Addition of oxides Fe$_2$O$_3$ and/or MnO to improve hydrogen storage properties of magnesium by reaction-involved milling

Myoung Youp Song$^a$, Sung Nam Kwon$^b$ and Hye Ryoung Park$^{c,*}$

$^a$Division of Advanced Materials Engineering, Research Center of Advanced Materials Development, Engineering Research Institute, Chonbuk National University, 664-14 1ga Deogjindong Deogjingu Jeonju, 54896, Korea

$^b$Professional Graduate School of Flexible and Printable Electronics, Department of Flexible and Printable Electronics, Chonbuk National University, 567 Baekje-daero Deokjin-gu Jeonju, 54896, Korea

$^c$School of Applied Chemical Engineering, Chonnam National University, 77 Yongbong-ro Buk-gu Gwangju, 61186, Korea

Mg-oxide and Mg-oxide-Ni hydrogen storage alloys, 90 wt% Mg + 10 wt% Fe$_2$O$_3$ (named Mg-10Fe$_2$O$_3$), 90 wt% Mg + 5 wt% Fe$_2$O$_3$ + 5 wt% MnO (Mg-5Fe$_2$O$_3$-5MnO), 90 wt% Mg + 3.3 wt% Fe$_2$O$_3$ + 3.3 wt% Ni + 3.3 wt% MnO (Mg-3.3Fe$_2$O$_3$-3.3Ni-3.3MnO), and 90 wt% Mg + 5 wt% Fe$_2$O$_3$ + 5 wt% Ni (Mg-5Fe$_2$O$_3$-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-5Fe$_2$O$_3$-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-5Fe$_2$O$_3$-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-5Fe$_2$O$_3$-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$_2$O$_3$ 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: H$_2$-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$_2$O$_5$, VN or VC [17], Cr$_2$O$_3$ [18], Nb$_2$O$_5$ [19-22], MgO [13], Cr$_2$O$_3$, Al$_2$O$_3$ and CeO$_2$ [24], CeO$_2$ [25], and Y$_2$O$_3$ [26].

Among the 90 wt% Mg + 10 wt% oxide samples (oxide = Fe$_2$O$_3$ purchased, Fe$_2$O$_3$ prepared by spray conversion, MnO purchased, SiO$_2$ prepared by spray conversion and Cr$_2$O$_3$ 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$_2$O$_3$ prepared by spray conversion had the highest hydriding rate, followed by the 90 wt% Mg + 10 wt% Fe$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ (named Mg-10Fe$_2$O$_3$), 90 wt% Mg + 5 wt% Fe$_2$O$_3$ + 5 wt% MnO (named Mg-5Fe$_2$O$_3$-5MnO), 90 wt% Mg + 3.3 wt% Fe$_2$O$_3$ + 3.3 wt% Ni + 3.3 wt% MnO (named Mg-3.3Fe$_2$O$_3$-3.3Ni-3.3MnO), and 90 wt% Mg + 5 wt% Fe$_2$O$_3$ + 5 wt% Ni (named Mg-5Fe$_2$O$_3$-5Ni), were prepared by milling under a hydrogen atmosphere (reaction-involved milling).
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), Fe₂O₃ (36 nm, prepared by spray conversion), MnO (88-250 μm, purity 99.8%, 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 sealed. The sample-to-ball weight ratio was thus 1 : 45. All steel balls, total weight = 360 g) which was hermetically enclosed in a stainless steel container (with 105 hardened steel balls, total weight of 360 g), and 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, H₂, was expressed on the basis of the sample weight. Fig. 1 shows the H₂ versus t curves of the first cycle at 593 K under 12 bar H₂ for Mg-10Fe₂O₃, Mg-5Fe₂O₃-5Ni, Mg-3.3Fe₂O₃-3.3Ni-3.3MnO, and Mg-5Fe₂O₃-5Ni. Mg-10Fe₂O₃ has the highest initial hydriding rate, followed in order by Mg-5Fe₂O₃-5Ni, Mg-3.3Fe₂O₃-3.3Ni-3.3MnO, and Mg-5Fe₂O₃-5Ni.

Fig. 2 shows the H₂ versus t curves after activation at 593 K under 12 bar H₂ for Mg-10Fe₂O₃, Mg-5Fe₂O₃-5MnO, Mg-3.3Fe₂O₃-3.3Ni-3.3MnO, and Mg-5Fe₂O₃-5Ni. Mg-3.3Fe₂O₃-3.3Ni-3.3MnO, Mg-5Fe₂O₃-5Ni, and Mg-5Fe₂O₃-5MnO. Mg-3.3Fe₂O₃-3.3Ni-3.3MnO and Mg-5Fe₂O₃-5Ni have similar initial hydriding rates and quantities of hydrogen absorbed for 60 min. Mg-10Fe₂O₃ 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-3.3Fe₂O₃-3.3Ni-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, H₂, was also expressed on the basis of the sample weight. Fig. 3 shows the H₂ versus t curves after activation at 593 K under 1.0 bar H₂ for Mg-10Fe₂O₃, Mg-5Fe₂O₃-5MnO, Mg-3.3Fe₂O₃-3.3Ni-3.3MnO, and Mg-5Fe₂O₃-5Ni. Mg-5Fe₂O₃-5Ni has both the highest initial dehydriding rate and the largest quantity of hydrogen released for 60 min, followed in order by Mg-3.3Fe₂O₃-3.3Ni-3.3MnO, Mg-10Fe₂O₃, and Mg-5Fe₂O₃-5MnO. Mg-5Fe₂O₃-5Ni releases 1.03 wt%H for 10 min, 2.10 wt%H for 30 min, and 2.84 wt%H for 60 min. Mg-3.3Fe₂O₃-3.3Ni-3.3MnO releases 0.66 wt%H for 10 min,
Addition of oxides $\text{Fe}_2\text{O}_3$ and/or $\text{MnO}$ to improve hydrogen storage properties of magnesium by reaction-involved milling

853

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 $\text{Mg-5Fe}_2\text{O}_3-5\text{MnO}$, $\text{Mg-3.3Fe}_2\text{O}_3-3.3\text{Ni-3.3MnO}$, and $\text{Mg-5Fe}_2\text{O}_3-5\text{Ni}$ are shown in Fig. 4. $\text{Mg-5Fe}_2\text{O}_3-5\text{Ni}$ has the highest initial dehydriding rate and the largest quantity of hydrogen released for 60 min, followed in order by $\text{Mg-3.3Fe}_2\text{O}_3-3.3\text{Ni-3.3MnO}$, and $\text{Mg-5Fe}_2\text{O}_3-5\text{Ni}$.

Among $\text{Mg-10Fe}_2\text{O}_3$, $\text{Mg-5Fe}_2\text{O}_3-5\text{MnO}$, $\text{Mg-3.3Fe}_2\text{O}_3-3.3\text{Ni-3.3MnO}$, and $\text{Mg-5Fe}_2\text{O}_3-5\text{Ni}$, 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 hydrogen storage properties of the $\text{Mg-5Fe}_2\text{O}_3-5\text{Ni}$ sample were investigated in more detail.

The quantity of the hydrogen absorbed for $x$ min is expressed by $H_a(x \text{ min})$. Fig. 5 shows the variations of $H_a(5 \text{ min})$, $H_a(10 \text{ min})$, and $H_a(60 \text{ min})$ at 593 K with the number of cycles, $n$, for $\text{Mg-5Fe}_2\text{O}_3-5\text{Ni}$.

The variations of $H_a(5 \text{ min})$, $H_a(10 \text{ min})$, and $H_a(60 \text{ min})$ at 593 K with hydrogen pressure for $\text{Mg-5Fe}_2\text{O}_3-5\text{Ni}$ are given in Fig. 6. $H_a(5 \text{ min})$, $H_a(10 \text{ min})$, and $H_a(60 \text{ min})$ increase very slightly with the hydrogen pressure, indicating that the influence of hydrogen pressure on the hydriding rate is
very weak. Under 10 bar H₂, 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 H₂, 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 Hₐ (5 min), Hₐ (10 min), and Hₐ (60 min) under 12 bar H₂ with temperature for Mg-5Fe₂O₃-5Ni 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 hydrogen released for x min is expressed by Hₕ (x min). Fig. 8 shows the variations of Hₕ (5 min), Hₕ (10 min), and Hₕ (60 min) at 593 K with hydrogen pressure from 1.0 to 1.8 bar H₂ for Mg-5Fe₂O₃-5Ni. Hₕ (5 min) and Hₕ (10 min) decrease...
slowly as the hydrogen pressure increases. $H_2$ (60 min) decreases rapidly as the hydrogen pressure increases. Under 1.0 bar $H_2$, Mg-5Fe$_2$O$_3$-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-5Fe$_2$O$_3$-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-10Fe$_2$O$_3$-5Ni alloy hydrided after 12 hydriding-dehydriding cycles. The Mg-10Fe$_2$O$_3$-5Ni sample had the composition of 85 wt% Mg + 10 wt% Fe$_2$O$_3$ + 5 wt% Ni. It contains MgH$_2$, Mg, Fe, Mg$_2$NiH$_4$, and MgO. This shows that Fe$_2$O$_3$ is reduced, Mg$_2$Ni is formed by the reaction of Mg with Ni during the hydriding-dehydriding cycling and Mg$_2$NiH$_4$ 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$_2$O$_3$ is reduced to Fe and MgO is formed.

The microstructures observed by SEM of Mg particles, and Mg-6Fe$_2$O$_3$-14Ni both after reaction-involved milling and after 4 hydriding-dehydriding cycles are exhibited in Fig. 10. The Mg-6Fe$_2$O$_3$-14Ni sample had the composition of 80 wt% Mg + 6 wt% Fe$_2$O$_3$ + 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-6Fe$_2$O$_3$-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-6Fe$_2$O$_3$-14Ni after 4 hydriding-dehydriding cycles is not homogeneous, and the particles of this sample are smaller than those of the Mg-5Fe$_2$O$_3$-5Ni after reaction-involved milling. The particles of the Mg-6Fe$_2$O$_3$-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-10Fe$_2$O$_3$, Mg-5Fe$_2$O$_3$-5MnO, Mg-3.3Fe$_2$O$_3$-3Ni-3.3MnO, and Mg-5Fe$_2$O$_3$-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$_2$O$_3$, 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-10Fe$_2$O$_3$, Mg-5Fe$_2$O$_3$-5MnO, Mg-3.3Fe$_2$O$_3$-3Ni-3.3MnO, and Mg-5Fe$_2$O$_3$-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$_2$O$_3$ 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-5Fe$_2$O$_3$-5Ni and Mg-3.3Fe$_2$O$_3$-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$_2$O$_3$, Ni, and/or MnO increases the initial dehydriding rate and the quantity of hydrogen released for 60 min.

Fig. 4 shows that Mg-5Fe$_2$O$_3$-5Ni, Mg-3.3Fe$_2$O$_3$-3Ni-3.3MnO, and Mg-5Fe$_2$O$_3$-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 $H_d$ (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 $H_d$ (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 $H_d$ (10 min) and the general decrease in $H_a$ (60 min) suggest that in the outside 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), $H_d$ (10 min), and $H_a$ (60 min) at 593 K with hydrogen pressure from 10 to 12 bar $H_2$ for Mg-5Fe$_2$O$_3$-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), $H_d$ (10 min), and $H_a$ (60 min) at 593 K with hydrogen pressure from 10 to 12 bar $H_2$ for Mg-5Fe$_2$O$_3$-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), $H_d$ (10 min), and $H_a$ (60 min) at 593 K with hydrogen pressure from 10 to 12 bar $H_2$ for Mg-5Fe$_2$O$_3$-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), $H_d$ (10 min), and $H_a$ (60 min) at 593 K with hydrogen pressure from 10 to 12 bar $H_2$ for Mg-5Fe$_2$O$_3$-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), $H_d$ (10 min), and $H_a$ (60 min) at 593 K with hydrogen pressure from 10 to 12 bar $H_2$ for Mg-5Fe$_2$O$_3$-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.
(60 min) under 12 bar \( H_2 \) with temperature for Mg-5FeO\(_2\)-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 \( H_2 \) (5 min), \( H_2 \) (10 min), and \( H_2 \) (60 min) at 593 K with hydrogen pressure from 1.0 to 1.8 bar \( H_2 \) for Mg-5FeO\(_2\)-5Ni given in Fig. 8 show that the hydrogen pressure strongly influences the dehydriding rate.

The XRD pattern of the Mg-10FeO\(_2\)-5Ni alloy hydrided after 12 hydriding-dehydriding cycles exhibited in Fig. 9 shows that the sample contains MgH\(_2\), Mg, Fe, Mg\(_2\)NiH\(_4\), and MgO. This shows that FeO\(_2\) is reduced, Mg\(_2\)Ni is formed by the reaction of Mg with Ni during hydriding-dehydriding cycling and Mg\(_2\)NiH\(_4\) is formed during hydriding, and a small part of Mg is oxidized. The values of the standard free energy change for the reactions \( \frac{4}{3}\text{Fe} + \text{O}_2 \rightarrow \frac{2}{3} \text{Fe}_2\text{O}_3 \) and \( 2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO} \) at 593 K were calculated to be -439,960 and -1,080,130 J/mol of \( \text{O}_2 \), 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, FeO\(_2\) 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-6FeO\(_2\)-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-6FeO\(_2\)-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-6FeO\(_2\)-14Ni after 4 hydriding-dehydriding cycles are smaller than those of the as-milled Mg-6FeO\(_2\)-14Ni.

The reaction-involved milling of Mg with FeO\(_2\), 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 FeO\(_2\), 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 Mg\(_2\)Ni phase [33-37], Mg\(_2\)Ni has higher storing and releasing rates than Mg [37-40]. Hydriding-dehydriding cycling makes the Mg and Mg\(_2\)Ni 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-10FeO\(_2\), Mg-5FeO\(_2\)-5MnO, Mg-3.3FeO\(_2\)-3.3NiO, and Mg-5FeO\(_2\)-5Ni, were prepared by mechanical milling under \( H_2 \) (reaction-involved milling). The reaction-involved milling with FeO\(_2\), 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 FeO\(_2\), Ni, and/or MnO increased the initial dehydriding rate and the quantity of hydrogen released for 60 min. Among these samples, Mg-5FeO\(_2\)-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 FeO\(_2\), 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 Mg\(_2\)Ni phase. Hydriding-dehydriding cycling makes the Mg and Mg\(_2\)Ni phase contract and expand, creating defects on the surface of the particles, making clean surfaces, and reducing the particle size.

**Acknowledgments**

This research was performed for the Hydrogen Energy R&D Center, one of the 21st Century Frontier R&D Programs, funded by the Ministry of Science and Technology of Republic of Korea. This research was
Addition of oxides $\text{Fe}_2\text{O}_3$ and/or $\text{MnO}$ to improve hydrogen storage properties of magnesium by reaction-involved milling

supported by “Research Base Construction Fund Support Program” funded by Chonbuk National University in 2015 (M.Y. Song). The authors appreciate Young Jun Kwak’s helpful assistance in experiments.

References