Research Article

Preparation and Hydrogen Storage Properties of Mg-Rich Mg-Ni Ultrafine Particles

Jianxin Zou,1,2 Haiquan Sun,1 Xiaoqin Zeng,1,2 Gang Ji,3 and Wenjiang Ding1,2

1 Shanghai Engineering Research Center of Magnesium Materials and Applications and National Engineering Research Center of Light Alloy Net Forming, Shanghai Jiao Tong University, Shanghai 200240, China
2 State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
3 Unité Matériaux Et Transformations (UMET), CNRS UMR 8207, Université Lille 1, 59655 Villeneuve d’Ascq, France

Correspondence should be addressed to Jianxin Zou, zoujx@sjtu.edu.cn

Received 29 August 2012; Accepted 16 October 2012

Academic Editor: Kemin Zhang

Copyright © 2012 Jianxin Zou et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In the present work, Mg-rich Mg-Ni ultrafine powders were prepared through an arc plasma method. The phase components, microstructure, and hydrogen storage properties of the powders were carefully investigated. It is found that Mg2Ni and MgNi2 could be obtained directly from the vapor state reactions between Mg and Ni, depending on the local vapor content in the reaction chamber. A nanostructured MgH2 + Mg2NiH4 hydrogen storage composite could be generated after hydrogenation of the Mg-Ni ultrafine powders. After dehydrogenation, MgH2 and Mg2NiH4 decomposed into nanograined Mg and Mg2Ni, respectively. Thermogravimetry/differential scanning calorimetry (TG/DSC) analyses showed that Mg2NiH4 phase may play a catalytic role in the dehydriding process of the hydrogenated Mg ultrafine particles.

1. Introduction

Mg-based alloys and composites are believed to be promising candidates as hydrogen storage carriers due to their high hydrogen storage capacity (7.6 wt% for MgH2 and 3.6 wt% for Mg2NiH4), great abundance, and low cost [1]. However, the sluggish hydrogen sorption kinetics and high operating temperature of Mg (>573 K) limit its practical applications. Different methods, such as alloying, catalyst addition, and nanocrystallization, have been used to improve the hydrogen thermodynamics and sorption kinetics of Mg [2–4]. Consequently, various Mg-based alloys, composites, and compounds have been developed with superior hydrogen sorption kinetics over pure Mg. Among those Mg-based materials, Mg2Ni intermetallic compound is well known to form Mg2NiH4 hydride with high reaction rate, which has a hydrogen storage capacity of 3.6 wt% [1]. However, it is difficult to obtain Mg alloys with accurately desirable compositions by conventional melt-cast methods due to following reasons: (1) Mg has low melting point (923 K) and high vapor pressure (133 Pa at 878 K); (2) Mg is quite active in the presence of oxygen. Especially in the case of Mg-Ni binary system, casting is quite difficult because of the large difference in melting point between Ni (1728 K) and Mg (923 K). Furthermore, based on the binary phase diagram [5, 6], single phase Mg2Ni cannot be simply obtained by casting as a phase separation occurs during solidification.

Mechanical alloying (MA) method has been widely used to produce nanostructured alloys or composites, especially to produce amorphous and nanocrystalline Mg2Ni alloys. However, it usually takes a long time to prepare alloys by the MA method, the sample can be contaminated during the milling process, oxidation occurs even in a protective atmosphere [7]. Moreover, it is difficult to obtain a homogenous sample by the MA method [8]. It is known that nano- or ultrafine particles have a lowered melting point because of the small size and large specific surface area of the particles, which implies a possibility of preparing the Mg2Ni compound by using magnesium and nickel nanoparticles. Lio et al. synthesized Mg2Ni intermetallic nanoparticles by a two-step method [9]. First, Mg and Ni nanoparticles were prepared by hydrogen plasma-metal reaction. Second,
The Mg-Ni ultrafine powders

2.1. Sample Preparation.

hydrogen pressure, Mg$_2$NiH$_4$ can be generated, and Mg$_2$Ni under a hydrogen pressure of about 40 bar to react. The mixture of Mg and Ni nanoparticles in a 2:1 molar ratio was compressed into a pellet and was heated up to 623 K. The equipment used to test the hydrogen sorption properties of the Mg-Ni powders was analyzed by thermo-gravimetry/differential scanning calorimetry spectroscopy (TG/DSC) technique.

2.2. Characterization. The phase identification of the Mg-Ni nanoparticles before and after hydrogen absorption was carried out by X-ray diffraction (XRD) using a D/max 2550VL/PCX apparatus equipped with Cu-K$_\alpha$ radiation source. The morphology and microstructure of the powders were observed by using a JEM-2100 transmission electron microscope (TEM), operated at 200 kV. The composition of the Mg-Ni powders was analyzed by inductive coupled plasma emission spectrometer (ICP). A conventional Sievett-type pressure-composition-temperature (P-C-T) apparatus, which means measuring hydrogen content versus pressure by recording the change of gas pressure in a constant volume, was used to test the hydrogen sorption properties of the Mg-Ni ultrafine powders. The testing temperatures were set at 400°C, 375°C, 350°C and 325°C. The hydrogen desorption property of the prepared powders was analyzed by thermo-gravimetry/differential scanning calorimetry spectroscopy (TG/DSC) technique.

3. Results and Discussions

3.1. XRD Analysis. Figures 2(a), 2(b), and 2(c) show the XRD patterns of the as-prepared Mg-Ni ultrafine particles, the samples obtained after the hydrogen absorption and after desorption, respectively. From Figure 2(a), it is seen that the main phases of the Mg-Ni ultrafine particles prepared by DC arc plasma are Mg and Ni, with a small amount of MgO. Besides, the presence of Mg$_2$Ni and MgNi$_2$ phases is also detected. The peaks corresponding to MgNi$_2$ phase are fairly weak, indicating that the volume content of Mg$_2$Ni in the powders is very low. The MgO phase was formed when the Mg-Ni nanoparticles were passivated in the mixture of argon and air. The MgO layer at the surface of the magnesium particles can effectively prevent the further oxidation or even burning of the Mg particles when exposed to air. The existence of Mg$_2$Ni and MgNi$_2$ shows that the following reactions have occurred during the arc plasma evaporation:

$$2\text{Mg} + \text{Ni} \rightarrow \text{Mg}_2\text{Ni} \quad (1)$$

$$\text{Mg} + 2\text{Ni} \rightarrow \text{MgNi}_2 \quad (2)$$

These reactions occurred in vapor state depending on the local vapor concentrations of Mg and Ni. Indeed, Mg has much higher vapor pressure than Ni at the same temperature, resulting in the generation of a vapor rich in Mg during arc evaporation. ICP analysis shows that the average Mg and Ni content in the Mg-Ni ultrafine powders is 7:1 in molar ratio, much higher than the ratio 1:2 in the original mixture. However, the local vapor content may not be homogeneous during arc evaporation of the Mg-Ni mixture. Ni concentration might be higher than Mg in local regions inside the plasma. As a result, both reaction (1) and reaction (2) were not homogeneous.

![Schematic illustration of the DC arc plasma evaporation equipment.](image-url)
and reaction (2) could occur in the mixed vapor, leading to the formation of \( \text{Mg}_2\text{Ni} \) and \( \text{MgNi}_2 \) phases. As the vapor is highly rich in Mg, reaction (1) should be more important than reaction (2). As a result, the amount of \( \text{Mg}_2\text{Ni} \) should be higher than the amount of \( \text{MgNi}_2 \). The fact that the majority phases in the Mg-Ni ultrafine powders are pure Mg and Ni indicates that most of Mg and Ni vapors do not react with each other during evaporation. It has been established that the evaporation rate of metals plays a major role for the generation of the metal particles. According to the Ohno’s model, the vapor generation rate of a metal through hydrogen plasma reaction method is proximately proportional to its reaction parameter, \( R_p \), which can be expressed by the following equation:

\[
R_p = \left( \frac{-\Delta H_r}{L_s} \right) \left[ \frac{N_{\text{H}_2}(T)}{N_{\text{H}_2}(273)} \right],
\]

where \( H_r \) is the reaction enthalpy between metal and hydrogen, \( L_s \) is the heat of vaporization of the metal at the temperature \( T \), and \( N_{\text{H}_2}(T) \) and \( N_{\text{H}_2}(273) \) are densities of the hydrogen molecules in the metal at temperature \( T \) and 273 K. By inputting parameters for Mg and Ni into (3), it is estimated that \( R_p = 1 \) for Mg and \( R_p = 0.17 \) for Ni. The large difference in \( R_p \) values indicates that the evaporation rate for Ni is much lower than that for Mg. This is consistent with the ICP result for which the Ni content in the composite is lower than that in the mixed powders before arc evaporation.

From the XRD pattern in Figure 2(b), it can be seen that most of the Mg-Ni powders have transformed into \( \text{MgH}_2 \) and \( \text{Mg}_2\text{NiH}_4 \) hydrides after the hydrogen absorption at 400°C and 4 MPa. The mechanism for the formation of \( \text{Mg}_2\text{NiH}_4 \) hydride is thought to be the reaction (4)
Mg$_2$NiH$_4$ transforms into Mg$_2$Ni compound, as described by reaction (5) occurred during the isothermal period:

$$\text{Mg} + \text{H}_2 \rightarrow \text{MgH}_2 \quad (4)$$

$$2\text{MgH}_2 + \text{Ni} \rightarrow \text{Mg}_2\text{NiH}_4 \quad (5)$$

As the atomic ratio of Mg: Ni is 7:1 in the Mg-Ni ultrafine powders, the reactions (4) and (5) can be combined together into reaction (6). That is, when Mg-Ni ultrafine powders are completely hydrogenated, the molar ratio of MgH$_2$ to Mg$_2$NiH$_4$ should be around 5:1:

$$\text{Mg}_2\text{Ni} + 7\text{H}_2 \rightarrow 5\text{MgH}_2 + \text{Mg}_2\text{NiH}_4 \quad (6)$$

There is still a small amount of Mg phase observed in the sample after hydrogenation at 400°C, as seen in Figure 2(b). This is due to the fact that some relatively large Mg particles cannot be completely hydrogenated. It is observed from Figure 2(c) that after hydrogen desorption, MgH$_2$ decomposes completely and transforms into Mg, and Mg$_2$NiH$_4$ transforms into Mg$_2$Ni compound, as described by the following reaction:

$$\text{Mg}_2\text{NiH}_4 \rightarrow \text{Mg}_2\text{Ni} + 2\text{H}_2 \quad (7)$$

This principle of the reactions (4), (5), and (7) is used to prepare Mg$_2$Ni compound by Shao et al. [12, 13]. Comparing Figures 2(a) and 2(b), it is worth noting that the diffraction peaks of MgNi$_2$ disappeared after hydrogen absorption. It is believed that MgNi$_2$ should react with MgH$_2$ to form Mg$_2$NiH$_4$ in the presence of high temperature and hydrogen atmosphere, as described by the following reaction:

$$3\text{MgH}_2 + \text{MgNi}_2 + \text{H}_2 \rightarrow 2\text{Mg}_2\text{NiH}_4 \quad (8)$$

3.2. TEM Observations of the Mg-Ni Ultrafine Particles.

Figures 3(a), 3(b), and 3(c) show typical bright field TEM micrographs of Mg-Ni composite powders before hydrogen absorption, the samples obtained after hydrogen absorption and after hydrogen desorption, respectively, with corresponding selected area electron diffraction (SAED) patterns. From Figure 3(a), it is observed that most of the particles have quasispherical shape with the particle size ranges from 50 to 200 nm. The corresponding SAED pattern consists of rings and overlapped dispersed spots. The rings are identified to be Mg and MgO phases. However, the spots are not indexed and could correspond to the Ni, Mg$_2$Ni, and MgNi$_2$ phases based on the result of XRD analysis (Figure 2(a)). Normally, Mg can be directly evaporated into gaseous atoms before melting in the high temperature plasma. This is due to the low melting point and small latent heat of evaporation for Mg. The fast vapor generation rate of the Mg results in the formation of relatively large particles [14]. After hydrogenation at 400°C in 4 MPa hydrogen atmosphere, MgH$_2$ and Mg$_2$NiH$_4$ phases formed in the composite. The typical morphology of these hydrides is shown in Figure 3(b). The particles became transparent having size in the range between 50 and 200 nm, smaller than the Mg particles shown in Figure 3(a). In the corresponding SAED pattern, diffracted rings belonging to MgH$_2$, Mg$_2$NiH$_4$, MgO, and Mg phases can be detected. It is found from Figure 3(c) that after 4 hydrogen absorption and desorption cycles, those large Mg particles have been cracked and broken into smaller particles. The corresponding SAED pattern is mainly composed of well-defined rings belonging to pure Mg. Besides this, MgO and Mg$_2$Ni are also identified. Compared with that of the as-prepared particles obtained using the same SAED aperture (Figure 3(a)), it indicates the grain refinement of Mg particles after hydrogen sorption cycles. The grain refinement of Mg particles is expected to benefit from the hydrogen storage properties owing to the increased surface areas and reduced diffusion length for hydrogen. As a consequence of the reduction in particle size, fresh surface was generated during the hydriding/dehydriding cycles. The presence of new surfaces makes the Mg particles easier to be oxidized. As a result, the amount of MgO increases after hydrogen sorption cycles, as can be observed from the comparison between diffraction peaks of MgO phase in Figures 2(c) and 2(a).

3.3. Hydrogen Storage Properties.

Figure 4 shows the P-C-T curves of the hydrogen absorption-desorption processes for the Mg-Ni ultrafine particles at 400°C, 375°C, 350°C, and 325°C. The data obtained from the P-C-T measurements are summarized in Table 1. Two plateaus of absorption and desorption are clearly visible on each profile. According to the XRD results given above, two types of hydrides, MgH$_2$ and Mg$_2$NiH$_4$, formed after hydrogenation. Therefore, the two plateaus of the absorption and desorption are attributed to the formation and decomposition of MgH$_2$ and Mg$_2$NiH$_4$. According to previous investigations on the Mg-rich Mg-Ni composite materials, the low plateaus are due to hydriding and dehydriding of Mg, while the high plateaus are the results of hydriding and dehydriding of MgNi [15, 16]. The maximum hydrogen absorption capacities at 400, 375, 350, and 325°C are 3.16, 3.05, 2.97, and 2.96 wt%, respectively, which are even lower than the theoretical value of 3.6 wt% for Mg$_2$Ni. This is due to the existence of MgO, the residual Mg and Ni in the hydrided Mg-Ni composite, as shown in Figure 2(b). Indeed, some large magnesium particles cannot be completely hydrogenated. From these PCT data, the van't Hoff plots (lnP versus 1000/T) for the Mg-Ni composite are drawn in Figure 5. According to the linear fitting lines from the experimental data, the van’t Hoff equations for the hydrogenation are

$$\ln(P_{\text{low}}) = -10/T + 15.16 \quad \text{for Mg}$$

$$\ln(P_{\text{high}}) = -7.77/T + 12.27 \quad \text{for MgNi}$$

The van’t Hoff equations for the dehydrogenation are

$$\ln(P_{\text{low}}) = -9.31/T + 13.84 \quad \text{for Mg}$$

$$\ln(P_{\text{high}}) = -7.96/T + 12.23 \quad \text{for MgNi}$$

Therefore, the obtained values of the hydride formation enthalpies ($\Delta H_{\text{f}}$) are $-83.1$ kJ/mol for Mg and $-64.6$ kJ/mol for Mg$_2$Ni, while the dehydrogenation enthalpies ($\Delta H_{\text{d}}$) are $77.4$ kJ/mol for Mg and $66.2$ kJ/mol for Mg$_2$Ni. These hydrogenation and dehydrogenation enthalpies of Mg and Mg$_2$Ni phases agree well with the values reported in the literature, for example, about $-66.3$ kJ/mol H$_2$ for hydrogenation of Mg$_2$Ni [10, 17] and $-74.5$ kJ/mol H$_2$ for hydrogenation of Mg [18].
Figure 3: Bright field TEM micrographs of Mg-Ni nanoparticles before hydrogen absorption with SAED patterns inset (a), after hydrogen absorption with SAED patterns inset (b), and after hydrogen desorption with SAED patterns inset (c).

Table 1: The data of P-C-T tests.

<table>
<thead>
<tr>
<th>Temperature/°C</th>
<th>Maximum H₂ absorption/wt%</th>
<th>Low plateau of absorption/MPa</th>
<th>Low plateau of desorption/MPa</th>
<th>High plateau of absorption/MPa</th>
<th>High plateau of desorption/MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>2.96</td>
<td>0.195</td>
<td>0.173</td>
<td>0.464</td>
<td>0.338</td>
</tr>
<tr>
<td>350</td>
<td>2.97</td>
<td>0.433</td>
<td>0.329</td>
<td>0.840</td>
<td>0.570</td>
</tr>
<tr>
<td>375</td>
<td>3.05</td>
<td>0.792</td>
<td>0.645</td>
<td>1.347</td>
<td>0.995</td>
</tr>
<tr>
<td>400</td>
<td>3.16</td>
<td>1.259</td>
<td>0.946</td>
<td>1.974</td>
<td>1.457</td>
</tr>
</tbody>
</table>

Figure 4: P-C-T curves of Mg-Ni ultrafine particles measured at 400°C, 375°C, 350°C, and 325°C.

Figure 6 shows the TG/DSC curves of the hydrided Mg-Ni composite obtained in 4 MPa hydrogen atmosphere at 400°C. It is observed that three endothermic peaks appeared on the DSC curve measured from room temperature to 500°C. The small peak in the temperature range between 235°C and 250°C comes from the phase transformation of Mg₂NiH₄ from its low temperature form to its high temperature form [19]. While in the same temperature range, TG curve does not show any mass loss. Two strong endothermic peaks in the high temperature range between 365°C and 425°C are observed on the DSC curve together with a mass loss of 3.3 wt%. They result from the dehydriding of Mg₂NiH₄ and MgH₂. In order to understand the dehydriding processes of the hydrogenated Mg-Ni composite, a partially hydrogenated sample is prepared and studied by using DSC technique. The sample is hydrogenated at 350°C with 0.89 wt% of hydrogen absorption. Figure 7 shows the XRD pattern of the partially hydrogenated composite. From Figure 7, one can see that both MgH₂ and Mg₂NiH₄ phases exist after absorbing 0.89 wt% of hydrogen. The intensity of peaks from MgH₂ is relative higher than that of the Mg₂NiH₄ phase, indicating that the main product in this partially...
Figure 5: Van’t Hoff plots based on the low plateaus (a) and high plateaus (b) on PCT curves for hydrogenation and dehydrogenation of the Mg-Ni composite.

Figure 6: TG/DSC curves of the hydrogenated Mg-Ni composite samples (a) after absorbing hydrogen in 4 MPa hydrogen atmosphere at 400°C and (b) after absorbing 0.89 wt% of hydrogen at 350°C.

The partially hydrided Mg-Ni composite. In Figure 6(b), two peaks are visible. A very weak endothermic peak appeared at 240°C, which corresponds to the phase transformation of Mg$_2$NiH$_4$. The other endothermic peak, with the onset point at 390°C and the peak point located at 420°C, must come from the dehydriding of MgH$_2$. Therefore, the endothermic peak located at 370°C observed in Figure 6(a) is confirmed from the dehydriding reaction of Mg$_2$NiH$_4$ → Mg$_2$Ni + 2H$_2$ while that of 395°C is from the dehydriding reaction of MgH$_2$ → Mg + H$_2$. It is worth noting here that the dehydriding temperature of MgH$_2$ in the fully hydrogenated powders is slightly lower than the partially hydrogenated powders. Also, the measured dehydrogenation enthalpy for MgH$_2$ (83.1 kJ/mol H$_2$) is slightly higher than its formation enthalpy (77.4 kJ/mol H$_2$). XRD analysis showed that the difference between the partially hydrogenated Mg-Ni powders and fully hydrogenated powders lies in the amount of Mg$_2$NiH$_4$ phase. Therefore, the Mg$_2$NiH$_4$ phase may play a role for the dehydriding of MgH$_2$ in the hydrogenated Mg-Ni composite powders. During dehydriding process, Mg$_2$NiH$_4$ decomposes prior to the MgH$_2$. The decomposition of Mg$_2$NiH$_4$ into nanostructured Mg$_2$Ni may act as “hydrogen channels” for the decomposition of MgH$_2$. Similar phenomena were also observed in Mg-Nb$_2$O$_5$ system for which the Nb$_2$O$_5$ act as hydrogen channels for hydrogen sorption of Mg [20, 21].
partially hydrogenated sample showed that Mg$_2$NiH$_4$ phase and XRD analyses on the fully hydrogenated sample and a nanostructured MgH$_2$+Mg$_2$NiH$_4$ hydrogen storage composite could be generated from the Mg-Ni ultrafine powders. After hydrogenation, reactions between Mg and Ni vapors, depending on the local vapor content in the reaction chamber. After hydrogenation, a nanostructured MgH$_2$+Mg$_2$NiH$_4$ hydrogen storage composite could be generated from the Mg-Ni ultrafine powders. After dehydrogenation, MgH$_2$ and Mg$_2$NiH$_4$ decomposed into nanograined Mg and Mg$_2$Ni, respectively. The hydrogenation enthalpy and dehydrogenation temperature of MgH$_2$ in the composite are significantly reduced. TG/DSC and XRD analyses on the fully hydrogenated sample and partially hydrogenated sample showed that Mg$_2$NiH$_4$ phase may play a catalytic role in the dehydriding process of the hydrogenated Mg ultrafine particles.

4. Conclusions

Mg-rich Mg-Ni ultrafine powders were prepared through a DC arc plasma method. The results showed that Mg$_2$Ni and MgNi$_5$ phases could be obtained directly from the vapor state reactions between Mg and Ni vapors, depending on the local vapor content in the reaction chamber. After hydrogenation, a nanostructured MgH$_2$+Mg$_2$NiH$_4$ hydrogen storage composite could be generated from the Mg-Ni ultrafine powders. After dehydrogenation, MgH$_2$ and Mg$_2$NiH$_4$ decomposed into nanograined Mg and Mg$_2$Ni, respectively. The hydrogenation enthalpy and dehydrogenation temperature of MgH$_2$ in the composite are significantly reduced. TG/DSC and XRD analyses on the fully hydrogenated sample and partially hydrogenated sample showed that Mg$_2$NiH$_4$ phase may play a catalytic role in the dehydriding process of the hydrogenated Mg ultrafine particles.

Acknowledgments

Professor J. Zou would like to acknowledge the financial support from Research Funds for the Doctoral Program of Higher Education of China (no. 20100073120007) and from Shanghai Education Commission (no. 12ZZ017). This work is partly supported by projects from the Science and Technology Committee of Shanghai no. 10JC1407700, 11ZR1417600, and no. 10dz2211000 and “Pujiang” project no. 11PJ1406000. This work was also partially supported by the French-Chinese collaboration project “XU Guangqi” (convention no. 27847SC).

References


![Figure 7: XRD pattern of the Mg-Ni particles after absorbing 0.89 wt% of hydrogen at 350°C.](image-url)

