Hydrogenation of MgNi₂ by Atomic Hydrogen at Elevated Temperatures

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Hydrogenation of MgNi₂ by atomic hydrogen was examined at elevated temperatures. Mg₂Ni powder was compacted into a disk and heated in vacuum at 773 K for outgassing. During this heat treatment, Mg₂Ni was transformed into MgNi₂ by evaporation of Mg. This specimen was hydrogenated at 573, 673 and 773 K by hydrogen gas of 30 Pa and atoms produced by rf-discharge. No significant hydrogenation took place by hydrogen gas. On the other hand, the specimen was hydrogenated by the exposure to atoms at 773 K up to [H]/[M] = 0.14 within 25 ks. New peaks appeared in the diffraction pattern of Cu K α X-rays at $2\theta = 34.0, 42.0, 48.9$ and 86.6° . This observation indicated that the hydride formed was in a cubic structure.

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1. Introduction

Hydrogen is promising energy carrier for sustainable energy systems. Storage of hydrogen in intermetallic compounds is favorable from the viewpoint of safety, and hence extensive studies have been carried out to improve hydrogen absorption capacity of intermetallic compounds.¹⁾ Hydrogenation by hydrogen at high chemical potential is one of the ways to synthesize high capacity hydrides. Recently, a technique for hydrogenation at high pressures (GPa) and high temperatures (up to 1473 K) has been developed,²⁾ and novel hydrides have been synthesized by using this kind of techniques.³⁻⁹⁾

Hydrogen at high chemical potential is also available by atomization and ionization. Hydrogenation by atoms and ions is non-equilibrium process, and hence this kind of techniques is inappropriate to determine thermodynamic characteristics of hydrides. Nevertheless, the use of atoms and ions provides high flexibility in designing hydrogenation apparatus in comparison with high pressure devices. It is also possible to understand the effect of compressive stress on hydride formation by comparing hydrogenation behaviors under high pressure with those by exposure to atoms and ions.

It has been reported that Ni hydride, which is formed in H₂ at high pressure,¹⁰⁾ was synthesized by use of atoms and ions at/below room temperature.^{11,12)} Hydrogenation at elevated temperatures, however, has been scarcely studied. From the viewpoint of synthesis of novel hydrides, hydrogenation at elevated temperatures where metal atoms are mobile is more interesting, because reconstruction of crystal structure occurs easily in comparison with hydrogenation at low temperatures. The release of hydrogen as molecules through surface recombination is thermally activated at elevated temperatures, whereas surface impurities such as oxygen significantly retard the surface recombination. Hence, the surface chemical state is the key factor in hydrogenation by atoms and ions for the accumulation of hydrogen in intermetallic compounds up to high concentration.

Magnesium-based alloys such as Mg₂Ni have large hydrogen absorption capacities, but the dissociation pressures of hydrides are generally too low at moderate temperatures

from the viewpoints of practical applications. The dissociation pressures of hydrides in Ni rich compositions are considered to be higher than those of Mg rich hydrides. Hence, it is important to explore Ni rich hydrides in Mg–Ni–H systems.

In the present study, the hydrogenation of MgNi₂ and the mixture of MgNi₂ and Ni by atomic hydrogen was examined at elevated temperatures. Sintered powders of MgNi₂ and the mixture of MgNi₂ and Ni were hydrogenated at 573, 673 and 773 K by atomic hydrogen produced by rf-discharge, and changes in crystal structure were examined by using X-ray diffraction (XRD).

2. Experimental

2.1 Apparatus

Figure 1 shows a schematic description of hydrogenation apparatus used in the present study. This apparatus is evacuated by a turbo-molecular pump (TMP) and an oil-sealed rotary pump (RP). The pressure and composition of residual gas are measured with an ionization gauge (IG) and a quadrupole mass spectrometer (QMS), respectively. Hydrogen gas is introduced from a cylinder through a variable leak valve. The pressure of hydrogen is measured by a capacitance manometer (CM). A specimen disk is held in a groove carved on the edge of a quartz tube and installed in a hydrogenation chamber made of quartz glass. A copper coil is attached to the

Fig. 1 Schematic description of hydrogenation apparatus.

outside of the hydrogenation chamber to apply rf-power. The specimen can be heated up to 1273 K by an electric furnace from the outside of the chamber. Temperature is measured with a thermocouple attached to the outside of the chamber.

2.2 Procedure

Two types of specimen disks (10 mm in diameter, 0.3 mm in thickness) were prepared by compacting powder of Mg_2Ni (> 200 mesh, 0.06 g) or mixture of powders of Mg_2Ni and Ni ($> 7\ \mu\text{m}$, 99.6%) at 590 MPa under vacuum. The former is hereafter denoted as specimen A and the latter as specimen B. In the latter case, the mole fractions of Mg_2Ni and Ni were adjusted to 0.25 and 0.75, respectively.

After installation of the specimen, the hydrogenation apparatus shown in Fig. 1 was evacuated to a pressure below 3×10^{-6} Pa. The major composition of residual gas was water vapor. The specimen disk was heated in vacuum at 773 K for 1.8 ks for outgassing and cooled to room temperature. Then the hydrogenation chamber was isolated from the pumping system by closing a valve V1, and hydrogen gas was introduced to 30 Pa. The specimen was heated to 573, 673 and 773 K in hydrogen gas. After cooling down to room temperature, the specimen was heated again under rf-discharge to the same temperatures. The rf-power was adjusted to 40 W. No bias voltage was applied between the specimen and the plasma produced by discharge. Hydrogen absorption was examined by measuring the change in pressure; the amount of hydrogen absorbed was estimated from the chamber volume and the extent of pressure change. Hydrogen pressure was restored to 30 Pa by admitting hydrogen gas when it became lower than 10 Pa.

The characteristics of plasma were not examined in the present study. Generally, however, ionization rates are significantly smaller than atomization rates in rf-plasmas. For example, the atomization and ionization rates were 0.22 and 2.4×10^{-6} , respectively, in the similar apparatus constructed by the present authors.¹³⁾ The amount of incident ions is negligibly small without bias voltage at this order of ionization rate. Therefore, hydrogenation is dominantly caused by atomic hydrogen under the present experimental conditions.

The crystal structure of the specimen was analyzed by means of XRD after compacting, outgassing and hydrogenating. The analysis was carried out also for the specimen kept in a desiccator at room temperature for 90 days after hydrogenation. The specimen was placed on a holder made of Al and analyzed in 2θ geometry in a range from 3 to 90° with Cu $K\alpha$ radiation. The incident angle of X-rays was adjusted to 1.5° to analyze a shallow region from the surface. The specimen hydrogenated by atoms was observed with a scanning electron microscope (SEM).

3. Results and Discussion

Figure 2 shows XRD patterns of specimen A before and after outgassing at 773 K. Before outgassing, almost all peaks were assigned to Mg_2Ni . After outgassing, the intensity of Mg_2Ni peaks drastically decreased, and MgNi_2 became dominant phase. Such phase transformation was ascribed to the selective evaporation of Mg. The mole fractions of Mg_2Ni and MgNi_2 after outgassing was determined to be 0.75 and 0.25,

Fig. 2 XRD pattern before (a) and after (b) outgassing.

Fig. 3 XRD pattern after hydrogenation by atoms.

respectively, from the change in mass by assuming that the mass change was caused only by evaporation of Mg. These observations indicate that Mg_2Ni remained inside the disk.

No significant hydrogen absorption was observed by heating the specimen in hydrogen gas up to 773 K at 30 Pa. Hydrogenation did not take place by atoms at 573 and 673 K, either. At 773 K, however, hydrogen atoms were absorbed up to $[\text{H}]/[\text{M}] = 0.14$ within 25 ks. The X-ray diffraction pattern after hydrogenation at 773 K is shown in Fig. 3. New peaks appeared at $2\theta = 34.0, 42.0, 48.9$ and 86.6° . This observation indicates that a hydride was formed by exposure to atomic hydrogen, though no significant hydrogen absorption was observed by molecular hydrogen under the present conditions. Hence, it is concluded that hydrogenation by atoms is effective method to synthesize hydrides at elevated temperatures.

Figure 4 shows XRD pattern of the hydride obtained by

Fig. 4 XRD pattern of hydride obtained by subtracting diffraction pattern shown in Fig. 2(b) from that in Fig. 3. ▼ indicates newly appeared hydride peak in Fig. 3 and ▽ shows the peak whose intensity increased significantly by hydrogenation.

Table 1 Characteristics of hydride peaks.

Peak no.	2θ	$\sin^2 \theta$	Ratio of $\sin^2 \theta$
1	23.9	0.0429	1
2	34.0	0.0855	2
3	42.0	0.128	3
4	48.9	0.171	4
5	71.7	0.343	8
6	86.6	0.470	11

subtracting the diffraction pattern before hydrogenation (Fig. 2(b)) from that after hydrogenation (Fig. 3). In addition to the four peaks newly observed in Fig. 3, two additional peaks appeared at 23.9 and 71.7°. Namely, the intensity of these peaks significantly increased by hydrogenation. Hence, these peaks were assigned to the hydride formed by exposure to atoms. The characteristics of the hydride peaks in this figure are summarized in Table 1. The ratios among the $\sin^2 \theta$ values gave figures very close to the integers in the right column of this table. This observation indicates that all peaks originate in the same hydride phase, and this hydride is in a cubic structure. These peaks appear to be the reflections from (100), (110), (111), (200), (220) and (311) planes of cubic cell whose lattice constant is 0.3725 nm.

It is difficult at the present to determine the hydrogen content in this hydride phase, because only average concentration in the specimen can be estimated from the pressure change. A large amount of MgNi₂ remained after hydrogenation as shown in Fig. 3. In addition, Mg₂Ni remained inside the disk as mentioned above. Although atomic hydrogen cannot directly reach the inside of the disk, Mg₂Ni can contribute to hydrogen absorption. This is because sintering of powder particles occurs at 773 K as reported in the previous paper.¹⁴⁾ A scanning electron micrograph of specimen A after hydrogenation is shown in Fig. 5. The powder particles were interconnected to each other, and such interconnection should allow hydrogen to diffuse through interface between the powder particles. Hence, the measurements of hydrogen content in MgNi₂ and Mg₂Ni phases are necessary to determine the hydrogen content in the hydride phase.

Fig. 5 Scanning electron micrograph of specimen A after hydrogenation by atoms.

It is, however, clear that the hydride detected in XRD analysis was formed from MgNi₂ phase and not from other phases such as Mg₂Ni remaining inside the specimen disks. This is because the amounts of other phases were negligibly small in the region analyzed by XRD as shown in Fig. 2(b). The hydride in the cubic structure whose lattice constant is 0.3725 nm has not been reported in Mg–Ni–H systems. Among known hydrides possible in the present system, only Ni hydride, NiH_x, has a cubic structure and comparable lattice constant. Irodova *et al.*¹⁵⁾ have reported that the crystal structure of NiH_x is NaCl type in which hydrogen atoms occupy octahedral sites of the fcc lattice of Ni. According to Baranowski *et al.*¹⁶⁾ who have examined relations between volume expansion and hydrogen content for various fcc metals, NiH_x takes the lattice constant comparable to that of the present hydride at $x = [\text{H}]/[\text{Ni}] = 0.7$. On the other hand, Chen *et al.*⁶⁾ reported that amorphous MgNi_{1.02}H_{2.2} was synthesized from MgH₂ and Ni at 6 GPa and 873 K, and a broad peak was observed at around 42° in XRD pattern. It appears to be difficult to detect the diffraction peak from this amorphous phase in the case where this phase coexists with NiH_x and MgNi₂. This is because the intensity of diffraction peak from amorphous phase should be significantly smaller than that of crystalline phase, and the peak from this amorphous phase should overlap with those from MgNi₂ and NiH_x. Hence, it is plausible that NiH_x and amorphous MgNiH_x were formed in the present study by hydrogen-induced disproportionation of MgNi₂ and only the former was detected by XRD.

The diffraction peaks from (100) and (110) planes are, however, normally not present in XRD patterns of fcc structures and observed only under particular conditions. Fukai and Okuma^{2,17)} have reported that a large amount of vacancies were formed in Ni and Pd by hydrogenation at high pressure (5 GPa), and the peaks from (100) and (110) planes of Pd were observed when Cu₃Au type (L1₂) structure was formed by ordering of vacancies. Therefore, the evidence of copious vacancy formation is necessary to draw a conclusion that the present hydride is NiH_x. Further investigation is necessary to identify the present hydride by taking account of the possibility of formation of a novel hydride phase.

Figure 6 shows the X-ray diffraction pattern of specimen

Fig. 6 XRD pattern of specimen A kept at room temperature for 90 days after hydrogenation by atoms.

Fig. 7 XRD pattern of specimen B after hydrogenation by atoms.

A kept at room temperature for 90 days after hydrogenation. A new peak was observed at 59.5° . The origin of this peak, however, has not been clarified. On the other hand, no significant difference was observed in the peak intensity ratio of the hydride to MgNi_2 in comparison with Fig. 3. This observation indicates that the decomposition rate of the formed hydride is very small at room temperature.

The diffraction pattern of specimen B after hydrogenation by atoms is shown in Fig. 7. The peaks of hydride appeared at the same positions as Fig. 3. It should be noted that the peak intensity ratio of hydride to MgNi_2 in Fig. 7 is comparable to that in Fig. 3. In addition, the mole ratio of absorbed hydrogen to MgNi_2 in specimen B was close to that in specimen A. No significant change was observed in the positions of Ni peaks. Hence, it is concluded that the hydride was formed only from MgNi_2 phase; Ni did not react with neither of MgNi_2 and atomic hydrogen during hydrogenation. This difference in hydrogenation behavior was ascribed to the difference in surface properties between MgNi_2 and Ni. According to the theoretical models for the interaction between metals and atomic hydrogen,^{18–20} the concentration of hydrogen in the specimen particles is determined by balance between the flux of penetrating hydrogen atoms and recombination release of hydrogen molecules. Here the influences of impurities adsorbed on the particle surfaces are quite different between penetrating process and recombination process. Since the internal

energy of hydrogen atoms is higher than that of molecules by 2.24 eV, the penetration flux of atoms is scarcely dependent on the concentration of surface impurities.^{18–20} On the other hand, the recombination release is markedly retarded by surface impurities.^{18–20} Hence, the concentration of hydrogen in the particles increases with that of surface impurities. Since H_2O was the major component of residual gas in the present apparatus as mentioned in Section 2.2, it is plausible that adsorption layer of oxygen is formed on the particle surfaces. The oxygen concentration on the surface of MgNi_2 particles should be higher than that of Ni particles because chemical affinity of Mg to oxygen is much higher than that of Ni. In fact, Ni oxide was reduced to metallic Ni by exposure to atomic hydrogen in different apparatus.¹³ Oxygen on the particle surfaces should have no significant influence on the penetration process of atomic hydrogen but retard the recombination release of hydrogen molecules as mentioned above. Hence, the hydrogen concentration in MgNi_2 particles is considered to be high in comparison with that in Ni particles. This should be the reason that hydride was formed only from MgNi_2 . Namely, Mg at the particle surfaces played key roles in the confinement of hydrogen in the alloy under the present conditions.

4. Conclusions

The sintered powder of MgNi_2 was hydrogenated by hydrogen gas and atoms at 573, 673 and 773 K, and changes in crystal structure were examined by using XRD. Hydrogenation took place only by the exposure to atomic hydrogen at 773 K, and the specimen absorbed hydrogen atoms up to $[\text{H}]/[\text{M}] = 0.14$. New peaks appeared in diffraction pattern at $2\theta = 34.0, 42.0, 48.9$ and 86.6° by hydrogenation. This observation indicated that the hydride formed was in a cubic structure. It was concluded that hydrogenation by atomic hydrogen is effective method to synthesize hydrides at elevated temperatures. The addition of Ni to MgNi_2 had no significant influence on hydrogenation behavior of MgNi_2 .

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