Improvement of Hydrogen Absorption Performance of Mechanically Alloyed Mg₂Ni Powders by Silver Doping

Chin-Yi Chen* and Shian-Ke Lin

Department of Materials Science and Engineering, Feng Chia University, Taichung, Taiwan 40724, Republic of China

In the present study, hydrogen-absorbed Mg₂Ni intermetallic powders were prepared by mechanical alloying under an Ar atmosphere. Modification of the Mg₂Ni powders was attempted by adding silver (0.5, 1.0, 2.5, and 5.0 at%) into starting elemental powder mixtures. The as-milled powders were examined as a function of milling time by X-ray diffraction and synchrotron X-ray absorption techniques. In addition, the hydrogen absorption performance of the 15 h as-milled powders were evaluated. The experimental results show that (Mg₂Ni)_{100-x}Ag_x powders exhibited a mixture of Mg₂Ni, magnesium and nickel solid solutions after 15 h of milling treatment. The maximum hydrogen absorption content and reversible hydrogen content of 15 h as-milled Mg₂Ni powders was 3.14 and 2.40 mass%, respectively. An improvement of hydrogen absorption properties can be noticed by doping silver, but the less silver addition the better performance. In the present study, (Mg₂Ni)_{99.5}Ag_{0.5} exhibited the best hydrogen absorption properties where the maximum hydrogen absorption content and reversible hydrogen content was increased significantly to 3.93 and 3.14 mass% respectively. More than 25% improvement of hydrogen absorption for Mg₂Ni intermetallic powders was achieved by doping silver. [doi:10.2320/matertrans.48.1113]

(Received January 17, 2007; Accepted March 6, 2007; Published April 25, 2007)

Keywords: intermetallics, hydrogen storage, mechanical alloying, Mg₂Ni, silver, synchrotron X-ray absorption techniques

1. Introduction

Researches and developments on high power density and clean energy technologies have been strongly promoted with the increase of pollution and requirement of energy sources. Hydrogen presents one of the best alternatives to petroleum as an energy carrier. It is non-polluting and can be easily produced from renewable energy sources. Extensive effort has been concentrated on the hydrogen technologies from the energy and environmental point of view. The major techniques for hydrogen storage include developing compressed high pressure gas cylinder, condensation into liquid or even solid hydrogen, hydrogen absorption on large-surface-area solids such as carbon nanotubes, and metal hydrides.¹⁾ Among these, hydrogen storage by metal hydrides has attracted numerous R&D interests due to the relatively lighter weight, higher hydrogen absorption percentage, 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.^{2,3)}

Hydrogen storage alloys can be classified into several groups, such as AB, AB₂, A₂B, and AB₅.⁴⁾ Among numbers of alloys, A₂B type Mg₂Ni intermetallic with its high hydrogen absorption capacity up to 3.6 mass% is a promising candidate for hydrogen storage applications. The low hydriding/dehydriding rate, however, limits its practicability. Mechanical alloying (MA) process has been used successfully to prepare metal hydrides.⁵⁻⁷⁾ By mechanically grounding starting materials, not only the grain size can be reduced but the introduced defect concentration and fresh surfaces can be increased. Thus, the hydrogen absorption properties can be improved.^{8,9)} Excluding mechanical alloying, the addition of extraneous elements such as Al,¹⁰⁾ Ti¹¹⁾ and Zr¹²⁾ generating lattice strains is also a thinkable methodology to improve the hydrogen storage properties.

Silver with good catalytic properties as well as its high

thermal conductivity may improve the hydrogen absorption properties of Mg₂Ni. For instances, Wang *et al.*¹³⁾ have demonstrated that the hydrogenation properties of Mg_{1.8}-Ag_{0.2}Ni alloy by grounding process were improved, such as low absorption temperature and long cycling life. Qian *et al.*^{14,15)} have also reported that the hydrogen absorption properties of Mg₂Ni can be improved by adding various contents of silver via hydriding combustion synthesis, such as absorption capacity and kinetics. Since there has been always a strong correlation between the synthesis route used to prepare a material and its hydrogenation properties, MA technique was used to prepare Mg₂Ni alloy powders with or without silver additions in the present study. The silver element was added into Mg₂Ni alloy with various contents. The effects of silver addition on the structural evolutions during MA were examined by X-ray diffraction and synchrotron X-ray absorption techniques. Meanwhile, the hydrogen absorption properties of as-milled Mg₂Ni/Ag powders were also investigated.

2. Experimental

Pure elemental powders of magnesium (99.8%, <50 mesh), nickel (99.98%, <300 mesh), and silver (99.9%, 1–3 μm) were mixed to yield the desired compositions: (Mg₂-Ni)_{100-x}Ag_x ($x = 0, 0.5, 1.0, 2.5, \text{ and } 5.0$), and then loaded into an SKH 9 high speed steel tank (40 mm in diameter and 50 mm in height) together with chromium steel balls (7 mm in diameter with ball-to-powder ratio = 5 : 1) under an argon-filled glove box, where a SPEX 8000D shaker ball mill was used for mechanical alloying. The overall MA process lasted 15 hours and were interrupted every 15 minutes for the first hour and every 30 minutes thereafter. Each interrupted interval was followed by an equal length of time (~15 min.) 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 structural evolution during milling was examined by

*Corresponding author, E-mail: chencyi@fcu.edu.tw

Fig. 1 X-ray diffraction patterns of (a) Mg_2Ni , (b) $(\text{Mg}_2\text{Ni})_{99.5}\text{Ag}_{0.5}$, (c) $(\text{Mg}_2\text{Ni})_{99}\text{Ag}_1$, and (d) $(\text{Mg}_2\text{Ni})_{95}\text{Ag}_5$ powders as a function of milling time.

using X-ray diffractometry and synchrotron X-ray absorption spectroscopy. The X-ray analysis was performed using a Philips X'pert PW3040 diffractometer with a $\text{Cu-K}\alpha$ radiation. A relatively slow scanning rate ($0.05^\circ 2\theta/\text{s}$) also was used to determine the lattice constants of the 15 h as-milled powders. A dilute silicon slurry was coated on the surface of the milled powders. The silicon powder was used as an internal standard, for accurate determination of the diffraction angles. X-ray absorption spectroscopy measurements¹⁶⁾ 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 $(\text{Mg}_2\text{Ni})_{100-x}\text{Ag}_x$ powders were evaluated by pressure-composition-temperature (P-C-T) measurements, differential scanning calorimetry, and thermogravimetric analysis (SDT2960 Simultaneous DSC-TGA, TA Instrument). The P-C-T measurements were performed at 350°C , while DSC/TGA measurements were performed under an Ar atmosphere at a heating rate of $5^\circ\text{C}/\text{min}$.

3. Results and Discussion

3.1 Structural Characterization

Figure 1(a) shows the X-ray diffraction patterns of the as-milled Mg_2Ni powders with various milling times. The diffraction peak intensities of magnesium and nickel were observed to decrease gradually with increasing the milling time at the early stage of milling. Formation of Mg_2Ni phase

with magnesium and nickel solid solutions can be noticed after 5 h of milling treatment. The diffraction peaks of Mg_2Ni tended to be broadened due to the decrease in crystallite size with prolonging the milling time.¹⁷⁾ Grain size reduction and/or residual strain arose from the MA treatment induced observable peak broadening in XRD data. Fig. 1(b), (c) and (d) show respectively the XRD patterns of the as-milled $(\text{Mg}_2\text{Ni})_{99.5}\text{Ag}_{0.5}$, $(\text{Mg}_2\text{Ni})_{99}\text{Ag}_1$ and $(\text{Mg}_2\text{Ni})_{95}\text{Ag}_5$ powder mixtures as a function of milling time. It can be noticed from the figures that the addition of silver influenced the structural evolution during MA. A similar trend can be observed between the XRD patterns of undoped Mg_2Ni , $(\text{Mg}_2\text{Ni})_{99.5}\text{Ag}_{0.5}$, and $(\text{Mg}_2\text{Ni})_{99}\text{Ag}_1$, Fig. 1(a), (b) and (c), where the Mg_2Ni phases from both the 5 h milled data showed no significant change. However, the formation of Mg_2Ni phase was delayed to a milling time of 10 h when silver addition was $\geq 2.5\text{ at\%}$ (Fig. 1(d), the XRD pattern of $(\text{Mg}_2\text{Ni})_{97.5}\text{Ag}_{2.5}$ is similar to that of $(\text{Mg}_2\text{Ni})_{95}\text{Ag}_5$). It was generally thought that silver elements dissolved into Mg_2Ni intermetallics and restricted the formation of Mg_2Ni . With increasing the silver content to 5 at% (Fig. 1(d)), the XRD pattern, however, shows a very small peak of silver after 15 h of milling. This indicates that the excess silver was detected to be elemental metal when silver content was higher than the solubility of silver in the Mg_2Ni intermetallics.

In order to further discuss the influence of silver addition, the XRD patterns of the as-milled powders after same processing time (5 h and 15 h) were plotted in Fig. 2.

Fig. 2 X-ray diffraction patterns of (a) 5 h-milled and (b) 15 h-milled $(\text{Mg}_2\text{Ni})_{100-x}\text{Ag}_x$ powders.

Figure 2(a) shows the XRD patterns of 5 h-milled $\text{Mg}_2\text{Ni}/\text{Ag}$ powders as a function of silver content. Similar behavior can be observed in the XRD patterns when silver content was ≤ 1.0 at%. No significant differences in the relative intensity of the diffraction peaks can be noticed. The intensity of nickel diffraction peak for silver content ≥ 2.5 at% is, however, significantly higher than those for silver content ≤ 1.0 at%. This indicates that a large amount of residual nickel can be observed in the 5 h-milled $\text{Mg}_2\text{Ni}/\text{Ag}$ powders when silver content increases to ≥ 2.5 at%. It can be found in Fig. 1 that the intensity of magnesium peaks decrease obviously at the early stage of milling. This may result from the reaction of magnesium with the doped silver, leading the peak of nickel to be more distinct. Though the excess nickel can be noticed in the high silver-doped powders after 5 h of milling, the Mg_2Ni phase was formed in all compositions after 10 h of milling treatment. Since no significant differences can be noticed with prolonged milling, Figure 2(b) shows the XRD patterns of 15 h-milled powders as a function of silver addition. The 15 h-milled powders exhibited a mixture of Mg_2Ni , magnesium and nickel solid solutions. Because the peaks of magnesium and nickel are close to those of Mg_2Ni after 10 h of milling, whether the existence of residual magnesium and nickel during MA process still required following verification.

A comparison to X-ray diffraction results revealing the long range order structure of as-milled powders, while extended X-ray absorption fine structure (*i.e.*, EXAFS)

Fig. 3 Ni *K*-edge absorption spectra for (a) $(\text{Mg}_2\text{Ni})_{99}\text{Ag}_1$ and (b) $(\text{Mg}_2\text{Ni})_{95}\text{Ag}_5$ powders with different milling times.

technique was used to investigate the change of local atomic configuration during MA. Figure 3 shows the EXAFS spectra (Ni *K*-edge, 8333 eV) of the as-milled $(\text{Mg}_2\text{Ni})_{99}\text{Ag}_1$ and $(\text{Mg}_2\text{Ni})_{95}\text{Ag}_5$ alloy powders as a function of milling time. The EXAFS spectra of as-milled silver-doped Mg_2Ni powders revealed no significant differences at the early stage of milling (up to 3 h of milling). The spectra are similar to those of undoped Mg_2Ni powders.¹⁸⁾ The EXAFS spectrum of 15 h-milled Mg_2Ni powders with silver addition was different from that of 3 h milled one, while 5 h spectrum is the transient stage. Because the EXAFS spectra of $(\text{Mg}_2\text{Ni})_{99}\text{Ag}_1$ and $(\text{Mg}_2\text{Ni})_{95}\text{Ag}_5$ powders shown in Fig. 3 exhibited no significant differences, further examinations were carried out by Fourier transformation of the EXAFS spectra to obtain the radial distribution functions (RDFs) where the local inter-atomic environment of the detected atom (*i.e.*, nickel) can be revealed.¹⁶⁾ Figure 4 shows the RDFs of as-milled $(\text{Mg}_2\text{Ni})_{99}\text{Ag}_1$ and $(\text{Mg}_2\text{Ni})_{95}\text{Ag}_5$ powders with various milling times. The magnitudes of the RDF indicate the coordination numbers of detected atom at various distances represented by the peak positions. Similar RDFs can be observed at the early stage of milling (3 h). This implies that the face-centered cubic structure of nickel persisted at least up to 3 h of milling. After 5 h of milling, not only an observable decrease in the relative peak intensities but a shift to the right of major peak position can be noticed, and indicate the formation of Mg_2Ni phase. It is interesting to note that the high order peaks (0.4~0.5 nm) exhibited in the 5 h-milled powders. This differed slightly from that without silver addition where the high order peaks of fcc nickel almost disappeared after 5 h of milling.

Fig. 4 Ni K-edge absorption spectra for (a) $(\text{Mg}_2\text{Ni})_{99}\text{Ag}_1$ and (b) $(\text{Mg}_2\text{Ni})_{95}\text{Ag}_5$ powders with different milling times.

In comparison to that of undoped Mg_2Ni intermetallic powders,¹⁸⁾ the effect of silver doping can be revealed. Though a similar behavior can be noticed for both Mg_2Ni intermetallic powders with or without silver doping, the Ag addition may delay the formation of Mg_2Ni phase. As shown in Fig. 1, the XRD results show that the formation of Mg_2Ni phase exhibited similar behavior (Mg_2Ni formed after 5 h milling) with limited amount of silver addition (≤ 1.0 at%) and was delayed to a longer milling time (10 h) when silver addition was ≥ 2.5 at%. EXAFS analysis and corresponding RDF examination, however, revealed that some residual nickel may still remain even with 1.0 at% silver addition (indicated by the high order peaks in Fig. 4(a)) and partial Mg_2Ni phase formed with 5.0 at% silver addition (the major peak shift to the right in Fig. 4(b)). A combination of XRD and EXAFS techniques can provide more phase evolution information during mechanical alloying process.

3.2 Hydrogen Absorption Properties

The hydrogen absorption measurements of $(\text{Mg}_2\text{Ni})_{100-x}\text{Ag}_x$ 15 h-milled powders were performed at 350°C . Figure 5 shows the hydrogen absorption kinetic curves of 15 h as-milled Mg_2Ni powders with various silver addition. It can be noted that the hydrogen absorption behavior of Mg_2Ni revealed a strong dependence on the silver content. A significant improvement of hydrogen absorption capacity can be observed by doping silver in Mg_2Ni . The maximum hydrogen absorption content increased when silver was added. However, the maximum hydrogen absorption content

Fig. 5 Kinetic curves for 15 h as-milled $\text{Mg}_2\text{Ni}/\text{Ag}$ powders with various silver additions.

Fig. 6 P-C-T curves for 15 h as-milled $\text{Mg}_2\text{Ni}/\text{Ag}$ powders with various silver additions.

achieved the highest value in the present study when the silver content was 0.5 at% indicating that the presence of a small amount of silver enhanced the hydrogen absorption content of Mg_2Ni . Then with increasing the silver content, the hydrogen absorption capacity of $\text{Mg}_2\text{Ni}/\text{Ag}$ powders decreases, but the values are still higher than that of undoped Mg_2Ni . Moreover, it can be noticed that the slope of the curves exhibited significant increase implying that the hydrogen absorption rate of Mg_2Ni powders was also enhanced by doping silver. As shown in Fig. 5, intermetallic Mg_2Ni powders with 0.5 at% silver addition exhibited the highest hydrogenation rate. The hydrogen absorption content of the $(\text{Mg}_2\text{Ni})_{99.5}\text{Ag}_{0.5}$ powders to its 80% (~ 2.8 mass%) of the saturated capacity (~ 3.5 mass%) can be accomplished within 8 minutes. This saturated value is comparable to the value (3.4 mass%) reported by Zaluski *et al.*¹⁹⁾ who also used MA technique to prepare nanocrystalline Mg_2Ni powders. The differences in the values of hydrogen absorption may be attributed to the MA processing and/or testing parameters. Moreover, the hydrogenation rate of 15 h as-milled $\text{Mg}_2\text{Ni}/\text{Ag}$ intermetallic powders is also higher than that of undoped Mg_2Ni due to the good catalytic properties of silver.

Figure 6 shows the P-C-T measurements for 15 h as-milled Mg_2Ni powders with various silver additions at 350°C . The absorbed hydrogen content and reversible hydrogen content of undoped Mg_2Ni were 3.14 and 2.40 mass%, respectively.

Table 1 Lattice parameters and c/a ratios of $(\text{Mg}_2\text{Ni})_{100-x}\text{Ag}_x$ powders.

	a (nm)	c (nm)	c/a
Mg_2Ni	0.522	1.325	2.517
$(\text{Mg}_2\text{Ni})_{99.5}\text{Ag}_{0.5}$	0.520	1.338	2.571
$(\text{Mg}_2\text{Ni})_{99}\text{Ag}_1$	0.520	1.332	2.560
$(\text{Mg}_2\text{Ni})_{97.5}\text{Ag}_{2.5}$	0.521	1.333	2.559
$(\text{Mg}_2\text{Ni})_{95}\text{Ag}_5$	0.523	1.307	2.526

The hydrogen absorption properties can be improved significantly with the additions of silver element. The hydrogen content reached 3.93, 3.83, 3.65, and 3.47 with 0.5, 1.0, 2.5, and 5.0 at% silver additions, respectively. Meanwhile, the reversible hydrogen content also increased (from 2.4 mass% for Mg_2Ni) to 3.14, 3.00, 2.73, and 2.86 mass%, respectively. A similar trend can be observed comparing to those of Fig. 6, the maximum hydrogen absorption content of 15 h as-milled $(\text{Mg}_2\text{Ni})_{99.5}\text{Ag}_{0.5}$ powder attained its highest value in P-C-T measurements. The maximum hydrogen absorption content of Mg_2Ni decreased when the addition of silver was more than 0.5 at%. It is known that the atomic radius of the silver (0.144 nm) is larger than that of nickel (0.124 nm) and smaller than that of magnesium (0.160 nm). Due to the assumption of silver substituting the site of nickel,²⁰ it is reasonable that a small amount of silver addition expanding the lattice structure may be attributed to the improvement of hydrogen absorption properties. These results showed a good agreement with those from the RDFs examination where the nearest neighbor bond length (the major peak position) increases after the formation of Mg_2Ni phase can be noticed. Excess silver addition (≥ 2.5 at%) tended to precipitate and resulted in the reduction of uniformity of silver in Mg_2Ni matrix. The poor distribution of the precipitated silver may cause the decrease of the lattice expansion. The hydrogen absorption content of Mg_2Ni with 1, 2.5 and 5 at% silver addition was thus decreased.

Moreover, it can be noted in Fig. 6 that the slope within the plateau region approached zero. This slope is related to the energy for hydrogen atom diffusion into the interstitial sites within the Mg_2Ni and/or $\text{Mg}_2\text{Ni}/\text{Ag}$ lattices.²¹ Though MA process commonly induces high lattice strains, the hydriding at a temperature over 300°C can eliminate the induced strains. This annealing-like effect may lead the lattice structure of the Mg_2Ni to a more uniform atomic arrangement. The flat slope within the plateau region for 15 h as-milled $\text{Mg}_2\text{Ni}/\text{Ag}$ powders indicated that hydrogen atom can diffuse into the alloy powders without overpowering a large energy barrier.

In order to evaluate the influence of silver addition on the lattice structure, detailed X-ray diffraction was used to examine the 15 h as-milled $\text{Mg}_2\text{Ni}/\text{Ag}$ powders. Table 1 summarizes the lattice parameters and c/a ratios of Mg_2Ni powders with or without silver additions. It can be noted that the c/a ratio of the initial Mg_2Ni powders was 2.517 and increased to 2.571, 2.560, 2.559, and 2.526 with a silver addition of 0.5, 1.0, 2.5 and 5.0 at%, respectively. In the present study, the c/a ratio of $\text{Mg}_2\text{Ni}/\text{Ag}$ intermetallics reached its highest value (2.571) with 0.5 at% of silver, and

Fig. 7 c/a ratio and hydrogen absorption content of $\text{Mg}_2\text{Ni}/\text{Ag}$ powders as a function of silver addition.

decreased gradually with superfluous silver additions. A correlation between the c/a ratio and the maximum hydrogen absorption content of $\text{Mg}_2\text{Ni}/\text{Ag}$ powders was attempted and the result was shown in Fig. 7. It is evident that the maximum hydrogen absorption content of $\text{Mg}_2\text{Ni}/\text{Ag}$ powders exhibited the similar trend as that of c/a ratio. The c/a ratio of Mg_2Ni without silver addition exhibited the lowest value, whereas the c/a ratio increased when silver was doped. It can be noticed that the c/a ratio of $\text{Mg}_2\text{Ni}/\text{Ag}$ powder reaches its highest value at a silver content of 0.5 at%. Correspondingly, at the same composition, the hydrogen absorption content of $\text{Mg}_2\text{Ni}/\text{Ag}$ powders also attains its highest value (3.93 mass%). The expanded lattice structure of $(\text{Mg}_2\text{Ni})_{99.5}\text{Ag}_{0.5}$ reveals significantly larger c/a ratio than those when silver additions are more than 0.5 at%, suggesting its correspondingly excellent hydrogen absorption content. In the present study, the trend of maximum hydrogen absorption content tends to be proportional to that of c/a ratio.

The expansion of lattice structure can also be contributed to explain the effect of silver addition on hydrogen absorption kinetics as shown in Fig. 5. The expansion of lattice structure may cause the ease of the hydrogen absorption for silver-doped Mg_2Ni . The full expansion of unit-cell volume for the composition of $(\text{Mg}_2\text{Ni})_{99.5}\text{Ag}_{0.5}$ thus revealed the rapidest rate of hydrogen absorption. In addition to the lattice expansion of Mg_2Ni by adding silver, it has been reported that the hydrogenation of Mg_2Ni may be improved by adding small amount of catalyst.²² Since silver is a good catalyst for hydrogen dissociation reaction, this may also attribute to the improvement in hydrogen absorption kinetics of Mg_2Ni powders.

The dehydriding reaction of Mg_2Ni alloy is another important issue during the practical application of the materials. It has been reported that Mg_2Ni intermetallics dehydride commonly at a temperature ranged from 250 to 300°C.^{23–25} The dehydriding behavior was examined by the thermal analysis where the hydrided Mg_2Ni powders were heated from room temperature to 350°C at a heating rate of 5°C/min under Ar gas flow. Figure 8 shows the TGA curves of $\text{Mg}_2\text{Ni}/\text{Ag}$ powders during dehydriding. It can be noticed that the 15 h as-milled Mg_2Ni exhibited a dehydriding temperature at 225°C. Fujii *et al.*²⁶ have reported that, during the hydriding process for nanocrystalline materials obtained from mechanical alloying, hydrogen atoms may

Fig. 8 Thermogravimetric analysis curves for hydrided 15 h as-milled $\text{Mg}_2\text{Ni}/\text{Ag}$ powders with various silver additions.

occupy the interstitial sites in crystallites and the intergranular regions. Dehydriding may occur as hydrogen atoms transfer from intra-grain to inter-grain region in this unstable structure of nanocrystalline powders. This suggests that unstable and/or nanocrystalline structure of hydrided Mg_2Ni alloy prepared by high-energy mechanical milling exhibits lower dehydriding temperature.

Additionally, the dehydriding temperature of mechanically milled $\text{Mg}_2\text{Ni}/\text{Ag}$ powders is relatively lower than those reported in literatures that ranged from 250 to 300 °C. In the present study, the hydrided $(\text{Mg}_2\text{Ni})_{99.5}\text{Ag}_{0.5}$ powders, curve (b) in Fig. 8, exhibited the lowest dehydriding temperature of ~190 °C. While the dehydriding temperature of undoped Mg_2Ni and those doped with more than 0.5 mass% Ag exhibited a dehydriding temperature in the range of 210–220 °C. It has been reported that, with a small amount of silver addition, dehydriding behavior can be observed at a somewhat lower temperature, resulting from the reduction of silver in the stability of hydrides.¹³⁾ Moreover, the ease of hydrogen diffusion in larger cell volume of the lattice structure may also contribute to the decrease in dehydriding temperature.

4. Conclusions

Hydrogen absorption $(\text{Mg}_2\text{Ni})_{100-x}\text{Ag}_x$ alloy powders were synthesized successfully by mechanical alloying. The 15 h-milled $(\text{Mg}_2\text{Ni})_{100-x}\text{Ag}_x$ powders exhibited a mixture of Mg_2Ni , magnesium, and nickel solid solutions. The addition of silver may delay the formation of Mg_2Ni phase. The maximum and reversible hydrogen content of 15 h-milled Mg_2Ni powders was 3.14 and 2.40 mass%, respectively. The maximum hydrogen content increased to 3.93, 3.83, 3.65, and 3.47 mass% with a silver addition of 0.5, 1.0, 2.5, and 5.0 at%, respectively. While the reversible hydrogen content also increased to 3.14, 3.00, 2.73, and 2.86 mass%, respectively. In the present study, $(\text{Mg}_2\text{Ni})_{99.5}\text{Ag}_{0.5}$ exhibited the

best hydrogen absorption properties and the lowest dehydriding temperature of ~190 °C. The cooperative effects of silver additions and MA treatment improved the hydrogen absorption performance of Mg_2Ni alloy.

Acknowledgements

This work was partially funded by the National Science Council of Taiwan (Grant No. NSC 95-2221-E-035-064). The authors wish to acknowledge the valuable discussions of Prof. C. K. Lin and his technical assistance in the measurements of synchrotron X-ray absorption spectroscopy. The entire staff at NSRRC were also thanked.

REFERENCES

- 1) J. Huot: *Nanoclusters and Nanocrystals*, Nalwa HS, Ed., (American Scientific Publishers, Stevenson Ranch, 2003).
- 2) Q. D. Wang, C. P. Chen and Y. Q. Lei: *J. Alloys Compd.* **629** (1997) 253–254.
- 3) V. Güther and A. Otto: *J. Alloys Compd.* **293–295** (1999) 889–892.
- 4) L. Schlapbach and A. Züttel: *Nature*. **414** (2001) 353–358.
- 5) C. Suryanarayana: *Inter. Mater. Rev.* **40** (1995) 41–64.
- 6) M. Abdellaoui, D. Cracco and A. Percheron-Guegan: *J. Alloys Compd.* **293–295** (1999) 501–507.
- 7) R. Schulz, J. Huot, G. Liang, S. Boily, G. Lalande, M. C. Denis and J. P. Dodelet: *Mater. Sci. Eng. A* **267** (1999) 240–245.
- 8) H. Aoyagi, K. Aoki and T. Masumoto: *J. Alloys Compd.* **231** (1995) 804–809.
- 9) S.-i. Orimo and H. Fujii: *Intermetallics*. **6** (1998) 185–190.
- 10) Q. Li, K.-C. Chou, K.-D. Xu, Q. Lin, L.-J. Jiang and F. Zhan: *Intermetallics*. **14** (2006) 1386–1390.
- 11) G. Liang, J. Huot, S. Boily, A. Van Neste and R. Schulz: *J. Alloys Compd.* **282** (1999) 286–290.
- 12) N. H. Goo and K. S. Lee: *Int. J. Hydrogen Energy*. **27** (2002) 433–438.
- 13) L.-b. Wang, Y.-h. Tang, Y.-j. Wang, Q.-d. Li, H.-n. Song and H.-b. Yang: *J. Alloys Compd.* **336** (2002) 297–300.
- 14) L. Qian, L. Qin, J. Lijun, K.-C. Chou, Z. Feng, Z. Qiang and W. Xiuying: *J. Alloys Compd.* **359** (2003) 128–132.
- 15) Q. Li, L.-j. Jiang, K.-c. Chou, Q. Lin, F. Zhan, K.-d. Xu, X.-g. Lu and J.-y. Zhang: *J. Alloys Compd.* **399** (2005) 101–105.
- 16) C. K. Lin, P. Y. Lee, J. L. Yang, C. Y. Tung, N. F. Cheng and Y. Hwu: *J. Non-Crys. Solids*. **232–234** (1998) 520–525.
- 17) T. Spassov, P. Solsona, S. Surinach and M. D. Baro: *J. Alloys Compd.* **349** (2003) 242–254.
- 18) C. K. Lin, C. K. Wang, P. Y. Lee, H. C. Lin and K. M. Lin: *Mater. Sci. Eng. A* **449–451** (2007) 1102–1106.
- 19) L. Zaluski, A. Zaluska and J. O. Ström-Olsen: *J. Alloys Compd.* **217** (1995) 245–249.
- 20) Q. Li, K.-C. Chou, Q. Lin, L.-J. Jiang and F. Zhan: *Int. J. Hydrogen Energ.* **29** (2004) 843–849.
- 21) S. Orimo and H. Fujii: *Appl. Phys. A* **72** (2001) 167–186.
- 22) L. Zaluski, A. Zaluska, P. Tessier, J. O. Ström-Olsen and R. Schulz: *J. Alloys Compd.* **217** (1995) 295–300.
- 23) J. J. Reilly and R. H. Wiswall, Jr.: *Inorg. Chem.* **7** (1968) 2254–2256.
- 24) J. Huot, E. Akiba and T. Takada: *J. Alloys Compd.* **231** (1995) 815–819.
- 25) Y. Zhang, H. Yang, H. Yuan, E. Yang, Z. Zhou and D. Song: *J. Alloys Compd.* **269** (1998) 278–283.
- 26) H. Fujii, S. Orimo and K. Ikeda: *J. Alloys Compd.* **253–254** (1997) 80–83.