Effects of SWNT and Metallic Catalyst on Hydrogen Absorption/Desorption Performance of MgH₂

Chengzhang Wu, Ping Wang, Xiangdong Yao, Chang Liu, Demin Chen, Gao Qing Lu, and Huiming Cheng

Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China, and ARC Centre for Functional Nanomaterials, School of Engineering, The University of Queensland, Brisbane, QLD 4072, Australia

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The microstructure and absorption/desorption characteristics of composite MgH₂ and 5 wt % as-prepared single-walled carbon nanotubes (MgH₂-5ap) obtained by the mechanical grinding method were investigated. Experimental results show that the MgH₂-5ap sample exhibits faster absorption kinetics and relatively lower desorption temperature than pure MgH₂ or MgH₂-purified single-walled carbon nanotube composite. Storage capacities of 6.0 and 4.2 wt % hydrogen for the MgH₂-5ap composite were achieved in 60 min at 423 and 373 K, respectively. Furthermore, its desorption temperature was reduced by 70 K due to the introduction of as-prepared single-walled carbon nanotubes (SWNTs). In addition, the different effects of SWNTs and metallic catalysts contained in the as-prepared SWNTs were also investigated and a hydrogenation mechanism was proposed. It is suggested that metallic particles may be mainly responsible for the improvement of the hydrogen absorption kinetics, and SWNTs for the enhancement of hydrogen absorption capacity of MgH₂.

1. Introduction

To develop a viable hydrogen storage system is becoming increasingly important for promoting the “hydrogen economy”. In recent years, various hydrogen storage materials, such as metal hydrides,1,2 nanocarbon materials,3,4 complex metal hydrides,5,6 metal−N−H systems,7 and metal−organic frameworks (MOFs),8 have been studied. Among them, a very attractive material is magnesium due to its high theoretical hydrogen storage capacity (7.6 wt %), abundance, and low cost. However, the practical application of magnesium as a hydrogen storage medium is greatly hindered by its high desorption temperature and slow absorption/desorption kinetics. Various additives with potential catalytic effect for H₂ absorption/desorption in Mg, including transition metals,9−14 H-storage alloys,15 metal oxides,16−18 metal hydrides,19 and graphite,20−24 have been utilized to prepare Mg-based composites by mechanical milling.

We recently found that, as an additive, single-walled carbon nanotubes (SWNTs) was superior to other carbon materials, such as activated carbon, carbon black, fullerene, and graphite, to improve the hydrogen absorption property of Mg. The pronounced catalytic effect of SWNTs allows the Mg-based composite to achieve a markedly improved hydrogen storage capacity and absorption kinetics. For example, the composite can absorb 6.7 wt % of hydrogen within 100 s at 573 K.25,26 Interestingly, in the subsequent investigation, we found that the as-prepared SWNTs had a higher catalytic effectiveness than purified SWNTs. This finding clearly indicates that the eliminated metal/alloy catalyst particles in SWNTs contribute to the catalytic enhancement of H-absorption of Mg. This article reports a systematic study of the hydrogen absorption/desorption properties of MgH₂ composite with as-prepared SWNTs. The different catalytic mechanisms of metallic particles and SWNTs contained in the as-prepared SWNTs are discussed.

2. Experimental Details

Magnesium hydride was prepared by mechanically grinding magnesium (purity >99.9%, 300 mesh) under hydrogen atmosphere with an initial pressure of ~1 MPa, followed by a long period of hydrogenation at 573 K. The process was repeated 3 times to achieve a hydrogenation ratio of ~80%, which was determined by using the volumetric method. The SWNTs used were synthesized by a hydrogen arc discharge method as detailed in ref 27. The as-prepared MgH₂ was mechanically ground with 5 wt % as-prepared SWNTs (the system was denoted as MgH₂-5ap) under argon atmosphere by using a SPEX 8000M mill and stainless steel pot and balls. The ball-to-powder weight ratio was around 40:1. As described in ref 28, the as-prepared SWNTs were entangled with amorphous carbon, carbon nanoparticles, and about 40 wt % of catalyst particles which were mainly made up of Fe, Co, and Ni. This means that the amount of metallic catalyst contained in the MgH₂-5ap is about 2 wt %. To clarify the roles of pure SWNTs and metallic catalysts played in the reversible desorption of MgH₂, the composites MgH₂−5 wt % purified SWNT (denoted as MgH₂-5ps) and MgH₂−2 wt % metallic catalysts (Fe, Co, and Ni elemental powder mixture, denoted as MgH₂-2FeCoNi) were also prepared. All the sample handling was performed in an Ar-filled glovebox (MBraun), in which the water/oxygen levels were below 1 ppm.

The structure of the samples was characterized by X-ray diffraction (XRD, Rigaku D/max 2400) with Cu Kα radiation, and high resolution transmission electron microscopy (HRTEM, JEM, 2100) equipped with an energy-dispersive X-ray (EDX) analysis unit (Oxford). The amount of Fe contamination introduced during mechanical milling was examined by inductively coupled plasma spectrometry (ICP, IRIS Intrepid).
Hydrogen storage properties of the composites were examined by an automated Sieverts’ apparatus. The typical sample mass for each measurement run was around 500 mg. Before measurements, the system was degassed for 2 h with the sample cell being heated to 673 K. Absorption/desorption measurements were performed at various temperatures with an initial pressure of 2 MPa and <10 Pa, respectively. The desorption performance of the re-hydrogenated samples was also examined by using diffraction scanning calorimetry (DSC, Netzsch STA 409C) with high-purity Ar (purity >99.999%) as the purge gas at a heating rate of 2–20 K/min.

3. Results and Discussion

3.1. Structural Characterization. Figure 1 presents the XRD patterns of the samples MgH2-5ap, MgH2-5ps, and MgH2-2(FeCoNi) milled for 10 h. In all composites, Mg can be detected due to incomplete hydrogenation in the process of preparing magnesium hydride. In addition, it was found that the intensive milling led to a partial transformation of MgH2 from a low-pressure \( \beta \)-phase (tetragonal) to a high-pressure metastable \( \gamma \)-phase (orthorhombic). The grain sizes of \( \beta \)-MgH2 were estimated according to the diffraction pattern and Sherrer equation, the results of which are shown in Table 1. It can be seen that the grain sizes of \( \beta \)-MgH2 of the three samples are close after long milling time.

Figure 2 gives the XRD patterns of MgH2-5ap ball-milled for 10 h before and after hydrogenation. It was observed that the diffraction peaks of Mg and \( \gamma \)-MgH2 disappeared after hydrogenation, and accordingly, the intensity of \( \beta \)-MgH2 diffraction peaks sharply increased.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgH2-2FeCoNi</td>
<td>5.5</td>
</tr>
<tr>
<td>MgH2-5ps</td>
<td>4.4</td>
</tr>
<tr>
<td>MgH2-5ap</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Table 1: Grain Sizes of \( \beta \)-MgH2 in Various Samples

The morphology and microstructure of the samples were further examined by electron microscopy. Figure 3a–c shows the SEM images of MgH2-5ap milled for 10 h before and after hydrogenation. It can be seen that the particle size of MgH2-5ap markedly decreased from around several micrometers before hydrogenation to several hundreds of nanometers after hydrogenation. However, most of the pulverized particles were agglomerated into large clusters with a size similar to that of the particles before hydrogenation. A TEM bright field image of the sample MgH2-5ap ball milled for 10 h is shown in Figure 4a, and the corresponding selected area electron diffraction (SAED) pattern is shown in Figure 4c. It was found that all the diffraction rings correspond to the Mg phase. As observed in the dark field image (Figure 4b), the average grain size of the
of the MgH$_2$ phase, and further hydrogen diffusion into bulk molecules into atoms, diffusion of hydrogen atoms, nucleation be understood in the following steps: dissociation of hydrogen account in the following mechanism discussion.

Therefore, the Fe contamination was not taken into any, would be similar in the various samples milled for the same period. It was highly expected that the effect of Fe contamination, if in the samples was around 0.5 wt %.

According to ICP examination, the amount of Fe contamination grinding process due to the hardened steal vial and balls used. In addition, it should be noted that Fe contamination would be unavoidably introduced into samples during the mechanical milling due to the formation of metallic particles. It has been well established that metallic catalysts may facilitate the dissociation of hydrogen molecules. The increase of hydrogen concentration chemisorbed on the surface of Mg particles will result in an enhanced thermodynamic driving force of hydrogenation. However, the favorable catalytic effect of metal/alloy additives is balanced by the capacity loss of the system due to their large molar mass. Therefore, the metal/alloy catalysts are generally controlled to a low molar ratio, which may largely limit the practically obtained catalytic performance. In this regard, SWNTs possess significant advantages. A large volume fraction, associated with a small capacity loss, can be easily achieved in Mg/C systems. Furthermore, the novel nanostructure of SWNTs may provide additional diffusion channels for diffusion of hydrogen atoms. This was supported by the observation that the hydrogen storage performance of the Mg/SWNTs composite will be degraded if the structural integrity of SWNTs was destroyed by performing a premilling before addition to Mg.26

For comparison, samples of MgH$_2$-2FeCoNi, MgH$_2$-5ps, and pure MgH$_2$ were also prepared and studied, the hydriding profiles of which together with MgH$_2$-5ap at 473 and 423 K are shown in Figure 6, parts A and B, respectively. The MgH$_2$-5ap and MgH$_2$-2FeCoNi samples exhibit a similar and high hydriding rate, both completing hydrogen absorption at 473 K within 5 min and at 423 K within 1 h. However, the hydrogen absorption capacity of MgH$_2$-2FeCoNi is about 20% lower than that of MgH$_2$-5ap. Therefore, MgH$_2$-5ap possesses the best overall hydrogen storage property, followed by the samples in the order of MgH$_2$-2FeCoNi, MgH$_2$-5ps, and pure MgH$_2$. In view of the above-mentioned similarity in the grain size of MgH$_2$ in the first three samples, these results clearly suggest that the metallic particles may be mainly responsible for kinetic enhancement, and SWNTs contribute to the H-capacity increase. In addition, it should be noted that Fe contamination would be unavoidably introduced into samples during the mechanical grinding process due to the hardened steel vial and balls used. According to ICP examination, the amount of Fe contamination in the samples was around 0.5–0.8 wt % after 10 h of milling. It was highly expected that the effect of Fe contamination, if any, would be similar in the various samples milled for the same period. Therefore, the Fe contamination was not taken into account in the following mechanism discussion.

It is well-known that the hydrogenation process of Mg can be understood in the following steps: dissociation of hydrogen molecules into atoms, diffusion of hydrogen atoms, nucleation of the MgH$_2$ phase, and further hydrogen diffusion into bulk magnesium through the formed MgH$_2$ layer. It has been well established that metallic catalysts may facilitate the dissociation of hydrogen molecules. The increase of hydrogen concentration

![Figure 5](image1.png)

Figure 5. Hydrogen absorption kinetics of the sample MgH$_2$-5ap milled for 10 h at the temperature range of 373 to 573 K with an initial hydrogen pressure of about 2.0 MPa.

![Figure 6](image2.png)

Figure 6. Hydrogen absorption kinetics of the sample (a) MgH$_2$, (b) MgH$_2$-5ps, (c) MgH$_2$-2FeCoNi, and (d) MgH$_2$-5ap milled for 10 h at 473 K (A) and at 423 K (B) with an initial hydrogen pressure of about 2.0 MPa.

Mg phase is around 10 nm, which agrees well with the estimated results on the basis of XRD examination. However, it should be noted that, due to the nanosize and the expected destruction of SWNTs after a long period of mechanical milling, we failed in direct observation of SWNTs in the composites.

3.2. Hydrogen Storage Performance. The as-prepared MgH$_2$-5ap sample exhibits superior hydriding kinetics and high hydrogen storage capacity. It should be pointed out that the material was directly measured after initial desorption at 623 K without any preactivation. As seen in Figure 5, the absorbed hydrogen amount of this composite at 573 K reached 5.7 wt % within 2 min, and 6.1 wt % in 20 min. Moreover, reducing the temperature from 573 to 473 K caused no influence on the hydrogen absorption capacity and kinetics. Even after further lowering the temperature, MgH$_2$-5ap could absorb 6.0 wt % of hydrogen at 423 K and 4.2 wt % of hydrogen at 373 K within 1 h.

![Figure 7](image3.png)

The dehydriding kinetics curves of MgH$_2$-5ap, MgH$_2$-5ps, MgH$_2$-2FeCoNi, and MgH$_2$ at varied temperatures from 553 to 623 K are shown in Figure 8. Again, it is found that the catalytic enhancement arising upon addition of the as-prepared SWNTs is more pronounced than that obtained with purified SWNT additive. At 573 K, MgH$_2$-5ap took about 30 min to desorb 6.1 wt % of hydrogen, about 60% higher than MgH$_2$-5ps. Unfortunately, the hydrogen desorption kinetics is decreased markedly when temperature decreased to 553 K, and the desorbed H-amount is only 3.2 wt % in 30 min, and below 4 wt % even after increasing the desorption time to 1 h.

![Figure 8](image4.png)
The desorption data were analyzed by using the Johnson–Mehl–Avrami (JMA) theory, where $R$ is the time-dependent phase fraction of MgH$_2$, $k$ is the rate constant that depends on pressure and temperature, and $n$ is the reaction order that is related to the transformation mechanism. A linear interpolation of the typical master plots, $\ln(-\ln(1 - R))$ vs $\ln(t)$, yields the values of $n$, the results of which are shown in Table 2. It was found that, for various MgH$_2$ samples, the values of $n$ are close to 1.5, indicating that the phase transformation of MgH$_2$ to Mg has a zero nucleation rate (i.e., negligible initial dimensions) and it is a diffusion-limited growth reaction of spheroids of any shape.\(^{30}\)

The desorption performance of the composites were further examined by thermal analysis. Figure 9 gives the DSC profiles (at a heating rate of 5 K/min) of the various composites after re-hydrogenation. The peak temperature of the endothermic effect associated to hydrogen desorption was observed to shift downward from 680 K for pure MgH$_2$, to 640 K for MgH$_2$-5ps, and further to 610 K for MgH$_2$-5ap. In addition, we measured the DSC profiles at different heating rates, from 2 to 20 K/min, and estimated the activation energy of the desorption process by using Kissinger method.\(^{31}\)

$$d[\ln(\beta/T_p^2)]/d(1/T_p) = -E_A/R$$  

Figure 9. DSC profiles of the rehydrogenated samples of (a) MgH$_2$, (b) MgH$_2$-5ps, and (c) MgH$_2$-5ap mechanically milled for 10 h. The heating rate was 5 K/min.

**TABLE 2: Results of the Interpolation of the Desorption Data in Figure 8**

<table>
<thead>
<tr>
<th>sample</th>
<th>temp (K)</th>
<th>$n \pm \Delta n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgH$_2$-5ap</td>
<td>573</td>
<td>1.5 $\pm$ 0.1</td>
</tr>
<tr>
<td></td>
<td>553</td>
<td>1.6 $\pm$ 0.1</td>
</tr>
<tr>
<td>MgH$_2$-5ps</td>
<td>623</td>
<td>1.4 $\pm$ 0.1</td>
</tr>
<tr>
<td></td>
<td>573</td>
<td>1.5 $\pm$ 0.1</td>
</tr>
<tr>
<td>MgH$_2$-2FeCoNi</td>
<td>573</td>
<td>1.7 $\pm$ 0.1</td>
</tr>
<tr>
<td>MgH$_2$</td>
<td>623</td>
<td>1.5 $\pm$ 0.1</td>
</tr>
</tbody>
</table>

Table 2: Results of the Interpolation of the Desorption Data in Figure 8

where $T_p$ is the peak temperature of the endothermic effect, $\beta$ is the heating rate, $E_A$ is the activation energy, and $R$ is the gas constant. The Kissinger plots, i.e., $\ln[\beta/T_p^2]$ as a function of the inverse of $T_p$, are given in Figure 10. From the slope of the fitted line, the activation energy of pure MgH$_2$, MgH$_2$-5ps, and MgH$_2$-5ap was estimated to be 126 $\pm$ 3, 122 $\pm$ 1, and 96 $\pm$ 1 kJ/mol, respectively. It was believed that the addition of SWNTs may facilitate the hydrogen diffusion in the bulk material, whereas according to the evaluated results, only a slight change on the activation energy exists between the samples MgH$_2$ and MgH$_2$-5ps. It was therefore suggested that the hydrogen diffusion was not an energy-consuming step in the desorption processes of MgH$_2$. In other words, the H-dissociation/recombination processes may consume most of the activation

**Figure 10.** The Kissinger plot for the hydrogen desorption reaction for (a) MgH$_2$, (b) MgH$_2$-5ps, and (c) MgH$_2$-5ap mechanically milled for 10 h. The heating rate used in DSC measurements was 2, 5, 10, and 20 K/min.
energy. The considerable decrease on activation energy (about 30 kJ/mol) achieved in the sample with as-prepared SWNTs additive clearly should be correlated to the well-known capability of metal catalyst in facilitating the recombination of H₂ molecules.

4. Conclusions

The as-prepared SWNTs possess a pronounced catalytic effect on the hydrogen storage of Mg. MgH₂-5ap composite exhibits faster absorption/desorption kinetics than MgH₂ with purified SWNT additive, and higher hydrogen capacity than MgH₂-2(FeCoNi) composite. For MgH₂-5ap, a hydrogen amount of 6.0 wt % can be absorbed within 1 h at 423 K and 0.5 h at 573 K. In addition, the nucleation and growth dynamics analysis by using the Johnson–Mehl–Avrami (JMA) theory suggests that the rate-limiting step is the hydrogen diffusion in the desorption process of MgH₂ at measurement temperature, and the activation energy of pure MgH₂, MgH₂-5ps, and MgH₂-5ap according to Kissinger method was estimated to be 126 ± 3, 122 ± 1, and 96 ± 1 kJ/mol, respectively. This indicates that the catalytic effect due to as-prepared SWNTs adding significantly decreases the activation energy for hydrogen desorption. Our results suggest that the metallic particles contained in the as-prepared SWNTs and SWNTs are mainly responsible for the kinetic enhancement and H-capacity increase, respectively. A favorable synergetic catalytic effect of SWNTs and metallic particles has been achieved in the Mg-base composite containing as-prepared SWNTs.

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References and Notes

(22) Shang, C. X.; Guo, Z. X. J. Power Sources 2004, 129, 73.