Enhancement of the Hydrogen-Storage Characteristics of Mg by Adding Mg$_2$Ni and Ni to MgH$_2$ via High Energy Ball Milling in Hydrogen Atmosphere

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Abstract: In this work, Mg$_2$Ni and Ni were added to MgH$_2$ in order to improve the hydrogen-storage properties of Mg. A 94 wt% MgH$_2$+5 wt% Mg$_2$Ni+1wt% Ni (named 94MgH$_2$+5Mg$_2$Ni+1Ni) sample was prepared by milling in a hydrogen atmosphere in a planetary ball mill for 5 h. The Mg$_2$Ni was hydrided during milling in a hydrogen atmosphere. The 94MgH$_2$+5Mg$_2$Ni+1Ni had an effective hydrogen-storage capacity (the quantity of hydrogen absorbed for 60 min) of near 5 wt%. At n=1, the sample released 0.18 wt% for 2 min, 2.14 wt% for 5 min, 4.65 wt% for 10 min, and 5.46 wt% for 60 min at 648 K. The reactive mechanical grinding of MgH$_2$ with Mg$_2$Ni and Ni is believed to facilitate nucleation (by creating defects, which serve as active sites for nucleation, on the surfaces and inside the Mg particles), increase reactivity with hydrogen (by making clean surfaces), and decrease the diffusion distances of hydrogen atoms (by reducing the particle size of Mg).

Keywords: hydrogen absorbing materials, mechanical milling, hydrogen, X-ray diffraction, Mg$_2$Ni and Ni addition

1. INTRODUCTION

Magnesium has drawn attention for its many advantages as a hydrogen storage material, including a high volumetric hydrogen-storage capacity (7.6 wt%), relatively low price, and ample reserves in the Earth’s crust. Magnesium hydride is expected to be used as a starting material for the preparation of Mg-based hydrogen-storage materials with an additive element; as a hydrogen-storage material that releases hydrogen by reaction with water; as a hydrogen-supply material for fuel cells; and as an anode material for lithium ion batteries [1].

However, in spite of these advantages, magnesium’s hydriding and dehydriding rates are very low [2]. Mg$_2$Ni is known to have higher hydriding and dehydriding rates than Mg [3-8]. The addition of Mg$_2$Ni is believed to increase the hydriding and dehydriding rates of Mg. Reilly et al. [3] and Akiba et al. [4] improved the reaction kinetics of Mg with H$_2$ by preparing Mg-Ni alloys. Song et al. [5-8] increased the hydriding and dehydriding rates of Mg by the mechanical alloying of Mg with Ni under Ar atmosphere. Cermak et al. [9] investigated the catalytic effects of Mg$_2$Ni and Mg$_2$NiH$_4$ on the hydrogen desorption kinetics of magnesium hydride (MgH$_2$) by preparing samples with a eutectic composition of the Mg-Mg$_2$Ni binary alloy. The components in the samples were mechanically contacted by grinding the mixture in a mortar. Zaluska et al. [10] reported that ball-milling of the mixtures of MgH$_2$ and Mg$_2$NiH$_4$ resulted in a synergetic effect, decreasing the desorption temperature and increasing the absorption / desorption kinetics of the mixture. We selected Mg$_2$Ni as a compound additive.

Bobet et al. [11] improved the hydrogen-storage properties of both magnesium and Mg+10 wt% Co, Ni, or Fe mixtures by mechanical grinding under H$_2$ (reactive mechanical grinding) for a short time (2 h). Zhenglong et al. [12] increased hydriding and
dehydriding rates by adding nano-sized Ni particles in a planetary ball mill. Niaz et al. [13] synthesized a Mg-Ni alloy by the thermal decomposition of bipyridyl complexes of Mg and Ni metals at 773 K for 24 h under dry argon gas atmosphere. The prepared alloy was nanostructured with a particle size in the range of 40–50 nm. They reported that the alloy exhibited superior hydrogen absorption and desorption behavior, with 3.2 wt% absorption within 1 min at 573 K and about 3 wt% desorption within 5–10 min at 573 K. We selected Ni as a transition element additive.

Too large an amount of Ni addition is considered to lead to a reduction in the hydrogen-storage capacity of the alloy. We thus chose a relatively small content of Ni, 1 wt% Ni, as the appropriate content of the additive.

The purpose of this work was to increase the dehydriding rate of MgH₂ by simultaneously adding Mg₂Ni and Ni as catalysts. Mg₂Ni and Ni were added to MgH₂. A sample with a composition of 94 wt% MgH₂+5 wt% Mg₂Ni+1 wt% Ni was prepared by milling in a hydrogen atmosphere in a planetary ball mill (reactive mechanical grinding) for 5 h. The hydrogen absorption and release properties of the prepared samples were investigated. The 94 wt% MgH₂+5 wt% Mg₂Ni+1 wt% Ni sample was named 94MgH₂+5Mg₂Ni+1Ni.

2. EXPERIMENTAL DETAILS

Pure MgH₂ powder (hydrogen storage grade, Aldrich), Mg₂Ni (High Purity Chemicals, Japan, shape powder, purity 99.9%), and Ni (Nano Technology, particle size 100 nm, purity 99.9%) were used to prepare the samples.

A mixture with a composition of 94 wt% MgH₂+5 wt% Mg₂Ni+1 wt% Ni (total weight=15 g) was mixed in a planetary ball mill with SUS balls (diameter=about 6 mm, total weight=about 416 g) for 5 h by repeating a cycle of 15 min milling and a 5 min pause. A mill container with a volume of 307 mL was filled with high-purity hydrogen gas of 15 bar before milling. The revolution speed was 250 rpm [1,14].

The quantity of hydrogen absorbed or released was measured as a function of time by a volumetric method with an automatic hydriding and dehydriding apparatus. The initial hydrogen pressures of the reactor were 17 bar H₂ for the hydriding measurement and 0 bar H₂ for the dehydriding measurement [1,14].

After measurement of the hydriding and dehydriding properties, the sample was furnace cooled under hydrogen atmosphere. X-ray diffraction (XRD) analysis was carried out with Cu Kα radiation for the as-milled powders and for the samples after desorption using an X-ray diffractometer, Rigaku D/max 2200. The scanning speed was 5°/min, and the range of the scanning diffraction angle (2θ) was 20°–80°. The microstructures of the prepared samples were observed by scanning electron microscope (SEM, JSM-5800, JEOL) [1,14].

Fig. 1. XRD patterns of the as-milled 94MgH₂+5Mg₂Ni+1Ni.

Fig. 2. XRD patterns of 94MgH₂+5Mg₂Ni+1Ni after being dehydrided at the fifth hydriding-dehydriding cycle.
3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the as-milled 94MgH$_2$+5Mg$_2$Ni+1Ni. The as-milled sample contains MgH$_2$, Mg$_2$NiH$_4$, and Ni, showing that the Mg$_2$Ni is hydrided during the reactive mechanical grinding. The reaction of 94MgH$_2$+5Mg$_2$Ni+1Ni during milling under hydrogen can be expressed as follows:

$$\text{MgH}_2 + \text{Mg}_2\text{Ni} + \text{Ni} + 2\text{H}_2 \rightarrow \text{MgH}_2 + \text{Mg}_2\text{NiH}_4 + \text{Ni}. \quad (1)$$

Figure 2 shows the XRD patterns of 94MgH$_2$+5Mg$_2$Ni+1Ni after being dehydrided at the fifth hydriding-dehydriding cycle. After hydriding-dehydriding cycling the sample contains Mg, MgH$_2$, Mg$_2$Ni, and Ni. A small amount of MgH$_2$ remains undecomposed, even after the sample was dehydrided. The background of this XRD pattern is lower than that of the XRD pattern of the as-milled 94MgH$_2$+5Mg$_2$Ni+1Ni, and the peaks of the sample after hydriding-dehydriding cycling are narrower than those of the as-milled sample, showing that the particles of the as-milled sample have micro-strain induced by plastic deformation during milling. The hydride of Mg$_2$Ni, Mg$_2$NiH$_4$, is less stable than MgH$_2$. Mg$_2$Ni and Mg form their hydrides under similar conditions of temperature and hydrogen pressure. Mg$_2$Ni has higher hydriding and dehydriding rates than Mg. The reactions during the dehydriding-hydriding cycling of 94MgH$_2$+5Mg$_2$Ni+1Ni can be expressed as follows:

$$2\text{MgH}_2 + \text{Mg}_2\text{NiH}_4 + \text{Ni} \leftrightarrow \text{MgH}_2 + \text{Mg} + \text{Mg}_2\text{Ni} + \text{Ni} + 3\text{H}_2.$$  \quad (2)

SEM micrographs at different magnifications of the as-milled 94MgH$_2$+5Mg$_2$Ni+1Ni are shown in Fig. 3. Very fine particles of the as-milled sample form agglomerates. In the as-milled sample, the agglomerates are irregular in shape and the agglomerate size is not homogeneous.

SEM micrographs at different magnifications of 94MgH$_2$+5Mg$_2$Ni+1Ni after being dehydrided at the fifth hydriding-dehydriding cycle (dehydrided at the fifth hydriding-dehydriding cycle) are shown in Fig. 4. Very fine particles of the

![Fig. 3. SEM micrographs at different magnifications of the as-milled 94MgH$_2$+5Mg$_2$Ni+1Ni.](image)

![Fig. 4. SEM micrographs at different magnifications of 94MgH$_2$+5Mg$_2$Ni+1Ni after being dehydrided at the fifth hydriding-dehydriding cycle.](image)

![Fig. 5. Variation in the hydrogen content vs. desorption time curve with the number of cycles for 94MgH$_2$+5Mg$_2$Ni+1Ni.](image)
sample dehydrided at the fifth hydriding-dehydriding cycle also form agglomerates. The agglomerates in the sample after hydriding-dehydriding cycling are irregular in shape and the agglomerate size is not homogeneous. The particle size of $94\text{MgH}_2+5\text{Mg}_2\text{Ni}+\text{Ni}$ after the hydriding-dehydriding cycling is similar to that of $94\text{MgH}_2+5\text{Mg}_2\text{Ni}+\text{Ni}$ after milling under hydrogen are similar.

The variation in the hydrogen content vs. absorption time curve with the number of cycles, $n$, at 573-673 K for $94\text{MgH}_2+5\text{Mg}_2\text{Ni}+\text{Ni}$ is shown in Fig. 5. At $n=1$, the hydriding curve shows negative values, indicating that hydrogen is not absorbed. The expansion of hydrogen, due to the introduction of hydrogen gas into the sample-containing reactor for hydriding measurement, is believed to lead to this result. Since a large fraction of the sample is a hydride ($94\text{ wt\% MgH}_2$) as a starting material, and a part of the sample is hydrided during reactive mechanical grinding, the sample absorbs no hydrogen. At $n=2$, at the beginning the hydriding rate is extremely high until 1 min and then becomes very low at 648 K. At 673 K, thereafter, the sample releases a small amount of hydrogen. At $n=3-4$, at the beginning the hydriding rate is extremely high until 10-14 min and then becomes very low. At $n=5$, the sample is dehydrided at 573 K and then at 623 K. The sample releases 2.42 wt\% H at 573 K and 2.52 wt\% H at 623 K, with the total quantity of hydrogen released at the 5th cycle being 4.94 wt\%. At $n=1$, the sample releases 0.18 wt\% for 2 min, 2.14 wt\% for 5 min, 4.65 wt\% for 10 min, and 5.46 wt\% for 60 min at 648 K. At $n=4$, the sample releases 0.11 wt\% for 2 min, 0.93 wt\% for 5 min, 3.18 wt\% for 10 min, and 4.82 wt\% for 60 min at 623 K. At $n=1$ the as-milled sample releases about 5.5 wt\% H for 125 min. Fig. 5 shows that at $n=2-5$ the sample absorbs about 5.0 wt\% H for 60 min and Fig. 6 shows that at $n=2-5$...
the sample releases about 5.0 wt% H for 125 min. The sample contains a larger amount of hydrogen after milling than at n=2-5, since a large fraction of the sample is a hydride (94 wt% MgH$_2$) as a starting material, and the Mg$_2$Ni is hydrided during milling. At n=2-5 all the Mg does not form MgH$_2$ (i.e. part of the sample does not absorb hydrogen) and less hydrogen (about 5.0 wt%) is thus released.

Figure 7 shows the variation in the hydrogen content vs. absorption time curve with the number of cycles, n, for as-purchased MgH$_2$ at 593K under nearly constant 12 bar H$_2$ [15]. This curve was obtained using another Sieverts’ type hydriding-dehydriding apparatus [16], in which hydrogen pressure can be maintained nearly constant. At n=1, the sample absorbs hydrogen extremely slowly. At n=1 the pure MgH$_2$ absorbs 0.04 wt% for 60 min and at n=2 the sample does not absorb hydrogen, showing that the sample absorbs a very small quantity of hydrogen for 60 min at n=1 and n=2. The initial hydriding rate and the quantity of hydrogen absorbed for 60 min increase as the number of cycles increases from n=1 to n=5. At n=5, the pure MgH$_2$ absorbs 0.17 wt% for 2.5 min, 0.19 wt% for 5 min, 0.23 wt% for 10 min, 0.24 wt% for 15 min, and 0.33 wt% for 60 min. On the other hand, the pure MgH$_2$ did not release hydrogen at 593 K under 1.0 bar H$_2$.

A SEM micrograph of as-purchased MgH$_2$ [17] showed that the as-purchased MgH$_2$ had small particles and large particles and the surfaces of the particles were quite flat with few defects.

A comparison of Fig. 5 and Fig. 7 shows that milling of MgH$_2$ with Mg$_2$Ni and Ni under a hydrogen atmosphere increases the hydriding rate of Mg. A comparison of Fig. 3 and the SEM micrograph of the as-purchased MgH$_2$ [17] shows that milling of MgH$_2$ with Mg$_2$Ni and Ni creates defects and greatly reduces the particle size of the MgH$_2$.

The reactive mechanical grinding of MgH$_2$ (with Mg$_2$Ni and Ni) is believed to facilitate nucleation (by creating defects, which serve as active sites for nucleation, on the surface of and inside the Mg particles), increase reactivity with hydrogen (by making clean surfaces), and decrease the diffusion distances of hydrogen atoms (by reducing the Mg particle size).

The rate-controlling steps of the dehydriding reaction of Mg$_2$Ni hydride were reported to be the Knudsen flow and bulk flow of the hydrogen molecules through pores, interparticle channels or cracks [18]. For the dehydriding reaction at 575–615 K and 0.52–2.6 bar H$_2$ of an activated, mechanically alloyed mixture of 90 wt% Mg + 10 wt% Ni, the rate-controlling steps were analyzed as both the bulk and Knudsen flows in the ranges of weight percentage of desorbed hydrogen (H$_d$) higher than 0.5 < H$_d$ ≤ 0.1. The dehydriding rate was considered controlled mainly by the Knudsen flow as the ranges of weight percentage of desorbed hydrogen become higher [19]. The contraction due to the relatively rapid desorption of Mg$_2$NiH$_4$ in 94MgH$_2$ +5Mg$_2$Ni+1Ni is believed to provide paths for the hydrogen released from neighboring MgH$_2$, facilitating the hydrogen desorption of MgH$_2$.

Takacs [20] pointed out that during mechanical grinding, size reduction, mixing, and defect formation take place. Suryanarayana et al. [21] reported that mechanical grinding is a powder metallurgy processing technique involving the cold welding, fracturing, and rewelding of powder particles in a high-energy ball mill, and is capable of synthesizing a variety of metastable phases including supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys.

Aoyaki et al. [22] reported that the ball milling of alloy powders like FeTi, Mg$_2$Ni, and LaNi$_5$ leads to a reduction in the particle size and the creation of new clean surfaces. Orimo and Fujii [23] pointed out that mechanical grinding produces nano-crystalline materials and the interesting hydriding properties of nanocrystalline materials are an increase in hydrogen solubility and the hydrogen diffusion rate depending on the hydrogen content in the grain boundaries.

Zaluska et al. [10] reported that the ball milling of MgH$_2$ can introduce internal and structural changes, such as the formation of defects and local imperfections, reduction in grain size, and induction of micro-stress in the structure. They also reported that
the ball milling of \( \text{Mg}_2\text{NiH}_4 \) brings about a reduction in grain size, the formation of a variety of defects, reduction of micro-twinning (a partial transformation of the high-temperature \( \text{Mg}_2\text{NiH}_4 \) (LT-II) into low-temperature \( \text{Mg}_2\text{NiH}_4 \) (LT-I)), and partial amorphisation of the hydride. In addition, they reported that, after milling, the \( \text{MgH}_2 \) and \( \text{Mg}_2\text{NiH}_4 \) powders were both refined and intermixed inside the particles that were newly formed by cold welding of \( \text{MgH}_2 \) and \( \text{Mg}_2\text{NiH}_4 \). The contraction due to the desorption of \( \text{Mg}_2\text{NiH}_4 \) applies strain to the attached \( \text{MgH}_2 \) neighbor, making the hydrogen desorption of \( \text{MgH}_2 \) easy. Song et al. [24] reported that the main effects of mechanical alloying in a planetary mill on the material are an increase in surface area and the creation of many defects on the surface and in the interior and the expansion and contraction of the lattice during hydriding-dehydriding cycling also stimulates a reduction in the effective particle size and create defects.

4. CONCLUSIONS

A \( 94\text{MgH}_2+5\text{Mg}_2\text{Ni}+1\text{Ni} \) sample was prepared by milling in a hydrogen atmosphere in a planetary ball mill for 5 h. The hydrogen absorption and release properties of the prepared samples were investigated. \( 94\text{MgH}_2+5\text{Mg}_2\text{Ni}+1\text{Ni} \) had an effective hydrogen-storage capacity of near 5 wt%. At \( n=2 \), the sample absorbed 4.71 wt% for 2 min, 4.73 wt% for 10 min, and 4.98 wt% for 60 min at 648 K. At \( n=1 \), the sample released 0.18 wt% for 2 min, 2.14 wt% for 5 min, and 5.46 wt% for 60 min at 648 K. At \( n=4 \), the as-purchased \( \text{MgH}_2 \) absorbed 0.50 wt% for 5 min and 0.90 wt% for 60 min at 593 K under 12 bar \( \text{H}_2 \). Milling of the \( \text{MgH}_2 \) with \( \text{Mg}_2\text{Ni} \) and \( \text{Ni} \) greatly increased the hydriding and dehydriding rates. The \( \text{MgH}_2 \) sample milled with \( \text{Mg}_2\text{Ni} \) and \( \text{Ni} \) had a much larger number of defects and much smaller particle sizes than the as-purchased \( \text{MgH}_2 \) sample. The reactive mechanical grinding of \( \text{MgH}_2 \) with \( \text{Mg}_2\text{Ni} \) and \( \text{Ni} \) is believed to facilitate nucleation, increase reactivity with hydrogen, and decrease the diffusion distances of hydrogen atoms. The contraction due to the relatively rapid desorption of \( \text{Mg}_2\text{NiH}_4 \) in \( 94\text{MgH}_2+5\text{Mg}_2\text{Ni}+1\text{Ni} \) is believed to provide paths for the hydrogen released from neighboring \( \text{MgH}_2 \), facilitating the hydrogen desorption of \( \text{MgH}_2 \).

ACKNOWLEDGEMENTS

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.

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