

Addition of oxides Fe_2O_3 and/or MnO to improve hydrogen storage properties of magnesium by reaction-involved milling

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Mg-oxide and Mg-oxide-Ni hydrogen storage alloys, 90 wt% Mg + 10 wt% Fe_2O_3 (named Mg-10 Fe_2O_3), 90 wt% Mg + 5 wt% Fe_2O_3 + 5 wt% MnO (Mg-5 Fe_2O_3 -5MnO), 90 wt% Mg + 3.3 wt% Fe_2O_3 + 3.3 wt% Ni + 3.3 wt% MnO (Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO), and 90 wt% Mg + 5 wt% Fe_2O_3 + 5 wt% Ni (Mg-5 Fe_2O_3 -5Ni), were prepared by mechanical milling under H_2 (reaction-involved milling). The hydrogen storage properties of the prepared alloys were then investigated. Among these samples, Mg-5 Fe_2O_3 -5Ni had the largest quantities of the hydrogen absorbed for 60 min at the first cycle and released for 60 min after activation, the highest initial hydriding rate at the first cycle, and the highest initial dehydriding rate after activation. The as-milled Mg-5 Fe_2O_3 -5Ni absorbed 1.75 wt%H for 2.5 min, 2.98 wt%H for 10 min, 3.82 wt%H for 30 min, and 4.24 wt%H for 60 min at 593 K under 12 bar H_2 . The activated Mg-5 Fe_2O_3 -5Ni released 1.70 wt%H for 10 min, 3.12 wt%H for 30 min, and 3.69 wt%H for 60 min at 603 K under 1.0 bar H_2 . Fe_2O_3 was reduced to Fe and Mg was oxidized to MgO, due to the large difference in the chemical affinities of Fe and Mg for oxygen.

Key words: H₂-storage properties of Mg, Mg-Oxide-Ni alloys, Reaction-involved milling, Hydriding and dehydriding rates, Phase transformation.

Introduction

Slow hydriding and dehydriding kinetics of Mg and high stability of MgH_2 are major obstacles to the hydrogen storage application of Mg. A lot of research has been conducted to ameliorate the low hydriding and dehydriding rates of Mg [1-12] by alloying it with certain metals, incorporating metal additives, or plating nickel on its surface.

The slow reaction kinetics of Mg with hydrogen were heightened by the addition to Mg of Co, Ni or Fe [13, 14], graphite [15], and graphite and organic additives (benzene, cyclohexene or cyclohexane) [16].

Mechanical milling can pulverize the ductile magnesium and brittle oxides. The added oxides and the oxides pulverized during mechanical milling can decrease the particle size of magnesium further. The hydriding and dehydriding kinetics of Mg was also improved by the addition to MgH_2 of V_2O_5 , VN or VC [17], Cr_2O_3 [18], Nb_2O_5 [19-22], MgO [13], Cr_2O_3 , Al_2O_3 and CeO_2 [24], CeO_2 [25], and Y_2O_3 [26].

Among the 90 wt% Mg + 10 wt% oxide samples (oxide = Fe_2O_3 purchased, Fe_2O_3 prepared by spray

conversion, MnO purchased, SiO_2 prepared by spray conversion and Cr_2O_3 prepared by spray conversion) prepared by milling for 2 hrs under high purity hydrogen of about 10 bar, the 90 wt% Mg + 10 wt% Cr_2O_3 prepared by spray conversion had the highest hydriding rate, followed by the 90 wt% Mg + 10 wt% Fe_2O_3 prepared by spray conversion, when these samples were hydrided at 593 K and 12 bar H_2 after activation. On the other hand, the 90 wt% Mg + 10 wt% MnO purchased had the highest dehydriding rate, followed by the 90 wt% Mg + 10 wt% Fe_2O_3 prepared by spray conversion, when these samples were dehydrided at 593 K and 1.0 bar H_2 after activation [27]. Based on these results, we chose Fe_2O_3 prepared by spray conversion and MnO purchased as the oxides to add to Mg. We also selected Ni as the metal to add, because there were reports that the addition of Ni to Mg greatly increased the hydriding and dehydriding rates of Mg [13, 28].

In this work, Mg-oxide and Mg-oxide-Ni hydrogen storage alloys, 90 wt% Mg + 10 wt% Fe_2O_3 (named Mg-10 Fe_2O_3), 90 wt% Mg + 5 wt% Fe_2O_3 + 5 wt% MnO (named Mg-5 Fe_2O_3 -5MnO), 90 wt% Mg + 3.3 wt% Fe_2O_3 + 3.3 wt% Ni + 3.3 wt% MnO (named Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO), and 90 wt% Mg + 5 wt% Fe_2O_3 + 5 wt% Ni (named Mg-5 Fe_2O_3 -5Ni), were prepared by milling under a hydrogen atmosphere (reaction-involved milling).

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The hydrogen storage properties of the prepared alloys were then investigated.

Experimental Details

The starting materials were pure Mg powder (particle size 100 ~ 297 μm or grit 50 ~ 150 mesh, purity 99%, Fluka), Fe_2O_3 (36 nm, prepared by spray conversion), MnO (88-250 μm , purity 99%, Aldrich), and Ni (~ 5 μm average, purity 99.9%, CERAC). The preparation by spray conversion is explained in detail in reference [29]. A mixture with the desired composition (total weight = 8 g) was mixed in a stainless steel container (with 105 hardened steel balls, total weight = 360 g) which was hermetically sealed. The sample-to-ball weight ratio was thus 1 : 45. All sample handling was performed in a glove box under Ar in order to prevent oxidation. The mill container was then filled with high purity hydrogen gas (≈ 12 bar). The disc revolution speed was 250 rpm and the milling time was 2 h.

The quantity of hydrogen absorbed or desorbed was measured as a function of time by a volumetric method with a Sievert's type hydriding and dehydriding apparatus [30]. X-ray diffraction (XRD) analysis was carried out for the as-milled powders and for the samples after hydriding-dehydriding cycling. The microstructures were observed by scanning electron microscopy (SEM).

Results

The quantity of the hydrogen absorbed by a sample, H_a , was expressed on the basis of the sample weight. Fig. 1 shows the H_a versus t curves of the first cycle at 593 K under 12 bar H_2 for Mg-10 Fe_2O_3 , Mg-5 Fe_2O_3 -5MnO, Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO, and Mg-5 Fe_2O_3 -5Ni. Mg-10 Fe_2O_3 has a relatively low initial hydriding rate, compared with those of the other samples, and then its hydriding rate decreases gradually. Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO has the highest initial hydriding rate, followed in order by Mg-5 Fe_2O_3 -5MnO, Mg-5 Fe_2O_3 -5Ni, and Mg-10 Fe_2O_3 . Mg-5 Fe_2O_3 -5Ni has the largest quantity of hydrogen absorbed for 60 min, followed in order by Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO, Mg-10 Fe_2O_3 , and Mg-5 Fe_2O_3 -5MnO. Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO absorbs 2.44 wt%H for 2.5 min, 3.19 wt%H for 10 min, 3.77 wt%H for 30 min, and 4.09 wt%H for 60 min. Mg-5 Fe_2O_3 -5Ni absorbs 1.75 wt%H for 2.5 min, 2.98 wt%H for 10 min, 3.82 wt%H for 30 min, and 4.24 wt%H for 60 min.

The H_a versus t curves after activation at 593 K under 12 bar H_2 for Mg-10 Fe_2O_3 , Mg-5 Fe_2O_3 -5MnO, Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO, and Mg-5 Fe_2O_3 -5Ni are shown in Fig. 2. Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO has the highest initial hydriding rate, followed in order by Mg-5 Fe_2O_3 -5Ni, Mg-10 Fe_2O_3 , and Mg-5 Fe_2O_3 -5MnO. Mg-10 Fe_2O_3 has the largest quantity of hydrogen absorbed for 60 min, followed in order by Mg-3.3 Fe_2O_3 -3.3Ni-

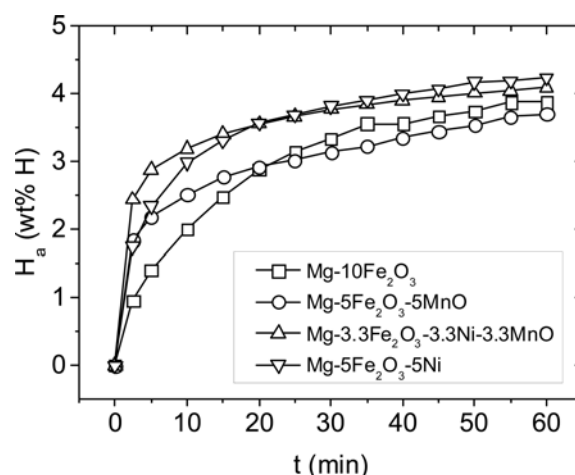


Fig. 1. H_a versus t curves of the first cycle at 593 K under 12 bar H_2 for Mg-10 Fe_2O_3 , Mg-5 Fe_2O_3 -5MnO, Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO, and Mg-5 Fe_2O_3 -5Ni.

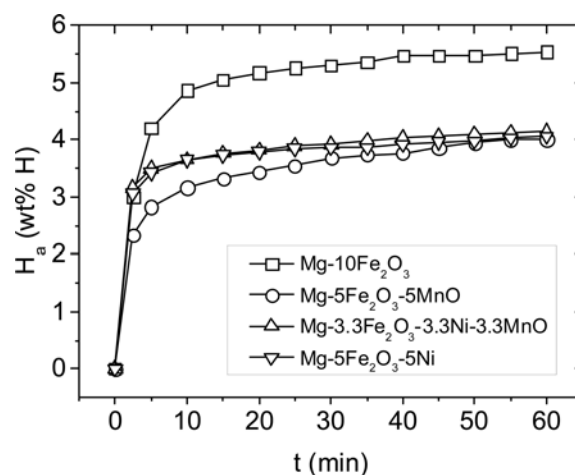


Fig. 2. H_a versus t curves after activation at 593 K under 12 bar H_2 for Mg-10 Fe_2O_3 , Mg-5 Fe_2O_3 -5MnO, Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO, and Mg-5 Fe_2O_3 -5Ni.

3.3MnO, Mg-5 Fe_2O_3 -5Ni, and Mg-5 Fe_2O_3 -5MnO. Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO and Mg-5 Fe_2O_3 -5Ni have similar initial hydriding rates and quantities of hydrogen absorbed for 60 min. Mg-10 Fe_2O_3 absorbs 2.99 wt%H for 2.5 min, 4.86 wt%H for 10 min, 5.30 wt%H for 30 min, and 5.54 wt%H for 60 min. Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO absorbs 3.15 wt%H for 2.5 min, 3.65 wt%H for 10 min, 3.91 wt%H for 30 min, and 4.15 wt%H for 60 min.

The quantity of the hydrogen released by a sample, H_d , was also expressed on the basis of the sample weight. Fig. 3 shows the H_d versus t curves after activation at 593 K under 1.0 bar H_2 for Mg-10 Fe_2O_3 , Mg-5 Fe_2O_3 -5MnO, Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO, and Mg-5 Fe_2O_3 -5Ni. Mg-5 Fe_2O_3 -5Ni has both the highest initial dehydriding rate and the largest quantity of hydrogen released for 60 min, followed in order by Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO, Mg-10 Fe_2O_3 , and Mg-5 Fe_2O_3 -5MnO. Mg-5 Fe_2O_3 -5Ni releases 1.03 wt%H for 10 min, 2.10 wt%H for 30 min, and 2.84 wt%H for 60 min. Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO releases 0.66 wt%H for 10 min,

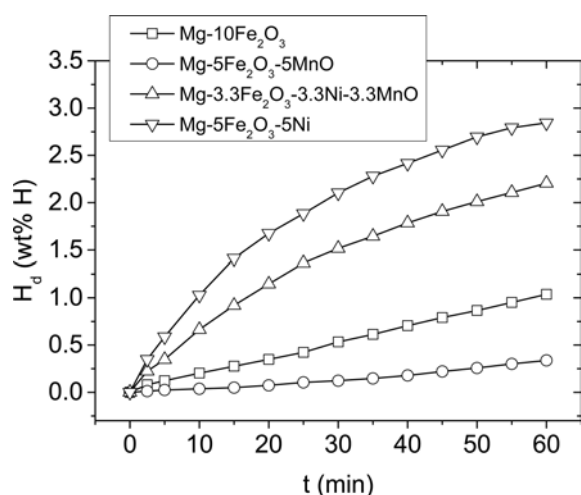


Fig. 3. H_d versus t curves after activation at 593 K under 1.0 bar H_2 for Mg-10Fe₂O₃, Mg-5Fe₂O₃-5MnO, Mg-3.3Fe₂O₃-3.3Ni-3.3MnO, and Mg-5Fe₂O₃-5Ni.

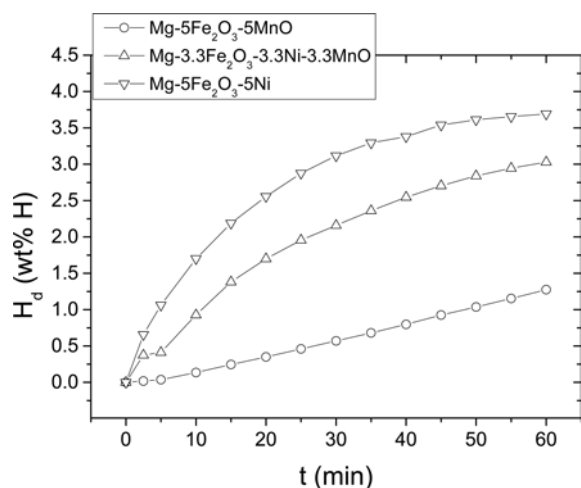


Fig. 4. H_d versus t curves after activation at 603 K under 1.0 bar H_2 for Mg-5Fe₂O₃-5MnO, Mg-3.3Fe₂O₃-3.3Ni-3.3MnO, and Mg-5Fe₂O₃-5Ni.

1.52 wt%H for 30 min, and 2.20 wt%H for 60 min.

The H_d versus t curves after activation at 603 K under 1.0 bar H_2 for Mg-5Fe₂O₃-5MnO, Mg-3.3Fe₂O₃-3.3Ni-3.3MnO, and Mg-5Fe₂O₃-5Ni are shown in Fig. 4. Mg-5Fe₂O₃-5Ni has the highest initial dehydrogenating rate and the largest quantity of hydrogen released for 60 min, followed in order by Mg-3.3Fe₂O₃-3.3Ni-3.3MnO, and Mg-5Fe₂O₃-5MnO. Mg-5Fe₂O₃-5Ni releases 1.70 wt%H for 10 min, 3.12 wt%H for 30 min, and 3.69 wt%H for 60 min. Mg-3.3Fe₂O₃-3.3Ni-3.3MnO releases 0.93 wt%H for 10 min, 2.16 wt%H for 30 min, and 3.03 wt%H for 60 min.

Among Mg-10Fe₂O₃, Mg-5Fe₂O₃-5MnO, Mg-3.3Fe₂O₃-3.3Ni-3.3MnO, and Mg-5Fe₂O₃-5Ni, Mg-5Fe₂O₃-5Ni had the largest quantities of the hydrogen absorbed for 60 min at the first cycle and released for 60 min after activation, the highest initial hydriding rate at the first cycle, and the highest initial dehydrogenating rate after

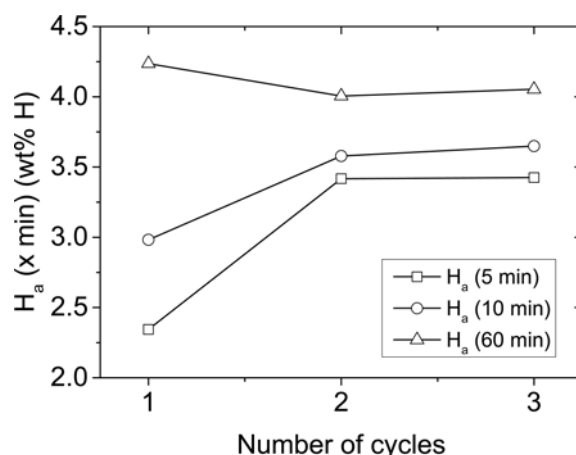


Fig. 5. Variations of H_a (5 min), H_a (10 min), and H_a (60 min) at 593 K under 12 bar H_2 with the number of cycles, n , for Mg-5Fe₂O₃-5Ni.

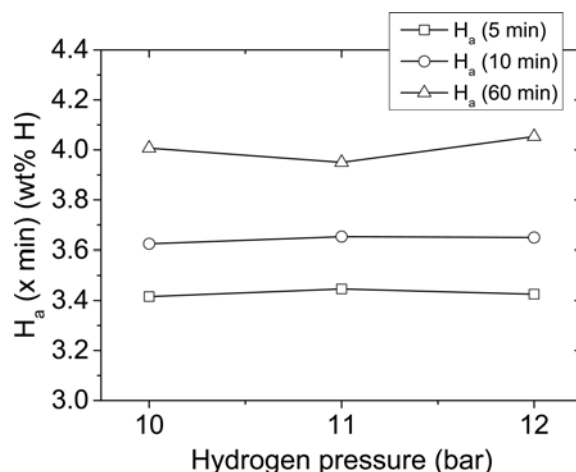


Fig. 6. Variations of H_a (5 min), H_a (10 min), and H_a (60 min) at 593 K with hydrogen pressure for Mg-5Fe₂O₃-5Ni.

activation. The hydrogen storage properties of the Mg-5Fe₂O₃-5Ni sample were investigated in more detail.

The quantity of the hydrogen absorbed for x min is expressed by H_a (x min). Fig. 5 shows the variations of H_a (5 min), H_a (10 min), and H_a (60 min) at 593 K under 12 bar H_2 with the number of cycles, n , for Mg-5Fe₂O₃-5Ni. H_a (5 min) and H_a (10 min) increase rapidly from $n = 1$ to $n = 2$ and increase very slowly from $n = 2$ to $n = 3$. H_a (60 min) decreases rapidly from $n = 1$ to $n = 2$ and remains almost constant from $n = 2$ to $n = 3$. At $n = 1$, Mg-5Fe₂O₃-5Ni absorbs 2.34 wt%H for 5 min, 2.98 wt%H for 10 min, and 4.24 wt%H for 60 min. At $n = 3$, Mg-5Fe₂O₃-5Ni absorbs 3.43 wt%H for 5 min, 3.65 wt%H for 10 min, and 4.05 wt%H for 60 min.

The variations of H_a (5 min), H_a (10 min), and H_a (60 min) at 593 K with hydrogen pressure from 10 to 12 bar H_2 for Mg-5Fe₂O₃-5Ni are given in Fig. 6. H_a (5 min), H_a (10 min), and H_a (60 min) increase very slightly with the hydrogen pressure, indicating that the influence of hydrogen pressure on the hydriding rate is

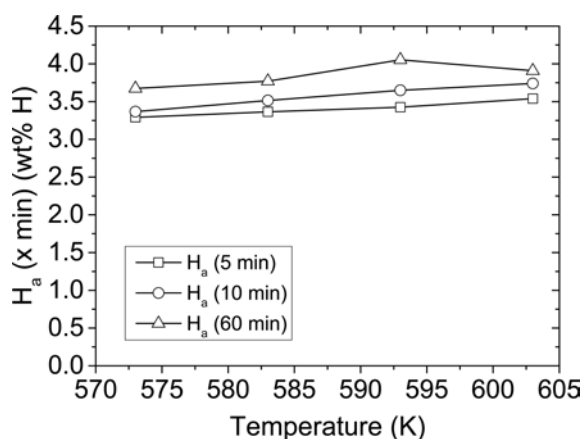


Fig. 7. Variations of H_a (5 min), H_a (10 min), and H_a (60 min) under 12 bar H_2 with temperature for Mg-5Fe₂O₃-5Ni.

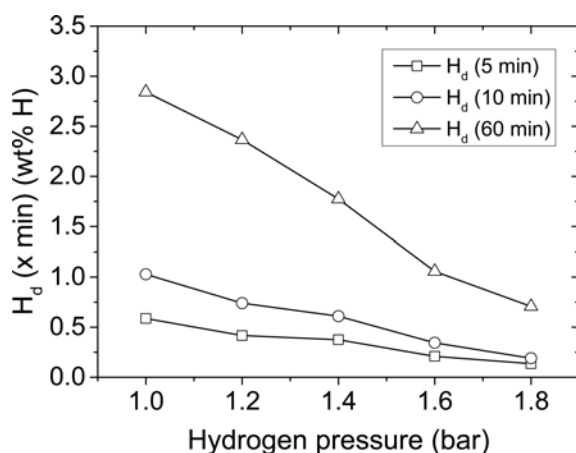


Fig. 8. Variations of H_d (5 min), H_d (10 min), and H_d (60 min) at 593 K with hydrogen pressure for Mg-5Fe₂O₃-5Ni.

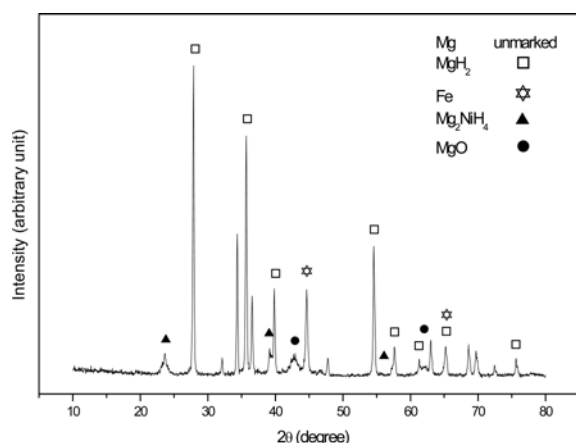
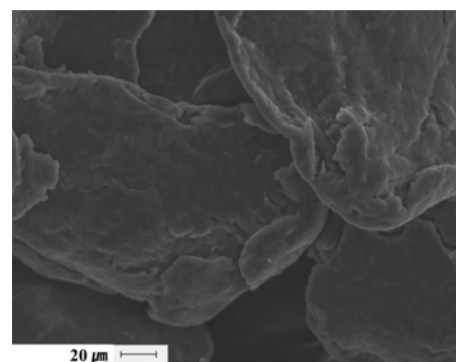


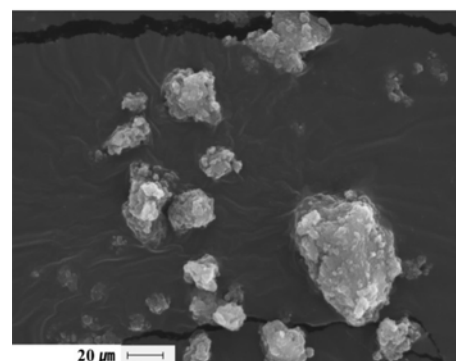
Fig. 9. XRD pattern of the Mg-10Fe₂O₃-5Ni alloy hydrided after 12 hydriding-dehydriding cycles.

very weak. Under 10 bar H_2 , Mg-5Fe₂O₃-5Ni absorbs 3.42 wt%H for 5 min, 3.62 wt%H for 10 min, and 4.01 wt%H for 60 min. Under 12 bar H_2 , Mg-5Fe₂O₃-5Ni absorbs 3.43 wt%H for 5 min, 3.65 wt%H for 10 min, and 4.05 wt%H for 60 min.

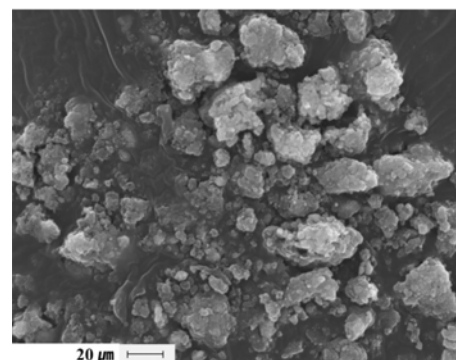
The variations of H_a (5 min), H_a (10 min), and H_a



(a)



(b)



(c)

Fig. 10. Microstructures observed by SEM of (a) Mg particles, (b) Mg-6Fe₂O₃-14Ni after reaction-involved milling, and (c) Mg-6Fe₂O₃-14Ni after 4 hydriding-dehydriding cycles.

(60 min) under 12 bar H_2 with temperature for Mg-5Fe₂O₃-5Ni are shown in Fig. 7. H_a (5 min), H_a (10 min), and H_a (60 min) increase slowly as the temperature increases. At 573 K, Mg-5Fe₂O₃-5Ni absorbs 3.29 wt%H for 5 min, 3.37 wt%H for 10 min, and 3.67 wt%H for 60 min. At 603 K, Mg-5Fe₂O₃-5Ni absorbs 3.54 wt%H for 5 min, 3.74 wt%H for 10 min, and 3.91 wt%H for 60 min. This shows that the hydriding rate increases slowly as the temperature increases from 573 to 603 K.

The quantity of the hydrogen released for x min is expressed by H_d (xs min). Fig. 8 shows the variations of H_d (5 min), H_d (10 min), and H_d (60 min) at 593 K with hydrogen pressure from 1.0 to 1.8 bar H_2 for Mg-5Fe₂O₃-5Ni. H_d (5 min) and H_d (10 min) decrease

slowly as the hydrogen pressure increases. H_d (60 min) decrease rapidly as the hydrogen pressure increases. Under 1.0 bar H_2 , Mg-5 Fe_2O_3 -5Ni releases 0.59 wt%H for 5 min, 1.03 wt%H for 10 min, and 2.84 wt%H for 60 min. Under 1.8 bar H_2 , Mg-5 Fe_2O_3 -5Ni releases 0.14 wt%H for 5 min, 0.19 wt%H for 10 min, and 0.71 wt%H for 60 min. This shows that the hydrogen pressure influences strongly the dehydriding rate.

Fig. 9 shows the XRD pattern of the Mg-10 Fe_2O_3 -5Ni alloy hydrided after 12 hydriding-dehydriding cycles. The Mg-10 Fe_2O_3 -5Ni sample had the composition of 85 wt% Mg + 10 wt% Fe_2O_3 + 5 wt% Ni. It contains MgH_2 , Mg, Fe, Mg_2NiH_4 , and MgO. This shows that Fe_2O_3 is reduced, Mg_2Ni is formed by the reaction of Mg with Ni during the hydriding-dehydriding cycling and Mg_2NiH_4 is formed during hydriding, and a small part of Mg is oxidized. The chemical affinity of Mg for oxygen is larger than that of Fe, and thus Fe_2O_3 is reduced to Fe and MgO is formed.

The microstructures observed by SEM of Mg particles, and Mg-6 Fe_2O_3 -14Ni both after reaction-involved milling and after 4 hydriding-dehydriding cycles are exhibited in Fig. 10. The Mg-6 Fe_2O_3 -14Ni sample had the composition of 80 wt% Mg + 6 wt% Fe_2O_3 + 14 wt% Ni. Mg particles are quite large and of spherical form, and have smooth surfaces with small numbers of cracks and defects. The Mg-6 Fe_2O_3 -14Ni after reaction-involved milling has small and large particles with more cracks than the Mg particles, even though this sample has particles with quite flat surfaces. Its particles are agglomerated. the Mg-6 Fe_2O_3 -14Ni after 4 hydriding-dehydriding cycles is not homogeneous, and the particles of this sample are smaller than those of the Mg-5 Fe_2O_3 -5Ni after reaction-involved milling. The particles of the Mg-6 Fe_2O_3 -14Ni after 4 hydriding-dehydriding cycles have minute particles on their surfaces.

The H_a versus t curves at 593 K under 12 bar H_2 and H_d versus t curves at 593 K under 1.0 bar H_2 at $n = 1$ -3 for Mg were examined. Mg has very low hydriding rates and does not release hydrogen. The initial hydriding rate and the quantity of hydrogen absorbed for 60 min decreased as the number of cycles increased. This is believed to be due to the coalescence of particles because the hydriding-dehydriding cycling was performed at a relatively high temperature of 593 K. At $n = 1$, Mg absorbed 0.04 wt%H for 2.5 min, 0.09 wt%H for 10 min, 0.29 wt%H for 30 min, and 0.45 wt%H for 60 min. At $n = 3$, Mg absorbed 0.01 wt%H for 2.5 min, 0.03 wt%H for 10 min, 0.11 wt%H for 30 min, and 0.22 wt%H for 60 min.

Discussion

Fig. 1 shows that Mg-10 Fe_2O_3 , Mg-5 Fe_2O_3 -5MnO, Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO, and Mg-5 Fe_2O_3 -5Ni have quite high initial hydriding rates and quite large quantities

of hydrogen absorbed for 60 min at the first cycle, compared with Mg. This shows that reaction-involved milling with Fe_2O_3 , Ni, and/or MnO increases the initial hydriding rate and the quantity of hydrogen absorbed for 60 min.

Fig. 2 shows that the hydriding-dehydriding cycling for activation of Mg-10 Fe_2O_3 , Mg-5 Fe_2O_3 -5MnO, Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO, and Mg-5 Fe_2O_3 -5Ni increases the initial hydriding rate and the quantity of hydrogen absorbed for 60 min. The effects of the hydriding-dehydriding cycling are strong when Fe_2O_3 is added. During the hydriding reaction, the hydride-forming material expands, and during the releasing reaction, it contracts. The expansion and contraction of the hydride-forming material with the hydriding-dehydriding cycling are considered to form defects, create clean surfaces, and make the particles smaller.

The results that Mg-5 Fe_2O_3 -5Ni and Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO have quite high initial dehydriding rates and quite large quantities of hydrogen released for 60 min after activation, compared with Mg, are shown in Fig. 3. This shows that reaction-involved milling with Fe_2O_3 , Ni, and/or MnO increases the initial dehydriding rate and the quantity of hydrogen released for 60 min.

Fig. 4 shows that Mg-5 Fe_2O_3 -5Ni, Mg-3.3 Fe_2O_3 -3.3Ni-3.3MnO, and Mg-5 Fe_2O_3 -5MnO have higher initial dehydriding rates and larger quantities of hydrogen released for 60 min at 603 K, compared with those at 593 K (shown in Fig. 3). This is believed to be due to the larger difference between the equilibrium plateau pressure and the applied hydrogen pressure (1.0 bar H_2) at 603 K than at 593 K, as well as the temperature effect for dehydriding reaction.

It is shown in Fig. 5 that H_a (5 min) and H_a (10 min) increase rapidly from $n = 1$ to $n = 2$ and increase very slowly from $n = 2$ to $n = 3$. H_a (60 min) decreases rapidly from $n = 1$ to $n = 2$ and remains almost constant from $n = 2$ to $n = 3$. The rapid increase in H_a (5 min) and H_a (10 min) and the rapid decrease in H_a (60 min) from $n = 1$ to $n = 2$ shows that the effects of the hydriding-dehydriding cycling are strong from $n = 1$ to $n = 2$. The general increase in H_a (5 min) and H_a (10 min) and the general decrease in H_a (60 min) suggest that in the outside of the agglomerates particles become finer while in the inside of the agglomerates particles coalesce due to the annealing effect caused by the hydriding-dehydriding cycling at the relatively high temperature.

The variations of H_a (5 min), H_a (10 min), and H_a (60 min) at 593 K with hydrogen pressure from 10 to 12 bar H_2 for Mg-5 Fe_2O_3 -5Ni given in Fig. 6 indicate that the influence of hydrogen pressure from 10 to 12 bar H_2 on the hydriding rate is very weak. It is considered that the influence of hydrogen pressure would be stronger if the hydrogen pressures of a wide range were applied.

The variations of H_a (5 min), H_a (10 min), and H_a

(60 min) under 12 bar H_2 with temperature for Mg-5Fe₂O₃-5Ni presented in Fig. 7 show that the influence of the temperature increase from 573 to 603 K on the hydriding rate is weak, but the hydriding rate increases as the temperature increases. The increase in temperature decreases the driving force for the hydriding reaction, which is related to the gap between the exerted hydrogen pressure (12 bar H_2 in this work) and the equilibrium plateau pressure at a given temperature, as well as accelerates the thermally activated process like the diffusion of hydrogen atoms through the thickening hydride layer. By the way, when the temperature increases from 573 K to 603 K, the influence of the acceleration of the thermally activated process is believed to prevail over the influence of the reduction in the driving force for the hydriding reaction, leading to an increase in the hydriding rate.

The results of the variations of H_d (5 min), H_d (10 min), and H_d (60 min) at 593 K with hydrogen pressure from 1.0 to 1.8 bar H_2 for Mg-5Fe₂O₃-5Ni given in Fig. 8 show that the hydrogen pressure strongly influences the dehydriding rate.

The XRD pattern of the Mg-10Fe₂O₃-5Ni alloy hydrided after 12 hydriding-dehydriding cycles exhibited in Fig. 9 shows that the sample contains MgH₂, Mg, Fe, Mg₂NiH₄, and MgO. This shows that Fe₂O₃ is reduced, Mg₂Ni is formed by the reaction of Mg with Ni during hydriding-dehydriding cycling and Mg₂NiH₄ is formed during hydriding, and a small part of Mg is oxidized. The values of the standard free energy change for the reactions $4/3Fe + O_2 \rightarrow 2/3 Fe_2O_3$ and $2Mg + O_2 \rightarrow 2MgO$ at 593 K were calculated to be -439,960 and -1,080,130 J/mol of O₂, respectively, using data in references [31, 32]. This indicates that the chemical affinity of Mg for oxygen is much larger than that of Fe. Thus, Fe₂O₃ will be reduced to Fe and Mg will be oxidized to MgO, because the chemical affinity of Mg for oxygen is much larger than that of Fe.

The microstructures observed by SEM of Mg particles, and Mg-6Fe₂O₃-14Ni both after reaction-involved milling and after 4 hydriding-dehydriding cycles exhibited in Fig. 10 show that Mg particles are quite large and of spherical form, and have smooth surfaces with small numbers of cracks and defects whereas the Mg-6Fe₂O₃-14Ni after reaction-involved milling has small and large particles, with more cracks than the Mg particles even though this sample has particles with quite smooth surfaces. The particle sizes of the Mg-6Fe₂O₃-14Ni after 4 hydriding-dehydriding cycles are smaller than those of the as-milled Mg-6Fe₂O₃-14Ni.

The reaction-involved milling of Mg with Fe₂O₃, Ni, and/or MnO produces defects on the surface and in the inside of the Mg particles. These produced defects and the additives themselves can act as active nucleation sites. The reaction-involved milling produces clean surfaces, leading to the increase in reactivity with hydrogen. It also

reduces the particle size of Mg, which decreases the diffusion distances of the hydrogen atoms. The reaction-involved milling of Mg with Fe₂O₃, Ni, and/or MnO is thus considered to increase the hydriding and dehydriding rates by making easy the nuclei formations of magnesium hydride and Mg-H solid solution, by increasing reactivity with hydrogen, and by shortening the diffusion distances of the hydrogen atoms. The hydriding-dehydriding cycling of the as-milled Ni-containing samples leads to the formation of the Mg₂Ni phase [33-37]. Mg₂Ni has higher storing and releasing rates than Mg [37-40]. Hydriding-dehydriding cycling makes the Mg and Mg₂Ni phase contract and expand, creating defects on the surface of the particles, making clean surfaces, and reducing the particle size. On the other hand, maintaining the mixture at a relatively high temperature (e. g. 593 K) during hydriding-dehydriding cycling causes the particles to coalesce by sintering, leading to the growth of particle size. This will bring about a decrease in the hydriding and dehydriding rates.

Conclusions

Mg-oxide and Mg-oxide-Ni hydrogen storage alloys, Mg-10Fe₂O₃, Mg-5Fe₂O₃-5MnO, Mg-3.3Fe₂O₃-3.3Ni-3.3MnO, and Mg-5Fe₂O₃-5Ni, were prepared by mechanical milling under H_2 (reaction-involved milling). The reaction-involved milling with Fe₂O₃, Ni, and/or MnO and the hydriding-dehydriding cycling increased the initial hydriding rate and the quantity of hydrogen absorbed for 60 min. The reaction-involved milling with Fe₂O₃, Ni, and/or MnO increased the initial dehydriding rate and the quantity of hydrogen released for 60 min. Among these samples, Mg-5Fe₂O₃-5Ni had the largest quantities of the hydrogen absorbed for 60 min at the first cycle and released for 60 min after activation, the highest initial hydriding rate at the first cycle, and the highest initial dehydriding rate after activation. The reaction-involved milling of Mg with Fe₂O₃, Ni, and/or MnO is considered to increase the hydriding and dehydriding rates by making easy the nuclei formations of magnesium hydride and Mg-H solid solution, by increasing reactivity with hydrogen, and by shortening the diffusion distances of the hydrogen atoms. The hydriding-dehydriding cycling of the as-milled Ni-containing samples led to the formation of the Mg₂Ni phase. Hydriding-dehydriding cycling makes the Mg and Mg₂Ni phase contract and expand, creating defects on the surface of the particles, making clean surfaces, and reducing the particle size.

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