Hydrogen Absorption Performance of Mechanically Alloyed (Mg$_2$Ni)$_{100-x}$Ti$_x$ Powder

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The hydrogen storage alloy (Mg$_2$Ni)$_{100-x}$Ti$_x$ ($x = 0, 2.5, 5.0, 7.5$ and $10.0$ at%) powders were synthesized from elemental powder mixture by mechanical alloying (MA) under an Ar atmosphere. The as-milled powders were examined as a function of titanium addition by X-ray diffraction and synchrotron X-ray absorption near-edge structure (XANES) techniques at various milling time. The hydrogen absorption kinetics of the 15-h as-milled powders were evaluated. The maximum hydrogen absorption content of 15-h as-milled Mg$_2$Ni powders can be improved from 3.14 mass% to 3.88 mass% when 5.0 at% of titanium was added. The hydrogenation rate of the Mg$_2$Ni powder was also obviously enhanced by introducing the titanium into Mg$_2$Ni lattices. More than 20% improvement of hydrogen absorption for Mg$_2$Ni intermetallic powders was achieved by adding titanium. [doi:10.2320/matertrans.MER2007169]

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1. Introduction

Extensive research efforts have been concentrated on seeking high power density and clean energy technologies with increasing the pollution and exploitation of energy sources. From the point of view, hydrogen, an abundant element in the universe, presents one of the best alternatives to petroleum as an energy carrier. It is also nonpolluting and can be easily produced from renewable energy sources, forming water as a harmless byproduct during use. In the last decade, hydrogen storage by metal hydrides has attracted considerable interests due to the relatively lighter weight, higher hydrogen storage, and low cost. Furthermore, metal hydrides can also be used in many other applications such as purification, hydride heat pump, transportation, nickel/metal hydride batteries, etc. [1, 2]

Among numbers of hydrogen storage alloys, A$_2$B type Mg$_2$Ni intermetallic possessing high hydrogen storage capacity up to 3.6 mass% has been a promising candidate for hydrogen storage applications. However, the low hydriding-dehydriding kinetics as well as the high absorption temperature limit its practicability. Numerous studies have demonstrated that Mg$_2$Ni hydrides can be synthesized by MA process. [3-5] Not only the grain size can be reduced but the introduced defect concentration and fresh surfaces can be increased. The hydrogen absorption properties can thus be improved. [5, 7] Excluding the means of MA, the addition of extraneous elements such as Al, Zr, and Ag introducing lattice strains is also a thinkable methodology to improve the hydrogen storage properties.

Titanium with good hydrogen storage as well as a relatively low density was added for improving the properties of Mg$_2$Ni alloys by MA process. For instances, Liang et al. [11] have demonstrated that the hydrogenation properties of nanocrystalline Mg$_{1.9}$Ti$_{0.1}$Ni alloy by MA process were improved comparing with those of polycrystalline Mg$_2$Ni, such as low hydrogenation kinetics and storage content. In the present study, the effects of titanium addition on the structural evolutions during MA were examined by X-ray diffraction and synchrotron X-ray absorption near-edge structure (XANES) techniques. Meanwhile, the hydrogen absorption kinetics of as-milled Mg$_2$Ni/Ti powders were also investigated.

2. Experimental

Pure elemental powders of magnesium (99.8%, <50 mesh), nickel (99.98%, <300 mesh), and titanium (99.7%, <100 mesh) were mixed to yield the desired compositions: (Mg$_2$Ni)$_{100-x}$Ti$_x$ ($x = 0, 5.0, 7.5$ and $10.0$). A SPEX 8000D shaker ball mill was used for mechanical alloying. Each 15-minute interrupted interval for every 30 minutes was used to cool down the tank. An appropriate amount of the as-milled powders was extracted in an argon-filled glove box to examine the progress of processing. The detailed milling procedures and conditions were also described in our previous studies. [10, 12-14]

The structural evolution during milling was examined using X-ray diffractometry and synchrotron X-ray absorption spectroscopy. The X-ray analysis was carried out using a Siemens D-5000 diffractometer with a Cu Kα radiation. X-ray absorption spectroscopy measurements were performed at the Wiggler-C beamline of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The hydrogen absorption properties of 15-h as-milled (Mg$_2$Ni)$_{100-x}$Ti$_x$ powders were evaluated using an automatic Sieverts apparatus performed at 300, 325 and 350°C.

3. Results and Discussion

X-ray diffractometry and synchrotron X-ray absorption spectroscopy were used to reveal respectively the long range and short range structure of the powder mixtures during MA in this study. Figures 1 show the X-ray diffraction patterns of the 3-h-milled, 5-h-milled and 15-h-milled Mg$_2$Ni/Ti pow-
ders. From Fig. 1(a), no significant reaction can be noticed from the XRD data for powder mixtures after 3 h of milling treatment. The diffraction peak of titanium can be found when titanium content was ≥2.5 at%. With prolonging the milling time, the formation of Mg$_2$Ni phase occurred in all compositions after 5 h of milling, as shown in Fig. 1(b). Though very small peaks of nickel can be observed in the undoped powder mixture, a large amount of residual nickel was revealed when titanium was added. A small amount of titanium addition tended to delay the formation of Mg$_2$Ni phase in this system. It was generally thought that titanium element dissolved into Mg$_2$Ni intermetallics and retarded the formation of Mg$_2$Ni, showing the influence on structural evolution during MA. When the milling time was further prolonged to 15 h, in Fig. 1(c), the diffraction peaks were identified the final phase as Mg$_2$Ni structure with small amounts of magnesium and nickel residuals for all Mg$_2$Ni/Ti compositions. Grain size reduction and/or residual strain arose from the MA treatment induced observable peak broadening in XRD data. Moreover, the diffraction peaks of the (Mg$_2$Ni)$_{97.5}$Ti$_{2.5}$ powder was noticed to be broader in width due to its poor crystallinity after 15 h of MA.

Based on the X-ray diffraction results, the titanium may form a mixture of solid solutions with Mg$_2$Ni, magnesium, and nickel in this system. Similarly, though not shown here, the electron-beam diffraction patterns from TEM analyses revealed the same results. However, it was still difficult to distinguish the exact locations of titanium elements within the lattice structure. From previous studies, titanium was assumed to substitute the magnesium sites based on their experimental expectations. It is also possible that titanium may form a mixture with Mg$_2$Ni, magnesium and nickel solid solutions to cause the higher lattice strain within the matrix structure, reducing the crystallinity of the Mg$_2$Ni interme-
tallics. Moreover, in all Figs. 1, the diffraction peak intensities of magnesium and nickel were observed to decrease with the increase of the milling time at the early milling stage. Formation of Mg$_2$Ni phase with magnesium and nickel solid solutions occurred after 5 h of milling treatment. Prolonging the milling time provided the further solid-state reaction between magnesium and nickel for the formation of Mg$_2$Ni intermetallics.

Except the long range order revealed by the X-ray diffraction technique, XANES was used to evaluate the electronic states of the selected atom in the as-milled powders. Figure 2(a) shows the XANES spectra (Ni K-edge, 8333 eV) of the as-milled powder mixtures as a function of milling time. As seen from the figure, the main absorption Ni K-edges of the milled powders shifted slightly toward the lower energy comparing to the spectrum of Ni standard. It showed that the solid-state reactions between nickel and magnesium occurred during the MA process. After determining the experimental thresholds (the XANES spectra in Fig. 2(a)), their differential curves were used to further reveal the detailed changes of Ni valence state in the as-milled powders. The main peaks (at ~8333 eV) indicated the absorption K-edges of nickel element in the as-milled powders. The main peak of the 3 h-milled powder mixture slightly shifted toward the lower energy, resulting from the formation of Mg$_2$Ni phase. Subsequently, the main peak shifted slightly backward the higher energy when the powders were milled after 15 h. This may attribute to the partial crystallization of nickel from the amorphous phase as the powder was treated with a long-time milling. Furthermore, the emergence of the absorption peak at ~8336 eV when powder was milled after 5 h implied the formation of amorphous nickel during the MA process, showing a good agreement with the results of the XRD data (Figs. 1). Because the long-time milling may cause the partial crystallization of nickel and magnesium, the final phases of the 15 h-milled powder mixture revealed to be Mg$_2$Ni structure with small amounts of residual nickel and magnesium after the XRD and XAS analyses.

In order to discuss the influences of titanium addition on the structural evolution of the powder mixtures during MA, the XAS analyses of the Mg$_2$Ni/Ti powder were investigated in this system. Figure 3(a) shows the XANES spectra of the (Mg$_2$Ni)$_{95}$Ti$_5$ powder as a function of milling time. No significant differences can be observed in these XANES spectra. Similarly, such the XANES spectra were differentiated for further analyses, as shown in Fig. 3(b). It can be noticed that the main peak (at ~8333 eV) of the 5 h-milled powder mixture slightly shifted toward the lower absorption energy, implying that the formation of Mg$_2$Ni phase. Comparing to the undoped Mg$_2$Ni powder mixture, the titanium additive may delay the formation of Mg$_2$Ni in MA process. Moreover, the amorphous Mg$_2$Ni phase indicated at the absorption energy of ~8336 eV formed after 15 h of
Hydrogen absorption behavior of Mg.

It can be noticed from the figure that the maximum hydrogen absorption content after the hydrogenation then attained a plateau value. Hydrogen absorption content rapidly increased at the early stage of the hydrogenation then attained a plateau value (maximum hydrogen absorption content) after the hydrogen absorption saturated. It can be noticed from the figure that the hydrogen absorption behavior of Mg revealed a strong dependence on the titanium addition. A significant improvement of hydrogen absorption capacity can be observed by adding the titanium into Mg intermetallics. The maximum hydrogen absorption content achieved the highest value when titanium content was 5 at%, suggesting that the presence of a relatively small amount of titanium enhanced the hydrogen absorption content of Mg. Then with increasing the titanium content, the hydrogen absorption capacity of Mg/Ti powder decreased, but the values are higher than that of undoped Mg. Moreover, it can be noticed that the slope of the curves exhibited significant increase implying that the hydrogen absorption rate of Mg/Ti powders was also enhanced by adding titanium. As seen in Fig. 4, intermetallic MgNi with 5 at% titanium addition exhibited the highest hydrogenation rate. The hydrogen absorption content of the (MgNi)100−xTi5 powder to its saturated capacity can be accomplished within 10 minutes.

Figure 5 shows the kinetic curves for 15 h as-milled MgNi/Ti powders at a hydrogenation temperature of 350 °C with various titanium additions. Similar trends of the hydrogenation behavior were observed for the powders measured at 325 °C. The addition of titanium significantly improved the hydrogen absorption capacity of MgNi. The maximum hydrogen absorption content attained the highest value when titanium content was 5 at%. Subsequently, with increasing the titanium content, the hydrogen absorption capacity of MgNi/Ti powder decreased. The values are still higher than that of undoped MgNi. And, the hydrogenation rate of the Ti-added MgNi was higher than that of the undoped one. However, the achievement of saturated hydrogen absorption content for (MgNi)100−xTi5 powder was prolonged to about 12 minutes. To further understand the hydrogenation behavior at higher temperature, the kinetic curves for 15 h as-milled MgNi/Ti powders with various titanium additions were performed at 350 °C, as shown in Fig. 6. As the same effect of the titanium addition at lower hydrogenation temperatures, the hydrogen absorption content of the intermetallic MgNi showed observable improvement at 350 °C. Similarly, the maximum hydrogen absorption capacity attained its highest value when titanium content was 5 at%, then decreased with the increase of titanium content. All the Ti-added MgNi powders possessed higher hydrogen absorption capacities than the undoped one. The hydrogenation rate of 15 h as-milled MgNi/Ti intermetallic powders is also higher than that of the undoped MgNi. The addition of titanium did improve the hydrogen absorption properties of the MgNi in MA process. However, it can be noticed that the achievement of the saturated hydrogenation value was further prolonged to over 30 minutes. Table 1 shows the hydrogen absorption properties of mechanically alloyed MgNi/Ti powders at 350 °C. As seen in this table, the hydrogen absorption capacity of MgNi was increased from 3.14 mass% to 3.88 mass% by adding titanium at a content of 5 at%. These saturated values are comparable to the value (3.4 mass%) reported by Zaluski et al.
al., who also used MA technique to prepare nanocrystalline Mg$_2$Ni powders. Moreover, in Table 1, the reversible hydrogen content also showed improvement when titanium was added. Similarly, the highest value occurred at the titanium content of 5 at%. It is claimed that the addition of titanium element increasing the partial lattice strains of the Mg$_2$Ni intermetallics and destabilizing their hydride phases during hydrogenation may be attributed to the improvement of hydrogen absorption performances.

Figure 7(a) shows the XRD patterns of the hydrided and dehydrided Mg$_2$Ni which was milled for 15 h by MA. It can be noticed that the hydrided phase of Mg$_2$NiH$_4$ formed after hydriding at 350°C. No obvious MgH$_2$ phase can be found in the hydrided alloy, suggesting the lower formation enthalpy of Mg$_2$NiH$_4$ during hydriding. The hydride phase of the reaction between Mg$_2$Ni and H$_2$ was thus proved to be Mg$_2$NiH$_4$. Comparing the different hydrogenation temperatures, in Figs. 4–6, the time to achieve the saturated hydrogenation capacity increased with the elevated temperature. The decrease in hydrogenation rate was believed to attribute to the exothermic reaction of the hydriding process. In such the exothermic hydriding process, the equilibrium pressure of hydrogen is increased when the hydriding temperature is elevated. However, the reaction is not predominated by the nucleation/growth mechanism during hydriding at temperatures above 300°C, whereas depends on the forced flow of hydrogen which chemisorbs onto the surface of the intermetallic powder. The hydrogenation rate was thus retarded due to the decrease in driving force of hydrogenation. Subsequently, the Mg$_2$NiH$_4$ phase transformed into Mg$_2$Ni phase after dehydriding. No diffraction peaks of magnesium and nickel can be found in the dehydrided powder. The peaks of Mg$_2$Ni phase are observed to be narrower and sharper after dehydriding, suggesting that the crystallinities of Mg$_2$Ni powders were enhanced after the hydriding/dehydriding reactions. It is generally thought that the annealing-like process during hydriding/dehydriding reaction may lead the lattice structure of the Mg$_2$Ni to be more uniform atomic arrangement, though the MA process usually arise the high defect density or high lattice strain within the milled structures. The presence of the marked grain growth of the Mg$_2$Ni phase is thus revealed. Furthermore, the XRD patterns of the hydrided and dehydrided 15 h-milled (Mg$_2$Ni)$_{92.5}$Ti$_{7.5}$ powder is shown in Fig. 7(b). Similarly trends can be found in the 7.5 at% Ti-added Mg$_2$Ni powder. The hydrided and dehydrided phases were identified as Mg$_2$NiH$_4$ and Mg$_2$Ni, respectively. The crystallinity of the dehydrided powder was enhanced. It shows, however, no obvious titanium peaks in these patterns, suggesting that the titanium element was introduced into the Mg$_2$Ni lattice.

### Table 1 Hydrogen absorption properties of (Mg$_2$Ni)$_{100-x}$Ti$_x$ powders at 350°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P$_s$ (Pa)</th>
<th>H$_{rev}$ (mass%)</th>
<th>H$_{max}$ (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$Ni</td>
<td>8.9 x 10$^5$</td>
<td>2.4</td>
<td>3.14</td>
</tr>
<tr>
<td>(Mg$<em>2$Ni)$</em>{97.5}$Ti$_{2.5}$</td>
<td>7.5 x 10$^5$</td>
<td>2.93</td>
<td>3.84</td>
</tr>
<tr>
<td>(Mg$<em>2$Ni)$</em>{95}$Ti$_{5}$</td>
<td>8.0 x 10$^5$</td>
<td>3.01</td>
<td>3.88</td>
</tr>
<tr>
<td>(Mg$<em>2$Ni)$</em>{92.5}$Ti$_{7.5}$</td>
<td>8.0 x 10$^5$</td>
<td>2.93</td>
<td>3.82</td>
</tr>
<tr>
<td>(Mg$<em>2$Ni)$</em>{90}$Ti$_{10}$</td>
<td>9.3 x 10$^5$</td>
<td>2.84</td>
<td>3.81</td>
</tr>
</tbody>
</table>

Fig. 7 X-ray diffraction patterns of 15 h-milled (a) Mg$_2$Ni and (b) (Mg$_2$Ni)$_{92.5}$Ti$_{7.5}$ before and after hydrogenation, and after dehydrogenation.
To further prove the introduction of titanium within the lattice structure of alloyed matrix, Figure 8 shows the differentiated Ti K-edge absorption spectra (differentiated XANES spectra) for \((\text{Mg}_2\text{Ni})_{95}\text{Ti}_5\) powders as a function of milling time, revealing the electronic structure change during MA. The position of the main differential peak corresponds to the energy (at 4966 eV) of titanium absorption K-edge, as indicated by a vertical line. No obvious differences for 5 h-milled powders can be observed when compared with those milled less than 3 h. It implied that the Mg$_2$Ni/Ti alloy powders exhibited elemental characteristics of titanium even after 5 h of milling treatment. As the milling time prolonged to 15 h, the differential peak significantly shifted toward the higher energy, showing the electronic structure change of the added titanium atoms. It suggested that the titanium atoms were introduced into the Mg$_2$Ni lattices after 15 h of milling.

4. Conclusions

Hydrogen storage alloy \((\text{Mg}_2\text{Ni})_{100-x}\text{Ti}_x\) powders were synthesized successfully by mechanical alloying. The 15 h-milled \((\text{Mg}_2\text{Ni})_{100-x}\text{Ti}_x\) powders exhibited a mixture of Mg$_2$Ni, magnesium, and nickel solid solutions. The addition of titanium may delay the formation of Mg$_2$Ni phase during MA. The maximum and reversible hydrogen content of 15 h as-milled Mg$_2$Ni powders were improved from 3.14 to 3.88 mass% and from 2.40 to 3.01 mass%, respectively, as the 5 at% titanium was added. The data of synchrotron XAS indicated that the effects may result from the introduction of titanium into Mg$_2$Ni lattice structure after the MA treatment. The cooperative effects of titanium additions and MA treatment did improved the hydrogen absorption performance of Mg$_2$Ni alloy.

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