formation of MgH₂ has been verified containing a nucleation stage^[12]. In this work, by monitoring the H₂ pressure variation combined with XRD, DSC, TGA and SEM-EDS measurements, three stages during the formation of Mg₂FeH₆ via milling Mg with Fe in H₂ can be deduced and the characteristics of the three stages are recognized. In the first stage (0 - 188 h), MgH₂ with very small grain size (i. e. 7.1 - 5.7 nm) is formed by Mg reacting with H₂. The second stage, which we term as incubation stage, is around 188 h to 210 h of milling. In this stage, XRD peaks of Fe are further broadened. However, peaks of crystalline Mg and MgH₂ disappear and no other crystalline hydride phase is detected by XRD. On the other hand, H₂ is found desorbed by DSC and TGA (the released gas is confirmed as H₂ by mass spectroscopy). Moreover, Mg element is detected uniformly distributed in the powder by picture mapping. Thus it looks reasonable to deduct that, just like Fe is progressively refined during milling, MgH₂ is also refined from its grain size of about 7 nm at 18 h and 5.7 nm at 188 h of milling to such a small size that it is unable to be detected by XRD. In the third stage (210 - 270 h), the new hydride phase Mg₂FeH₆ is formed via the reaction of fully refined Fe and MgH₂.



From point view of solid-state reaction, particle size and grain size of MgH₂ and Fe, energy induced by the balls (related to milling mode, ball-powder ratio, ball density, milling rate) will all exert influences on the formation of Mg₂FeH₆ via reaction of MgH₂ with Fe. In this work, the grain size of MgH₂ and Fe are less than 5.7 nm and about 25 nm. The particle size of the two reactants are in the order of 200 - 300 nm. As a result, the actual contact surface between MgH₂ and Fe is substantially increased. If the energy

is accumulated high enough to surpass the energy barrier for the forming reaction of Mg₂FeH₆. In the second stage, Fe is further refined and energy is accumulated by the impact of the balls, which are both necessary for the formation of Mg₂FeH₆. As a result, the incubation stage can keep for a long period of time.

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