Hydrogen Storage Properties of a Mg–Ni Nanocomposite Coprecipitated from Solution

Yana Liu, Jianxin Zou, Xiaqin Zeng, Xiaomei Wu, Dejiang Li, and Wenjiang Ding

ABSTRACT: Reducing Mg particles to nanoscale and doping with various catalysts are considered as efficient approaches for improving the hydrogen storage properties of Mg/MgH2. It has been established that doping Ni or Mg2Ni into nano-Mg/MgH2 through physical routes remarkably improves the hydrogen sorption kinetics. In this work, a Mg–Ni nanocomposite has been coprecipitated from a tetrahydrofuran (THF) solution containing anhydrous magnesium chloride (MgCl2), nickel chloride (NiCl2), and lithium naphthalide (LiNp) as the reducing agent. TEM observations reveal that Ni nanoparticles are distributed homogeneously on the surface of those larger Mg particles with sizes ranging from 10 to 20 nm in the nanocomposite. It is observed that γ-MgH2 phase appears when the nanocomposite is hydrogenated at temperatures below 225 °C. Pressure–composition–temperature (PCT) measurements reveal that the Mg–Ni nanocomposite has superior hydrogen storage properties over the pure Mg prepared using the same method. For instance, the Mg–Ni nanocomposite can absorb 85% of its maximum hydrogen capacity within 45 s at 125 °C, and a hydrogen capacity of 5.6 wt % can be obtained within 10 h at room temperature. In addition, the dehydrogenation temperature of the hydrogenated Mg–Ni nanocomposite is also much lower than that of the hydrogenated pure Mg. The hydrogenation and dehydrogenation enthalpies of the Mg–Ni nanocomposite are determined to be −70.0 and 70.7 kJ/mol H2, slightly lower than those for the reduced pure Mg. The excellent hydrogen sorption properties of the Mg–Ni nanocomposite can be attributed to the nanosize effect of Mg particles and the gateway effect of MgNi formed in the composite after hydrogenation/dehydrogenation cycles.

1. INTRODUCTION

Magnesium hydride is considered to be one of the most promising hydrogen storage materials due to its high hydrogen storage capacity (7.6 wt %), environment friendliness, and low cost. However, the sluggish hydrogenation and dehydrogenation kinetics at practical operating temperatures and the high desorption temperature limit its practical application.1–3 The low dehydrogenation kinetics of MgH2 is mainly due to the slow dissociation rate of molecular H2 on the Mg surface, the low H diffusion rate in bulk Mg/MgH2, and formation of MgO on the surface of Mg/MgH2.4 Moreover, its high desorption temperature is related to the high stability of the Mg–H bonds.5 Various attempts have been undertaken to overcome the kinetic limitations and improve the potential thermodynamics for pure Mg, which can be divided into two groups: (i) reducing Mg particles to nanoscale and (ii) introducing various catalysts into the Mg system. Indeed, nanosized Mg has outstanding advantages for hydrogen storage, such as increased surface area when it reacts with hydrogen and shortened hydrogen diffusion distances for H atoms.6–8 Consequently, many methods have been attempted to synthesize Mg nanoparticles to improve the hydrogen thermodynamic and kinetic properties for pure Mg, such as ball milling,9,10 gas-phase condensation,11–13 nanococondensation14–17 and chemical reduction in the solution.18,19 Ball milling is the most often used method for synthesis of Mg nanoparticles. However, this method cannot ensure the particle size distribution within a desired narrow range. Moreover, the products of ball milling are usually in a metastable state and thus tend to aggregate to large particles upon de/rehydrogenation cycles.17 The arc plasma method is one of the gas-phase condensation techniques for synthesis of Mg nanoparticles, which has advantages such as high production rate, low cost, and low reactivity to air. However, the particle size of Mg prepared through the arc plasma method ranges from 50 to 500 nm with an average size of about 300 nm, which is larger than the particle size of Mg prepared by other methods.11 Nielsen et al.7 pointed out that the thermodynamic improvement is suggested to occur only for small MgH2 nanoparticles with a size less than 5 nm, while the kinetic enhancement occurs for larger Mg nanoparticles below 50 nm. Therefore, the reduction of Mg particles down to 50 nm may be more effective for improving sorption properties of Mg-based hydrogen storage materials. MgH2 nanoparticles with a size of <3 nm were prepared by direct hydrogenation of MgBu2 inside the pores of carbon scaffold.14 However, MgH2 weight percentage in MgH2@ACF composite was not more than 22 wt percent.
% since only a portion of pores in ACF can be filled with MgH2.

The Rieke method is a general approach for preparing highly reactive metal powders by reducing metal salts in ethereal or hydrocarbon solvents using alkali metals. Many metals can be prepared by the Rieke method, such as Mg, Zn, Al, In, Th, U, Ti, Cr, Mn, Fe, Ni, Co, Cd, Pt, Pd, and Ca. Recently, an adapted Rieke method has been developed to synthesize Mg nanoparticles by reducing magnesocene (MgCp2) dissolved in 1,2-dimethoxyethane or THF, which allows one to control the particle size and phase purity. These Mg particles with an average size of 25 nm can absorb 95% of their maximum capacity within 60 s at 300 °C. An air-stable composite containing Mg nanocrystals embedded in PMMA was synthesized through an adapted Rieke method, which enables hydrogen sorption with both high density and rapid kinetics (uptake < 30 min at 200 °C). Therefore, the adapted Rieke method is a promising method to produce Mg nanoparticles and provides a simple route to dramatically enhance hydrogen sorption kinetics of Mg. Considering the high cost of MgCp2, cheaper anhydrous MgCl2 is used to prepare Mg-based nanoparticles by the adapted Rieke method in the present work.

Various catalysts have been added into Mg/MgH2 to improve their hydrogen storage properties, including transition metals, metal oxides, and graphite. Among them, transition-metal compounds show high efficiency due to the high affinity of transition-metal cations toward hydrogen. Liang et al. found that the sorption kinetics of MgH2 could be improved dramatically after doping with 5 mol % transition metals (Ti, V, Mn, Fe, and Ni). MgH2 doped with 2 mol % Ni nanoparticles could desorb a large amount of hydrogen (6.5 wt %) in the temperature range from 150 to 250 °C at a heating rate of 5 °C/min under He gas flow. These results show that Ni is an effective catalyst for improving the sorption kinetics of MgH2. Recently, Shao et al. reported superior hydrogen sorption kinetics in Mg−Ni materials and attributed the improvement to the unique nanostructure formed after the special synthesis procedures, the catalytic effect of the Mg−Ni nanophase, and the synergistic effects between the Mg2Ni and the Mg in the materials. Therefore, Mg2Ni formed during de/rehydrogenation cycles may act as a good catalyst for improving the hydrogen sorption properties of Mg-based materials. In the present work, in order to find a new route toward improving hydrogen sorption kinetics of Mg nanoparticles, a Mg−Ni nanocomposite was copercolated from a homogeneous THF solution containing anhydrous MgCl2, NiCl2, and lithium naphthalide (LiNp) as the reducing agent. The synthetic approach to produce the Mg−Ni nanocomposite is shown in Figure 1.

Figure 1. Synthetic approach of the Mg−Ni nanocomposite using an adapted Rieke method.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. All steps were performed in a glovebox filled with purified argon to avoid the influence of oxygen and moisture. Both the oxygen and the water vapor levels inside the glovebox were kept below 1 ppm. First, naphthalene (11.265 g) and lithium (0.610 g) were added in the freshly distilled THF (100 mL) while stirring vigorously to form a deep green solution at room temperature. Second, anhydrous MgCl2 (3.808 g) and NiCl2 (0.239 g) were dissolved in THF (400 mL), which form a light yellow solution after stirring vigorously at 60–70 °C. The solution was then cooled down to room temperature. Third, the light yellow solution (containing MgCl2, NiCl2) was added into deep green solution (containing LiNp) under stirring at room temperature. Lastly, the resultant products were isolated by centrifugation, washed with THF three times, and dried by vacuum pumping to remove the residual THF. For the sake of comparison, pure Mg was also reduced from MgCl2/THF solution by LiNp using the same processing.

2.2. Characterization. Structure characterization of as-prepared samples was performed by X-ray diffraction (XRD) using an apparatus (D/max 2550VL/PCX) equipped with a Cu Kα radiation source. In order to isolate the sample from air, the sample powder was put on a designed XRD holder and sealed with scotch tape in the glovebox. Scherrer’s equation was used to calculate the average crystallite size of as-prepared composites, which can be expressed by the following equation:

\[
D = \frac{K\lambda}{B \cos \theta}
\]

where D is the crystallite diameter, λ is the X-ray wavelength, and B is the full width at half-maximum of a diffraction peak. The morphology and microstructure of as-prepared samples were observed using a JEM-2100F transmission electron microscopy (TEM). The composition of the Mg−Ni nanocomposite was analyzed by an energy-dispersive spectrometer (EDS). The hydrogen absorption/desorption properties of as-prepared samples were examined using a Sievert-type pressure−composition−temperature (PCT) volumetric apparatus at various temperatures. The activation process is not needed for all samples before hydrogen storage properties measurements. Ten hydrogenation/dehydrogenation cycles measurements were performed for the sample as follows: absorption at 150 °C about 2 h under 3 MPa hydrogen pressure, followed by desorption at 325 °C about 2 h under vacuum. Desorption performance of as-prepared samples was examined using TGA analysis. A reduction in calorimetry (DSC, Netzsch STA 449F3) at heating rates of 3, 5, and 10 °C/min under Ar gas flow.

2. RESULTS AND DISCUSSION

3.1. Microstructural Characterization. Figure 2a and 2b shows the XRD patterns of the reduced pure Mg and the Mg−Ni nanocomposite, respectively. As can be seen, almost all broad diffraction peaks of the Mg−Ni nanocomposite match for the hexagonal Mg phase with the lattice parameters of a = b = 0.3206 nm and c = 0.5206 nm, and the average crystallite size of Mg is calculated to be about 11.6 nm. Only a weak broad diffraction peak located in the 2Theta range of 42–46° can be determined to be the characteristic peak of Ni. This is in accordance with the XRD pattern of pure Ni prepared using the adapted Rieke method, as shown in the inset of Figure 2. It is possible that Ni synthesized from solution is in the form of

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extremely fine particles or amorphous. In contrast, the lattice parameters and average crystallite size of the reduced pure Mg are determined to be $a = b = 0.3196$ nm and $c = 0.5199$ and $16.1$ nm, respectively. Therefore, addition of Ni could reduce the crystallite size of Mg and increase the lattice parameters of Mg phase. Such a size reduction of Mg may be due to the fact that the reduced Ni could provide more nucleation sites for Mg and inhibit the crystallites of Mg from growing up or aggregating to larger crystallites during the preparation process. In addition, some Ni atoms may dissolve into the lattice of Mg phase during the vigorously stirring, leading to the increase in lattice parameters. A small amount of MgO can be detected in the reduced pure Mg and the Mg–Ni nanocomposite, which is likely due to the possible oxidation that occurred during sample preparation for the XRD analysis. Figure 2c and 2d shows the XRD patterns of the Mg–Ni nanocomposite hydrogenated at 150 and 250 °C, respectively. (Inset) XRD pattern of pure Ni.

**Figure 2.** XRD patterns of (a) the reduced pure Mg, (b) the Mg–Ni nanocomposite, and (c, d) the Mg–Ni nanocomposite hydrogenated at 150 and 250 °C, respectively. (Inset) XRD pattern of pure Ni.
The typical TEM micrographs of the reduced pure Mg and the Mg−Ni nanocomposite are shown in Figure 4a and 4b. It is observed that plate-shaped pure Mg particles are stacked together, forming a shape like "chicken claws" structure. The length of plate-shaped particles ranges from 50 to 200 nm, while the thickness ranges from 10 to 20 nm. In contrast, the Mg−Ni nanocomposite is composed of irregular shaped particles aggregating together with their particle sizes ranging from 10 to 20 nm, as shown in Figure 4b. This result is consistent with XRD analysis (Mg with an average crystallite size of 11.6 nm). The above results indicate that Ni could dramatically change the morphology of Mg particles and reduce the particle size of Mg. In the corresponding selected area electron diffraction (SAED) pattern shown in the inset of Figure 4b the diffraction rings or points can be indexed with (100), (002), (101), (102), (110), (103), and (201) for Mg, (111), (200), and (220) for MgO, and (111) for Ni. Formation of MgO phase is likely due to the possible oxidation occurred during TEM sample preparation. In order to analyze the morphology of Ni nanoparticles, a dark field image taken from the diffraction ring of the Ni (111) plane and MgO (200) plane is shown in Figure 4c. It can be seen that Ni and MgO

Figure 3. XRD patterns of (a) the reduced pure Mg hydrogenated at 150 °C and (b, c, d, e) the Mg−Ni nanocomposite hydrogenated at 100, 150, 200, 225, and 250 °C, respectively.

Figure 4. (a) TEM micrograph of the reduced pure Mg. (b) TEM micrograph of the Mg−Ni nanocomposite and (c) the corresponding dark field TEM image of Ni/MgO nanoparticles. (d) TEM micrograph of the Mg−Ni nanocomposite hydrogenated at 150 °C. Insets in a, b, and d show the corresponding SAED patterns.
nanoparticles, having bright contrasts and a particle size of several nanometers, are distributed homogeneously on the surface of those large Mg particles. In order to qualitatively evaluate the homogeneity of the Ni distribution in Mg particles, a scanning transmission electron microscope (STEM) micrograph of the Mg–Ni nanocomposite (Figure 5a) along with energy-dispersive spectrometer (EDS) elemental maps of Mg (Figure 5b) and Ni (Figure 5c) are shown in Figure 5. As can be seen, Ni is homogeneously distributed in the Mg–Ni nanocomposite. The actual Ni weight content in the prepared Mg–Ni nanocomposite is determined to be about 7.8 wt % by EDS. The TEM micrograph and corresponding SAED pattern of the Mg–Ni nanocomposite hydrogenated at 150 °C for 10 h are shown in Figure 4d. The diffraction rings or points correspond to Mg, MgO, β-MgH₂, and Mg₂Ni phases. Only a few diffraction points can be indexed with β-MgH₂ phase. However, XRD analysis has shown that hydrogenated nanocomposite consists of β-MgH₂ phase as the majority phase, together with minority MgO and Mg₂NiH₄ phases. The same phenomenon was also observed in previous research works, which can be attributed to hydrogen release from nanosized MgH₂ during the TEM measurement under high-vacuum condition and exposure to the electron beam. As can be seen, the particle size of hydrogenated Mg–Ni nanocomposite ranges from 10 to 30 nm, which is in accordance with XRD results.

3.2. Hydrogen Sorption Properties of the Mg–Ni Nanocomposite. The PCT curves of the reduced pure Mg and the Mg–Ni nanocomposite measured at different temperatures in a hydrogen pressure range from 0.02 to 4 MPa are shown in Figure 6a and 6c. The data obtained from PCT measurements are summarized in Table 1. Each PCT curve of the Mg–Ni nanocomposite shows only a single plateau region. This is attributed to the fact that the amount of Mg₂NiH₄ or Mg₂Ni is too low to form an obvious upper plateau region. The maximum hydrogen absorption capacities of the Mg–Ni nanocomposite at 225, 250, 275, 300, 325, 350, and 375 °C are 5.6, 5.7, 5.8, 5.8, 5.9, 5.9, and 6.0 wt %, respectively, with a fairly close amount of reversible hydrogen sorption capacity. It is observed that the maximum hydrogen absorption capacity of the Mg–Ni nanocomposite is lower than the theoretical capacity of 7.6 wt % for MgH₂, which is mainly due to addition of Ni. The Mg–Ni nanocomposite can absorb and release hydrogen at temperatures down to 225 °C. In contrast, the reduced pure Mg cannot release hydrogen even at 300 °C, as shown in Figure 6a. It is found that the absorption and desorption plateaus of the Mg–Ni nanocomposite from the PCT curves are quite flat with a very small gap between them,
indicating a good thermodynamic property of the Mg\textendash\text{Ni} nanocomposite. The reaction enthalpy can be calculated using the van’t Hoff equation. The van’t Hoff plots (ln $P$ versus $1/T$) of the reduced pure Mg and the Mg\textendash\text{Ni} nanocomposite are shown in Figure 6b and 6d. According to the fitting lines, the van’t Hoff equations for the Mg\textendash\text{Ni} nanocomposite are determined to be $\ln(P_{ab}) = -8.42 \times 10^3/T + 15.20$ for absorption and $\ln(P_{de}) = -8.51 \times 10^3/T + 15.23$ for desorption. Therefore, the hydrogenation enthalpy ($\Delta H_{ab}$) is $-70.0 \text{ kJ/mol H}_2$, while the dehydrogenation enthalpy ($\Delta H_{de}$) is $70.7 \text{ kJ/mol H}_2$. $\Delta H_{de}$ values dehydrogenation of the Mg\textendash\text{Ni} nanocomposite are slightly lower than the standard values for Mg ($\pm 74.7 \text{ kJ/mol H}_2$) and the reduced pure Mg ($\Delta H_{de} = 74.8 \text{ kJ/mol H}_2$, $\Delta H_{de} = 76.3 \text{ kJ/mol H}_2$). These results indicate that the thermodynamics of hydrogenation and dehydrogenation of the Mg\textendash\text{Ni} nanocomposite is slightly improved by addition of Ni nanoparticles, which is in accordance with recent experimental observations and theoretical calculations for nanosized Mg.\textsuperscript{43,45} For instance, H values of nanostructured MgH$_2$\textendash\text{Ni} prepared by ultra-high-energy high-pressure and MgH$_2$\textendash\text{Ni/Ti (4:1, with 26.7 atom % Ni) prepared by ball milling under hydrogen atmosphere were determined to be 68 and 67.8 kJ/mol H$_2$, respectively.\textsuperscript{46,47} In addition, Dai\textsuperscript{45} and Shevlin\textsuperscript{43} carried out theoretical calculations and showed that doping the MgH$_2$ with Ni would improve the dehydrogenation properties of MgH$_2$ because (i) the presence of the empty d states of the Ni dopant modifies the binding and lessens the charge of H ions, (ii) the bonding between the Mg and the H atoms is weakened, and (iii) there is a higher probability of forming the thermodynamically less stable Mg$_2$NiH$_4$ phase. In this work, XRD results have shown that Ni atoms may dissolve in the lattice of Mg/MgH$_2$ during the absorption process and react with Mg to form Mg$_2$Ni phase. Considering the above, it is thus reasonable to have altered thermodynamic properties for the Mg\textendash\text{Ni} nanocomposite synthesized using an adapted Rieke method.

In order to investigate the hydrogen absorption kinetic of the Mg\textendash\text{Ni} nanocomposite, the hydrogen absorption curves of the reduced pure Mg and the Mg\textendash\text{Ni} nanocomposite measured at different temperatures under 3 MPa hydrogen pressure are shown in Figures 7 and 8, respectively. The data obtained from hydrogen absorption kinetics measurements are summarized in Table 2. As can be seen in the first absorption curves of the reduced pure Mg at different temperatures (Figure 7a), pure Mg can absorb 85% of its maximum hydrogen capacity within 52 and 1004 s at 250 and 200 °C, respectively. This rapid hydrogen absorption kinetics is similar to the cases reported by

<table>
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<th>sample name</th>
<th>temp (°C)</th>
<th>max hydrogen absorption (wt %)</th>
<th>absorption plateau (MPa)</th>
<th>desorption plateau (MPa)</th>
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<td>0.508</td>
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<td></td>
<td>375</td>
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<td>0.920</td>
<td>0.880</td>
</tr>
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<td>Nano Mg\textendash\text{Ni}</td>
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<td>0.012</td>
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<tr>
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<td>375</td>
<td>6.0</td>
<td>0.950</td>
<td>0.854</td>
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Figure 7. Hydrogen absorption curves of the reduced pure Mg measured at different temperatures under 3 MPa hydrogen pressure: (a) 1st hydrogen absorption and (b) the corresponding $\ln k - 1000/T$ plot; (c) 1st and 3rd hydrogen absorption measured at 250 °C.

Figure 8. Hydrogen absorption curves of the Mg–Ni nanocomposite measured at different temperatures under 3 MPa hydrogen pressure: (a) 1st hydrogen absorption; (b) 1st–10th hydrogen absorption measured at 150 °C; (c) 5th hydrogen absorption and (d) the corresponding $\ln k - 1000/T$ plot.
Norberg and Jeon. In contrast, for the Mg–Ni nanocomposite, 85% of its maximum hydrogen capacity is obtained after 670 and 1049 s at 250 and 200 °C respectively, while 4.0 wt% of hydrogen is absorbed after 2 h at 150 °C, as shown in Figure 8a. It can be found that the hydrogen absorption kinetics of the Mg–Ni nanocomposite in its first sorption cycle is slightly lower than that for the reduced pure Mg. This result is likely due to the fact that Mg particles are covered by Ni nanoparticles, resulting in the reduction of active surface area for Mg to absorb hydrogen. In addition, MgNi is not formed in considerable amounts at the beginning of the first H absorption; thus, the gateway effect from MgNi on H absorption in Mg is still weak. The 1st–10th hydrogen absorption curves of the Mg–Ni nanocomposite measured at 150 °C are shown in Figure 8b. It can be found that the absorption kinetics of the Mg–Ni nanocomposite increases quickly with increasing absorption cycles in the first several cycles and reaches a plateau value after 4 cycles. In particular, the nanocomposite could absorb 85% of its maximum hydrogen capacity within 45 s at 125 °C. Such an excellent hydrogen absorption kinetics at low temperature of the Mg–Ni nanocomposite is much better than that of the reduced pure Mg and the Mg–Ni composites prepared by mechanical milling (~2.09 wt% of hydrogen at 120 °C within 1800 s). The improved absorption kinetics can be further understood by calculating the hydrogenation activation energy of the Mg–Ni composite. Several solid-state reaction mechanism models have been tested to select the best-fitting form, such as the nucleation and growth processes, phase-boundary-controlled reactions, and diffusion-controlled reactions. The hydrogen absorption data (50, 75, 100, 125 °C) of the Mg–Ni nanocomposite can be best modeled by the Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory, and the linear equation is described as follows

$$\ln\left(\frac{\ln(1-\alpha)}{\ln1}\right) = \eta \ln k + \eta \ln t$$  

(2)

where $\alpha$ is the fraction of Mg transformed into MgH$_2$ at time $t$, $k$ is an effective kinetic parameter, and $\eta$ is the Avrami exponent or reaction order. The values of $\eta$ (the slope) and $\eta$ ln$k$ (the intercept) can be obtained from the fitting linear of $\ln[-\ln(1-\alpha)]$ vs ln $t$ at each temperature. Thus, the value of $k$ and $\eta$ at different temperatures can be obtained. The apparent activation energy ($E_a$) for the absorption process can be calculated according to Arrhenius equation as

$$k = A \exp(-E_a/RT)$$

(3)

where $A$ is a temperature-independent coefficient, $R$ is the universal gas constant, and $T$ is the absolute temperature. The Arrhenius type plot of ln $k$ vs 1000/$T$ is drawn in Figure 8d. The apparent activation energy ($E_a$) for hydrogenation in the Mg–Ni nanocomposite is determined to be 57.4 kJ/mol H$_2$. This value is much lower than that of the reduced pure Mg (73.1 kJ/mol H$_2$ calculated from hydrogen absorption data (150, 175, 200 °C)). Such a low energy barrier explains the excellent absorption kinetics of the Mg–Ni nanocomposite at low temperatures. The improved hydrogen absorption kinetics can be mainly attributed to two factors: the nanosize effect and catalytic effect of MgNi. Fernández et al. pointed out that formation of metal hydrides involves a number of steps: (1) H$_2$ adsorption onto the surface, (2) H$_2$ dissociation, (3) H chemisorption, (4) H migration from surface to bulk, (5) H diffusion and nucleation of hydride, and (6) growth of hydride phase. The rate-controlling step is considered to be the slowest step. The reduction of particle size can shorten the diffusion length of hydrogen and increase the ratio of surface to bulk atoms, which can provide more nucleation sites for formation of magnesium hydride and enhance the diffusion of hydrogen into the magnesium grains. MgNi is also a good catalyst for the hydrogen chemisorption in the composite, and the phase boundaries between Mg and MgNi enhance hydrogen diffusion. The interface between Mg–MgNi can provide active nucleation sites for MgH$_2$ and $\alpha$-solution (MgNiH$_x$, $x \leq 0.3$) could act as channels for hydrogen atoms to spill over into the Mg matrix. In addition, MgNi may play a role as the grain growth inhibitor that prevents the coarsening of Mg or MgH$_2$ particles during the hydrogenation/dehydrogenation cycles. All of these positive factors contribute to the excellent hydrogen absorption kinetics of the Mg–Ni nanocomposite.

In order to investigate the desorption performance of the Mg–Ni nanocomposite, DSC curves of the reduced pure Mg and the Mg–Ni nanocomposite hydrogenated at 150 °C for 10

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Hydrogen Capacity after 2 h (wt %)</th>
<th>Time Needed to 85% of its Maximum Hydrogen Capacity (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Mg</td>
<td>2.6</td>
<td>4862</td>
</tr>
<tr>
<td>150</td>
<td>5.9</td>
<td>1004</td>
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<tr>
<td>200</td>
<td>7.0</td>
<td>52</td>
</tr>
<tr>
<td>250</td>
<td>7.0</td>
<td>670</td>
</tr>
<tr>
<td>Nano Mg–Ni</td>
<td>4.0</td>
<td>2025</td>
</tr>
<tr>
<td>200</td>
<td>5.8</td>
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<td>75</td>
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</tr>
<tr>
<td>100</td>
<td>5.8</td>
<td>45</td>
</tr>
</tbody>
</table>
As can be seen, there is a broader endothermic peak corresponding to desorption of $\beta$-MgH$_2$ and $\gamma$-MgH$_2$ phase in the Mg–Ni nanocomposite at all heating rates. Peak temperatures of DSC curves of hydrogenated nanocomposite at heating rates of 3, 5, and 10 °C/min are reduced to 266.2, 276.2, and 291.1 °C, respectively, and the onset dehydrogenation temperature at a heating rate of 3 °C/min was dramatically reduced to 244.6 °C. In contrast, peak dehydrogenation temperatures of the hydrogenated pure Mg at heating rates of 3, 5, and 10 °C/min are 332.7, 340.8, and 352.9 °C, respectively, as shown in Figure 9a. The onset dehydrogenation temperature of the hydrogenated Mg–Ni nanocomposite is 66.5 °C lower than that of the hydrogenated pure Mg. The improved desorption property can be further understood by calculating the activation energy of the dehydrogenation reaction of the hydrogenated Mg–Ni nanocomposite. The activation energy, $E_d$, for the hydrogen desorption mechanism of the Mg–Ni nanocomposite is obtained from DSC measurements at different heating rates by the Kissinger equation

$$\ln(\beta/T_p^2) = A - E_d/(RT_p)$$

where $\beta$ is the heating rate, $T_p$ is the peak temperature, and $A$ is a linear constant. The $E_d$ values for all samples can be estimated from the slope of the plot of $\ln(\beta/T_p^2)$ vs $1000/T_p$ as shown in Figure 9b. The apparent activation energy ($E_d$) for dehydrogenation of the hydrogenated Mg–Ni nanocomposite is determined to be 139.1 kJ/mol H$_2$. This value is slightly lower than that of the reduced pure Mg (147.4 kJ/mol H$_2$ calculated from Figure 9d). The reduction in the $E_d$ values is in good agreement with desorption curves shown in Figure 9c, resulting in extremely rapid desorption kinetics of the Mg–Ni nanocomposite. The particle size of the Mg–Ni nanocomposite hydrogenated at 150 °C is about 10–30 nm, which is much smaller than that of MgH$_2$ prepared by other methods. According to previous studies, the size reduction of MgH$_2$ could decrease the hydrogen desorption temperature and improve the first hydrogen desorption kinetics. In addition, $\gamma$-MgH$_2$ phase can destabilize $\beta$-MgH$_2$ and thereby lower the dehydrogenation temperature. Furthermore, Zalusk et al. found that the ball-milled mixtures of MgH$_2$ and Mg$_2$NiH$_4$ exhibited a synergetic effect for the hydrogen desorption. Those fine Mg$_2$NiH$_4$ particles on the surface of large MgH$_2$ grains serve as gateways for hydrogen desorption from the interior of the MgH$_2$ grains. Therefore, the effects from nanosize, the existence of $\gamma$-MgH$_2$ phase, and Mg$_2$NiH$_4$ contribute to the superior hydrogen desorption property of the hydrogenated Mg–Ni composite.

3. CONCLUSIONS

In the present work, the Mg–Ni nanocomposite was coprecipitated for the first time from a homogeneous solution using an adaption of Rieke method. The main conclusions are as follows.

1. TEM observations revealed that the Mg–Ni nanocomposite was composed of Ni nanoparticles with sizes of several nanometers distributed homogeneously on the surface of those large Mg particles with sizes ranging from 10 to 20 nm.
2. $\gamma$-MgH$_2$ phase formed when the Mg–Ni nanocomposite was hydrogenated below 225 °C for its first sorption cycle.
3. The hydrogenation and dehydrogenation enthalpies of the Mg–Ni nanocomposite changed as compared to those for the reduced pure Mg, indicating that the...
The thermodynamic property of Mg in the Mg–Ni nano-composite was slightly improved by Ni addition.

(4) The Mg–Ni nanocomposite showed extremely fast hydrogen absorption kinetics at lower temperatures: the composite can absorb 85% of its maximum hydrogen capacity within 45 s at 125 °C, and a hydrogen capacity of 5.6 wt % can be obtained within 10 h at room temperature. Absorption apparent activation energy is determined to be 57.4 kJ/mol H₂ for the Mg–Ni nanocomposite.

(5) The hydrogen desorption temperature of the hydrogenated Mg–Ni nanocomposite was much reduced with respect to that of the hydrogenated pure Mg. For example, the onset dehydrogenation temperature of the hydrogenated Mg–Ni nanocomposite is 66.5 °C lower than that of the hydrogenated pure Mg. The desorption apparent activation energy of the Mg–Ni nanocomposite is determined to be 139.1 kJ/mol H₂.

(6) The superior hydrogen sorption properties of the Mg–Ni nanocomposite can be mainly attributed to factors involving nanosized Mg, formation of γ-MgH₂ phase, and the gateway effect of MgNi formed after hydrogenation/dehydrogenation cycles.

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Notes
The authors declare no competing financial interest.

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