Protium Absorption/Desorption Characteristics of $\text{Mg}_2\text{Ni}/\text{LaNi}_5$ Composite ^{*1}

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In this study, an attempt is made to form composites by mechanical alloying (MA) or pulse-electric-current-sintering (PECS) for utilization of synergy effect to acquire both high capacity and ability to absorb/desorb protium at low temperatures. The composites have well-bonded structure consisting of Mg_2Ni alloy that has high hydrogenation capacity and LaNi_5 alloy that is capable of protium absorption/desorption at relatively low temperatures. During the absorption process, the protium content of MA + PECS and MA specimens at 80°C is over the theoretical value corresponding to the ratio of LaNi_5 phase. After absorption of the maximum protium content at 40°C by MA + PECS specimen, the desorption process was evaluated by TG/DTA analysis and the specimen starts desorbing protium at about 100°C. Consequently, the result suggests the occurrence of synergy effect during the absorption/desorption process of the obtained composites.

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1. Introduction

Presently, negative changes in the earth's environment and the depletion of fossil fuel are advancing due to human economic activities. Therefore, attention is being paid to hydrogen energy for breaking away from the dependence on fossil fuel and for protection from the global warming effect that results from the utilization of fossil fuel. However, hydrogen is very dangerous to handle because it exists in gaseous state at room temperature and atmospheric pressure, and its ignitability is high. Thus, we need the safest methods for utilizing hydrogen energy effectively. Therefore, hydrogen absorbing alloys that can store hydrogen compactly are attracting a lot of attention, and moreover, they are safer than liquefied hydrogen gas. Presently, researches for the development of various applications of hydrogen are being carried out. Among such applications, the research and development of new generation vehicles that utilize hydrogen energy is extremely fierce, and fuel cell electric vehicles that utilize various methods of supplying hydrogen are being developed simultaneously. The sources of hydrogen considered include: methanol modification, gasoline modification, high pressure cylinder of 25 MPa, hydrogen absorbing alloys and so on. Generally, it is said that the use of hydrogen absorbing alloys as fuel tank is the safest method of supplying hydrogen. However, in spite of the safety, Mm-Ni-Co-Al-Mn hydrogen absorbing alloys¹⁾ could not be satisfactorily utilized because of little hydrogen content and the mileage is too small compared to gasoline car. Therefore, attention is being paid to Mg_2Ni alloy among hydrogen absorbing alloys that are most suitable for transport applications because its theoretical protium storage capacity per unit weight is more than twice that of other alloys. Moreover it is cheaper than other hydrogen absorbing alloys. However, it has problems of high protium absorption/desorption

temperature and slow reaction kinetics. Therefore, numerous studies are being carried out on the use of nanocrystalline and amorphous phases obtained by mechanical alloying²⁻⁴⁾ for the purpose of lowering the protium absorption and desorption temperature. Furthermore, development of new protium absorbing Magnesium system alloys is also being vigorously pursued.^{5,6)}

It has been confirmed that in an alloy whose microstructure consists of intermingled fine Mg and Mg_2Ni phases, protium absorption/desorption characteristics at low temperatures are improved by synergy effect.^{7,8)} This phenomenon occurs when the phase capable of protium absorption/desorption at low temperatures undergoes expansion/contraction during the reaction with protium and this expansion/contraction applies strain to the other neighbouring phase that can only absorb/desorb protium at high temperatures, thereby facilitating the reaction of the latter at low temperatures. The same result was also obtained by Zaluska *et al.*⁹⁾ Furthermore, Orimo *et al.*²⁾ reported that synergy effect occurred in ball-milled Mg-Ni alloys during hydrogen desorbing process for the nano-amorphous region. Similarly, Nagai *et al.*¹⁰⁾ reported that in Mg- x mass% LaNi_5 ($x = 10-60$) sintered composite, LaNi_5 addition significantly lowered the temperature at which the hydrogen absorption of magnesium was initiated during the initial hydrogenation process, and the subsequent hydriding rate was also accelerated by the addition of up to 30% LaNi_5 , beyond which the hydriding rate decreased steeply. Liang *et al.*¹¹⁾ reported that mechanically milled Mg-50 mass% LaNi_5 composite consists of Mg, Mg_2Ni and LaNi_5 phases, and the composite has excellent hydrogen absorption kinetics while the amount of protium absorption is 4.1 mass% at 250 to 300°C. These results show that hydrogen absorption kinetics become fast, but hydrogen absorbing/desorbing temperature could not be lowered. Thus the characteristic advantage of each phase could not be utilized because the microstructure of the composite shows that other phases crystallize, too.

Therefore in this study, an attempt is made to use mechanical alloying (MA) or pulse-electric-current-sintering (PECS) methods to synthesize composites that have well-bonded

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structure consisting of Mg₂Ni alloy that has comparatively high hydrogenation capacity and LaNi₅ alloy that is capable of protium absorption/desorption at low temperatures in order to acquire both high capacity and ability to absorb/desorb protium at low temperatures. Mg₂Ni–50 mass%LaNi₅ mixed powder was used to prepare the specimens. At first, conditions that made it possible to obtain specimens in which the two phases are well-bonded were determined. Then, the microstructures of the obtained specimens were analyzed, and their protium absorption/desorption characteristics were also evaluated.

2. Experimental Procedure

Mg₂Ni alloy was prepared by melting Mg of 99.98% purity and Ni of 99.99% purity in high frequency induction furnace in argon atmosphere, while commercial LaNi₅ alloy was used. Table 1 shows the chemical composition of Mg₂Ni alloy. The as-cast specimens were degassed in vacuum condition for 4 h and then crushed in a glovebox in argon atmosphere into particles with sizes of less than 75 μm and 355 μm for PECS and MA, respectively, and then, both specimens were mixed using mass ratio of Mg₂Ni to LaNi₅ of 1:1. During MA, both the samples and stainless steel balls were placed in a pot mill, and using a conventional horizontal mill at a rotating speed of 105 min^{-1} (roll surface speed is 31.0 m/s), the specimens were mechanically alloyed from 1 h through 16 h at ambient temperature. The mass ratio of stainless steel balls to the specimen was 100:1. The raw materials used for PECS were mixed in a mortar and the weight of the mixture was about 11.1 g. The sintering occurs while applying an even pressure of 30 MPa after filling into a die of 20 mm diameter made of graphite. The PECS was carried out by changing the heating rate, holding temperature and time in argon atmosphere of 0.14 MPa. The condition of pulse current was turning on

the electricity for 39.6 ms and turning it off for 6.6 ms. At first, PECS conditions that made it possible to obtain specimens in which the Mg₂Ni and LaNi₅ phases are well-bonded and preserved were determined. Consequently, PECS specimens were prepared under the following conditions: heating rate of 0.86°C/s; holding temperature of 620°C and holding time of 0 s. For MA + PECS specimens, the heating rate of 0.83°C/s, holding temperature of 550°C and holding time of 0 s were utilized after mechanical alloying for 16 h.

The microstructures of the obtained composite samples were observed using both optical and scanning electron microscopes. They were also analyzed using X-ray diffractometer and EPMA analysis. The protium absorption/desorption characteristics were evaluated using as-mechanically alloyed specimens, in the case of MA specimen, while PECS, mixed powder and MA + PECS specimens were first crushed into particles with sizes of less than 75 μm . Hydriding properties were evaluated using Siverts' method by measuring the change in protium pressure during heating from room temperature to 300°C at a constant rate of 0.5°C/min and an initial protium pressure of 0.88–0.90 MPa (Hydrogen purity: 7 N). The protium desorbing characteristics was evaluated by measuring the change in quantity of protium desorbed during heating from 30 to 400°C at a constant rate of 0.5°C/min in Ar atmosphere (6 N) using TG/DTA. Specimens whose surfaces were activated by absorption and desorption cycles were used for the evaluation of the desorption characteristics. The absorption process during activation was carried out at 250°C and 40°C under protium pressure of about 0.2 MPa and 0.7 MPa, respectively, for 3 h and the activation was determined to be finished when there was no further change in the absorption curve.

3. Results and Discussion

3.1 Microstructure

Figure 1 shows changes in (a) X-ray diffraction patterns and (b) scanning electron micrographs of Mg₂Ni–50 mass%LaNi₅ composite with mechanical alloying time. Diffraction peaks from Mg₂Ni phase decrease in intensity and broaden with mechanical alloying time. However, LaNi₅

Table 1 Chemical composition of Mg₂Ni alloy (mass%).

Alloy	Ni	Mg
Mg ₂ Ni	54.8	bal.

Fig. 1 Changes in (a) X-ray diffraction patterns and (b) scanning electron micrographs of Mg₂Ni–50 mass%LaNi₅ composites with mechanical alloying time.

Fig. 2 X-ray diffraction patterns and microstructures of (a) mixed powder, (b) MA, (c) PECS and (d) MA + PECS specimens of Mg_2Ni -50 mass% LaNi_5 composite.

phase peaks are observed clearly after mechanically-alloyed for 16 h. Therefore, Mg_2Ni phase becomes nano-crystalline with mechanical alloying time. The grain size is below $5\text{ }\mu\text{m}$ after mechanical alloying for 16 h as shown in Fig. 1(b).

Figure 2 shows X-ray diffraction patterns and microstructures of (a) mixed powder, (b) MA, (c) PECS and (d) MA + PECS specimens of Mg_2Ni -50 mass% LaNi_5 composite, while Fig. 3 shows the result of quantitative analyses of (a) PECS and (b) MA + PECS specimens of Mg_2Ni -50 mass% LaNi_5 composite. The microstructure of the mixed powder specimen consists of α (Mg), Mg_2Ni , MgNi_2 and LaNi_5 phases as observed from X-ray diffraction analysis as shown in the Fig. 2(a). In the MA specimen, which was mechanically-alloyed for 16 h, both Mg_2Ni and LaNi_5 phases decrease in intensity and the diffraction peaks of Mg_2Ni become broad as shown in the Fig. 1. As shown in Fig. 2(b), fine particles of Mg_2Ni phase are obtained, and LaNi_5 phase of 1 to $8\text{ }\mu\text{m}$ uneven particle sizes are embedded in Mg_2Ni particles by mechanical alloying for 16 h. However, there is no X-ray diffraction peak from an intermediate phase. The microstructure of the PECS specimen consists of Mg_2Ni , LaNi_5 and LaMg_2Ni_6 ¹²⁾ phases as observed from X-ray diffraction analysis as shown in Fig. 2(c). From the result of quantitative analysis shown in Fig. 3(a), the PECS specimen consists of an unknown phase having Mg:Ni ratio of 4:6. LaMg_2Ni_6 phase is formed along the phase boundaries of Mg_2Ni and LaNi_5 phases as an intermediate phase as observed from the SEM image and its schematic illustration. This means that Mg_2Ni and LaNi_5 phases are well bonded. Also, in the microstructure of the MA + PECS specimen shown in Fig. 2(d) and Fig. 3(b), the same phases observed in PECS specimen are observed, too. Furthermore, though there are unknown peaks in the X-ray diffraction pattern, the phase may be the unknown phase having Mg:Ni ratio of 4:6 obtained by EPMA. In the specimen mechanically-alloyed for 16 h, the particles of LaNi_5 phase is smaller than those in the PECS specimen,

which are embedded in Mg_2Ni particles.

3.2 Protium absorbing characteristics

Figure 4 shows the changes in protium content absorbed by different specimens of Mg_2Ni -50 mass% LaNi_5 composite during heating under a rate of $0.5^\circ\text{C}/\text{min}$ and an initial hydrogen pressure of 0.88–0.90 MPa, (a) before and (b) after activation of the specimens surface. The result obtained for as-cast specimen of Mg_2Ni is also shown in the figure. The LaNi_5 phase of the composite is expected to absorb protium of 0.7 mass%, which is half of the theoretical absorption content of LaNi_5 single phase. Similarly, the protium content of the Mg_2Ni phase of that composite should be 1.8 mass%, which is half of the theoretical absorption content of Mg_2Ni single phase. Therefore, the maximum theoretical absorption content of Mg_2Ni -50 mass% LaNi_5 composite is 2.5 mass%. Consequently, due to the circumstances mentioned above, the composite material is expected to be able to absorb protium over the theoretical value for LaNi_5 phase around room temperature due to the occurrence of synergy effect. Before activation process is carried out, as-cast specimen of Mg_2Ni can absorb protium from about 80°C . However, all of the specimens of the composite starts absorbing protium at about 40°C , but subsequently absorb protium slowly. This is because LaNi_5 phase can absorb protium under the condition of 0.9 MPa at room temperature. The MA and MA + PECS specimens absorb protium of about 1.2 mass% and 0.9 mass% at around 80°C , respectively, which is over the theoretical value for LaNi_5 phase. When LaNi_5 phase expands by protium absorption, strain is induced into Mg_2Ni phase if it is intermingled with the LaNi_5 phase, thereby accelerating protium absorption by Mg_2Ni phase even at 50°C , indicating the occurrence of synergy effect. Vucht *et al.*¹³⁾ reported that the volume expansion associated with protium absorption by LaNi_5 phase is about 25% based on X-ray diffraction analysis. Therefore, such a high volume expansion must have gen-

(a) heating rate: $0.86^\circ\text{C}/\text{min}$, temperature: 620°C (b) heating rate: $0.83^\circ\text{C}/\text{min}$, temperature: 550°C

Chemical composition of each parts (mol%)

	Mg	Ni	La
A	69.0	30.6	0.4
B	0.1	82.6	17.3
C	43.1	56.8	0.1
D	9.5	73.5	17.0
E	69.0	30.9	0.1
F	0.2	84.1	15.7
G	43.9	56.0	0.1
H	25.7	62.5	11.8

A,E Mg_2Ni **B,F** LaNi_5 **C,G** $\text{Mg:Ni}=4:6$ **D,H** LaMg_2Ni_6 Fig. 3 Result of quantitative analyses of (a) PECS and (b) MA + PECS specimens of Mg_2Ni -50 mass% LaNi_5 composites. Fig. 4 Changes in protium content absorbed by different specimens of Mg_2Ni -50 mass% LaNi_5 composite during heating under a rate of $0.5^\circ\text{C}/\text{min}$ and initial hydrogen pressure of 0.88–0.90 MPa (a) before and (b) after activation of the specimens surface.

erated enough strain to cause the neighboring Mg_2Ni phase to react with protium. It is thought that the difference in starting absorption temperature may be due to the different ratio of oxidized surface of each specimen. The surface area of MA specimen is larger than other specimens, because the grain size of the MA specimen is below $5\mu\text{m}$, while the grain size of the PECS and MA + PECS specimens varies up to $75\mu\text{m}$. Moreover, the MA specimen has very reactive surface, so the specimen is oxidized easily even with only a small amount of oxygen in the Ar gas. Therefore, the difference in starting ab-

sorption temperature may vanish after activation. The heating rate of $0.5^\circ\text{C}/\text{min}$ that was used during the test is faster than the equilibrium condition, because during heating test maximum protium content is not reached at the respective temperatures. Therefore, the test condition is an additional kinetics factor. The protium content of MA specimen is 1.7 mass% at 300°C and this is more than that of the other specimens because in MA specimen, grain size is smaller than that of the other specimens, and therefore protium diffusion path is short and the specimen surface area is large.

After carrying out activation process, the as-cast specimen of Mg_2Ni absorbs 0.2 mass% protium at around room temperature to form $\text{Mg}_2\text{NiH}_{0.3}$ phase or protium combines with Magnesium to form Magnesium hydride. However, Mg_2Ni phase absorbs protium quickly from temperatures higher than 150°C .¹⁴⁾ All of the specimens start to absorb protium at nearly the same temperature, because during the activation process, the specimens become fine and then the surface area of the specimens is increased with a lot of new active surface area. The starting protium absorption temperature of MA specimen is remarkably low. This may be because the oxygen component of the atmosphere absorbed by the specimen surface is removed by the activation process. In the mixed powder and PECS specimens of the composite, initially, protium is absorbed at about 30°C and desorbed at about 70°C , and then another absorption occurs at about 150°C . The absorption and desorption that occurs at about 30°C and 70°C , respectively, correspond to the absorption/desorption of LaNi_5 phase while the absorption that occurs at about 150°C corresponds to the absorption of Mg_2Ni phase. Therefore, it appears that the bonded particles dissociate at the boundaries due to the repetitive process of expansion/contraction that occurs during the absorption/desorption cycle of the activation process because the constituent particles are coarse. On the other hand, MA and MA + PECS specimens indicate an absorption curve similar to that obtained before activation pro-

Fig. 5 X-ray diffraction patterns and microstructures of cross section of Mg_2Ni -50 mass% LaNi_5 composite of (a) MA and (b) MA + PECS specimens after absorbing protium at 250°C and 40°C, respectively.

cess. In the MA and MA+PECS specimens, the desorption of protium from LaNi_5H_6 phase is not observed at 70°C, instead the protium content gradually increases with rising temperature. This means that Mg_2Ni phase starts absorbing protium at about 70°C. This result suggests the occurrence of synergy effect because the joined parts are retained.

Figure 5 shows X-ray diffraction patterns and microstructures of cross sections of Mg_2Ni -50 mass% LaNi_5 composite of (a) MA and (b) MA+PECS specimens after absorbing protium at 250°C and 40°C, respectively. In (a), the MA specimen that absorbed protium at 250°C under hydrogen pressure of 0.9 MPa, Mg_2NiH_4 and LaNi_5 phases are observed from X-ray diffraction peaks; but LaNi_5H_6 is not observed. Mg_2Ni phase can absorb protium at 250°C, while LaNi_5 phase could not absorb protium probably due to no occurrence of synergy effect from Mg_2NiH_4 to LaNi_5 phase. In (b), MA + PECS specimen that absorbed protium at 40°C, LaNi_5 and Mg_2Ni phases together with their corresponding hydrides are observed from the X-ray diffraction pattern. The existence of Mg_2NiH_4 at 40°C indicates the occurrence of synergy effect from LaNi_5H_6 to Mg_2Ni . On the other hand, existence of LaNi_5 phase means that LaNi_5H_6 phase desorb protium or the LaNi_5 phase could not absorb protium due to the presence of neighboring Mg_2Ni phase at 40°C. Moreover, only a small amount of protium of about 0.05 mass% is desorbed at 40°C under hydrogen pressure of 0.11 MPa.

3.3 Protium desorbing characteristics

Figure 6 shows the mass changes in hydride specimens of Mg_2Ni -50 mass% LaNi_5 composite during heating under a rate of 0.5°C/min with Ar flow by TG/DTA after protium absorption up to the maximum protium content at 40°C for MA + PECS specimen and at 250°C for the other specimens. The result obtained for as-cast specimen of Mg_2Ni is also shown in the figure. The amount of change of ther-

Fig. 6 Mass changes in hydride specimens of Mg_2Ni -50 mass% LaNi_5 composite during heating under a rate of 0.5°C/min with Ar flow by TG/DTA after protium absorption up to the maximum protium content at 40°C for MA + PECS specimen and at 250°C for the other specimens.

mogravimetry represents the amount of protium desorption. The as-cast specimen of Mg_2Ni alloy starts desorbing protium from Mg_2NiH_4 phase at about 180°C, and the reaction finishes at about 230°C. And subsequently, magnesium solid-solution desorbs protium at about 320°C.¹⁴⁾ However, the MA + PECS specimen starts desorbing protium at about 100°C, and the reaction finishes at about 210°C. The amount of desorption is about 0.73 mass% which is equivalent to 64% of absorbed protium content. If it is assumed that LaNi_5H_6 phase at the grain surface has already desorbed protium during holding at room temperature for about 100 h in argon atmosphere because LaNi_5H_6 phase can desorb protium even at room temperature, and since the amount of desorption is over the theoretical absorption content of LaNi_5 phase in the composite, then it is possible that protium is desorbed from Mg_2NiH_4 phase. Therefore, the desorption of protium at such a low temperature of 100°C by the Mg_2NiH_4 phase suggests the occurrence of synergy effect from LaNi_5 to Mg_2NiH_4 during the desorption process. In other words, in the case where LaNi_5 hydride is located around Mg_2Ni hydride, synergy effect occurs when LaNi_5H_6 phase contracts due to protium desorption and contraction strain is exerted on the surrounding Mg_2NiH_4 phase. Furthermore, Higuchi *et al.*¹⁵⁾ reported that in nano-composite three-layered Mg/Pd/Mg film prepared by RF-associated magnetron sputtering method, hydrogen in the palladium film becomes unstable and easily desorbs from both surfaces of the palladium films. This induces compression stress on both the top and bottom surfaces of the magnesium film and the hydrogen in the magnesium film becomes unstable, leading to low temperature dehydrogenation. This phenomenon is the so-called 'cooperative phenomenon that hydrogen exhibits in nano-composite systems by elastic interactions'.^{2,16)} Other specimens start desorbing protium like as-cast Mg_2Ni alloy.¹⁴⁾ Since protium absorption at 250°C is done by only Mg_2Ni phase as shown in Fig. 5, synergy effect does not occur from Mg_2NiH_4 to LaNi_5 phase.

4. Conclusions

(1) In PECS and MA + PECS specimens, LaMg_2Ni_6 phase is formed as an intermediate phase along the phase boundaries of Mg_2Ni and LaNi_5 phases, and as a result the phase boundaries are well-bonded by pulse-electric-current-

sintering. But, in mechanically-alloyed specimen, no intermediate phase appears as observed by the result of X-ray diffraction analyses.

(2) It is confirmed that synergy effect occurs in MA + PECS and MA specimens before and after activation process. This indicates that the well-bonded interface between Mg₂Ni and LaNi₅ phases remain intact even after activation.

(3) MA + PECS specimen of Mg₂Ni–50 mass%LaNi₅ composite absorbs protium of 1.09 mass% at 40°C. Moreover, it starts desorbing protium from Mg₂NiH₄ phase at about 100°C.

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