

Mg-Ni 금속 간 화합물 나노입자의 형성과 수소저장 특성

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Formation and Hydrogen Absorption Properties of Intermetallic Mg-Ni Compound Nanoparticles

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Abstract >> Mg-Ni nanoparticles were synthesized by a physical vapor condensation method (DC arc-discharge) in a mixture of argon and hydrogen atmosphere, using compressed mixture of micro powders as the raw materials. The crystal phases, morphology, and microstructures of nanoparticles were analyzed by means of X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). It was found that the intermetallic compounds of Mg₂Ni and MgNi₂ formed with existence of phases of Mg, Ni, and MgO in Mg-Ni nanoparticles. After one cycle of hydrogen absorption/desorption process (activation treatment), Mg-Ni nanoparticles exhibited excellent hydrogen absorption properties. Mg₂Ni phase became the main phase by a phase transformation during the hydrogen treatments. The phenomenon of refinement of grain size in the nanoparticle was also observed after the hydrogen absorption/desorption processes, which was attributed to the effect of volume expansion/shrinkage and subsequent break of nanoparticles. Maximum hydrogen absorption contents are 1.75, 2.21 and 2.77 wt.% at 523, 573 and 623 K, respectively.

Key words : Mg-Ni nanoparticles(Mg-Ni 나노입자), Intermetallic compound(금속 간 화합물), Arc discharge(아크 방전), Hydrogen(수소), Storage(수소저장)

1. Introduction

Mg-based alloys are considered to be one of the promising hydrogen storage materials for their high hydrogen storage capacity (7.6 wt.%), light weight, the abundance of Mg in the earth's crust, and low-cost compared with other hydrogen storage materials. Since Reilly et al.¹⁾ reported that Mg₂Ni can form Mg₂NiH₄ phase, in which the corresponding hydrogen content can achieve 3.6 wt.%, Mg₂Ni attracts more and more attention for its relatively high capacity and favorable thermodynamics. However, conventional Mg₂Ni alloy absorbs hydrogen at high temperature and exhibits poor absorption/desorption kinetics. To improve hydrogen absorption/desorption properties, much effort has been carried out with various approaches, such as element substitution^{2,3)}, surface modification^{4,5)}, forming nanometer-scale structures⁶⁻⁸⁾, forming composite etc⁹⁻¹¹⁾. Forming nanometer-scale structures offers new ways of addressing those issues emerged in Mg-based alloys by taking advantage of the distinctive chemical and physical properties caused by nanostructures¹²⁾. Nanoparticles often show excellent hydrogen storage properties because they possess more surface area and defects, which mean more nucleation sites with hydrogen. In addition, particle size reduction gives shorter diffusion distance for hydrogen. Thus, extensive work have been done to improve the kinetic properties of Mg-based alloys by preparing nanostructured Mg-based materials using various methods including ball-milling method^{6,7)}, Hydrogen-driven metallurgical reactions (HDMR)⁸⁾, hydriding combustion synthesis¹³⁾, etc.

However, there were few studies on the formation of Mg₂Ni by a physical vapor condensation method, i.e., DC arc-discharge method. In addition, most of the samples were prepared by a ball-milling method

in the past, with which the impurities were inevitably doped into the as-prepared powders. As a typical method to fabricate nanoparticles, DC arc-discharge has many unique advantages, such as low impurity introduction, distinct "core/shell" nanostructure, etc. Considering the large difference in vapor pressure and melting point between Mg and Ni, it is difficult to obtain Mg₂Ni by conventional melting method or vacuum arc melting technique. In this work, Mg-Ni nanoparticles were in situ synthesized by a modified arc-discharge method and the hydriding/dehydriding properties were explored by a volumetric method. The main purpose of this investigation is to gain some understanding on hydrogen storage kinetic and thermodynamic properties of Mg-Ni nanoparticles.

2. Experimental

The experimental equipment for production of Mg-Ni nanoparticles is similar to our previous work¹⁴⁾. In the experimental setup a tungsten rod was used as the cathode. Micron-sized Mg and Ni powders (99% purity) as the raw materials were weighed prorata and compressed into acylindrical block which served as the anode to be evaporated. A series of the compacted master blocks were prepared with different molar ratios of Mg to Ni (2:1, 1:1, and 1:2), and the resultant nanoparticles were labeled as sample (A)-(C), respectively. After the chamber was evacuated, a mixture of hydrogen and argon was introduced as the source of hydrogen plasma and a condensing atmosphere. Arc current and voltage were maintained at 240 A and 30 V, respectively. Before removing the nanoparticles from the chamber, they were experienced a passivation process for stabilization.

The phases in as-prepared nanoparticles were determined by X-ray diffraction (XRD) using a Shimadzu XRD-6000 instrument. The morphology, size and mi-

crostructure of the nanoparticles were observed by high-resolution transmission electron microscopy (HRTEM) using a Tecnai220 S-TWIM instrument. The Mg-Ni samples were activated sufficiently under thermal treatment conditions (heating at 673 K for 2 hours in 4.0 MPa hydrogen atmosphere and then annealing at the same temperature for 2 hours in vacuum). If the change in hydrogen pressure is less than about 1 Pa per second during the process of activation to avoid the absorbing of hydrogen and give the sufficient activation. The pressure-composition-isotherms (P-C-I) curves were measured using a conventional volumetric method

3. Results and discussion

3.1 The phases in Mg-Ni nanoparticles

Fig. 1 shows XRD patterns of Mg-Ni nanoparticles with different molar ratios of Mg to Ni. Five phases, i.e. Ni, Mg₂Ni, MgNi₂, Mg and MgO, coexist in all nanoparticle samples. MgO in nanoparticles is attributed to the oxidation reaction between Mg and oxygen during the passivation process. A trace of Mg(OH)₂ was observed in the as-prepared nano-

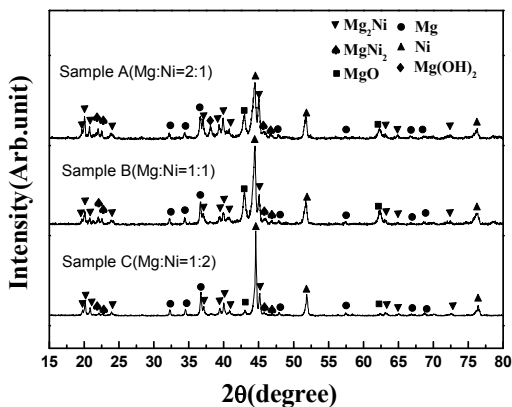


Fig. 1. XRD patterns of Mg-Ni nanoparticles produced by arc-discharge with different molar ratio of Mg to Ni

particles sample (A), which may be attributed to the reaction between MgO and H₂O vapor as nanoparticles were exposed to air. It is indicated from the experimental results that the single phase of Mg₂Ni was difficult to be formed by co-evaporating Mg and Ni raw materials, although the stoichiometric composition of master bulk was set as the molar ratio of 2:1 for Mg and Ni. In present preparation, the thermal non-equilibrium condition and the significant difference between melting points of Mg and Ni would result in the complex phase constitution. It was also reported that the main phase of Mg₂Ni in Mg-Ni powders can be obtained by hydriding combustion synthesis and the ball milling methods^{13,15}. A similar XRD result to present work was also obtained by the laser sintering method by which five phases, i.e. Mg₂Ni, MgNi₂, Mg, Ni and MgO, were founded¹⁶. It is well known from the equilibrium phase diagram¹⁷ that two kinds of intermetallic compounds (Mg₂Ni and MgNi₂) exist in binary bulk Mg-Ni alloy system. Mg₂Ni is considered to be a good candidate for a hydrogen storage material; nevertheless, MgNi₂ is unable to absorb hydrogen¹. It is suggested that the ordered intermetallic compounds (Mg₂Ni) would be formed by solid state diffusion and transition, neither in gas nor in liquid states. The free-energy and strains at surfaces or interfaces are mainly responsible for the formation of Mg₂Ni and MgNi₂ during the arc discharge process¹⁸. Pure metallic phases of Mg and Ni are due to the non-equilibrium condition in arc-discharge process, namely it is short diffusion time to exhaust out to form the stable intermetallic compound phases.

3.2 Kinetic properties during the activation process

In this work, sample A was taken as a typical one to measure its hydrogen storage properties, which has

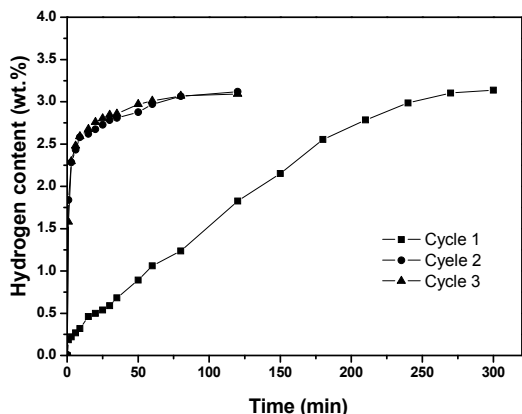


Fig. 2. Hydrogen absorption kinetic curves of the Mg-Ni nanoparticles at 673 K under a hydrogen pressure of 4.0 MPa: (a) Cycle 1, (b) Cycle 2, and (c) Cycle 3

the most quantity of active Mg_2Ni phase in comparison to that in other samples. Fig. 2 shows hydrogen absorption kinetic curves of Mg-Ni nanoparticles (sample A) at 673 K under a hydrogen pressure of 4.0 MPa. The maximum hydrogen contents are 3.14 wt.% in 300 min. for cycle 1, while it is 3.12 wt.% and 3.09 wt.% in 120 min. for cycle 2 and cycle 3, respectively. It is indicated that both of hydrogen absorption rates in cycles 2 and 3 are sharp higher than that in cycle 1. Compared with Mg_2Ni alloy prepared by a conventional melting method^{1,19)}, the activation property of this nanoparticles sample is largely improved. For instance, the hydrogen absorption content of 0.46 wt.% is reached in 15 min. during the first cycle, while it becomes 2.62 wt.% and 2.68 wt.% in the same time for cycle 2 and cycle 3, respectively. It seems that oxide layer on the surface of Mg-based nanoparticles act as a barrier for hydrogen diffusion during first activation process. To crack this kind of oxide layer leaves as the key factor for excellent hydrogen absorption properties²⁰⁾. The nanoparticles without exposure to air can be activated with ease under a moderate activation condition¹⁶⁾ or do not need further activation process at all¹⁴⁾. However, an oxygen-free condition is quite money-consuming

or time-consuming and reduces the possibility of its practical applications. It is speculated that the improved kinetics in cycle 2 and 3 are mainly attributed to the fracture of oxide surface layers of nanoparticles after first cycle and the resultant fresh surfaces facilitate hydrogen absorption in the following cycles. Furthermore, the other reason may be the refinement of grain size in a nanoparticle during the hydrogen absorption/desorption process, which was observed and will be analyzed in next section. It is also well known that nanoparticles possess various kinds of defects, such as phase boundaries, interfaces, dislocations, etc. All of these defects are favorable to diffuse hydrogen atoms and store an excess energy that may facilitate hydrogen absorption¹⁴⁾. As a result, Mg-Ni nanoparticles can exhibit excellent hydrogen absorption properties by only one absorption/desorption cycle.

3.3 The microstructure change through hydrogen absorption and desorption

Fig. 3 presents the change of phase constitution between as-prepared Mg-Ni nanoparticles (sample A) and the treated one through hydrogen absorption/desorption processes (three cycles). It is well shown in Fig. 3 that Mg_2Ni becomes the main phase instead of Ni, meanwhile Mg is consumed out. This phenomenon indicates that the phase transformations occur during the hydrogen process accompanying the change of microstructure in nanoparticles. An energy dispersive spectroscopy (EDS) analysis reveals that the measured composition in Mg-Ni nanoparticles is almost the same to the nominal one in raw bulk (Mg:Ni=2:1 in molar ratio). Part of Mg is consumed by MgO layers on the surface of nanoparticles and result in the lack of Mg resource to form Mg_2Ni phase in comparison to the Ni counter part. Therefore, the residual pure Ni

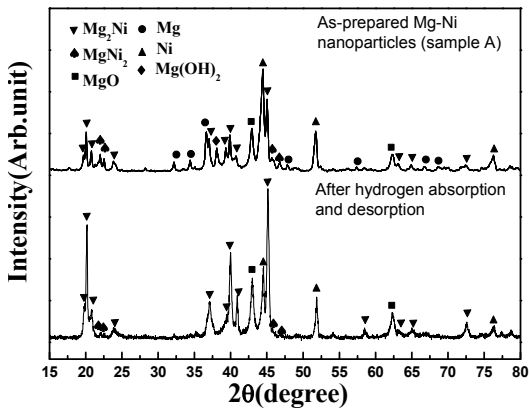


Fig. 3. X-ray patterns of the as-prepared Mg-Ni nanoparticles (sample A) and its variation by hydrogen absorption/desorption processes

phase is found in the treated sample without pure Mg phase appeared. It was reported that single phase of Mg_2Ni can be formed by treating the mixture of separated pure Mg and Ni nanoparticles under proper temperature and pressure with existence of hydrogen. The lowest temperatures to form Mg_2Ni were 703 K in argon and 603 K in hydrogen atmosphere, respectively²¹⁾. In addition, the trace of $Mg(OH)_2$ disappears after hydrogen treatment, indicating change of $Mg(OH)_2$ into MgO and H_2O during the hydrogen absorption/desorption process.

Fig. 4 is TEM images of the as-prepared Mg-Ni nanoparticles (sample A, Fig. 4(a) and (c)) and its variation after hydrogen absorption/desorption treatments (Fig. 4(b) and (d)). Significant changes were observed in the morphologies and microstructures between two samples. Based on the analysis of TEM images, the sizes of original nanoparticles are about in the range of 50-200 nm, and the particles' shape are spherical with smooth surface. After several cycles, the outline of nanoparticles is indistinct and some smaller particles are observed because of the separation of between shell and core parts. As shown in Fig. 4(b) and (d), some of broken nanoparticles are labeled with arrows. A broken nanoparticle and its

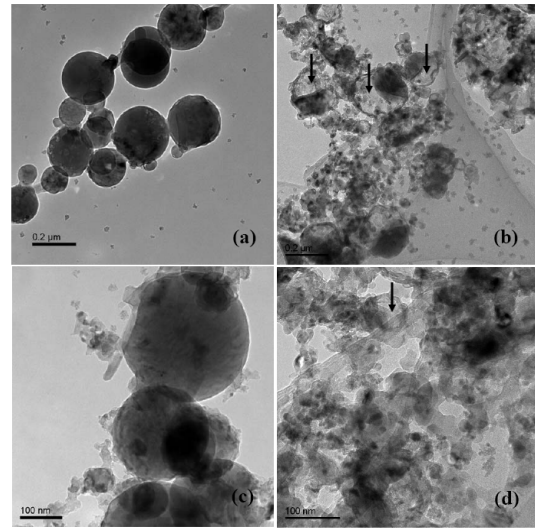


Fig. 4. TEM image of the as-prepared Mg-Ni nanoparticles (sample A, (a) and (c)) and its variation by hydrogen absorption/desorption processes ((b) and (d)).

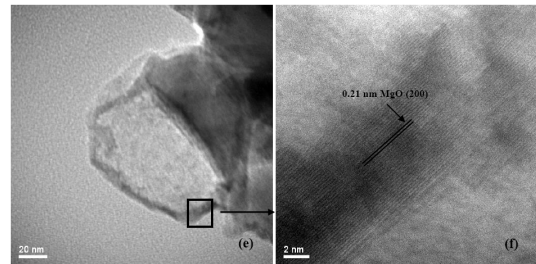


Fig. 5. HRTEM images of a fractured Mg-Ni nanoparticle by hydrogen treatment (partly hollow within nanoparticle) (a) and its shell part of MgO (b)

shell part are displayed as HRTEM images in Fig. 5. The largest interplanar spacing of crystal MgO is about 0.21 nm for (200) plane, which agrees with the observed value (0.21 nm) of MgO in the shell of nanoparticle (Fig. 5(b)).

If the pressure and temperature are high enough, the adsorbed hydrogen is then dissociated at the surface and becomes chemisorbed. Chemisorption is the chemical combination of hydrogen with the metal to form a new compound accompanied with phase transition. This phase transition is usually characterized by a crystalline structure change, a volume expansion, and

a nucleation energy barrier associated with volume expansion and interface energy between the phases⁸⁾. In this work, a volume expansion/shrinkage is expected to take place in the hydriding/dehydriding process as long as the existence of active phases, such as Mg or Mg₂Ni. Nevertheless, as a shell of nanoparticle, the phase of MgO can not absorb hydrogen with a volume expansion, which result in the maintenance of its original states and the separation between shell and coreparts. This interesting phenomenon may play an important role to improve of hydrogen absorption kinetics. Some larger particles will be divided in to smaller ones and this refinement of grain and particle sizes will bring out lots of defects, i.e. new fresh surfaces, boundaries, etc. All the changes maybe facilitate hydriding/dehydriding and give a chance to improve the hydrogen storage properties.

It is well known that grain growth is a serious problem in nanostructured materials. Generally, large numbers of grain boundaries with excess energy will increase the free energy and drive recrystallization in nanostructure materials²²⁾. Recrystallization occurs by the migration of the grain boundary of a growing crystal into surrounding particles and results in the partial lost of the nanostructure properties. Boundary migration can be reduced by doping with incoherent second phase particles to limit recrystallization²³⁾. In this work, MgO can act as a second phase which disperses in active materials and prohibits the grain growth. This phenomenon may be potentially beneficial to stabilize nanoparticles and leads to better cycling properties, as indicated in this work after several hydrogen absorption/desorption cycles.

3.4 The hydrogen absorption properties of Mg-Ni nanoparticles

As shown in Fig. 6, P-C-I curves of Mg-Ni nano-

particles (sample A) were measured at different temperatures to reveal the hydrogen absorption/desorption properties. The maximum hydrogen absorption contents are 1.75, 2.21 and 2.77 wt.% at 523, 573 and 623K, respectively. In the case of Mg-Ni bulk or film with an excess Mg, P-C-I curves exhibit two plateaus^{1,24)}. Nevertheless, only one plateau occurs in the present nanoparticles. As discussed in 3.3, pure Mg component in the original Mg-Ni nanoparticles was consumed out to form Mg₂Ni during the hydrogen absorption/desorption process. It can be concluded that the single plateau in P-C-I curve of Mg-Ni nanoparticles mainly attribute to the absorption/desorption reactions of Mg₂Ni phase with the absence of pure Mg. As shown in Fig. 6, the P-C-I curves show a large hysteresis between the measured absorption and desorption plateau pressure, which can be ascribed to coherency strain between the phases²⁵⁾. The coherency strain introduces an unsurmountable energy barrier between the transforming phases, which prevents the coexistence of the phase and results in a reversible hysteresis in the P-C-I curves. It is obvious that the hysteresis is incomplete, which indicates that hydrides are not completely desorbed. The residual hydrides may reduce the capacity of future cycles. Similar results were also reported in other reports^{16,26)}. Generally, the

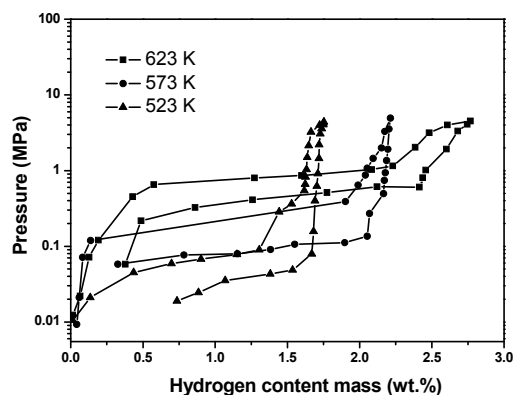


Fig. 6. P-C-I curves of the Mg-Ni nanoparticles (sample A)

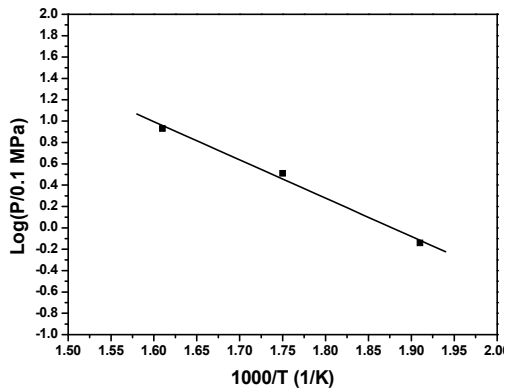


Fig. 7. Van't Hoff curve for sample A

hydrogen solubility is expected to decrease at higher temperatures and this should be reflected in the length of the corresponding plateau in LaNi₅-type alloys. However, it displays an inverse behavior and the maximum hydrogen absorption capacity is found to decrease remarkably with decreasing temperature in this work. This phenomenon is a common case in Mg-Ni alloys and more details are discussed by Kuji et al.²⁶⁾

To further explore the thermal properties of nanoparticles, the van't Hoff curve (Log P versus 1/T) is usually employed to estimate the thermal stability of hydrides. The van't Hoff curve of Mg-Ni nanoparticles (sample A) is displayed in Fig. 7. The resulting van't Hoff equation is $\text{Log } P = -3578/T + 6.719$. From van't Hoff equation, the hydride formation enthalpy (ΔH) is calculated to be $-68.52 \text{ kJ/mol H}_2$ and the entropy (ΔS) is $-0.129 \text{ kJ/K/mol H}_2$. It was reported that ΔH and ΔS of hydriding reaction are -64.4 kJ/mol H_2 and $-0.121 \text{ kJ/K/mol H}_2$ for pure Mg₂Ni system, respectively²⁷⁾. The measured values in this study are close to the reported ones, indicating thermodynamic properties of Mg₂Ni can not be improved by fabricating nanoparticles.

4. Conclusion

In this study, Mg-Ni nanoparticles are prepared by

arc discharge using micro-sized metallic powders as the raw materials. It was found that the intermetallic compounds of Mg₂Ni and MgNi₂ are generated and coexist with the phases of Mg, Ni, and MgO in nanoparticles. Mg-Ni nanoparticles exhibit excellent kinetic properties after only one hydrogen absorption/desorption cycle. After this kind of hydrogen treatment, Mg₂Ni becomes the main phase by a phase transformation. The absorption/desorption of hydrogen atoms causes the expansion and shrinkage of the crystal lattice, which lead to fracture and refinement of grain size in nanoparticles. P-C-I curves exhibit single plateau which attributes to the absorption/desorption reactions of Mg₂Ni phase with the absence of pure Mg. The hydride formation enthalpy ($-68.52 \text{ kJ/mol H}_2$) and the entropy (ΔS) ($-0.129 \text{ kJ/K/mol H}_2$) are close to the reported ones.

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References

1. J. J. Reilly and R. H. Wiswall, "Reaction of hydrogen with alloys of magnesium and nickel and the formation of Mg₂NiH₄", *Inorg. Chem.* Vol. 7, 1968, p. 2254.
2. E. Grigorova, M. Khristov, M. Khrussanova, J. L. Bobetb, and P. Pesheva, "Effect of additives on the hydrogen sorption properties of mechanically alloyed composites based on Mg and Mg₂Ni" *Int. J. Hydrogen Energy*, Vol. 30, 2005, p. 1099.
3. Y. Feng, L. F. Jiao, H. T. Yuan, and M. Zhao, "Effect of Al and Ce substitutions of the electrochemical properties of amorphous MgNi-based alloy electrodes", *Int. J. Hydrogen Energy*, Vol. 32, 2007, p. 1701.
4. X. L. Wang, N. Haraikawa, and S. Suda, "A study of the surface composition and structure of fluorinated Mg-based alloys", *J. Alloy Compd.*, Vol. 231, 1995, p. 397.
5. M. D. Hampton and J. K. Lomness, "Water activation of

- Mg₂Ni for hydrogen uptake Original Research Article”, *Int. J. Hydrogen Energy*, Vol. 24, 1999, p. 175.
6. A. Zaluska, L. Zaluski, and J. O. Ström-Olsen, “Nanocrystalline magnesium for hydrogen storage”, *J. Alloy Compd.*, Vol. 288, 1999, p. 217.
 7. F. C. Gennari, F. J. Castro, and G. Urretavizcaya, “Hydrogen desorption behavior from magnesium hydrides synthesized by reactive mechanical alloying”, *J. Alloy Compd.*, Vol. 321, 2001, p. 46.
 8. J. Graetz and J. J. Reilly, “Nanoscale Energy Storage Materials Produced by Hydrogen-Driven Metallurgical Reactions”, *Advanced Engineering Materials*, Vol. 7, 2005, p. 597.
 9. M. Terzieva, M. Khruasanova, and P. Peshev, “Hydriding and dehydriding characteristics of Mg-LaNi₅ composite materials prepared by mechanical alloying”, *J. Alloy Compd.*, Vol. 267, 1998, p. 235.
 10. H. Miyaoka, T. Ichikawa, S. Isobe, and H. Fujii, “Hydrogen storage properties of nano-structural carbon and metal hydrides composites”, *Physica B*, Vol. 383, 2006, p. 51.
 11. D. Sun, H. Enoki, M. Bououdina, and E. Akiba, “Phase components and hydriding properties of the sintered Mg-xwt.% LaNi₅ (x=20-50) composites”, *J. Alloys Compd.*, Vol. 282, 1999, p. 252.
 12. V. Bérubé, G. Radtke, M. Dresselhaus, and G. Chen, “Size effects on the hydrogen storage properties of nano-structured metal hydrides: A review”, *Int. J. Energy Res.*, Vol. 31, 2007, p. 637.
 13. I. Saita, L. Q. Li, K. Saito, and T. Akiyama, “Hydriding combustion synthesis of Mg₂NiH₄”, *J. Alloys Compd.*, Vol. 356-357, 2003, p. 490.
 14. X. L. Dong, Z. D. Zhang, X. G. Zhao, Y. C. Chuang, S. R. Jin, and W. M. Sun, “The preparation and characterization of ultrafine Fe-Ni particles”, *J. Mater. Res.*, Vol. 14, 1999, p. 398.
 15. G. Liang, S. Boily, J. Huot, A. V. Neste, and R. Schulz, “Mechanical alloying and hydrogen absorption properties of the Mg-Ni system”, *J. Alloy Compd.*, Vol. 267, 1998, p. 302.
 16. T. Z. Si, D. M. Liu, and Q. A. Zhang, “Microstructure and hydrogen storage properties of the laser sintered Mg₂Ni alloy”, *Int. J. Hydrogen Energy*, Vol. 32, 2007, p. 4912.
 17. M. H. G. Jacob and P. J. Spencer, “A critical thermodynamic evaluation of the system MG-NI”, *CALPHAD*, Vol. 22, 1998, p. 513.
 18. S. Yu, D. M. Li, H. P. Sun, H. D. Li, H. B. Yang, and G. T. Zou, “Microanalysis of single-phase AlN nanocrystals and AlN-Al nanocomposites prepared by DC arc-discharge”, *J. Cryst. Growth*, Vol. 183, 1998, p. 284.
 19. P. Selvam, B. Viswanathan, and V. Srinivasan, “XPS and XAES studies on hydrogen storage magnesium-based alloys”, *Int. J. Hydrogen Energy*, Vol. 14, 1989, p. 899.
 20. J. L. Bobet, E. Akiba, Y. Nakamura, and B. Darriet, “Study of Mg-M (M=Co, Ni and Fe) mixture elaborated by reactive mechanical alloying—hydrogen sorption properties”, *Int. J. Hydrogen Energy*, Vol. 25, 2000, p. 987.
 21. H. Y. Shao, T. Liu, X. G. Li, and L. F. Zhang, “Preparation of Mg₂Ni intermetallic compound from nanoparticles”, *Scripta Mater*, Vol. 49, 2003, p. 595.
 22. V. Y. Gertsman and R. Birringer, “On the room-temperature grain growth in nanocrystalline copper”, *Scripta Metall. Mater.*, Vol. 30, 1994, p. 577.
 23. H. Gleiter, “Nanostructured materials: basic concepts and microstructure”, *Acta Mater.*, Vol. 48, 2000, p. 1.
 24. L. Z. Ouyang, S. Y. Ye, H. W. Dong, and M. Zhu, “Effect of interfacial free energy on hydriding reaction of Mg-Ni thin films”, *Appl. Phys. Lett.*, Vol. 90, 2007, Art No. 021917.
 25. R. B. Schwarz and A. G. Khachatryan, “Thermodynamics of Open Two-Phase Systems with Coherent Interfaces”, *Phys. Rev. Lett.*, Vol. 74, 1995, p. 2523.
 26. T. Kuji, H. Nakano, and T. Aizawa, “Hydrogen absorption and electrochemical properties of Mg_{2-x}Ni (x=0-0.5) alloys prepared by bulk mechanical alloying”, *J. Alloys Compounds*, Vol. 330-332, 2002, p. 590.
 27. Y. Q. Tong, L. Z. Ouyang, and M. Zhu, “Effect of Ni on Mg based hydrogen storage alloy Mg₃Nd”, *Rare Metals*, Vol. 25, 2006, p. 289.