Synthesis and Hydrogen Storage Behaviour of Pure Mg$_2$FeH$_6$ at Nanoscale

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Pure Mg$_2$FeH$_6$ compounds with two different morphologies have been successfully synthesized directly by mechanical milling (MM) and sintering of a mixture of 2Mg+Fe nanoparticles under an H$_2$ atmosphere, respectively. The successful preparation of pure Mg$_2$FeH$_6$ can be attributed to the small particle sizes of Mg and Fe nanoparticles prepared by hydrogen plasma-metal reaction (HPMR), which provides shorter diffusion distance for hydrogen and the metals. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) results show that the Mg$_2$FeH$_6$ synthesized by mechanical milling has larger particle size but smaller crystallite size compared with the Mg$_2$FeH$_6$ synthesized by sintering. The Mg$_2$FeH$_6$ synthesized by mechanical milling can desorb more than 4.5 mass% hydrogen in 10 min under an initial hydrogen pressure of 0.001 bar at 573 K. Compared with the Mg$_2$FeH$_6$ synthesized by sintering under the same conditions as the Mg$_2$FeH$_6$ synthesized by mechanical milling, it is suggested that decrease of crystallite size is beneficial for enhancing desorption property of Mg$_2$FeH$_6$.

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1. Introduction

Mg-based hydrogen storage materials are considered to be a promising candidate for fuel cell technologies and battery materials due to their large hydrogen storage capacity, reversibility, great abundance and low cost. However, the high operating temperature, and the poor reaction kinetics are the main drawbacks of Mg with respect to fuel cell technologies. Forming Mg-based 3d transition metal hydrides is a classical method to reduce the reaction temperature. Among them, Mg$_2$FeH$_6$, with the largest hydrogen storage capacity as 5.47 mass% (3.6 mass% for Mg$_2$NiH$_4$, 4.5 mass% for Mg$_2$CoH$_5$, and 2.6 mass% for Mg$_2$Cu-H system (3MgH$_2$+MgCu$_2$)), is an attractive hydride. Different from Mg-Ni-H and Mg-Co-H system, Mg and Fe do not form stable binary alloy. Therefore, Fe as a catalysts can be in-situ separated out to improve the dehydrogenation kinetics during the desorption process. On the other hand, due to the immiscibility of Mg and Fe, the large difference in vapor pressure, density and melting point between them, the synthesis of pure Mg$_2$FeH$_6$ is very difficult by conventional methods.

For the preparation of Mg$_2$FeH$_6$ compounds, many methods such as sintering the 2Mg+Fe mixture under high pressure hydrogen$^{3,6}$ and mechanical milling the 2Mg+Fe or 2MgH$_2$+Fe mixture$^{5,10}$ have been developed. The Mg$_2$FeH$_6$ compound has been first synthesized and described in 1984.$^3$ In that report, the obtained samples, synthesized by sintering the 2Mg+Fe mixture at about 793 K under 12 MPa H$_2$ pressure during 10–20 days, just contained less than 50% Mg$_2$FeH$_6$. There were a large amount of unreacted MgH$_2$ and Fe in the obtained samples which were difficult to remove. Mechanical milling was introduced to make progress on the synthesis of Mg$_2$FeH$_6$. Huot et al. milled the 2Mg+Fe mixture under 1 MPa hydrogen atmosphere, and then sintered it at 623 K under 5 MPa of hydrogen pressure for 1 day.$^{15}$ However, the obtained sample still contained unreacted MgH$_2$ and Fe and the content of Mg$_2$FeH$_6$ was still below 70 mass%. Subsequently, the synthesis of Mg$_2$FeH$_6$ was developed by reactive mechanical alloying (RMA), the milling condition and the ratio of the Mg/MgH$_2$ and Fe played an important role for the synthesis of Mg$_2$FeH$_6$. Raman et al. milled the 2Mg+Fe mixture under 1 MPa hydrogen pressure in a single step, and 63 mass% Mg$_2$FeH$_6$ was obtained.$^{11}$ In addition, the samples are often got polluted and oxidized during the milling process with the RMA method. All the obtained samples so far in literature inevitably contained unreacted materials. The pure Mg$_2$FeH$_6$ sample could hardly be obtained with the normal Mg and Fe particles. Metals in the nano-scale showed special properties and could provide shorter diffusion distance for the metals and gas in the solid-gas reaction. Therefore, we introduced the Mg and Fe nanoparticles prepared by hydrogen plasma metal reaction (HPMR) as the reactant, in order to prepared pure Mg$_2$FeH$_6$.

In this work, we successfully synthesized the pure Mg$_2$FeH$_6$ compound at mild condition both using the RMA and the sintering method with Mg and Fe nanoparticles which were produced by HPMR. The pure Mg$_2$FeH$_6$ compound synthesized with the two methods showed different morphologies. The dehydrogenated properties of Mg$_2$FeH$_6$ sample were further investigated. In addition, the size effect of the Mg$_2$FeH$_6$ on the dehydrogenated properties was also discussed.

2. Experimental Details

A schematic illustration of the experimental equipment...
which was used for production of ultra-fine particle (UFP) samples by HPMR was given. Magnesium and iron UFPs were prepared by the same method as illustrated before. The Mg nanoparticles were hexagonal in structure and the average particle size was about 300 nm, which was bigger than the Fe nanoparticles whose average particle size was about 30 nm.

Using the RMA method, the Mg and Fe nanoparticles prepared by HPMR were mechanically milled for 30 min, 3 h, 10 h, 20 h and 30 h at 300 rpm under 0.5 MPa hydrogen using a planetary ball milling apparatus (Pulverisette 5). The materials of grinding pots and balls are Cr-Mn-Ni stainless steels. The sample mass was 1.0 g and the ball-to-sample weight ratio was 40 : 1 in each milling process. The samples before and after milling were handled in an argon-filled glovebox in order to minimize oxidation and hydrolysis.

Using the sintering method, a mixture of Mg and Fe nanoparticles in a 2 : 1 molar ratio was put in tetrachloromethane and then ultrasonically dispersed by an ultrasonic homogenizer for 60 min (30 min each time, twice). After being dried in a container under 0.01 MPa H\textsubscript{2}, the mixture was milled for 30 min in a glove box, and then pressed at 75 MPa into pellets (13 mm in diameter, 0.3–0.4 mm in height and 0.1–0.15 g in weight) under air atmosphere. The pellets were put into the reactor, and the system was evacuated to 10\textsuperscript{-3} Pa. Then the samples were heated up to 673 K under 4 MPa hydrogen pressure to make the Mg and Fe mixtures react with hydrogen for 24 h, 48 h and 60 h.

Structural analysis of the samples before and after the synthesis reaction was carried out by X-ray diffraction (XRD) using monochromatic Cu K\textalpha\textsubscript{1} radiation. The size distribution and morphology of the samples before and after the preparation reaction was investigated by scanning electron microscopy (SEM) Hitachi S-4800 at 10 kV.

To determine the desorption temperature and thermodynamic properties, differential scanning calorimetry (DSC) was performed by using a Netzsch DSC 204 HP calorimeter at heating rates of 1.5, 2.5, 5, 10 and 20 K/min under Ar from room temperature to 773 K.

A conventional pressure-volume-temperature technique, which means measuring hydrogen content versus time by recording the change of gas pressure in a constant volume, was used to obtain the hydrogen absorption/desorption kinetics curves and pressure-composition isotherm (P-C-I) curves of the obtained samples. The kinetic measurements were carried out under an initial hydrogen pressure about 100 Pa for desorption. The hydrogen absorption and desorption measurements were thought to reach equilibrium and are stopped when the change of hydrogen pressure is less than about 10 Pa per second. The P-C-I curves are measured during the first hydrogen desorption cycle of the as-prepared samples.

3. Results and Discussion

Figure 1 presents the XRD patterns of the as-prepared samples by ball milling for various durations at room temperature. In Fig. 1(a), the peaks of MgH\textsubscript{2} can be observed clearly and there are no peaks of Mg\textsubscript{2}FeH\textsubscript{6}, which indicates that the Mg nanoparticles can be absorb hydrogen by the catalysis of Fe during the ball milling at room temperature. However, there are still unreacted Mg and Fe in the sample with the 30 min ball milling. When the milling time is prolonged to 3 h, the peaks of Mg have almost disappeared and the peaks of MgH\textsubscript{2} have been enhanced, which indicates that Mg nanoparticles have reacted with hydrogen further as shown in Fig. 1(b). But there is still no peak of Mg\textsubscript{2}FeH\textsubscript{6} in the sample. In Fig. 1(c) and (d), as the milling time have been prolonged to 10 h and 20 h, the peaks of MgH\textsubscript{2} became weak and the peaks of Mg\textsubscript{2}FeH\textsubscript{6} come out and became strong. In 30 h ball milling, the peaks of MgH\textsubscript{2} and Fe have disappeared and the pure Mg\textsubscript{2}FeH\textsubscript{6} have been successfully obtained as shown in Fig. 1(e). The peaks of Mg\textsubscript{2}FeH\textsubscript{6} are broadened because the crystallite sizes became smaller during the milling process. As the Mg powder could not reacted with hydrogen directly under such low hydrogen pressure at room temperature, the result showed that the hydrogenation of Mg should be contributed to the catalysis of Fe. From the XRD results of the as prepared samples by ball milling for various durations, it can be concluded that the Mg and Fe nanoparticles firstly formed MgH\textsubscript{2} phase and finally converted to Mg\textsubscript{2}FeH\textsubscript{6} during the ball milling reaction.

As can be seen in Fig. 2, pure Mg\textsubscript{2}FeH\textsubscript{6} can be also obtained by sintering the Mg and Fe nanoparticles mixture under 4 MPa hydrogen at 673 K. Figure 2(a) shows that the main phases of the mixture is ultrasonically dispersed Mg and Fe. Figure 2(d) shows that the obtained Mg\textsubscript{2}FeH\textsubscript{6} produced at 673 K under 4 MPa hydrogen for 60 h by directly hydriding the Mg and Fe nanoparticles mixture. Moreover, there is a very weak peak of MgO and nearly no peak of Fe, which shows that the obtained sample is pure Mg\textsubscript{2}FeH\textsubscript{6} phase. Thus, the dark green powder obtained is pure Mg\textsubscript{2}FeH\textsubscript{6}. In Fig. 2(b), when the Mg and Fe nanoparticles mixture is sintered for 24 h, we can observe the peaks of unreacted Mg.
and Fe, and the peaks of MgH$_2$ in the as prepared sample, however, no peaks of Mg$_2$FeH$_6$ is observed. As the mixture was sintered for 48 h, the Mg$_2$FeH$_6$ phase has been formed as shown in Fig. 2(c). The peaks of Mg are disappeared and the peaks of unreacted MgH$_2$ and Fe still exist, which indicates that the reaction firstly formed MgH$_2$ phase and finally converted to Mg$_2$FeH$_6$. After dehydrogenation of Mg$_2$FeH$_6$, the sample remains the Mg-Fe mixture which shows in Fig. 2(e).

The pure Mg$_2$FeH$_6$ compounds are obtained in mild condition, due to the smaller size of the pure Mg and Fe nanoparticles prepared by HPMR and the well-mixing, which provides shorter diffusion distance for hydrogen and the particles. In addition, compared with the method of sintering of the Mg and Fe nanoparticles mixture, it takes shorter time to form pure Mg$_2$FeH$_6$ with the method of ball milling. That is because the MgH$_2$, Fe and H$_2$ can be contacted adequately during the ball milling process.

The morphology and microstructure of the samples are further investigated by electron microscopy. Figure 3 presents SEM micrographs of the Mg$_2$FeH$_6$ obtained by ball milling and by sintering under 4 MPa hydrogen atmosphere. The two graphs show the Mg$_2$FeH$_6$ samples obtained by the two methods have different morphologies. The samples prepared at 673 K under a 4 MPa hydrogen atmosphere for 60 h were smaller and have more fine structures. However, comparing the XRD pattern of Mg$_2$FeH$_6$ in Fig. 1 and Fig. 2, the crystallite size of Mg$_2$FeH$_6$ obtained by ball milling is smaller than that of Mg$_2$FeH$_6$ obtained by sintering under 4 MPa hydrogen atmosphere.

It can be seen from Fig. 4 that the samples of completely dehydrogenated Mg$_2$FeH$_6$ obtained by ball milling and by sintering under 4 MPa hydrogen atmosphere also have different morphologies. The decomposed samples should be the mixtures of Mg and Fe particles in Fig. 4(a), and have smaller particle size compared with the Mg$_2$FeH$_6$ particles obtained by ball milling in Fig. 3(a). It is suggested that the Mg$_2$FeH$_6$ particles obtained by ball milling can crack into smaller nanoparticles during the decomposition process. In comparison, Mg$_2$FeH$_6$ particles obtained by sintering seem to remain the main shape of the nanoparticles, and separate out smaller particles which are considered to be Fe nanoparticles in the main nanoparticles. It can be explained that the crystallite size of Mg$_2$FeH$_6$ obtained by ball milling is much smaller and the sample had more grain boundaries and higher defect concentration, thus it is easier to crack into smaller nanoparticles.

Figure 5 presents the hydrogen desorption curves of the pure Mg$_2$FeH$_6$ compounds obtained by 30 h ball milling and sintering at 573 K under a 4 MPa hydrogen atmosphere for 60 h under an initial hydrogen pressure of $C_24$100 Pa, which shows that the Mg$_2$FeH$_6$ compounds desorbs hydrogen very quickly, which is not usually observed. In comparison, MgH$_2$ can hardly release hydrogen at 573 K without catalysis.$^{17}$ It can be seen that the sample obtained by ball milling has more than 4.5 mass% hydrogen desorption in 10 min at 573 K, and 5.0 mass% in 1 h, which is close to the theoretical value 5.47 mass%. At the same temperature, the sample obtained

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Fig. 2 X-ray diffraction patterns of (a) Mg and Fe nanoparticles mixture, (b) Mg-Fe-H (4 MPa hydrogen, 673 K, 24 h), (c) Mg-Fe-H (4 MPa hydrogen, 673 K, 48 h), (d) Mg$_2$FeH$_6$ (4 MPa hydrogen, 673 K, 60 h) and (e) Mg$_2$FeH$_6$ after complete dehydrogenation.

Fig. 3 SEM micrographs of: (a) Mg$_2$FeH$_6$ particles prepared by 30 h ball milling; (b) Mg$_2$FeH$_6$ particles prepared at 673 K under a 4 MPa hydrogen atmosphere for 60 h.
by sintering under a 4 MPa hydrogen atmosphere has less than 3 mass% hydrogen desorption in 10 min, and 4.7 mass% in 2 h. The hydrogen released more quickly from the samples prepared by ball milling, which should be contributed to the significantly less energy consumption and the smaller crystallite sizes.

Figure 6 shows DSC curves obtained by heating the pure Mg$_2$FeH$_6$ compounds prepared by RMA up to 723 K at heating rates of 5, 10 and 20 K min$^{-1}$ under Ar. The activation energy of the desorption process for the sample was estimated using the Kissinger equation:

\[ d \left( \ln \frac{\beta}{T_p^2} \right) / d \left( \frac{1}{T_p} \right) = \frac{E}{R} \]

where $T_p$ is the peak temperature corresponding to the heating rate $\beta$, $E$ the activation energy and $R$ the gas constant. From the obtained results, the activation energy of the desorption of pure Mg$_2$FeH$_6$ prepared by RMA is $86.0 \pm 17.8$ kJ mol$^{-1}$. Figure 7 shows DSC curves obtained by heating the pure Mg$_2$FeH$_6$ compounds prepared by sintering up to 723 K at heating rates of 1.5, 2.5, 5 and 10 K min$^{-1}$ under Ar. The activation energy of the desorption of pure Mg$_2$FeH$_6$ prepared by sintering can also be estimated as $165.7 \pm 8.4$ kJ mol$^{-1}$. The result is similar with the result $174 \pm 36$ kJ mol$^{-1}$ H$_2$ for Mg$_2$FeH$_6$ which has been reported by Gennari et al.\textsuperscript{7} Compared with the sintering sample, the activation energy of the desorption of pure Mg$_2$FeH$_6$ prepared by RMA is much smaller, which should be contributed to the crystallite sizes reduction and crystal structure modification by ball milling. As the particle size of
the sintering sample is much smaller than that of the RMA samples, it is suggested that decrease of crystallite size played a more important role compared with particle size for enhancing desorption property of Mg$_2$FeH$_6$. The mechanism has to be further investigated.

Figure 8 shows the P-C-I curves of hydrogen desorption and absorption of the obtain samples at 673 K. The P-C-I curves are measured during the first hydrogen desorption/absorption cycle without any activation process. Only one plateau is observed corresponding to the transformation from during the desorption process. The two plateaus of the P-C-I curves during the absorption course indicate the two steps of the formation of Mg$_2$FeH$_6$. Both P-C-I curves of absorption and desorption can reach more than 5 mass% hydrogen content, which suggests good recyclability of Mg$_2$FeH$_6$.

4. Conclusions

In conclusion, with the Mg and Fe nanoparticles, pure Mg$_2$FeH$_6$ compounds could be successfully synthesized using either RMA method or sintering method. The nano-scale effect played an important role in synthesis of the pure phase at relatively moderate condition. The pure Mg$_2$FeH$_6$ compound synthesized by mechanical milling had larger particle size but smaller crystallite size compared with the Mg$_2$FeH$_6$ synthesized by sintering. The formation of Mg$_2$FeH$_6$ from 2Mg+Fe nanoparticle mixture involved two reaction steps either using RMA method or using sintering method. First, Mg absorbed hydrogen to form MgH$_2$, and then MgH$_2$ react with Fe and H$_2$ to form Mg$_2$FeH$_6$. The desorption of Mg$_2$FeH$_6$ synthesized by RMA was very fast, which could desorb more than 4.5 mass% hydrogen in 10 min at 573 K. Using the Kissinger equation, the activation energy of the desorption of pure Mg$_2$FeH$_6$ compounds prepared by RMA and sintering methods were estimated as 86.0 ± 17.8 kJ mol$^{-1}$ and 165.7 ± 8.4 kJ mol$^{-1}$ respectively. The smaller activation energy suggested that decrease of crystallite size played a more important role compared with particle size for enhancing desorption property of Mg$_2$FeH$_6$.

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