Hydrogen Absorption at a Low Temperature by MgH$_2$ after Reactive Mechanical Grinding

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Abstract Pure MgH$_2$ was milled under a hydrogen atmosphere (reactive mechanical grinding, RMG). The hydrogen storage properties of the prepared samples were studied at a relatively low temperature of 423 K and were compared with those of pure Mg. The hydriding rate of the Mg was extremely low (0.0008 wt% H/min at n = 4), and the MgH$_2$ after RMG had higher hydriding rates than that of Mg at 423 K under 12 bar H$_2$. The initial hydriding rate of MgH$_2$ after RMG at 423 K under 12 bar H$_2$ was the highest (0.08 wt% H/min) at n = 2. At n = 2, the MgH$_2$ after RMG absorbed 0.39 wt% H for 5 min, and 1.21 wt% H for 60 min at 423K under 12 bar H$_2$. At 573 K under 12 bar H$_2$, the MgH$_2$ after RMG absorbed 4.86 wt% H for 5 min, and 5.52 wt% H for 60 min at n = 2. At 573 K and 423 K under 1.0 bar H$_2$, the MgH$_2$ after RMG and the Mg did not release hydrogen. The decrease in particle size and creation of defects by reactive mechanical grinding are believed to have led to the increase in the hydriding rate of the MgH$_2$ after RMG at a relatively low temperature of 423 K.

Key words pure magnesium hydride, activation, hydriding rate, microstructure, X-ray diffraction.

1. Introduction

Magnesium has advantages as a hydrogen storage material from the viewpoints of hydrogen storage capacity, cost and reserves in the earth’s crust. The hydrogen storage capacity of Mg is comparatively high (7.6 wt%) partly since it is a light element. However, its reaction rate with H$_2$ is very low since it is hard to be pulverized due to high ductility.

A lot of work to improve the hydriding and dehydriding rates of magnesium has been performed by alloying with magnesium metals$^{2,3}$ such as Cu,$^4$ Ni,$^5$ In,$^6$ Sn,$^7$ V,$^8$ and Ni and Y,$^9$ by synthesizing compounds such as CeMg$_{12}$,$^{10}$ and Mg$_9$Ti$_2$Fe$_{12-x}$Ni$_x$ (x = 4, 8),$^{11}$ and by making composites such as Mg - 20 wt% Fe$_{23}$Y$_8.$$^{12}$ Aminoroaya et al.$^{13}$ added Nb and multi-walled carbon nanotubes to Mg-Ni alloys, and Cho et al.$^{14}$ added transition metals to cast Mg-Ni alloys for the improvement of the reaction rates of Mg with H$_2$. Milanese et al.$^{15}$ mixed Ni and Cu with Mg, Tanguy et al.$^{16}$ mixed metal additives with magnesium, and Eisenberg et al.$^{17}$ plated nickel on the surface of magnesium to improve the hydriding-dehydriding kinetics of MgH$_2$.

Mao et al.$^{18}$ investigated doping MgH$_2$ with NiCl$_2$ and CoCl$_2$ in an effort to develop MgH$_2$ with a low dehydriding temperature and fast sorption kinetics. Both the dehydrogenation temperature and the absorption/desorption kinetics were improved by adding either NiCl$_2$ or CoCl$_2$, and a significant enhancement was obtained in the case of the NiCl$_2$-doped sample.

Cermak and David$^{19}$ studied separate catalytic effects of Ni, Mg$_3$Ni and Mg$_3$NiH$_4$ on the hydrogen desorption characteristics of MgH$_2$. It was observed that the catalytic capacity of Mg$_3$NiH$_4$ was considerably higher than that of pure Ni and non-hydrated intermetallic Mg$_3$Ni.

By use of the first-principles density functional theory

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for a cluster model, the alloying effect of transition element M on the electronic structure of magnesium hydride, MgH$_2$, was investigated by Chen et al. They concluded that the chemical interaction between Mg and H may play a dominant role in the pure MgH$_2$ system. Such a strong interaction remained in the alloyed Mg(M)H$_2$ when the central Mg was replaced by an alloying element M. In view of the reasonably good agreement between the calculated M(or Mg)-H interactions and the enthalpies of formation for some pure dihydrides, they reported that 70% chemical(ionic plus covalent) interactions would appear to be ionic but the covalent interaction of an adjacent Mg to M with a H atom around it would be sensitive to the substitution of M.

The paper of Matovic et al. dealt with non-isothermal kinetics models of hydrogen desorption from MgH$_2$ altered by ion bombardment and stressed the importance of the MgH$_2$ surface during its decomposition. The concentration and good dispersion of defects in near-surface region were important factors.

Bobet et al. investigated the influence of mechanical grinding and those after hydriding-dehydriding cycling were characterized by X-ray diffraction(XRD) for these measurements. Samples after reactive mechanical grinding was performed for 2 h by repeating 15 min milling and 5 min rest. The mill container was refilled with hydrogen every two hours. These milling conditions were the optimum ones to improve hydriding and dehydriding rates of magnesium hydride in our previous work.

At a given temperature, after hydriding reaction measurement under 1.0 bar H$_2$ was performed for 1 h, and then the sample was dehydrided at 623 K in vacuum for 2 h. 0.5 g of the samples was used for these measurements. Samples after reactive mechanical grinding and those after hydriding-dehydriding cycling were characterized by X-ray diffraction(XRD) with Cu Kα radiation, using a Rigaku D/MAX 2500 powder diffractometer. The microstructures of the samples after reactive mechanical grinding and after hydriding-dehydriding cycling were observed by a JSM-6400 scanning electron microscope(SEM) operated at 20 kV. ASAP2010(Accelerated Surface Area and Porosimetry analyzer, Micromeritics, USA) was used for analyzing the particle size distribution of the MgH$_2$ after RMG.

The amount of absorbed hydrogen, $H_a$, is expressed with respect to sample weight. Fig. 1 shows the variation of $H_a$ versus t curve at 573 K under 12 bar H$_2$ with the number of cycles, n, for the MgH$_2$ after RMG. In the beginning, the hydriding rate is very high, and it be-

![Graph showing variation of $H_a$ versus t curve at 573 K under 12 bar H$_2$](image_url)
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after Reactive Mechanical Grinding

comes very low after 10 min. The \(H_a\) versus \(t\) curves at \(n = 1\) to \(n = 3\) are very similar. The \(H_a\) values for 5 min and 60 min increase from \(n = 1\) to \(n = 2\) and decrease from \(n = 2\) to \(n = 3\), showing that the activation of the MgH\textsubscript{2} after RMG was completed after the first hydriding-dehydriding cycle. At \(n = 1\), the MgH\textsubscript{2} after RMG absorbs 4.86 wt% H for 5 min and 5.51 wt% H for 60 min. At \(n = 2\), the MgH\textsubscript{2} after RMG absorbs 4.86 wt% H for 5 min and 5.52 wt% H for 60 min. Table 1 presents the variation of the quantity of hydrogen absorbed by the MgH\textsubscript{2} after RMG at 573 K under 12 bar H\textsubscript{2} with time at \(n = 1\) and at \(n = 2\).

The variation of \(H_a\) versus \(t\) curve at 423 K under 12 bar H\textsubscript{2} with the number of cycles for the Mg is shown in Fig. 2. The hydriding rates of the Mg are extremely low. The Mg absorbs 0.05 wt% H for 60 min at \(n = 4\), corresponding to a hydriding rate of 0.0008 wt% H/min.

Fig. 3 shows the variation of \(H_a\) versus \(t\) curve at 423 K under 12 bar H\textsubscript{2} with the number of cycles for the MgH\textsubscript{2} after RMG. The hydriding rates are not high, and the \(H_a\) values for 60 min are not large, either. However, the MgH\textsubscript{2} after RMG absorbs hydrogen at a relatively low temperature of 423 K. Roughly speaking, the initial hydriding rate and the \(H_a\) value for 60 min increase from \(n = 1\) to \(n = 2\) and decrease from \(n = 2\) to \(n = 4\). At \(n = 1\), the MgH\textsubscript{2} after RMG absorbs 0.14 wt% H for 5 min and 1.21 wt% H for 60 min. At \(n = 2\), the MgH\textsubscript{2} after RMG absorbs 0.39 wt% H for 5 min and 1.21 wt% H for 60 min. Table 2 presents the variation of the quantity of hydrogen absorbed by the MgH\textsubscript{2} after RMG at 423 K under 12 bar H\textsubscript{2} with time at \(n = 1\) and at \(n = 2\).

Fig. 2 and Fig. 3 show that the hydriding rate of the Mg is extremely low, absorbing 0.05 wt% H for 60 min at \(n = 4\), the initial hydriding rate 0.0008 wt% H/min at \(n = 4\), and the MgH\textsubscript{2} after RMG has a higher initial hydriding rate(0.08 wt% H/min) than the Mg, absorbing 1.21 wt% H for 60 min at \(n = 2\), at 423 K under 12 bar H\textsubscript{2}.

Fig. 4 shows the variations, with the number of cycles, of the initial hydriding rate and \(H_a\) for 60 min under 12 bar H\textsubscript{2} for the MgH\textsubscript{2} after RMG at 573 K and 423 K. The initial hydriding rates were obtained from the \(H_a\) values from 0 min to 5 min. The initial hydriding rates at 573 K remain almost constant and they are very similar from \(n = 1\) to \(n = 3\). The initial hydriding rate at 423 K increases from \(n = 1\) to \(n = 2\) and decreases from \(n = 2\) to \(n = 4\). The values of \(H_a\) for 60 min at 573 K are much larger than those at 423 K. The value of \(H_a\) for 60 min at 573 K remains almost constant and decreases from \(n = 2\) to \(n = 4\). The values of \(H_a\) for 60 min at 573 K are much larger than those at 423 K.

| Table 1. Variation of the quantity of hydrogen absorbed by the MgH\textsubscript{2} after RMG at 573 K under 12 bar H\textsubscript{2} with time at \(n = 1\) and at \(n = 2\). |
|---|---|---|
| \(H_a\) (wt% H) at 573 K | \(n = 1\) | \(n = 2\) |
| time (min) | | |
| 0 | 0.00 | 0.00 |
| 5 | 4.86 | 4.86 |
| 10 | 5.23 | 5.22 |
| 30 | 5.42 | 5.45 |
| 60 | 5.51 | 5.52 |

| Table 2. Variation of the quantity of hydrogen absorbed by the MgH\textsubscript{2} after RMG at 423 K under 12 bar H\textsubscript{2} with time at \(n = 1\) and at \(n = 2\). |
|---|---|---|
| \(H_a\) (wt% H) at 423 K | \(n = 1\) | \(n = 2\) |
| time (min) | | |
| 0 | 0.00 | 0.00 |
| 5 | 0.14 | 0.39 |
| 10 | 0.25 | 0.51 |
| 30 | 0.73 | 0.84 |
| 60 | 1.21 | 1.21 |

Fig. 2. Variation of \(H_a\) versus \(t\) curve at 423 K under 12 bar H\textsubscript{2} with the number of cycles for the Mg.

Fig. 3. Variation of \(H_a\) versus \(t\) curve at 423 K under 12 bar H\textsubscript{2} with the number of cycles for the MgH\textsubscript{2} after RMG.
they are very similar from \( n = 1 \) to \( n = 3 \). But the value of \( H_a \) for 60 min at 423 K increases from \( n = 1 \) to \( n = 2 \) and decreases from \( n = 2 \) to \( n = 4 \). The initial hydriding rates of the MgH\(_2\) after RMG at \( n = 2 \) are 0.97 and 0.08 wt% H/min at 573 and 423 K, respectively. The values of \( H_a \) for 60 min of the MgH\(_2\) after RMG at \( n = 2 \) are 5.52 and 1.21 wt% H at 573 and 423 K, respectively.

At 573 K and 423 K under 1.0 bar H\(_2\), the MgH\(_2\) after RMG and the Mg did not release hydrogen.

The XRD pattern of the MgH\(_2\) after RMG showed that this sample contained \( \beta \)-MgH\(_2\), and small amounts of Mg, \( \gamma \)-MgH\(_2\), and MgO. \( \beta \)-MgH\(_2\) is a low pressure form of MgH\(_2\) that has a tetragonal structure. \( \gamma \)-MgH\(_2\) is one of the high pressure forms of MgH\(_2\) having an orthorhombic structure. This showed that \( \gamma \)-MgH\(_2\) was formed during reactive mechanical grinding. The XRD pattern of the MgH\(_2\) after RMG exhibited a quite strong background and broad peaks, indicating that the MgH\(_2\) after RMG...
was slightly amorphous.

Fig. 5 shows the SEM micrographs of the MgH2 after RMG. The sample has small and large particles. The particle size is not homogeneous.

The SEM micrographs of the MgH2 after RMG dehydrated at n = 5 are shown in Fig. 6. The particle size is not homogeneous. During hydriding reaction, the particles expand. The particles after hydriding-dehydriding cycling are larger than those after reactive mechanical grinding.

Fig. 7 shows the particle size distribution of the MgH2 after RMG. The particle sizes are from 0 to 5 µm. The curve has two peaks at about 0.7 and 3.5 µm. The mean particle size is 1.39 µm.

The hydriding reaction of magnesium can be classified by the following: transfer of hydrogen molecules to the surface of Mg, chemisorption of H2 molecules on the surface of Mg, transition of hydrogen atoms from the chemisorbed state to the absorbed state, and nucleation of magnesium hydride and growth. If a continuous layer of magnesium hydride is formed, diffusion of hydrogen atoms through a growing Mg hydride layer occurs, and then phase transformation from β Mg-H solid solution to magnesium hydride takes place at the magnesium hydride-β Mg-H solid solution interface.

As mentioned above, the hydriding and dehydriding reactions of Mg are reportedly nucleation-controlled under certain conditions and the hydriding rates of Mg are controlled by the diffusion of hydrogen atoms through a growing Mg hydride layer.33)

Reactive mechanical grinding is considered to decrease the particle size of magnesium hydride and create defects. The diminution in the particle size decreases the diffusion distances of hydrogen atoms, and the creation of defects facilitates nucleation. These effects are believed to have led to the increase in the hydriding rate of the MgH2 after RMG at a relatively low temperature of 423 K.

On the other hand, the Mg has a small surface area and a few defects, leading to its low hydriding and dehydriding rates.

The reactive mechanical grinding of MgH2 was performed in a planetary ball mill under the high purity hydrogen gas of about 12 bar at a disc revolution speed of 400 rpm for 2 h. The initial hydriding rate of the MgH2 after RMG at 423 K under 12 bar H2 was the highest (0.08 wt% H/min) at n = 2.

4. Conclusions

Pure MgH2 was milled under hydrogen atmosphere. Hydrogen storage properties of the prepared samples were studied at a relatively low temperature of 423 K, and compared with those of pure Mg. The hydriding rate of the Mg was extremely low (0.0008 wt% H/min at n = 4), and the MgH2 after RMG had higher hydriding rates than the Mg, at 423 K under 12 bar H2. At n = 2, the MgH2 after RMG absorbed 0.39 wt% H for 5 min and 1.21 wt% H for 60 min at 423K under 12 bar H2. The initial hydriding rate of the MgH2 after RMG at 423 K under 12 bar H2 was the highest (0.08 wt% H/min) at n = 2. At 573 K under 12 bar H2, the MgH2 after RMG absorbed 4.86 wt% H for 5 min and 5.52 wt% H for 60 min at n = 2. At 573 K and 423 K under 1.0 bar H2, the MgH2 after RMG and the Mg did not release hydrogen. The decrease in particle size and creation of defects by reactive mechanical grinding are believed to have led to the increase in the hydriding rate of the MgH2 after RMG at a relatively low temperature of 423 K.

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