Hydriding Properties of $(\text{Mg}_{1-x}\text{M}_x)\text{Ni}_2$ C15-Type Laves Phase Alloys

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Mg-based Laves phase alloys $(\text{Mg}_{0.7}\text{M}_{0.3})\text{Ni}_2$, where M elements were Ca, La, Ce, Pr, Nd and Gd were successfully developed. The alloys can be synthesized by a conventional induction melting and annealing method from intermetallic compounds MgNi_2 and MNi_2 as a source of Mg, Ni and M elements. The crystal structures of the major phases of annealed $(\text{Mg}_{0.7}\text{M}_{0.3})\text{Ni}_2$ alloys were C15-type for M = Ca and C15_b-type for M = La, Ce, Pr, Nd and Gd Laves structures, respectively. In the alloys except M = Ce, hydrogenation and dehydrogenation reversibly occurred. The maximum hydrogen contents of the alloys are 1.2–1.6 mass% (H/M:0.6–0.8) under hydrogen pressure of 5 MPa at 243–273 K. As the results of measurements of *p*-*c* isotherms, in the case of the M = Pr and Nd, two step plateaus were clearly observed. After a few hydrogenation/dehydrogenation cycles, the alloys kept C15-type or C15_b-type Laves structures without hydrogen-induced amorphization, disproportionation and decomposition. [doi:10.2320/matertrans.47.1890]

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1. Introduction

Hydrogen attracts attention from both environmental and energy resource issues. In order to transport and store a large amount of hydrogen in safely, compactly and economically, a system which uses a hydrogen absorbing material is suitable as compared with the other systems such as high pressure hydrogen gas container or liquid hydrogen dewar vessel. Development of hydrogen absorbing materials which can reversibly absorb and desorb a large amount of hydrogen at ambient temperature and ambient hydrogen absorption/desorption pressure is indispensable to establish hydrogen transportation and storage systems using hydrogen absorbing materials.

Pure Mg metal absorbs and desorbs hydrogen to form MgH_2 and their hydrogen content is as high as 7.6 mass%.¹⁾ However, because reaction kinetics of MgH_2 is quite low even at temperature above 600 K for 0.1 MPa of hydrogen desorption pressure, It has not been applied for actual applications. On the other hand, intermetallic compound Mg_2Ni also reversibly absorbs and desorbs hydrogen to forms Mg_2NiH_4 and its hydrogen content is as high as 3.6 mass%.²⁾ Moreover, reaction kinetics of Mg_2NiH_4 is very rapid as compared with MgH_2 . Therefore Mg-based hydrogen absorbing alloys represented by Mg_2Ni have a great potential for applications such as hydrogen transportation and storage systems. In addition, it is rich in natural resources and less expensive as compares with the other hydrogen absorbing metals. However, because working temperature of Mg_2NiH_4 is above 550 K under 0.1 MPa of hydrogen desorption pressure, it has not been applied for room temperature applications.

To lower hydrogen desorption temperature under 0.1 MPa of hydrogen pressure, amorphization or substitution of third elements for Mg or Ni site of Mg_2Ni in order to improve hydrogenation/dehydrogenation properties have been performed briskly.^{3,4)} Attempts to improve the reaction kinetics of MgH_2 by mechanical alloying have also been performed. However, the satisfying results have not been obtained yet. It

has been reported that, almost all the Mg-based hydrogen absorbing alloys except Mg_2Ni disproportionate to form MgH_2 and other phases.⁵⁾ Therefore, they are unfavorable for most of the applications to be used in practical hydrogen energy systems.

Recently, a few studies on novel hydrogen absorbing alloys containing Mg have been published. For example, these are the hexagonal PuNi_3 -type alloys RMg_2Ni_9 (R = rare earth) reported by Kadir *et al.*,^{6–8)} the La-Mg-Ni system alloys reported by Kohno *et al.*⁹⁾ and the C15_b-type Laves phase alloys MgYNi_4 reported by Aono *et al.*¹⁰⁾ We also have developed the novel Mg-based hydrogen absorbing alloy $(\text{Mg}_{0.67}\text{Ca}_{0.33})\text{Ni}_2$ with C15-type Laves structure which can reversibly absorb and desorb hydrogen at room temperature.¹¹⁾ The maximum hydrogen capacity of $(\text{Mg}_{0.67}\text{Ca}_{0.33})\text{Ni}_2$ is 1.4 mass% (H/M = 0.7) under hydrogen pressure of 4 MPa at temperature of 278 K. We have also reported on the improvement of flatness of the plateau and cycle durability of $(\text{Mg}_{0.7}\text{Ca}_{0.2}\text{Y}_{0.1})\text{Ni}_2$ C15-type Laves phase alloy.¹²⁾

In this study, we develop a novel hydrogen absorbing alloy $(\text{Mg}_{1-x}\text{M}_x)\text{Ni}_2$ with C15-type Laves structure by melting method. We synthesize $(\text{Mg}_{1-x}\text{M}_x)\text{Ni}_2$ alloys, where M elements are Ca, La, Ce, Pr, Nd and Gd and $x = 0.3$, crystalline structures, and hydrogenation/dehydrogenation properties.

2. Experimental Details

2.1 Sample preparation

$(\text{Mg}_{1-x}\text{M}_x)\text{Ni}_2$ alloys, where M elements were Ca, La, Ce, Pr, Nd and Gd and $x = 0.3$ were synthesized by melting in a high-purity (more than 97%) alumina crucible using a conventional induction furnace and casting into a water cooling board mold made of iron under 0.05–0.1 MPa argon or helium atmosphere. Commercial grade Mg (3–5 mm in diameters, 99.9%), Ca (3–5 mm in diameters, 99.5%), Ni (10–15 mm in diameters, 99.99%) and Rare earth elements (5–10 mm in diameters, 99.9%) granules were used as raw

materials. In order to avoid evaporation of Mg and reaction of Mg to alumina crucible during melting process, we divided our alloying process into two steps. Namely we synthesized (Mg_{1-x}M_x)Ni₂ alloys from two kinds of the intermetallic compounds MgNi₂ and MNi₂ prepared in advance as a source of Mg, Ni and M element, instead of direct syntheses from simple Mg, Ni and M metals. The reason for this is as follows: there is a quite large difference of melting points between Mg and Ni. On the other hand melting points of both MgNi₂ and MNi₂ are close to 1200 K. Therefore we can avoid boiling of Mg during melting. We decide the values of $x = 0.3$ to avoid an increase of the atomic radius ratio $R_{(\text{Mg,M})}/R_{\text{Ni}}$ than 1.37,^{13,14)} which is a dominant factor for controlling the occurrence of hydrogen-induced amorphization. Here, $R_{(\text{Mg,M})}$ and R_{Ni} are the atomic radii of Mg_{1-x}M_x and Ni atoms in the (Mg_{1-x}M_x)Ni₂ alloys.

The shape of the cast alloys was a flat plate with one-two centimeters in thickness. The weight of each cast alloy was approximately two-three kilograms. The annealing-treatments were carried out at temperature 873 and 1173 K for 100 hours under an argon atmospheric flow. The ingots were powdered to the size appropriate for each measurement using a hand mill in argon atmosphere for preventing ignition and oxidation.

2.2 Characterizations

The chemical compositions of the cast alloys were analyzed using a conventional Inductively Coupled Plasma analyzer (ICP, Seiko Instruments Inc., SPS4000). The crystal structures of each phase were determined by powder X-Ray Diffraction (XRD) using Rigaku RINT2500V. The pressure-composition (p - c) isotherms were measured at temperatures 243–373 K under hydrogen pressure from 1.0×10^{-3} to 5 MPa by use of a homemade automatic Sieverts'-type apparatus. Before and after measurements of p - c isotherms, we measured XRD profiles under the air to confirm the occurrence of hydrogen-induced amorphization, disproportionation and decomposition.

3. Results and Discussions

3.1 Chemical analysis

Table 1 shows the results of chemical analysis, melting points of M elements and intermetallic compounds MNi₂ and annealing conditions of (Mg_{0.7}M_{0.3})Ni₂ alloys. The results of chemical analysis agreed with those of the target compositions. We successfully synthesized (Mg_{0.7}M_{0.3})Ni₂ alloys

without a heavy evaporation of Mg and reactions between alumina crucible and Mg during melting by use of inter-metallic compounds MgNi₂ and MNi₂ instead of Mg, Ni and M elements.

It should be pointed out that the estimation of the amount of evaporation of Mg during melting, temperatures of molten metal, a period of melting time and sufficient stir are keys to synthesize by melting the alloys close to the target composition. Our applied estimations and calculations of a yield rate and melting conditions were suitable.

3.2 Crystal structures

Figure 1 shows the X-ray diffraction profiles of annealed (Mg_{0.7}M_{0.3})Ni₂ alloys. From Fig. 1, it can be seen that the crystal structure of the major phase of annealed (Mg_{0.7}M_{0.3})Ni₂ alloys was C15-type Laves structure indicated by open circles. In the case of the alloys with M = La, Ce, Pr,

Fig. 1 The XRD profiles of annealed (Mg_{0.7}M_{0.3})Ni₂ alloys (M = Ca, La, Ce, Pr, Nd and Gd). The open circles and solid triangles indicate Bragg peaks from C15-type and C15_b-type Laves structures, respectively.

Table 1 The results of chemical compositions analysis, melting points of M elements and intermetallic compounds MNi₂ and annealing conditions.

M elements	Mg (at%)	M (at%)	Ni (at%)	Compositions formula	Melting points (K)		Annealing conditions
					M	NNi ₂	
M (Target)	22.22	11.11	66.67	(Mg _{0.7} M _{0.3})Ni ₂	—	—	—
Ca	23.29	10.09	66.61	(Mg _{0.70} Ca _{0.30})Ni _{2.00}	1111	1170	1173 K–100 hours
La	22.86	9.74	67.41	(Mg _{0.70} La _{0.30})Ni _{2.07}	1193	1068	873 K–100 hours
Ce	21.16	10.32	68.52	(Mg _{0.67} Ce _{0.33})Ni _{2.18}	1077	1103	873 K–100 hours
Pr	22.48	9.98	67.54	(Mg _{0.69} Pr _{0.31})Ni _{2.08}	1192	1183	873 K–100 hours
Nd	22.98	9.90	67.11	(Mg _{0.70} Nd _{0.30})Ni _{2.04}	1292	1213	873 K–100 hours
Gd	23.72	9.15	67.13	(Mg _{0.72} Gd _{0.28})Ni _{2.04}	1585	1283	1173 K–100 hours

Fig. 2 The relation between the lattice parameters of C15_b-type Laves phases and atomic radii of M elements.

Nd and Gd, additional two Bragg peaks indicated by solid triangles appeared. These peaks fitted for X-ray diffraction from (200) and (420) planes of C15-type Laves structure. It has been suggested that the elementally orders of 8a (0, 0, 0) sites in C15-type Laves structures (Space Group: Fd-3m, No. 227) occurred and C15-type Laves structures converted to C15_b-type Laves structures (Space Group: F-43m, No. 216). The relation between the lattice parameters of the C15_b-type phases and the atomic radii of M elements is shown in Fig. 2. The Lattice parameters of the C15_b-type phases increased with increasing the atomic radii of M elements. The crystal structure of Mg, La, Pr, Nd and Gd is hexagonal close-packed (hcp), however only the crystal structure of Ce is face centered cubic (fcc). The atomic radii should change by crystal structure. Therefore in the case of substitution Ce with fcc for Mg with hcp, the atomic radius of Ce doesn't apply the same as other rare earth elements with hcp. It is assume that this difference appears in Fig. 2.

3.3 Hydriding/dehydriding properties

Figure 3 shows the *p*-*c* isotherms of annealed (Mg_{0.7}M_{0.3})Ni₂ alloys except M = Ce alloy at temperatures of 243, 273, 323 and 373 K. In the case of the M = Ce, we could not hydrogenate at temperatures of 243 K and hydrogen pressure of 5 MPa after evacuation using a turbo molecular pump at 423 K for 6 hours. As shown in Fig. 3, the reversible *p*-*c* isotherms of hydrogenation/dehydrogenation were clearly observed. The maximum hydrogen contents of these alloys are 1.2–1.6 mass% (H/M:0.6–0.8) under a hydrogen pressure of 5 MPa at 243–273 K. In the case of the M = Pr and Nd, two step plateaus were clearly observed. The maximum hydrogen contents and its hydrogenation conditions are summarized in Table 2.

3.4 Structural stability of the C15-type and C15_b-type Laves phases

From X-ray diffraction profiles after a few hydrogenation/dehydrogenation cycles, it was found that all alloys kept C15-type or C15_b-type Laves structure without occurrence of

Fig. 3 The *p*-*c* isotherms for annealed (Mg_{0.7}M_{0.3})Ni₂ alloys (M = Ca, La, Pr, Nd and Gd). The open squares, open triangles, open circles and cross marks indicate the measurements at 373, 323, 273 and 243 K, respectively. Figure 3-A to E shows M = Ca, La, Pr, Nd and Gd, respectively.

Table 2 The maximum hydrogen contents and conditions of hydrogenation.

M elements	Hydrogen contents		conditions
	mass%	H/M	
Ca	1.7	0.8	273 K, 5 MPa
La	1.1	0.7	273 K, 5 MPa
Ce	—	—	—
Pr	1.2	0.7	273 K, 4 MPa
Nd	1.3	0.7	273 K, 5 MPa
Gd	1.1	0.6	243 K, 5 MPa

hydrogen-induced amorphization, disproportionation and decomposition. Figure 4 shows the X-ray diffraction profiles of the M = Ca, Gd and Nd after a few hydrogenation/dehydrogenation cycles. Aoki *et al.*^{13,14} reported that, the atomic radii ratio R_A/R_B is a dominant factor for controlling the occurrence of hydrogen-induced amorphization and in the case of R_A/R_B is larger than 1.37, hydrogen-induced amorphization occurs. Here, R_A and R_B are the atomic radii of A and B atoms in C15-type AB₂ Laves phases. In the estimations for the (Mg_{0.7}M_{0.3})Ni₂ alloys, R_A is the average

Table 3 The lattice parameters of C15-type or C15_b-type Laves phases before and after measurements of *p-c* isotherms, atomic radii of M elements and atomic radii ratios R_A/R_B .

M elements	Lattice parameters of C15 or C15 _b phases (nm)		Atomic radii of M elements/nm	R_A/R_B
	Before PCT	After PCT		
Ca	6.979	6.987	0.197	1.369
La	7.151	—	0.188	1.347
Ce	6.979	—	0.183	1.335
Pr	7.058	—	0.183	1.335
Nd	7.000	6.997	0.182	1.333
Gd	6.980	6.972	0.178	1.323

Fig. 4 The XRD profiles of after measurements of *p-c* isotherms on (Mg_{0.7}M_{0.3})Ni₂ alloys (M = Ca, Nd and Gd). The open circles and solid triangles indicate Bragg peaks from C15-type and C15_b-type Laves structures, respectively.

of atomic radii of Mg and M. In this study R_A/R_B of all (Mg_{0.7}M_{0.3})Ni₂ alloys were smaller than 1.37. Therefore we conclude that hydrogen-induced amorphization, disproportionation and decomposition did not occur in the present study. The lattice parameters of C15-type or C15_b-type Laves phases before and after measurements of *p-c* isotherms, atomic radii of M elements and R_A/R_B are summarized in Table 3.

4. Conclusions

Based on the above-mentioned results and discussions, we conclude:

- (1) (Mg_{0.7}M_{0.3})Ni₂ alloys with C15-type or C15_b-type Laves structure were successfully synthesized by induc-

tion melting and annealing method from intermetallic compounds MgNi₂ and MNi₂ as a source of Mg, Ni and M elements.

- (2) The crystal structures of the major phases of annealed (Mg_{0.7}M_{0.3})Ni₂ alloys were C15-type for M = Ca and C15_b-type for M = La, Ce, Pr, Nd and Gd.
- (3) The lattice parameters of the C15_b-type Laves phases increased with the atomic radii of M elements.
- (4) A reversible *p-c* isotherms were clearly observed at 243–273 K on (Mg_{0.7}M_{0.3})Ni₂ alloys except M = Ce. The maximum hydrogen contents of these alloys are 1.2–1.6 mass% (H/M:0.6–0.8) under a hydrogen pressure of 5 MPa at 243–273 K. In the case of the M = Pr and Nd alloys, two step plateaus were clearly observed.
- (5) (Mg_{0.7}M_{0.3})Ni₂ alloys kept C15-type or C15_b-type crystalline structures without hydrogen-induced amorphization, disproportionation and decomposition after a few hydrogenation/dehydrogenation cycles.

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