

Development of High-Capacity MgMH Alloy for Hydrogen Storage

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ABSTRACT

A method of mechanical grinding using nanoparticle catalyst was applied to create hydrogen-absorbing magnesium alloy with a chemical composition of Mg-0.33 Ni-0.17 Fe (at%). The use of nanoparticle catalyst made it possible to achieve a 15-minute process time that was one-fortieth or less in comparison with the conventional method with an acceleration of 13.3 G. The synthesized hydrogen storage magnesium alloy possessed a microstructure with catalyst metal distributed uniformly across the powder surface and throughout the matrix. As a result, the alloy yielded significantly improved hydrogen storage capacity, achieving a maximum capacity of 7.49 wt%. This rate of hydrogen absorption places it in the world's top level of hydrogen-absorbing alloys that are currently being reported.

1. Introduction

There are many hydrogen absorbing alloys that function at or below 50 °C, typical examples being LaNi₅ and MmNi₅. Of these, the largest amounts of hydrogen absorption range from 1.0 to 1.4 wt%. A familiar example of the use of hydrogen absorbing alloys is an Ni-MH battery, in which a hydrogen absorbing alloy is used for the negative electrode. Furthermore, the large amount of research that has been conducted in the field of fuel cells for automobiles in recent years has been accompanied by a great deal of research activity in BCC-type alloys (with a maximum absorption amount ranging from 1.8 to 2.4 wt%) composed of V, Ti, etc.⁽¹⁾.

Hydrogen-absorbing magnesium alloy (MgMH) is classified as a high-temperature hydride since it functions at temperatures in excess of 300 °C. A feature of MgMH is that at a hydrogen desorption temperature of 290 °C at 0.1 MPa and the generation enthalpy of MgH₂ is high at 74.5 kJ. But the hydrogen storage capacity is extremely large (theoretical value of pure Mg: 7.6 wt%)⁽¹⁾. However, the initial activation of the pure Mg requires that extreme conditions, such as a temperature of 350 °C and a hydrogen pressure of 5 MPa, be maintained for a week. In addition, the rate of hydrogen absorption/desorption is markedly slow. Because of these obstacles, there are hardly any examples of practical

application of this material⁽¹⁾.

Two conventional methods of producing MgMH with a high absorption amount are mechanical grinding (MG) using ball milling, and mechanical alloying (MA)⁽²⁾⁻⁽⁷⁾. Particles of catalyst metal that were on the order of tens of micrometers when added are distributed throughout the matrix in the form of small grains ranging from tens to hundreds of micrometers in size. Additionally, there are reports of absorption amounts being improved in the case of nanosized grain particles⁽²⁾⁻⁽⁷⁾. However, the MG and MA processes require tens or hundreds of hours, making them impractical. In addition, in order to improve rates of absorption/desorption by switching from micron-sized catalyst to nanoparticle catalyst metal and achieving a microstructure in which the catalyst metal is distributed uniformly, the MG and MA processes require acceleration well in excess of tens of gravity (G). As a result, energy input will be increased as to make this approach impractical. In order to create a practical MH alloy through MG with ball milling or through MA, the time required for production needs to be greatly reduced, and the required acceleration needs to be reduced.

In light of this situation, the purpose of this research was to bring the absorption amount of MgMH alloy as close as possible to the theoretical value, and to produce the alloy by a method that required less time and less linear acceleration than conventional methods.

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2. Aims

As a means of achieving the objectives, attention focused on moving from micron-sized catalyst metal to nanoparticle catalyst metal at the catalyst introduction stage, so the MG process was performed using nanometer-sized catalyst metal particles (“nanosized”) as the introduced material. For the catalyst metal, the decision was made to use a combination of Ni, which has a large catalytic effect on the reaction between Mg and H₂, and Fe, the most inexpensive of the group VIII transition metals, the same group to which Ni belongs. Even with the MgMH alloy, reducing the amount of catalyst metal is directly linked to improving the absorption amount and reducing the cost. However, because reducing the amount of catalyst metal too much will lead to a clear decreasing of the rate of hydrogen absorption/desorption, it is essential that the storage capacity be increased while maintaining a fast rate of absorption/desorption. This research assumed a base composition of Mg-2Ni-1Fe (at%) (maximum amount of absorption: 6.5 wt%, theoretical absorption content = 7.17 wt%), and studied the reduction of the catalyst metal fraction from that base composition.

3. Experimental Procedures

3.1. Production Method

The alloy was synthesized using the MG process, since it permits uniform distribution of the nanosized metal catalyst. Synthesizing MgMH by a conventional MG process requires tens or even hundreds of hours, therefore reduction of the process time is an extremely important issue from an industrial standpoint. Energy consumption can also be reduced by reducing the amount of energy required in the MG process. Therefore, MG range of 1 minute to 10 hrs was studied. Also, an optimization study was conducted, substituting the acceleration of gravity on the pot wall varying from 0.5-23.7 G for the energy input into MG. Fritsch P-5 planetary ball milling apparatus was used for the MG. The MG pot is a gas replacement type with a capacity of 80 cc.

Each metallic element was weighed out at a total mass of 2.5 g in order to produce the target composition in the MG process. After the material was set in the MG pot, a vacuum was created in the pot at room temperature. Then the pot was filled with H₂ at 1 MPa, and the MG process was performed.

3.2. Material Powder

Metal powders of the purity and diameter shown in Table 1 were used. The nanosized catalyst particle powders were checked for O₂ impurities through composition analysis by the inert gas fusion - infrared absorption method. Because Fe more readily oxidizes than Ni, there were more O₂ impurities in the Fe powder. The metal powders that were used had granular diameters of less than 180 μm in the case

of Mg and of approximately 20 nm in the case of Ni and Fe. The Ni and Fe powders were produced by the evaporation method in inert gas, and oxidized slowly in the air in order to prevent combustion.

FeNi alloy nanoparticle catalyst powders were used in order to study reduction of the MG time when using nanoparticle catalysts. The composition of the FeNi nanoparticle catalyst powders were Fe-20Ni (wt%), with a diameter of 20 nm.

3.3. Analysis Method

The composition of the MgMH powder that was synthesized was checked using X-ray diffraction measurement (XRD). Transition Electron Microscope (TEM) was used to observe the microstructure of the MgMH powder, the morphology, location and diameter of the catalyst metal. The powder was also analyzed using a Scanning Electron Microscope (SEM) and an Energy Dispersive X-ray Spectrometer (EDX) in order to check the surface condition of the MgMH particles and distribution of the component elements. Pressure-Composition Isotherms (PCT) measurement equipment was used to evaluate the hydrogen absorption characteristics of the powder. For the PCT measurement, samples weighing from 0.25 g to 0.30 g were tested, with a convergence time of 15 minutes and a convergence judgement time of 5 minutes.

4. Test Results

4.1. Reduction of MG Time

4.1.1. Results of absorption amount measurement

Figure 1 shows the relationship between MG time and the maximum hydrogen absorption amount of Mg-3FeNi alloy that was synthesized with an MG acceleration of 23.7 G. This graph shows that the majority of this alloy's theoretical capacity to absorb hydrogen is achieved after 15 minutes of MG. This is likely to be due to two major factors. The first is that the nanoparticle catalysts used are highly activated as a catalyst from the start. The second is that, Fe and Ni surface oxides are easily reduced and the MG process is performed within hydrogen atmosphere, so that the surfaces of the nanoparticle catalysts become highly activated after a short period of time.

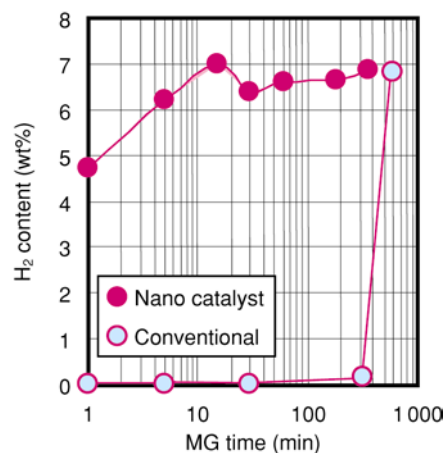


Fig. 1 Relationships between MG time and H₂ contents of Mg-3FeNi alloy

Table 1 Purity and diameter of each material

Material	Mg	Ni	Fe
Purity	3N	O: 6.9wt%	O: 18wt%
Diameter	<180 μm	26nm	20nm

Figure 2 shows the PCT property of the Mg-2Ni-1Fe alloy at 310 °C. Figure 3 shows the PCT property of the MgMH alloy produced by the conventional method, with a 10-hour MG process and a catalyst metal particle diameter of less than 150 μm . The 2:1 ratio of Ni to Fe results from retaining the composition which previous studies have found to be effective in terms of both absorption amount and plateau properties. Even if the MG time shown in Fig. 2 is reduced to 15 minutes (1/40 or less of MG time conventionally required), the hydrogen desorption amount exceeds 6.3 wt%, and has an absorption amount that is roughly equivalent to that of conventional materials.

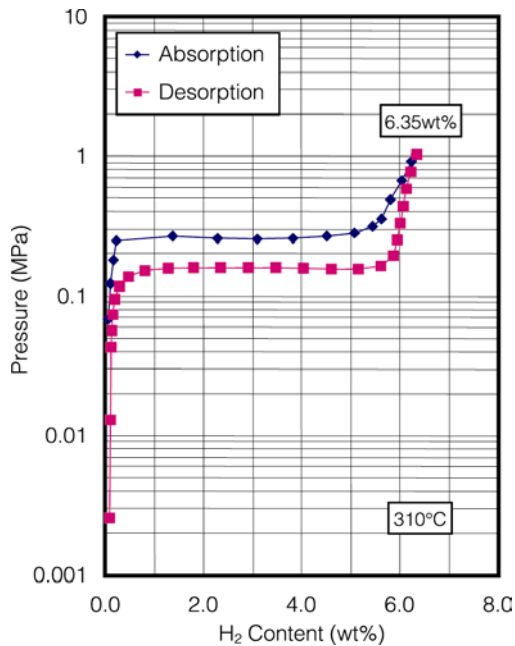


Fig. 2 PCT property of Mg-2Ni-1Fe alloy using nano meter sized catalyst (MG time 15 min)

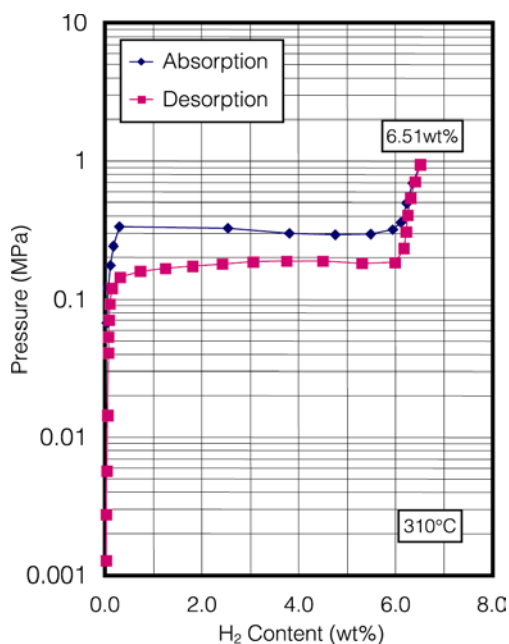


Fig. 3 PCT property of conventional method (10hr, 150 μm cat.)

In addition, the alloys shown in Fig. 2 and Fig. 3 were collected in a controlled glove box with an Ar gas atmosphere. Then, in order to reduce the danger of ignition of the Mg metal powder in air and to improve the safety of the material while handling it in the air, the material was left exposed to the open air for more than 24 hours. After its controlled oxidation, its PCT property was measured. The PCT property confirmed that there was practically no reduction of the hydrogen absorption/ desorption properties even if the material was handled in the open air. This PCT measurement also clearly indicated that, as shown in Fig. 4, it was still possible to obtain approximately the maximum absorption amount even if initial activation was not performed. This demonstrates that the extreme initial activation treatment that was typically performed for conventional alloys is not needed when using nanoparticle catalysts.

Based on the above, using nanoparticle catalysts permitted a reduction of the MG time using planetary ball milling from the conventional 10 hours to 15 minutes (1/40 the previous amount of time). It also became clear that initial activation was no longer necessary, and that once the material had become oxidized there was no reduction in the hydrogen absorption/desorption properties even when the material was handled in the open air.

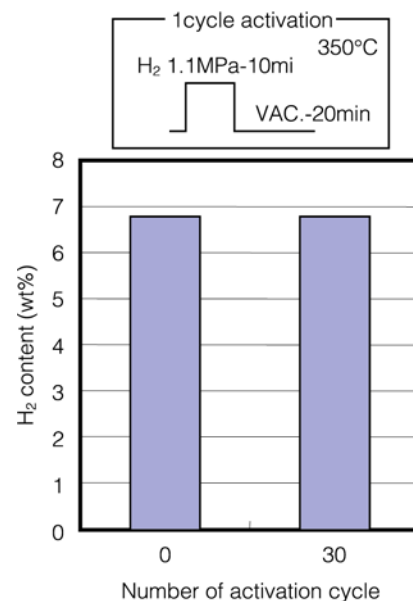


Fig. 4 Relationship of H₂ contents and Number of activation cycle

4.1.2. Results of identification of component phases of the Mg-2Ni-1Fe alloy

An XRD measurement was performed in order to identify the component phase of the MgMH powder that was produced. Figure 5 shows the XRD diffraction pattern of the Mg-2Ni-1Fe (at%) that was collected after MG using nanoparticle catalysts. In the conventional method, MG was performed for at least 6 hours to generate MgH₂, but in this method, using nanoparticle catalysts, MgH₂ was generated after 15 minutes.

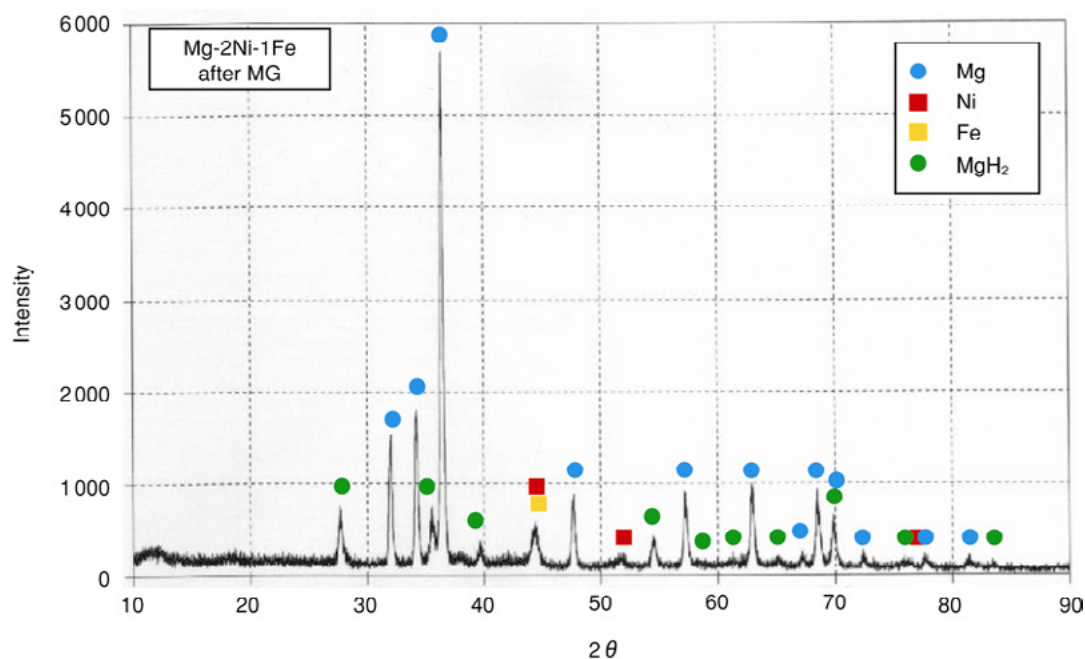


Fig. 5 XRD pattern of Mg-2Ni-1Fe alloy using nano meter sized catalyst (after MG)

As described earlier, the mechanism that renders initial activation unnecessary is likely as follows, based on the results shown in Fig. 5. Because MgH_2 is already synthesized in the MG process, the hydrogen in the alloy is released by heating over 300°C . As a result, the released hydrogen removes the adsorbed gases and part of the oxidation layer on the surface of the MgMH powder. This puts the surface of the MgMH powder in a state equivalent to post-activation treatment state. Because the above phenomenon occurs continuously, initial activation is completed simply by desorbing hydrogen and maintaining the temperature at over 300°C .

4.2 Reduction of MG Acceleration

4.2.1. Absorption amount measurement results

The reduction of MG acceleration reduces the amount of energy that is input into the process, which contributes to lower product cost. In addition, large acceleration requires equipment that is larger and that produces greater output. Therefore, methods for decreasing MG acceleration were studied for the purpose of reducing energy requirements.

The reduction of acceleration was studied by changing the acceleration generated on the inner wall of the pot in the planetary ball milling equipment; this was accomplished by changing the rotational speed of the pot. Applied accelerations in this research were 0.5 G, 13.3 G, 21.8 G, and 23.7 G. The MG time was established as 15 minutes, based on the study results described in section 4.1, “Reduction of MG time.” For the purposes of comparison, an MgMH powder that was synthesized by mixing Mg powder and catalyst metal particles with an agate mortar was also studied. Specifically, the Ni and Fe metal particles (diameter = less than $150\ \mu\text{m}$) that were used in the conventional material were mixed together for five minutes with an agate mortar as the “Coarse As Mix,” while nanoparticle metallic powder was used as the “Nano As Mix.”

Figure 6 shows the relationship between the PCT desorption property and the acceleration. It became clear that

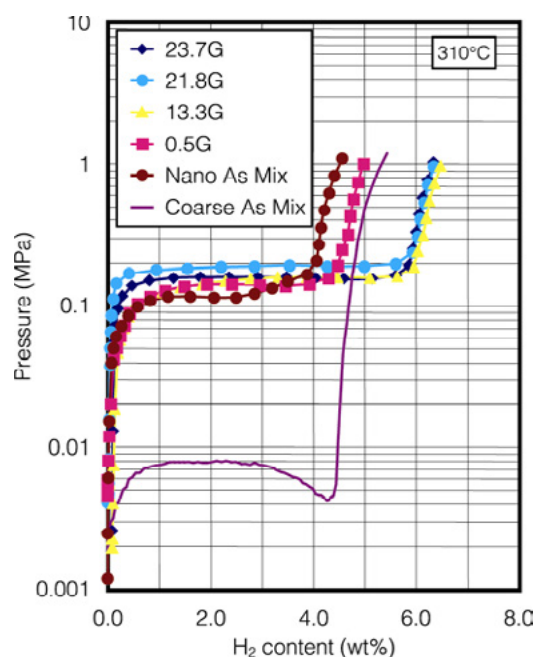


Fig. 6 Relationships between PCT desorption property and MG acceleration

even though the nanoparticle catalyst MG process was reduced to 15 minutes the hydrogen desorption property and the plateau property for 10 hours MG treated conventional material at 23.7 G were achieved with nanoparticle catalysts at 13.3 G to 23.7 G. These results show that the MG acceleration can be reduced by 44%, from 23.7 G to 13.3 G when using nanoparticle catalysts.

It is also clear that the “Nano As Mix” that was synthesized using an agate mortar has a plateau pressure that is equivalent to that of a sample produced by the MG process. The fact that the “Nano As Mix” material has a plateau pressure equivalent to that of the MG material means that the rate of desorption of the “Nano As Mix” is equivalent

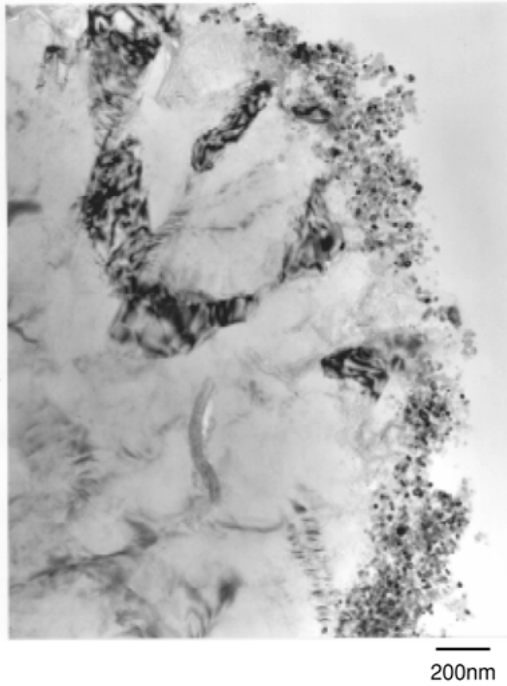


Fig. 7 TEM image of Mg-2Ni-1Fe after MG-0.5G

to that of the MG material. Given these results, it is likely that even simple mixing with nanoparticles easily increases the hydrogen activation at the periphery of the powder where the nanoparticle catalysts have adhered, although the activation towards hydrogen is low within the Mg grains where no nanoparticle exist. As a result, it was possible to measure the amount of hydrogen desorption in the highly activated region near the surface of the Mg powder.

Based on the above, when using nanoparticle catalysts it is possible to reduce the MG acceleration by 44% compared with conventional materials, and the rate of reaction is able to be greatly increased by even simple mixing with nanoparticle catalysts.

4.2.2 Results of microstructure observation

Observation by TEM was used in order to gain a clear understanding of the microstructure of the MgMH powder that was produced. Among the samples shown in Fig. 6, observation by TEM was made on the 0.5 G and 13.3 G samples immediately after the MG process. Figure 7 and 8 show typical TEM images of the 0.5 G and 13.3 G samples, respectively.

It is believed that, in a normal MH alloy, catalyst metal on the surface promotes the dissociation of the atoms in hydrogen molecules, or the reverse reaction. In other words, when hydrogen is absorbed, the catalysts promote the dissociation of the atoms in hydrogen molecules; when hydrogen is desorbed, it has the effect of bonding hydrogen atoms to form molecules.

As Fig. 7 clearly shows, the nanoparticle catalysts in the 0.5 G material are only present on the outermost surface, and do not exist within the matrix of the Mg powder. On the other hand, in the case of the 13.3 G material that is shown in Fig. 8, the nanoparticle catalysts are distributed both within the Mg matrix and on the surface. The nanoparticle catalysts are distributed within the matrix, and this is a likely reason why the MgMH powder overall has a high rate of absorption/desorption, and exhibits a large absorption amount in excess of 6 wt%, similar to 23.7 G material.

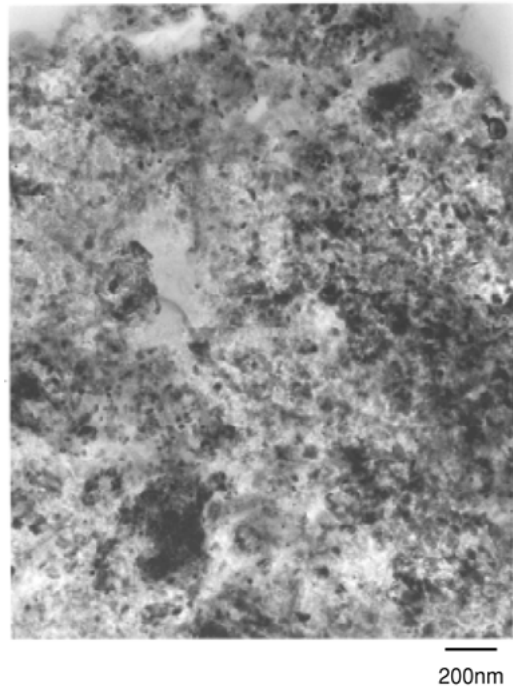
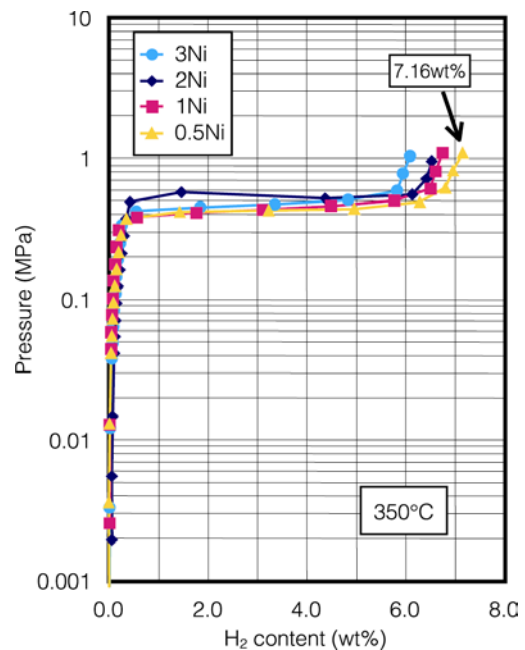


Fig. 8 TEM image of Mg-2Ni-1Fe after MG-13.3G

These results clearly indicate the importance of uniform distribution of nanoparticle catalyst on the surface of the MgMH powders and within the matrix.

4.3. Reduction of Amount of Catalyst

After studying Mg-xNi two-element alloys ($x = 0.5, 1.0, 2.0, 3.0$ at %), the results were fed back into Mg-Ni-Fe alloys, and alloys with compositions based on that feedback were created and the amount of hydrogen absorption was measured. As it was considered difficult to stably obtain the

Fig. 9 Relationships between PCT desorption property and contents of Ni catalyst ($x=0.5, 1.0, 2.0, 3.0$)

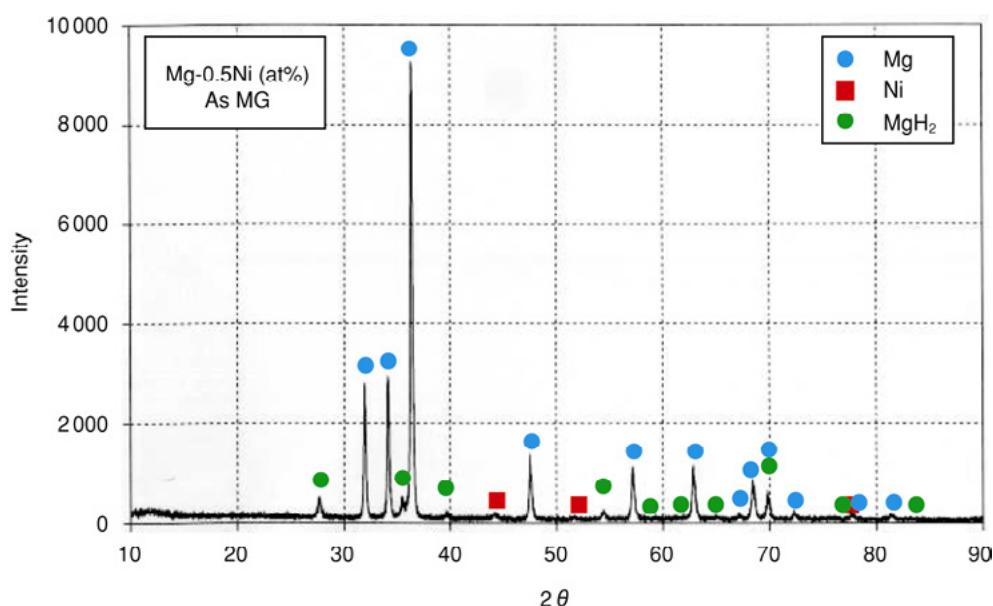


Fig. 10 XRD pattern of Mg-0.5Ni alloy after MG using nanometer sized catalyst

target composition in the range below 0.5 at%, this range is excluded from the study.

Figure 9 shows the results of PCT property measurement in Mg-xNi binary alloys that were produced with different amounts of catalyst. In the case of the alloy using the nanoparticle catalysts reduced the amount of catalyst as low as 0.5 at% which did not accompany decreasing of the hydrogen storage capacity; the maximum amount of desorption exceeds 7 wt%. The hydrogen desorption rate did not drop even when the amount of the catalyst was 0.5 at%. So the amount of hydrogen desorption increased with the decrease in the amount of the catalyst.

4.3.1. Results of XRD measurement

Of the two-element alloys, XRD observation was carried out of the Mg-0.5 Ni (at%) alloy (which exhibited an absorption amount in excess of 7 wt%) immediately after MG (As MG). Figure 10 shows the XRD diffraction pattern. Because the MG process was short, Mg exhibits no broad peak; instead, the pattern is very peaky with high crystallization. Regarding Ni, only small peaks are observed, since the amount that was added was 0.5 at%.

A chief characteristic of the conventional method is that, once MgH_2 is generated after six or more hours of the MG process in a hydrogen atmosphere, the MgH_2 peak is observed in XRD measurement after MG. In the case of the new alloy, the generation of MgH_2 was confirmed even with only 0.5 at% Ni and just 15 minutes of MG. In addition, hydrogen storage capacity in excess of 7 wt% was confirmed for the series of alloys regardless of whether the initial activation treatment was performed or not, just as described in section 4.1.2, "Results of identification of component phases of the Mg-2Ni-1Fe alloy."

4.3.2 Expansion to Mg-Ni-Fe alloys

It was decided to apply that amount of catalyst to Mg-Ni-Fe alloys (Ni:Fe = 2:1), and a chemical composition of Mg - 0.33Ni - 0.17Fe (at%) was selected, as it became clear that hydrogen storage capacity in excess of 7 wt% could be reached with catalyst amounts of 0.5 at%. Similar to the MG conditions described previously, a vacuum was created in an 80 cc pot, then 1 MPa of H_2 was added, and the MG

process was performed for 15 minutes. After a series of MG process, the MgMH powder was collected in the open air and the PCT property was measured. Figure 11 shows the PCT property at 310 °C under convergent conditions for 15 minutes. Figure 12 shows the PCT property at 350 °C under convergent conditions for 5 hours.

In Fig. 11, the maximum hydrogen storage capacity reaches 7.33 wt%, and it clearly exceeds the previous data that has been reported⁽⁸⁾. In Fig. 12, the hydrogen storage capacity reaches 7.49 wt%; although this doesn't reach the theoretical value (7.57 wt%) for this alloy composition, the difference is a mere -0.08 wt%. Figure 13 shows a comparison of the absorption amount of this alloy compared with other types of alloys and an MgMH alloy produced by industrial melting methods^{(1), (8), (9)}. Although the working

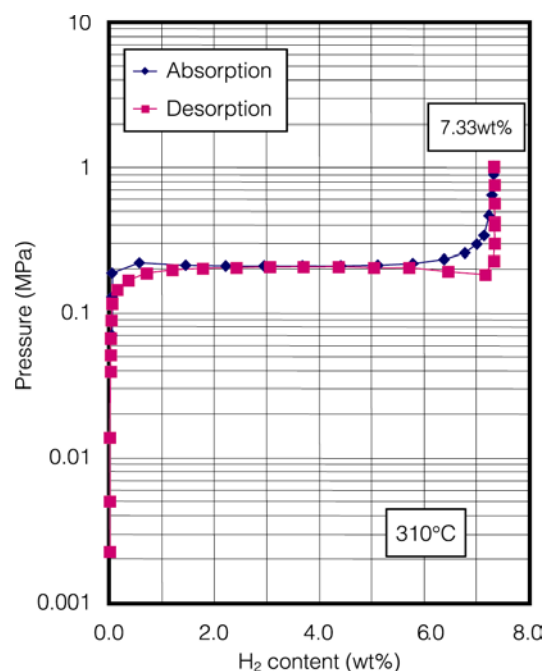


Fig. 11 PCT property of Mg-0.33Ni-0.17Fe alloy

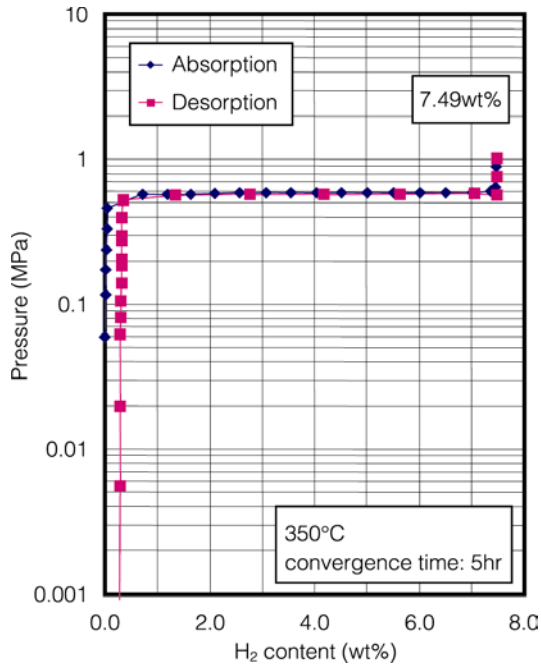


Fig. 12 PCT property of Mg-0.33Ni-0.17Fe alloy with 5 hr convergence time

temperature is higher than that of low-temperature alloys, these graphs show that an absorption amount that is 99% of the theoretical value has been reached, and that this alloy has a hydrogen storage capacity that far exceeds that of other hydrogen absorbing alloys.

4.3.3. Results of component phase identification of Mg-Ni-Fe alloys

Figure 14 shows the XRD diffraction pattern for a dehydrogenated Mg - 0.33Ni - 0.17Fe alloy after PCT measurement. Recrystallization occurs and a Mg peak is observed with extremely high degree of crystallization, as the PCT measurement was performed at 310 °C. And, it is clear that the Ni catalyst now exists in the form of $\alpha\text{Mg}_2\text{Ni}$ compound. Even if the Ni existed in the Mg_2Ni state, it would not reduce absorption/desorption properties as the

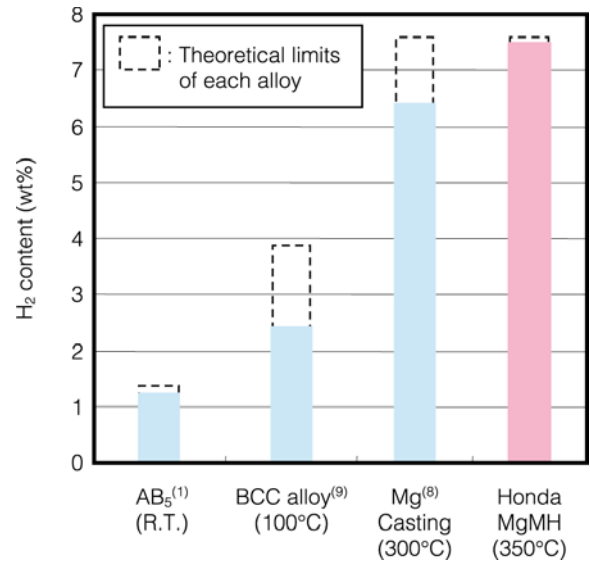


Fig. 13 Comparison of H storage capacity between MgMH in this research and another MH alloy

MgMH have maintained its absorption/desorption properties. Fe is thought to exist in independent domains within the MgMH powder, as Fe does not synthesize a compound with Mg. Although the XRD diffraction pattern of MgMH powder immediately after MG, the generation of MgH_2 has been confirmed in the MgMH powder, initial activation is unnecessary for this alloy.

4.3.4. Results of microstructure observation

TEM observation was carried out in order to clarify the microstructure of the Mg - 0.33Ni - 0.17Fe alloy that was produced. Figure 15 shows a TEM observation image of the dehydrogenated MgMH powder after PCT measurement of the Mg - 0.33Ni - 0.17Fe alloy. Introduced dislocations and defects during MG and hydrogen absorption/desorption disappear and clear crystal grains are formed, as the PCT measurement is performed in a high temperature range around 300 °C. The diameter of the crystal grains likely ranges from several hundred nanometers to several

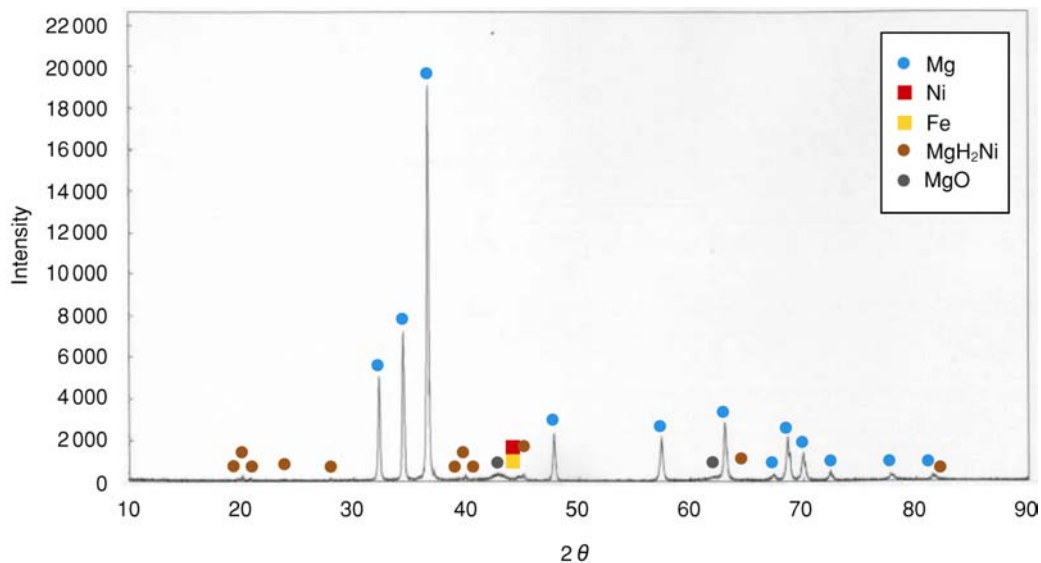


Fig. 14 XRD pattern of Mg-0.33Ni-0.17Fe after PCT measurement

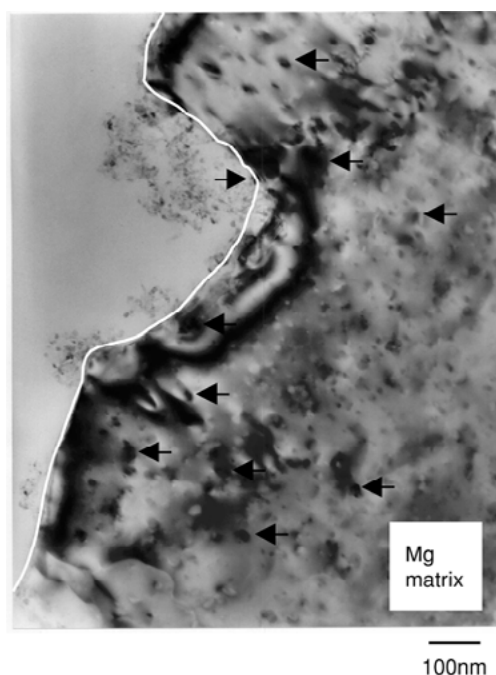


Fig. 15 TEM image of Mg-0.33Ni-0.17Fe after PCT measurement (Arrows indicate some catalysts and white line is a surface of Mg particle)

micrometers. Metallic images that are thought to be nanoparticle catalysts were confirmed in the matrix. It became clear that even though most of these are less than 100 nm in diameter and the PCT measurement was made at high temperature, most of the catalyst particles are distributed uniformly as nanoparticle on the surface of the MgMH particles and throughout the matrix. Regarding the Ni particles, their existence in Mg_2Ni was confirmed as described earlier in section 4.3.3, "Results of component phase identification of Mg-Ni-Fe alloys." In addition, the results of EDX also confirmed that the particles are composed of Mg and Ni.

These TEM observation results clearly indicated that the microstructure that achieves an absorption capacity in excess of 7 wt% in MgMH consists of under 100 nm sized catalyst particles distributed uniformly on the surface of the Mg powder and within the crystal grains.

5. Conclusion

The goal of this research was to produce a practical, easily manufactured Mg hydrogen absorbing alloy with the greatest possible hydrogen storage capacity.

As a result of this research, MgMH alloy was synthesized using nanoparticle catalysts with a chemical composition of Mg - 0.33Ni - 0.17Fe (at%) and 15 minute MG process with an acceleration of 13.3 G. And, it was shown that initial activation was completed through the first hydrogen desorption at 300 °C. In addition, the hydrogen storage capacity approached its theoretical value thereby greatly increasing the rate of hydrogen absorption/desorption. The maximum hydrogen storage capacity of this alloy achieved in this research was 7.49 wt%. This value is among the highest in the world for currently known practical hydrogen absorbing alloys.

This research enabled a simple and effective utilization of nanoparticle catalysts, a type of nanotechnology.

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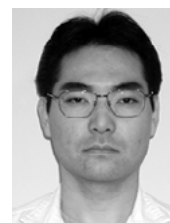
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