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Hydriding–dehydriding characteristics of aged Mg–10%Ni alloy hydride and water resistance of sol–gel encapsulated composite

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Abstract

Thermodynamic assessments of a 20-year-old Mg–10%Ni alloy hydride, which had been stored under a dry atmosphere, was carried out. More than 80 mol% of the magnesium in the aged sample was reactive to hydrogen. After a further two-year aging in an ambient atmosphere, formation of magnesium hydroxide proved to be significant. The hydrogen absorbing ability was diminished through consumption of magnesium, and the rate of deterioration was accelerated due to the increased surface area brought by decomposition of magnesium hydroxide on dehydriding at elevated temperatures. The presence of water would favor the formation of magnesium hydroxide. Encapsulation of the hydride with the siliceous shell prepared by the sol–gel method provided a water resistant composite which had fair hydriding–dehydriding characteristics.

Keywords: Hydrogen storage materials; Intermetallics; Surfaces and interfaces; Chemical synthesis; Thermodynamic properties

1. Introduction

Water resistant metal hydrides are required for specified applications where a selective uptake of hydrogen from hydrogen–water mixtures is intended or a steady supply of hydrogen under humidified atmospheres is aimed at. The former is related to the solar splitting of water and the latter to fuel cell systems.

In our previous work [1], it was found that water resistance was imparted to hydrides by the encapsulation within hydrophobic siliceous shells carrying organic functional groups. The effectiveness of the encapsulation was so high that $ZrMn_2$ was able to be handled in air without ignition and retained the hydrogen capacity after an overnight stirring in water. On the contrary, the encapsulation of Mg–10%Ni alloy showed only a little effect on the water resistance.

According to Song et al. [2], the hydrogen capacity of Mg_2Ni at 573 K almost linearly decreased with the number of hydriding cycles to reach about 80% of the initial value after 36 cycles under 0.7 MPa of hydrogen containing 9 ppm of oxygen and 19 ppm of water. In a recent study by Song [3], a similar lowering of the hydrogen capacity was reported for Mg_2Ni at 543–583 K under 0.35–0.8 MPa of hydrogen containing 9 ppm of oxygen. The variation of the hydrogen capacity was not linear with the cycle number, but drastically changed at around the 30th cycle; the lowering was accelerated from there. Why the cycling behavior differed was not discussed nor was how the water impurity affected that.

According to Ono et al. [4], the water had no effect on the reactions of Mg_2Ni, whereas the dehydriding of Mg–5%Ni hydride was partly inhibited by water. Further, they pointed out that carbon dioxide inhibited hydriding reactions of both Mg_2Ni and Mg–5%Ni alloys owing to methanation with hydrogen to form water. It appears that water has some hazardous influence on the Mg–Ni alloys, but the mechanism of the plausible poisoning effect is not known. More experimental studies are now required for phenomenological understanding.

The purpose of the present work is to clarify whether the sol–gel encapsulation is effective for a hydride the oxidative inactivation of which is much milder than $ZrMn_2$. A twenty-year old Mg–10%Ni alloy hydride (Mg–Ni–H(20)) is thus employed, since it is stable in air not undergoing any rapid changes in hydriding–dehydriding characteristics. Firstly the present state of the aged hydride

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is analyzed, and secondly the effectiveness of the sol–gel encapsulation is discussed from the viewpoint of the protecting ability to oxidative damage by water. The conventional sol–gel method is employed for simplicity.

2. Experimental

The hydride, Mg–Ni–H(20), was prepared in 1976 starting from an ingot having a precise nickel concentration of 10.31%. Hydriding was performed at 623 K under 5 MPa of hydrogen, and dehydriding at 623 K in vacuo. Thirty cycles of hydriding–dehydriding gave a steady state hydride having a H/Mg ratio of two. After the intended kinetic study [5] was completed, the hydrided sample was packed in a 500 ml polyethylene bottle under nitrogen (the volume of the sample was about two thirds of that of the bottle), sealed with adhesive tape and stocked in a silica gel desiccator. The sample was taken out twenty years later for the thermodynamic measurements in the present work.

Mg–Ni–H(20) was further aged for two years in an ambient atmosphere. Most of the following measurements were carried out on this sample (Mg–Ni–H(20+2)).

Pressure–composition isotherms were automatically measured at 473 K using a Sieverts type apparatus. The hydride was heated at 573 K under 0.5 Pa for 10 h, a dose of hydrogen was admitted at 473 K, and the pressure was monitored every 2 min. When the ratio of the pressure 2 min before to the present value fell into 0.999–1.005, the next dose of hydrogen was admitted. Typically it took about 6 h to get one equilibrium point.

Thermogravimetric analysis was done using a Cahn 2000 electrobalance at a heating rate of 10 K min^{-1} in vacuo. Decomposition behaviors of treated and non-treated hydrides were measured by two types of temperature programmed desorption (TPD) at a heating rate of 10 K min^{-1}. An Edwards EQ80F mass analyzer was used in vacuo (mass TPD) and a TCD detector for Yanagimoto G-1880 gas chromatograph was used in an argon stream (TCD TPD).

A transparent solution containing 3.8 g of $Si(OEt)_4$, 1.5 g of water, 10.2 g of methanol and 0.5 g of 85% phosphoric acid was stirred at room temperature for 1 h and diluted with 144 g of methanol. The hydrophobic encapsulation was carried out by adding 18.8 g of this solution to 5.0 g of the hydride. After filtration and gelation at room temperature for 24 h, a solid composite was obtained which had a weight ratio of the shell to the alloy of 0.04.

The water resistance of the encapsulated material was evaluated by subjecting it to an accelerated aging treatment; it was stirred in water for 24 h and then dried in air at room temperature for 24 h.

3. Results

Mg–10%Ni alloy, which was obtained by heating Mg–Ni–H(20) at 573 K in vacuo, occluded hydrogen at 473 K as shown in Fig. 1. The hydrogen concentration in the solid phase monotonously increased with the pressure and no plateaux were observed. According to the published relationships between log P and $1/T$ [6], the equilibrium dissociation pressure for $Mg–H_2$ system is calculated to be 4.8 kPa at 473 K and that for $Mg_2Ni–H_2$ system is 20 kPa. The Mg–Ni alloy derived from Mg–Ni–H(20) required higher pressures to occlude hydrogen to a substantial extent.

The Mg–Ni alloy, as prepared by the dehydriding of Mg–Ni–H(20+2), occluded much less hydrogen under the same hydrogen pressure. In other words, it required much higher pressures to react with hydrogen with comparable H/Mg ratios. The activity of this alloy was severely diminished during the further two-year aging under an ambient atmosphere. Higher evacuating temperatures, 623 K and 673 K, did not alter the shape of the isotherm for Mg–Ni–H(20+2) shown in Fig. 1. The hydrogen capacity was not as low as H/Mg = 0.1 or so. It was observed that the saturated amount of hydrogen in the solid phase was about 5 wt% under 3.8 MPa of hydrogen at 623 K.

Fig. 2 shows a little but observable effect of the sol–gel encapsulation on the resistance to the model damage. The original isotherm for Mg–Ni–H(20) shifted to the left hand side on damaging treatment. After the sol–gel encapsulation, the isotherm also shifted to the left hand side on water immersion, but the deviation from the

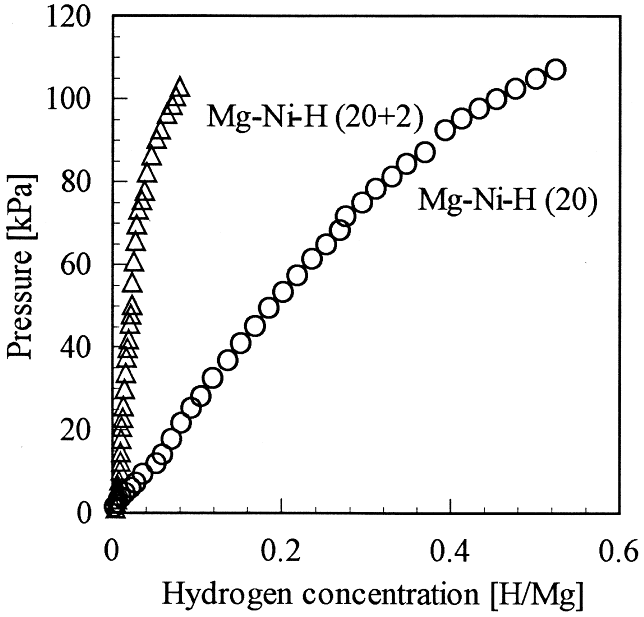


Fig. 1. Absorption isotherms for the aged samples at 473 K.

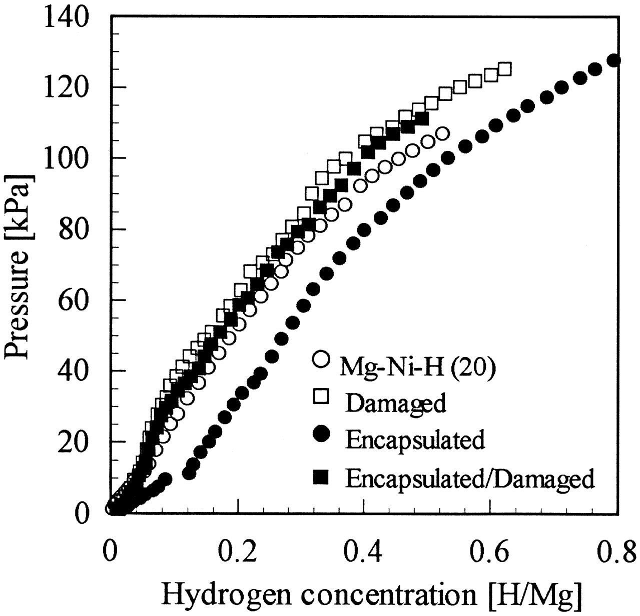


Fig. 2. Absorption isotherms for treated and non-treated Mg–Ni–H (20) at 473 K.

original isotherm was half as large as that for the non-coated material. The encapsulation imparted water resistance to Mg–Ni–H(20), and, at the same time, lowered the hydrogen pressure required to reach a certain H/Mg ratio.

If the Mg–10%Ni alloy does not include any impurities nor carry adsorbed gases, the theoretical weight loss on dehydriding is calculated to be 6.9%. As shown in Fig. 3, the observed weight loss of Mg–Ni–H(20+2) was 23%, much larger than the theoretical value. This was caused by evolution of other gases as described later. A hydride sample, which was obtained by evacuating Mg–Ni–H(20+2) at 623 K for 12 h and hydriding at the same temperature under 3.8 MPa of hydrogen for 12 h, showed a different profile and the total weight loss was 5% as also shown in Fig. 3. This was 70% of the theoretical value.

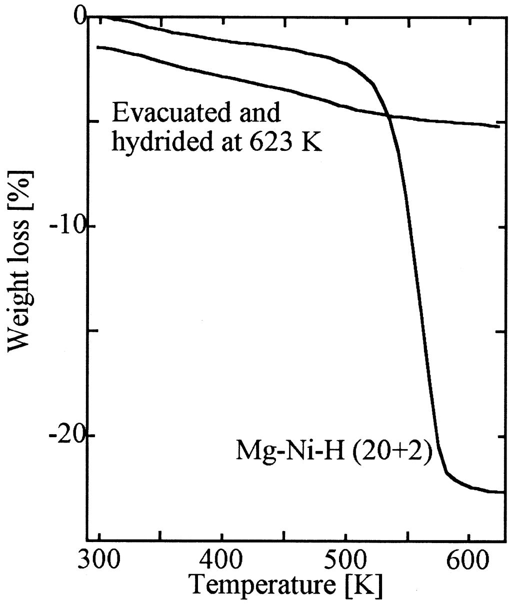


Fig. 3. Thermogravimetric curves for the aged hydride and rehydrided one.

Fig. 4 shows powder X-ray diffraction (XRD) patterns for Mg–Ni–H(20+2) and treated ones. The starting sample, Mg–Ni–H(20+2), was composed of Mg, Mg_2NiH_4 and $Mg(OH)_2$ and no diffraction peaks from MgH_2 phase were observed. Evacuation at 553 K caused decomposition of Mg_2NiH_4 to form Mg_2Ni. $Mg(OH)_2$ did not decompose at 553 K, but was absent after evacuation at 623 K. MgO was present instead. The XRD pattern recorded after evacuation at 673 K (not shown) was exactly the same as that at 623 K.

Dehydriding at a temperature below 553 K and decomposition of $Mg(OH)_2$ at a temperature between 553 K and 623 K were confirmed by the mass TPD spectra shown in Fig. 5. Two peaks were observed when the mass to charge ratio, m/e, was fixed at 2. The stronger peak at the lower temperature was assigned to hydrogen released from Mg_2NiH_4, and the other at the higher temperature to the H_2^+ fragment formed by electron impact ionization of

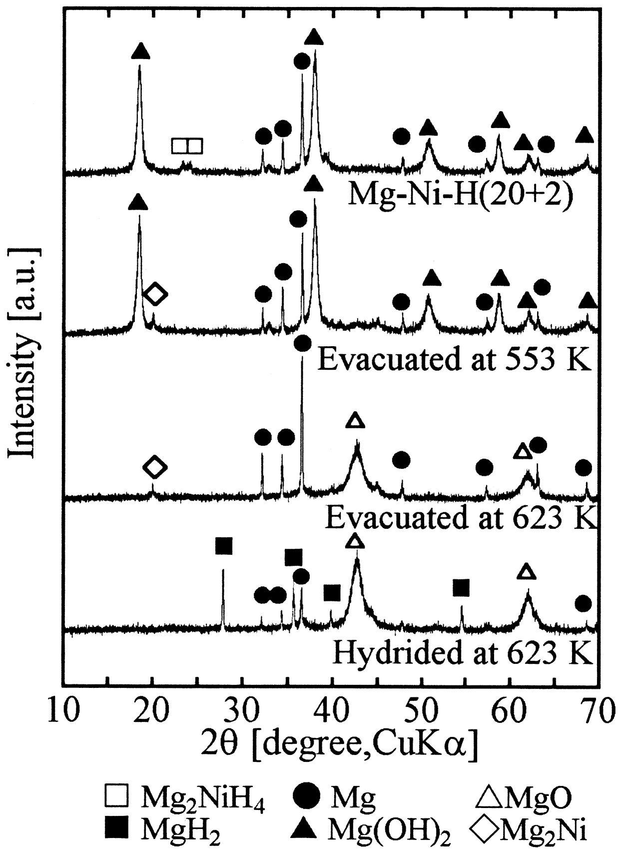


Fig. 4. XRD patterns for Mg–Ni–H(20+2) as well as evacuated and rehydrided ones.

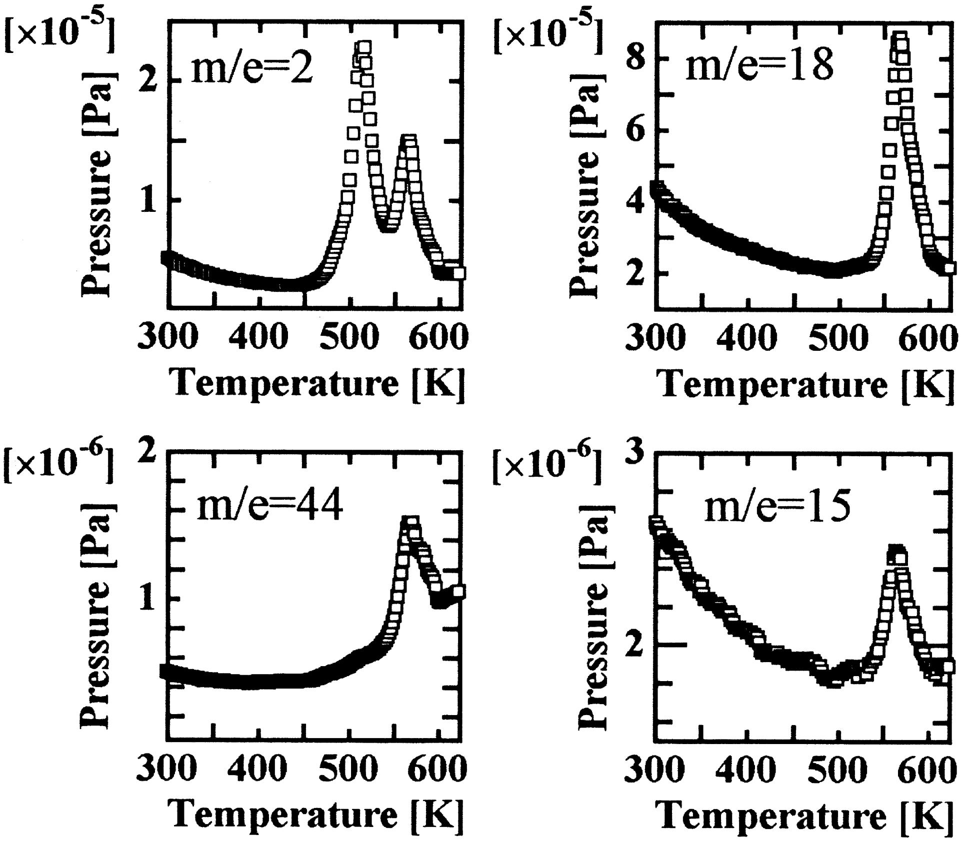


Fig. 5. Mass TPD spectra for Mg–Ni–H(20+2).

released water. At this temperature, water was undoubtedly released from the sample as evidenced by the sharp TPD peak for $m/e = 18$.

At the same temperature as $Mg(OH)_2$ decomposed, carbon dioxide and methane evolved. This was consistent with the fact that methane was formed from Mg–Ni alloy hydrides and carbon dioxide in air reported by Ono et al. [4]. The large weight loss observed in Fig. 3 should be attributed to the evolution of the other gases rather than hydrogen.

The sample hydrided at 623 K under 3.8 MPa, the thermogravimetric curve of which was shown in Fig. 3, did not show any substantial TPD peaks for $m/e = 15$, 18 nor 44. Thus, the observed weight loss, 5%, would be due to hydrogen. Knowing that the components of the sample varied from Mg, Mg_2Ni and MgO to Mg, MgH_2 and MgO on rehydriding, as shown in Fig. 4, we can calculate the molar fraction of reactive Mg to be 80%.

Eventually, the aged sample, Mg–Ni–H(20+2), contained Mg, Mg_2NiH_4 and $Mg(OH)_2$ phases as well as adsorbed gases, and 80 mol% of Mg was reactive to hydrogen after evacuation in vacuo. Hydrogen occluded by the regenerated alloy was easily released as demonstrated in Fig. 3 by the premature weight loss prior to heating.

The encapsulation by the sol–gel method imparted water resistance to Mg–Ni–H(20+2) as can be distinctly seen from Fig. 6. Here the samples were dehydrided and rehydride in the TPD apparatus prior to the measurements. Dehydriding was carried out at 603 K under argon and hydriding at 553 K in a hydrogen flow for 1 h. After cooling to room temperature under hydrogen, the samples

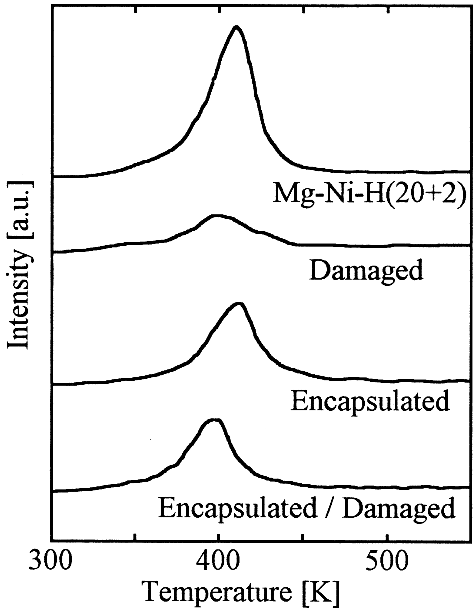


Fig. 6. TCD TPD spectra for treated and non-treated Mg–Ni–H(20+2).

were heated in an argon flow and released hydrogen was detected. The amount of hydrogen released from Mg–Ni–H(20+2) was 0.12 as represented by the H/Mg ratio. After damage through the water immersion, this ratio decreased to 0.043. On the contrary, the immersed alloy still showed a high H/Mg ratio, 0.063, when it was beforehand encapsulated by the sol–gel method. The encapsulation imparted water resistance to Mg–Ni–H(20+2). Since this value was slightly lower than 0.073 for the encapsulated sample without the water damage, the present recipe for the encapsulation should not be optimum. The lowering to 0.073 on the sol–gel treatment is another problem to be solved.

The XRD peaks from Mg_2NiH_4 disappeared through the sol–gel treatment as shown in Fig. 7. This tendency was the same as that on the water damage. Loss of the hydride phase was also confirmed by the mass TPD measurements. The XRD peak near $2\theta=40°$ for Mg–Ni–H(20+2) was assigned to MgH_2, but it was possible to be assigned to Mg_2NiH_4. Anyhow, the sample had no hydride phases after the water damage or the encapsulation.

The water damage lowered the intensities of the Mg peaks, whereas the encapsulation did not. The water damage after the encapsulation also weakened the Mg peaks, but the extent was slightly smaller than that without the encapsulation. The ratio of the peak intensity at $2\theta=37°$ to that of the neighboring $Mg(OH)_2$ peak was larger for the encapsulated/damaged sample than that for the damaged one without the encapsulation.

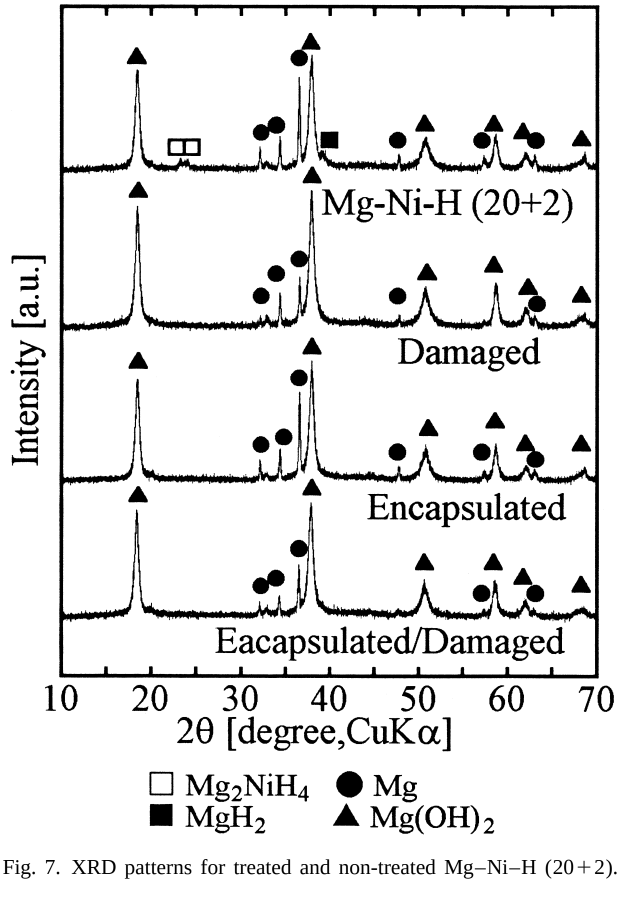


Fig. 7. XRD patterns for treated and non-treated Mg–Ni–H (20+2).

The sol–gel encapsulation did not change the surface morphology of Mg–Ni–H(20+2) as demonstrated in Fig. 8. Calculating from the surface area, 10 m^2 g^{-1}, which was measured by krypton adsorption after heat treatment at 473 K in vacuo, we estimated the mean diameter to be 0.16 μm. The appearances in the photographs (a) and (c) in Fig. 8 were suited for this particle size. Through water immersion, the surface seemed to become smooth as if the particles agglomerated. Apparently the sol–gel encapsulation considerably prevented the surface change during the water damage.

4. Discussion

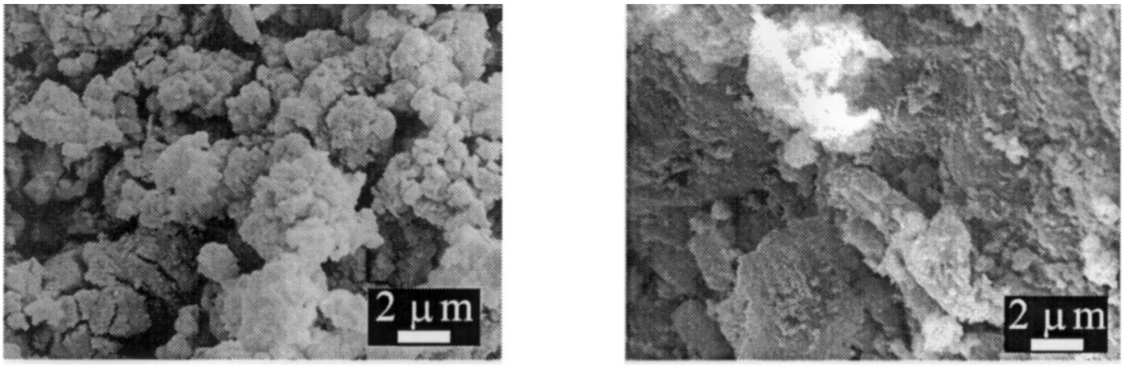
According to Ishido et al. [7], Mg–10%Ni hydride exposed to air for more than 4 years lost about 10% of its hydrogen capacity. In the present study, the alloy which was stored in a dry atmosphere for 20 years and exposed to air for 2 years lost 20% of its capacity. It is notable that a dry condition is profitable to store the hydride. This has been demonstrated in Fig. 1, where the further two-year aging of Mg–Ni–H(20) in the ambient atmosphere has severely lowered its hydrogen capacity to give the isotherm for Mg–Ni–H(20+2). Eventually, more than 80 mol% of magnesium in Mg–Ni–H(20) should be reactive to hydrogen.

Cracking, typically shown in the lower half on the left of the photograph (a) in Fig. 8, would promote the degradation of the hydrogen capacity. As a matter of fact, the surface area of Mg–Ni–H(20+2) was much higher than that of the starting hydride, 2.6 m^2 g^{-1}. Weathering would take place through cracking and the newly exposed surfaces would be poisoned by oxidative gases.

Carbon dioxide detected in Fig. 5 would be formed by decomposition of carbonate groups in the sample. The surface carbonate is easily formed by exposing the hydride to carbon dioxide or air and it protects the active surface of Mg–Ni alloy [7]. The long term storability of Mg–10%Ni alloy hydride in the present study would be due to the protecting effect of the surface carbonate.

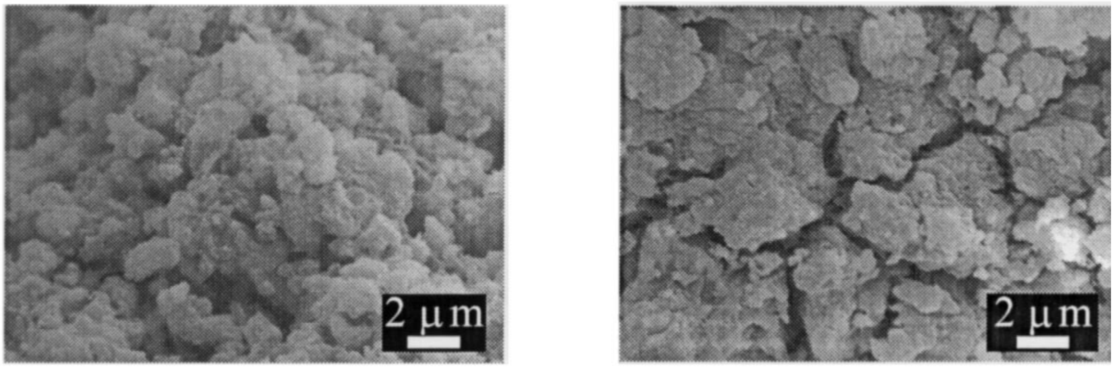
On the other hand, it has also been reported that carbon dioxide has hazardous effects on the hydriding/dehydriding reactions through methanation with hydrogen to form water [4]. Carbon dioxide, therefore, has the advantageous and the disadvantageous sides in aging. This could be why Mg–Ni–H(20+2) contained Mg_2NiH_4 instead of MgH_2 as shown in Fig. 4. It is probable that the protecting effect of surface carbonate favored the survival of Mg_2NiH_4 and that the hazardous effects of the aqueous products caused decomposition of MgH_2.

The predominance of Mg_2NiH_4 rather than MgH_2 in Mg–Ni–H(20+2) was further supported by estimation of



(a) Mg-Ni-H (20+2)

(b) Damaged



(c) Encapsulated

(d) Encapsulated / Damaged

Fig. 8. SEM images for treated and non-treated Mg–Ni–H(20+2).

the hydrogen content. As mentioned earlier, the weight loss on heating was caused by evolution of several gas species. The mass fraction of hydrogen was roughly estimated as 2.8% from the mass-TPD results as shown in Fig. 5, with the molecular weights taken into consideration. Thus, the weight loss attributed to the release of hydrogen should amount to 0.6% as calculated by multiplication of the total weight loss observed in Fig. 3 by the hydrogen fraction. This is close to the theoretical concentration when hydrogen is carried only by the Mg_2NiH_4 phase in the Mg–10%Ni alloy hydride.

Though MgH_2 was lost and strong XRD peaks from $Mg(OH)_2$ were observed, the molar fraction of reactive Mg in Mg–Ni–H(20+2) was as high as about 80%. On evacuation at 623 K, $Mg(OH)_2$ decomposed to MgO, and the formed MgO did not chemically change during the subsequent hydriding. The formation of $Mg(OH)_2$ during the stock period and that of MgO on heating were not fatal to the hydrogen capacity. The decomposition of $Mg(OH)_2$ was accompanied by a significant increase of the surface area to 180 $m^2\ g^{-1}$. It is likely that this accelerated the reaction velocity as was typically shown as a premature hydrogen evolution at room temperature in Fig. 3. Repeated hydriding/dehydriding cycles were able to be done at 623 K with a steady H/Mg ratio, but hydriding was completely inhibited after the hydrided sample was exposed to air for 1 month. High surface area would be favorable for kinetics, but adverse to storability.

The sol–gel encapsulation imparted water resistance to Mg–Ni–H(20+2) as already seen in Fig. 6. Before the TPD measurements, the samples were heated to 603 K and hydrided at decreasing temperatures from 553 K to room temperature under the atmospheric pressure of hydrogen. This would be why the observed H/Mg ratio was higher than that in Fig. 1 for Mg–Ni–H(20+2). It is noted that the peak temperature of hydrogen evolution was lowered by the model damage of the water immersion. Moreover the peak temperature for Mg–Ni–H(20+2) was by itself 100 degrees lower than that in Fig. 5. Both of these facts would be related to the increase in the surface area brought about by the decomposition of $Mg(OH)_2$ on heating. The surface areas for Mg–Ni–H(20+2), damaged, encapsulated and encapsulated/damaged ones were 180, 190, 180 and 190 $m^2\ g^{-1}$, respectively. The temperature difference of 100 K would be due to the increase from 10 to 180 $m^2\ g^{-1}$, and the little shifts in Fig. 6 to the increase from 180 to 190 $m^2\ g^{-1}$.

It is here assumed that an additional amount of

$Mg(OH)_2$ was formed during the water immersion. The larger amount of $Mg(OH)_2$ would provide the higher surface area. This picture implies that the sol–gel capsule does not interfere with the access of water to the encapsulated core. The sol–gel treatment in the present work should be further optimized to exclude water besides being improved so as not to break the Mg_2NiH_4 phase.

It is unclear why the protecting effect of the sol–gel encapsulation was more significant for Mg–Ni–H(20+2) than for Mg–Ni–H(20). Weathering through cracking on the formation of $Mg(OH)_2$ should be less for Mg–Ni–H(20), since this was not subjected to the prolonged aging at an ambient atmosphere. Thus, the access of water would be slower and cause less deterioration during water immersion. Since the extent of the damage was not large for the control experiment, the sol–gel effect would not be significant for Mg–Ni–H(20). The unexpected increase in the hydrogen concentration of the encapsulated hydride observed in Fig. 2 could be brought about by an increased permeability through the natural shell modified by the sol–gel treatment.

In Fig. 8, several cracks can be seen for the encapsulated/damaged Mg–Ni–H(20+2) in the photograph (d). If the cracks pass the encapsulated cores, it would bring about a large drop in the hydrogen capacity. In the photograph (b), the powdery surfaces are scarcely seen, which suggests that the powders were caked through the binding of $Mg(OH)_2$ on the surfaces. Since the sol–gel encapsulation prevented the caking, the cracks in (d) should run between the capsules.

The discussed optimization is now in progress with fresh Mg–Ni alloy hydrides employed.

5. Conclusion

More than 80 mol% of magnesium in a twenty-year old Mg–10%Ni alloy hydride, which had been stored under dry atmosphere, was reactive to hydrogen. After a further two-year aging in an ambient atmosphere, the presence of magnesium hydroxide proved to be significant. The hydroxide formation diminished the hydrogen absorbing ability and accelerated the rate of deterioration through increasing the surface area on heating in vacuo for dehydriding. The presence of water would favor the formation of magnesium hydroxide. The ceramic encapsulation of the hydride provided a water resistant composite which had fair hydriding–dehydriding characteristics.

Acknowledgements

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