

Comparison of hydrogen storage properties of pure Mg and milled pure Mg

MYOUNG YOUP SONG^{a,*}, YOUNG JUN KWAK^b, SEONG HO LEE^b and HYE RYOUNG PARK^c

^aDivision of Advanced Materials Engineering, Hydrogen & Fuel Cell Research Centre, Engineering Research Institute, Chonbuk National University, 567 Baekje-daero Deokjin-gu Jeonju 561-756, South Korea

^bDepartment of Materials Engineering, Graduate School, Chonbuk National University, 567 Baekje-daero Deokjin-gu Jeonju 561-756, South Korea

^cSchool of Applied Chemical Engineering, Chonnam National University, 77 Yongbong-ro Buk-gu Gwangju 500-757, South Korea

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Abstract. Hydrogen storage properties of pure Mg were studied at 593 K under 12 bar H₂. In order to increase the hydriding and dehydriding rates, pure Mg was ground under hydrogen atmosphere (reactive mechanical grinding, RMG) and its hydrogen storage properties were subsequently investigated. Pure Mg absorbed hydrogen very slowly. At the number of cycles (*n*) of 1, pure Mg absorbed 0.05 wt% H for 5 min, 0.08 wt% H for 10 min and 0.29 wt% H for 60 min at 593 K under 12 bar H₂. Activation was completed at the fifth cycle. At *n* = 6, pure Mg absorbed 1.76 wt% H for 5 min, 2.17 wt% H for 10 min and 3.40 wt% H for 60 min. The activation of pure Mg after RMG was completed at the sixth cycle. At *n* = 7, pure Mg after RMG absorbed 2.57 wt% H for 5 min, 3.21 wt% H for 10 min and 4.15 wt% H for 60 min.

Keywords. Hydrogen absorbing materials; pure magnesium; mechanical alloying/milling; microstructure; X-ray diffraction.

1. Introduction

Magnesium has many advantages as a hydrogen storage material in terms of hydrogen storage capacity, cost and reserves in the earth's crust. However, the reaction rate of Mg with H₂ is very low (Hong *et al* 2013a). Extensive research has been conducted to improve the hydriding and dehydriding rates of magnesium by alloying with certain magnesium metals (Hong *et al* 2013b; Kwak *et al* 2013; Song *et al* 2013a,b,c,d), including Cu (Reilly and Wiswall 1967), Ni (Reilly and Wiswall 1968; Akiba *et al* 1982), In (Mintz *et al* 1978), Sn (Zhong *et al* 2011), V (Pei *et al* 2012) and Ni and Y (Li *et al* 2007), by synthesizing compounds such as CeMg₁₂ (Boulet and Gerard 1983) and Mg₇₆Ti₁₂Fe_{12-x}Ni_x (*x* = 4, 8) (Lucaci *et al* 2009), and by fabricating composites such as Mg–20 wt%Fe₂₃Y₈ (Li *et al* 2006). Aminorroaya *et al* (2011) added Nb and multi-walled carbon nanotubes to Mg–Ni alloys and Cho *et al* (2011) added transition metals to cast Mg–Ni alloys to improve the reaction rate of Mg with H₂. Milanese *et al* (2010) mixed Ni and Cu with Mg, Tanguy *et al* (1976) mixed metal additives with magnesium and Eisenberg *et al* (1980) plated nickel on the

surface of magnesium to improve the hydriding–dehydriding kinetics of MgH₂.

In this work, hydrogen storage properties of pure Mg were studied. In order to increase the hydriding and dehydriding rates, pure Mg was ground under hydrogen atmosphere (reactive mechanical grinding, RMG) and its hydrogen storage properties were investigated. The hydrogen storage properties of pure Mg and pure Mg after RMG were then compared.

2. Experimental

Pure Mg powder (–100 + 200 mesh, 99.6%, Alfa Aesar) or pure MgH₂ (hydrogen storage grade, Aldrich) was used as a starting material.

Reactive mechanical grinding was performed in a planetary ball mill (Planetary Mono Mill; Pulverisette 6, Fritsch). Pure Mg or pure MgH₂ (total weight = 8 g) was mixed in a hermetically sealed stainless steel container with 105 hardened steel balls (total weight = 360 g); the sample to ball weight ratio was 1:45. All sample handling was performed in a glove box under Ar in order to prevent oxidation. The disc revolution speed was 250 rpm. The mill container (volume, 250 mL) was then filled with high purity hydrogen gas (~12 bar). The

*Author for correspondence (songmy@jbnu.ac.kr)

reactive mechanical grinding was performed for 6 h by repeating 15 min milling and 5 min rest. The mill container was refilled with hydrogen every 2 h.

The quantity of absorbed or desorbed hydrogen was measured as a function of time by a volumetric method using a Sivert's type hydriding and dehydriding apparatus, which has been described in previous research (Song *et al* 2010). The sample weight used for this measurement was 0.5 g. The samples after reactive mechanical grinding and after hydriding–dehydriding cycling were characterized by X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation using a Rigaku D/MAX 2500 powder diffractometer. The microstructures of the powders were examined with a JSM-6400 scanning electron microscope (SEM) operated at 20 kV.

3. Results and discussion

The weight percentage of absorbed hydrogen, H_a , is expressed with respect to sample weight. Figure 1 shows variation of H_a vs t curve with the number of cycles, n , for pure Mg at 593 K under 12 bar H_2 . The pure Mg sample absorbs hydrogen very slowly. At $n = 1$, pure Mg absorbs 0.05 wt% H for 5 min, 0.08 wt% H for 10 min, 0.17 wt% H for 30 min and 0.29 wt% H for 60 min. The hydriding rate increases as the number of cycles increases from $n = 1$ to $n = 6$ and the hydriding rate decreases as the number of cycles increased from $n = 6$, indicating that activation is completed at the fifth cycle. At $n = 6$, pure Mg absorbs 1.76 wt% H for 5 min, 2.17 wt% H for 10 min, 2.87 wt% H for 30 min and 3.40 wt% H for 60 min.

SEM micrographs of pure Mg and pure Mg dehydrided at the tenth hydriding–dehydriding cycle are shown in figure 2. The particles of pure Mg have a few cracks with quite flat surfaces. The pure Mg dehydrided at the tenth

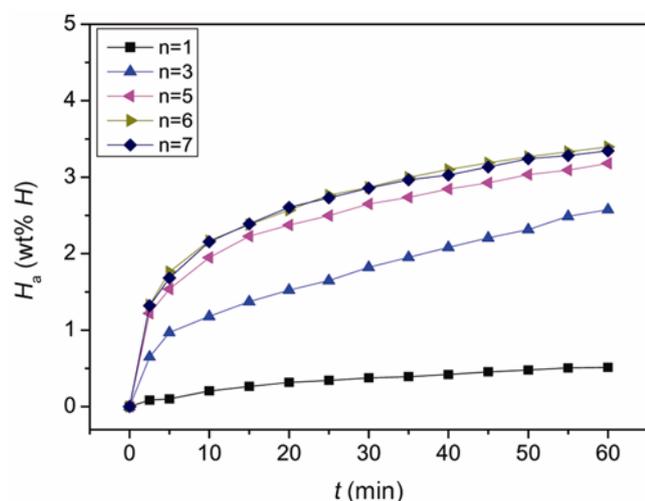


Figure 1. Variation of H_a vs t curve with number of cycles for pure Mg at 593 K under 12 bar H_2 .

hydriding–dehydriding cycle, quite small particles coexist with larger particles and particles are smaller than those of the pure Mg before hydriding–dehydriding cycling, with fine particles on their surfaces. Quite small particles and fine particles are created with hydriding–dehydriding cycling. The expansion and contraction of Mg with hydriding and dehydriding reactions are believed to be responsible for the formation of these quite small and fine particles.

Figure 3 shows XRD pattern of pure Mg. The sample contains only Mg phase.

The variation of H_a vs t curve with the number of cycles for pure Mg after RMG at 593 K under 12 bar H_2 is shown in figure 4. At $n = 1$, the sample absorbs a very small amount of hydrogen. At $n = 1$, pure Mg after RMG absorbs 0.08 wt% H for 2.5 min and 0.14 wt% H for 60 min. The hydriding rate of pure Mg after RMG increases as the number of cycles increases from $n = 1$ to $n = 7$ and decreases as the number of cycles increases

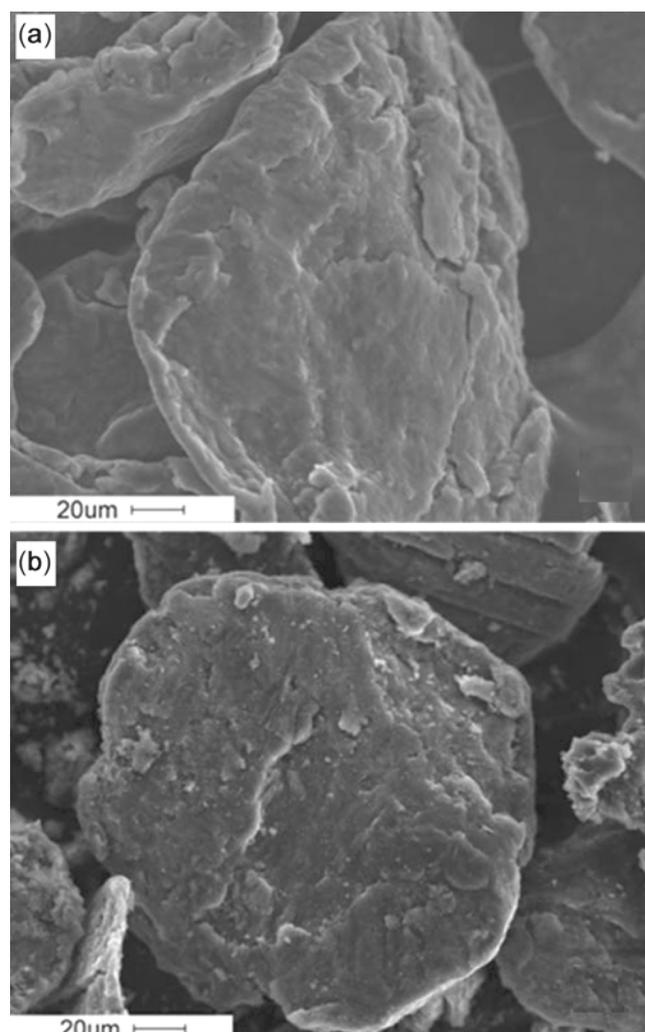


Figure 2. SEM micrographs of (a) pure Mg and (b) pure Mg dehydrided at tenth hydriding–dehydriding cycle.

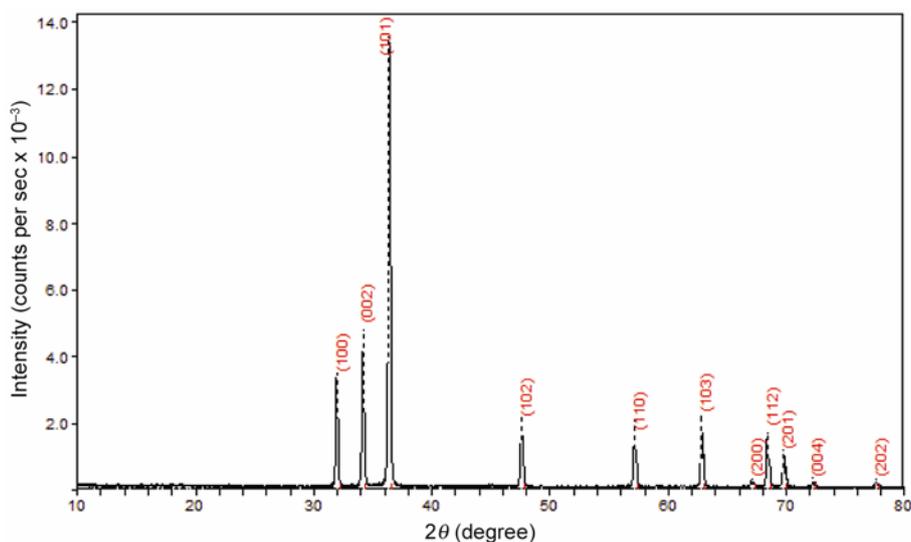


Figure 3. XRD pattern of pure Mg.

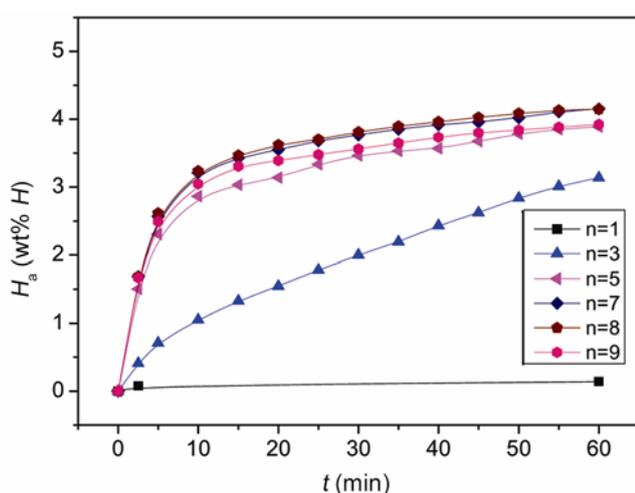


Figure 4. Variation of H_a vs t curve with number of cycles for pure Mg after RMG at 593 K under 12 bar H_2 .

from $n = 7$ to $n = 8$. At $n = 7$, pure Mg after RMG absorbs 2.57 wt% H for 5 min, 3.21 wt% H for 10 min, 3.77 wt% H for 30 min and 4.15 wt% H for 60 min.

Figure 5 shows SEM micrographs of pure Mg after RMG and pure Mg after RMG dehydrided at the twelfth hydriding–dehydriding cycle. After reactive mechanical grinding, ductile Mg particles formed plastically into elongated and flat shapes via collisions with the steel balls and fine cracks formed by repeated impact forces during ball milling. However, growth rate of microcracks was very slow and fine powder could not be obtained by milling for 6 h. Therefore, pure Mg after RMG absorbs a very small amount of hydrogen at the first cycle, as shown in figure 4. In the pure Mg after RMG dehydrided at the twelfth hydriding–dehydriding

cycle, quite small particles coexist with larger particles and particles are much smaller than those of pure Mg after RMG, with fine particles on their surfaces. Cracks are observed. Cracks, quite small particles and fine particles are created with hydriding–dehydriding cycling. The expansion and contraction of Mg with hydriding and dehydriding reactions is believed to be responsible for the formation of these cracks, quite small particles and fine particles. Compared with pure Mg dehydrided at the tenth hydriding–dehydriding cycle (figure 2), the particles are smaller or finer and more cracks are observed in pure Mg after RMG dehydrided at the twelfth hydriding–dehydriding cycle.

XRD pattern of pure Mg after reactive mechanical grinding is shown in figure 6. The sample contains Mg and a very small amount of MgH_2 , which is formed by the reaction of Mg with hydrogen during milling under H_2 .

The variations in the quantity of hydrogen absorbed at 593 K under 12 bar H_2 for 60 min, H_a (60 min), with the number of cycles for pure Mg and pure Mg after RMG are shown in figure 7. The value of H_a (60 min) for pure Mg increases as the number of cycles increases from $n = 1$ to $n = 6$ and decreases from $n = 6$ to $n = 7$. The values of H_a (60 min) for pure Mg are 0.51, 3.40 and 3.35 wt% H at $n = 1, 6$ and 7 , respectively. The value of H_a (60 min) for pure Mg after RMG increases as the number of cycles increases from $n = 1$ to $n = 7$ and decreases from $n = 7$ to $n = 9$. The values of H_a (60 min) for pure Mg after RMG are 0.14, 4.15 and 3.93 wt% H at $n = 1, 7$ and 9 , respectively. Pure Mg after RMG has smaller H_a (60 min) values than pure Mg at $n = 1$ and $n = 2$. After reactive mechanical grinding, the particles of pure Mg after RMG do not become smaller than those of pure Mg. Ductile Mg particles formed plastically into elongated

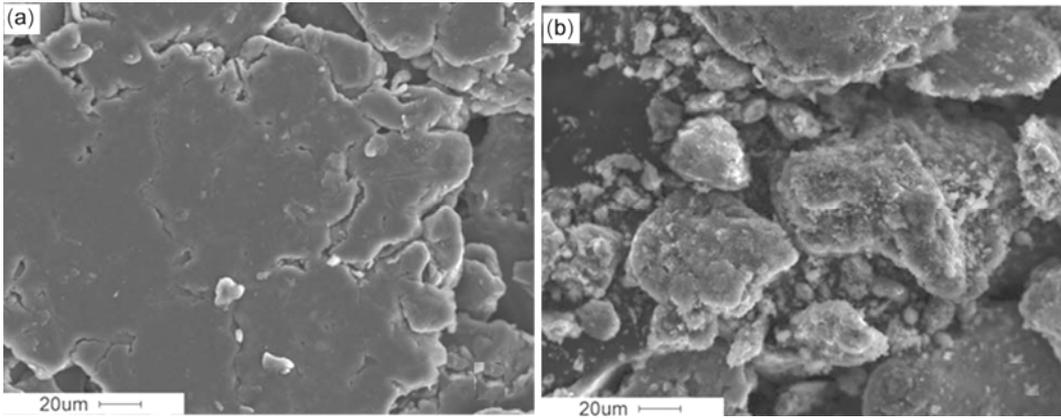


Figure 5. SEM micrographs of (a) pure Mg after RMG and (b) pure Mg after RMG dehydrided at twelfth hydriding-dehydriding cycle.

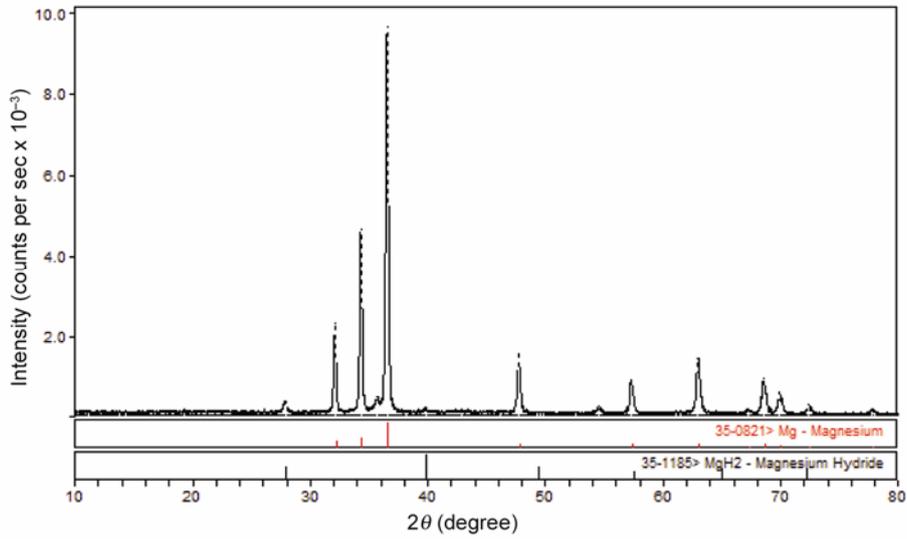


Figure 6. XRD pattern of pure Mg after reactive mechanical grinding.

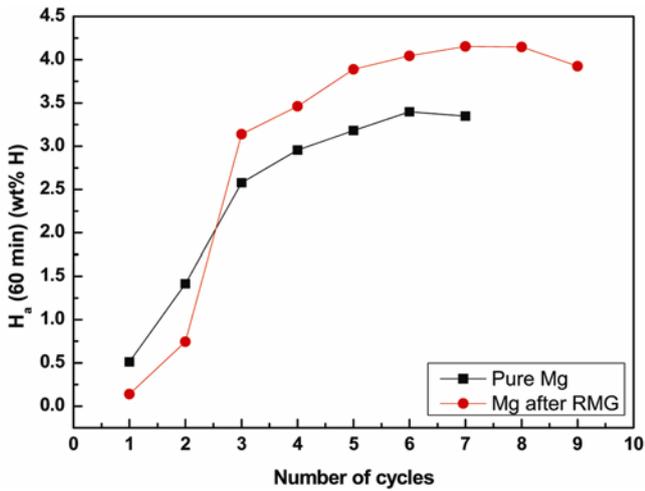


Figure 7. Variations in quantity of hydrogen absorbed at 593 K under 12 bar H_2 for 60 min (H_a (60 min)) with the number of cycles for pure Mg and pure Mg after RMG.

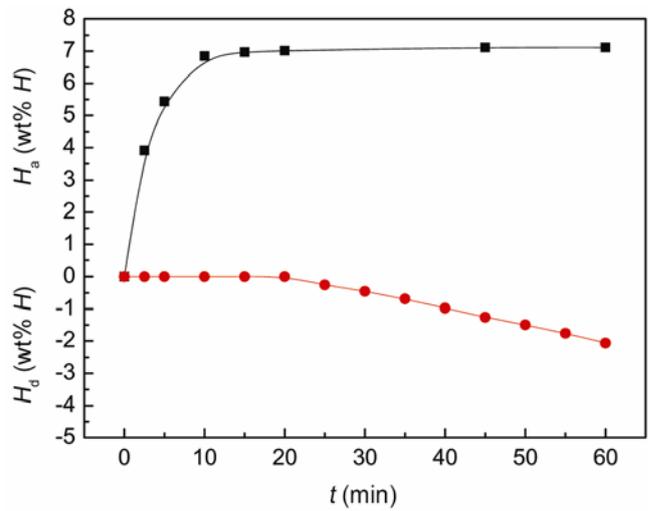


Figure 8. H_a vs t curve under 12 bar H_2 and H_d vs t curve under 1 bar H_2 at 593 K at $n = 1$ for MgH_2 after RMG.

and flat shapes with a few cracks. This is believed to be responsible for the smaller H_a (60 min) values of pure Mg after RMG than pure Mg at $n = 1$ and $n = 2$. Pure Mg after RMG has larger H_a (60 min) values than pure Mg from $n = 3$ to $n = 9$. Pure Mg after RMG dehydrided at the twelfth hydriding–dehydriding cycle has smaller particles and a much larger number of defects, with some cracks, than pure Mg dehydrided at the tenth hydriding–dehydriding cycle. This is believed to lead to the larger H_a (60 min) values of pure Mg after RMG than pure Mg from $n = 3$ to $n = 9$.

The reactive mechanical grinding of Mg and the hydriding–dehydriding cycling of pure Mg after RMG is believed to facilitate nucleation by creating defects on the surface and in the interior of Mg which can act as active sites for nucleation, and shorten the diffusion distances of hydrogen atoms by forming cracks in Mg and reducing Mg particle size.

Hydrided pure Mg and hydrided pure Mg after RMG did not release hydrogen at 593 K under 1 bar H_2 . A pure magnesium sample with smaller particle sizes was prepared by reactive mechanical grinding of MgH_2 . The weight percentage of desorbed hydrogen, H_d , is also expressed with respect to the sample weight. Figure 8 shows H_a vs t curve under 12 bar H_2 and the H_d vs t curve under 1 bar H_2 at 593 K at $n = 1$ for MgH_2 after RMG. MgH_2 after RMG has very high hydriding rate. This sample absorbs 5.44 wt% H for 5 min, 6.85 wt% H for 10 min, 7.02 wt% H for 20 min and 7.11 wt% H for 60 min. This sample shows an incubation period of 20 min and desorbs 0.26 wt% H for 25 min, 0.46 wt% H for 30 min, 0.98 wt% H for 40 min and 2.07 wt% H for 60 min.

4. Conclusions

The hydrogen storage properties of pure Mg were studied. To increase the hydriding and dehydriding rate, pure Mg was ground under hydrogen atmosphere and its hydrogen storage properties were investigated. Pure Mg absorbed hydrogen very slowly. At $n = 1$, pure Mg sample absorbed 0.05 wt% H for 5 min, 0.08 wt% H for 10 min and 0.29 wt% H for 60 min at 593 K under 12 bar H_2 . Activation was completed at the fifth cycle. At $n = 6$, pure Mg absorbed 1.76 wt% H for 5 min, 2.17 wt% H for 10 min and 3.40 wt% H for 60 min. The activation of pure Mg after RMG was completed at the sixth cycle. At $n = 7$, pure Mg after RMG absorbed 2.57 wt% H for 5 min, 3.21 wt% H for 10 min and 4.15 wt% H for

60 min. The reactive mechanical grinding of Mg and the hydriding–dehydriding cycling of pure Mg after RMG is believed to facilitate nucleation by creating defects on the surface and in the interior of Mg which can act as active sites for nucleation, and shorten the diffusion distances of hydrogen atoms by forming cracks in Mg and reducing the Mg particle size.

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