Hydrogen Sorption of Pure Mg and Niobium (V) Fluoride-Added Mg Alloys Prepared by Planetary Ball Milling in Hydrogen

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Abstract: In this work, niobium (V) fluoride was selected as an additive to heighten the hydrogen sorption rates of Mg. Specimens of pure Mg, 5 wt% niobium fluoride-added Mg, and 10 wt% niobium fluoride-added Mg were prepared by planetary ball milling in hydrogen. The hydrogen sorption properties of the specimens were then examined. An Mg-based hydrogen-storage alloy with an effective hydrogen-storage capacity of about 5.5 wt% was developed. At 593 K in 12 bar hydrogen at the first cycle (Cn = 1), the 5 wt% niobium fluoride-added Mg stored 4.37 wt% hydrogen in 5 min and 5.50 wt% hydrogen in 30 min. At 593 K in 1.0 bar hydrogen at Cn = 1, the 5 wt% niobium fluoride-added Mg released 2.11 wt% hydrogen in 10 min, 4.66 wt% hydrogen in 30 min, and 5.43 wt% hydrogen in 60 min. The planetary ball milling of Mg with NbF5 in hydrogen, which generated MgF2, NbH2, and NbF3, is believed to have produced imperfections both on the surface and in the interior of the Mg particles, created clean surfaces, and diminished the particle size of the Mg. The 5 wt% niobium fluoride-added Mg specimen stored a larger quantity of hydrogen in 30 min and a larger quantity of hydrogen was released in 60 min compared with the 10 wt% niobium fluoride-added Mg, or the pure Mg.

Keywords: hydrogen absorbing materials, mechanical milling, microstructure, X-ray diffraction, niobium (V) fluoride-added Mg alloys

1. INTRODUCTION

Among many metal hydrides, magnesium hydride has been studied by many researchers since it has many advantages as a hydrogen storage material. However, the hydrogenation rate of magnesium (Mg) and the dehydrogenation rate of magnesium hydride (MgH2) are very low, and relatively high temperatures are required for the hydrogenation of Mg and the dehydrogenation of MgH2 [1,2].

A great deal of research has been performed to improve the hydrogen storage and release rates of magnesium [3-9] by alloying the magnesium with certain metals [10-12]. The hydrogen storage and release temperatures of MgH2 were decreased or the hydrogen sorption kinetics of MgH2 was improved by adding transition metal fluorides such as FeF3 [13], NbF5, and TiF5 [14], and by adding various halides including ZrF4, TaF5, NbF5, VCl3, and TiCl3 [15]. Malka et al. [15] reported that, of the halides studied, NbF5 is one of the best catalysts for the hydrogen release from magnesium hydride.

Malka et al. [16] ball-milled magnesium hydride with 7 wt% of ZrF4, TaF5, NbF5, and TiCl3, and investigated the influence of these dopants on the hydrogen storage and released kinetics of magnesium hydride. They reported that TaF5, NbF5, and TiCl3 participated in the partial and full disproportionation reactions directly after milling and the first hydrogen release-storage cycle.

Malka et al. [17] reported results on the thermal stability of nanocrystalline magnesium hydride milled with 7 wt% of metal halide additives such as ZrF4, NbF5, TaF5, FeF2, FeF3, TiCl3 and VCl3 after 1 year of storage in a glovebox under a continuously purified argon atmosphere. The oxidation of MgH2 at low oxygen and water vapor pressures led to an increase in the hydride decomposition temperatures of the samples, compared with their initial (as-prepared) counterparts.
Table 1. Variations in $H_h$ with $t$ at 593 K in 12 bar hydrogen for Pure Mg, 95Mg + 5NbF$_5$, and 90Mg + 10NbF$_5$ at $C_n = 1$.

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Fig. 1. Variations in $H_h$ with $t$ at 593 K in 12 bar hydrogen for Pure Mg, 95Mg + 5NbF$_5$, and 90Mg + 10NbF$_5$ at $C_n = 1$.

In the current work, niobium (V) fluoride was selected as an additive to heighten the hydrogen sorption rates (the hydrogenation and dehydrogenation rates) of Mg. Specimens with compositions of pure Mg, 95 wt% Mg + 5 wt% NbF$_5$, and 90 wt% Mg + 10 wt% NbF$_5$ were prepared by planetary ball milling in hydrogen. The hydrogen sorption properties of the specimens were then examined. The pure Mg, 95Mg + 5NbF$_5$, and 90Mg + 10NbF$_5$ samples were named Pure Mg, 95Mg + 5NbF$_5$, and 90Mg + 10NbF$_5$, respectively.

2. EXPERIMENTAL DETAILS

We employed pure Mg powder (particle size 74-149 μm, purity 99.6%, Alfa Aesar) and NbF$_5$ (purity 98%, Aldrich) as starting materials.

Planetary ball milling in hydrogen of about 12 bar was carried out in a planetary ball mill (Planetary Mono Mill; Pulverisette 6, Fritsch) for 6 h by repeating 15 min periods of milling interspersed with 5 min periods of rest. Hydrogen was refilled every two hours. A mixture with the desired composition was mixed in a 250 ml stainless steel container (with 105 hardened steel balls) which was sealed hermetically. The sample weight (8 g) to ball weight (360 g) ratio was 1:45. The sample handling was performed in a glove box under Ar to prevent oxidation. The number of revolutions per minute (rpm) was 250. This process of planetary ball milling in hydrogen is explained in detail in previous works [4,8].

The quantities of hydrogen absorbed by hydrogenation at 593 K in 12 bar hydrogen or released by dehydrogenation at 593 K in 1.0 bar hydrogen, as hydrogenation or dehydrogenation progressed, were measured using a volumetric method in a Sievert’s type hydrogen sorption apparatus, as described previously [18]. During hydrogenation and dehydrogenation, the hydrogen pressures were maintained as nearly constant. The quantity of the specimens used to identify the hydrogenation and dehydrogenation properties was 0.5 g.

The phases in the samples after planetary ball milling in hydrogen and after hydrogenation-de-hydrogenation cycling were analyzed by obtaining powder X-ray diffraction (XRD) patterns with Cu Kα radiation in a diffractometer (Rigaku D/MAX 2500). A scanning electron microscope (SEM) (JSM-6400) was used to observe the microstructures of the powders after planetary ball milling in hydrogen and after hydrogenation-dehydrogenation cycling. Particle size distributions of the as-milled samples were analyzed using Mastersizer 3000 (Malvern Instruments, UK).

3. RESULTS AND DISCUSSIONS

The percentage of hydrogen stored by hydrogenation, $H_h$, was expressed with respect to the weight of the specimen. Figure 1 shows the variations in $H_h$ with $t$ at 593 K in 12 bar hydrogen for Pure Mg, 95Mg + 5NbF$_5$, and 90Mg + 10NbF$_5$ at the number of cycles, $C_n$, of 1 ($C_n = 1$). The hydrogenation rate of Pure Mg was very low. Mg stored 0.08 wt% hydrogen in 2.5 min and 0.11 wt% hydrogen in 30 min [19]. 95Mg + 5NbF$_5$ and 90Mg + 10NbF$_5$ had quite high hydrogenation rates, with 95Mg + 5NbF$_5$ having a higher hydrogenation rate than 90Mg + 10NbF$_5$ [20,21]. 95Mg + 5NbF$_5$ stored 4.37
Table 2. Variations in $H_r$ with $t$ at 593 K in 1.0 bar hydrogen for Pure Mg, $95\text{Mg} + 5\text{NbF}_5$, and $90\text{Mg} + 10\text{NbF}_5$ at $C_n = 1$.

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Fig. 2. Variations in $H_r$ with $t$ at 593 K in 1.0 bar hydrogen for Pure Mg, $95\text{Mg} + 5\text{NbF}_5$, and $90\text{Mg} + 10\text{NbF}_5$ at $C_n = 1$.

The percentage of hydrogen released by dehydrogenation, $H_r$, was also expressed with respect to the weight of the specimen. The variations in $H_r$ with $t$ at 593 K in 1.0 bar hydrogen for Pure Mg, $95\text{Mg} + 5\text{NbF}_5$, and $90\text{Mg} + 10\text{NbF}_5$ at $C_n = 1$ are shown in Fig. 2. The dehydrogenation rate of Pure Mg was zero [19]. $90\text{Mg} + 10\text{NbF}_5$ had an incubation period of 2.5 min. $95\text{Mg} + 5\text{NbF}_5$, and $90\text{Mg} + 10\text{NbF}_5$ (after the incubation period) had quite high dehydrogenation rates, with $95\text{Mg} + 5\text{NbF}_5$ having a higher dehydrogenation rate than $90\text{Mg} + 10\text{NbF}_5$ [20,21]. $95\text{Mg} + 5\text{NbF}_5$ released 2.11 wt% hydrogen in 10 min and 5.43 wt% hydrogen in 60 min. $90\text{Mg} + 10\text{NbF}_5$ released 0 wt% hydrogen in 2.5 min, 0.17 wt% hydrogen in 5 min, 0.74 wt% hydrogen in 10 min, and 2.81 wt% hydrogen in 60 min [22]. Table 2 presents the variations in $H_r$ with $t$ at 593 K in 1.0 bar hydrogen for Pure Mg, $95\text{Mg} + 5\text{NbF}_5$, and $90\text{Mg} + 10\text{NbF}_5$ at $C_n = 1$. Milling with NbF$_3$ in hydrogen atmosphere is believed to have facilitated the nucleation rate of Mg and increased the dehydrogenation rate of MgH$_2$.

The variation in $H_r$ with $t$ according to the number of cycles, $C_n$, for $90\text{Mg} + 10\text{NbF}_5$ at 593 K in 1.0 bar hydrogen was investigated [22]. At $C_n = 1-3$, the $H_r$ vs. $t$ curves exhibited an incubation period of approximately 2.5 min. As the dehydrogenation temperature increased, the equilibrium plateau pressure (which can be found in P-C-T curves) increases and the dehydrogenation rate increased. As the dehydrogenation temperature increases, the gap between the equilibrium plateau pressure and the applied hydrogen pressure for dehydrogenation (1.0 bar hydrogen in this figure) increases, which is the driving force for dehydrogenation [18]. The incubation periods are believed to have appeared due to a small driving force for dehydrogenation. Tanguy et al. [23] reported the equilibrium plateau pressures in the Mg-H system at various temperatures. With their results, the relation between the equilibrium plateau pressure ($P_{eq}$) and temperature in the Mg-H system was obtained as the following:

\[
\ln P_{eq} \text{(bar)} = 17.65 - \frac{9,844}{T} \quad (1)
\]

Stampfer et al. [24] also reported a similar relation between the equilibrium plateau pressure ($P_{eq}$) and temperature in the Mg-H system. From the equation (1), the equilibrium plateau pressure was calculated as 2.87 bar. After the incubation period, the initial dehydrogenation rate increased from $C_n = 1$ to $C_n = 3$. The quantity of hydrogen released for 60 min, $H_r (60$
Table 3. Variations in $H_r$ with $t$ at $C_n = 1$ and $C_n = 3$ for $90\text{Mg} + 10\text{NbF}_5$ at 593 K in 1.0 bar hydrogen.

<table>
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Fig. 3. Variations in $H_h$ with $t$ at 593 K in 12 bar hydrogen for Pure Mg, 95Mg + 5NbF$_5$, and 90Mg + 10NbF$_5$ at $C_n = 3$.

Table 4. Variations in $H_h$ with $t$ at 593 K in 12 bar hydrogen for Pure Mg, 95Mg + 5NbF$_5$, and 90Mg + 10NbF$_5$ at $C_n = 3$.

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<th>Stored hydrogen quantity (wt% hydrogen)</th>
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min), decreased from $C_n = 1$ to $C_n = 2$, and then increased from $C_n = 2$ to $C_n = 3$. At $C_n = 1$, the specimen released 0.74 wt% hydrogen in 10 min and 2.81 wt% hydrogen in 60 min. At $C_n = 3$, the specimen released 1.03 wt% hydrogen in 10 min and 3.08 wt% hydrogen in 60 min. The variation in $H_r$ with $t$ according to the number of cycles showed that the $H_r$ vs. $t$ curve for $90\text{Mg} + 10\text{NbF}_5$ at 593 K in 1.0 bar hydrogen did not change significantly from $C_n = 2$ to $C_n = 3$, i.e., it was stabilized at $C_n = 3$. We therefore compared the $H_h$ vs. $t$ curves and $H_r$ vs. $t$ curves for Pure Mg, 95Mg + 5NbF$_5$, and 90Mg + 10NbF$_5$ at $C_n = 3$. Table 3 shows the variation in $H_r$ with $t$ at $C_n = 1$ and $C_n = 3$ for $90\text{Mg} + 10\text{NbF}_5$ at 593 K in 1.0 bar hydrogen.

The variations in $H_h$ with $t$ at 593 K in 12 bar hydrogen for Pure Mg, 95Mg + 5NbF$_5$, and 90Mg + 10NbF$_5$ at $C_n = 3$ are shown in Fig. 3. Pure Mg had a much higher hydrogenation rate at $C_n = 3$ than at $C_n = 1$ [19]. 95Mg + 5NbF$_5$ had the highest initial hydrogenation rate and the largest quantity of hydrogen stored for 30 min, followed in order by 90Mg + 10NbF$_5$ and Mg. Pure Mg stored 0.41 wt% hydrogen in 2.5 min, 0.71 wt% hydrogen in 5 min, and 2.00 wt% hydrogen in 30 min. 95Mg + 5NbF$_5$ stored 3.99 wt% hydrogen in 5 min and 5.16 wt% hydrogen in 30 min. 90Mg + 10NbF$_5$ stored 3.54 wt% hydrogen in 5 min and 4.21 wt% hydrogen in 30 min [22]. Table 4 presents the variations in $H_h$ with $t$ at 593 K in 12 bar hydrogen for Pure Mg, 95Mg + 5NbF$_5$, and 90Mg + 10NbF$_5$ at $C_n = 3$. Hydrogenation-dehydrogenation cycling increased the initial hydrogenation rate and increased the quantity of hydrogen stored in 30 min of the Pure Mg due to the expansion of the material by hydrogenation and contraction of the material by dehydrogenation. Expansion and contraction of the material are considered to have produced imperfections, created clean surfaces, and diminished the Mg particle size.

Figure 4 shows the variations in $H_h$ with $t$ at 593 K in 1.0 bar hydrogen for Pure Mg, 95Mg + 5NbF$_5$, and 90Mg + 10NbF$_5$ at $C_n = 3$. Mg did not release hydrogen [19]. This is believed to be due to the small driving force for dehydrogenation. 90Mg + 10NbF$_5$ had an incubation period of 2.5 min. 95Mg + 5NbF$_5$ and 90Mg + 10NbF$_5$ (after the incubation period) had quite high dehydrogenation rates, with 95Mg + 5NbF$_5$ having a higher dehydrogenation rate than
Table 5. Variations in H_r with t at 593 K in 1.0 bar hydrogen for Pure Mg, 95Mg + 5NbF_5, and 90Mg + 10NbF_5 at C_n = 3.

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<td>90Mg + 10NbF_5</td>
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Fig. 5. SEM images of (a) 95Mg + 5NbF_5 and (b) 90Mg + 10NbF_5 after planetary ball milling in hydrogen.

90Mg + 10NbF_5 [20,21]. 95Mg + 5NbF_5 released 1.92 wt% hydrogen in 10 min and 5.14 wt% hydrogen in 60 min. 90Mg + 10NbF_5 released 1.03 wt% hydrogen in 10 min and 3.08 wt% hydrogen in 60 min [22]. Table 5 presents the variations in H_r with t at 593 K in 1.0 bar hydrogen for Pure Mg, 95Mg + 5NbF_5, and 90Mg + 10NbF_5 at C_n = 3.

As the number of cycles increased from C_n = 1 to C_n = 3, the initial hydrogenation rate and the quantity of hydrogen absorbed in 30 min of 95Mg + 5NbF_5 decreased. As the number of cycles for 90Mg + 10NbF_5 increased from C_n = 1 to C_n = 3, the initial hydrogenation rate increased and the quantity of hydrogen stored in 30 min decreased. As the number of cycles increased from C_n = 1 to C_n = 3, the initial dehydrogenation rate and the quantity of hydrogen released in 60 min of 95Mg + 5NbF_5 decreased. As the number of cycles for 90Mg + 10NbF_5 increased from C_n = 1 to C_n = 3, after the incubation period, the initial dehydrogenation rate and the quantity of hydrogen released in 60 min increased. The overall trends of the hydrogenation and dehydrogenation rates and the quantities of hydrogen stored in 30 min and released in 60 min showed that the activation of 95Mg + 5NbF_5 and 90Mg + 10NbF_5 was not required.

Figure 5 shows the SEM images of 95Mg + 5NbF_5 and 90Mg + 10NbF_5 after planetary ball milling in hydrogen. 95Mg + 5NbF_5 and 90Mg + 10NbF_5 had a wide range of particle sizes and the particles of these samples had fine particles on their surfaces. Pure Mg had particles of various sizes, the surfaces of which were very flat. The particles had a few imperfections [20,21]. 95Mg + 5NbF_5 had the largest number of fine particles, followed in order by 90Mg + 10NbF_5 and Pure Mg. This agrees well with the results that Pure Mg absorbed hydrogen very slowly, Pure Mg did not release hydrogen, and 95Mg + 5NbF_5 and 90Mg + 10NbF_5 had quite high hydrogenation and dehydrogenation rates, with 95Mg + 5NbF_5 having higher hydrogenation and dehydrogenation rates than 90Mg + 10NbF_5.

Figure 6 shows the particle size distributions of 95Mg + 5NbF_5 and 90Mg + 10NbF_5 after planetary ball milling in hydrogen. These two samples have relatively narrow particle size distributions, with particle sizes between 0 μm and about 2 μm. 95Mg + 5NbF_5 had the strongest peak at 0.5 μm and the second strongest peak at 1.2 μm. 90Mg + 10NbF_5 had the strongest peak at 1.0 μm and the second strongest peak at 0.3 μm.
μm. The average particle size of the as-milled 95Mg + 5NbF5 was analyzed as 0.732 ± 0.390 μm and that of the as-milled 90Mg + 10NbF5 was analyzed as 0.742 ± 0.372 μm. The average particle size of the as-milled 95Mg + 5NbF5 was slightly smaller than that of the as-milled 90Mg + 10NbF5. The surface areas of the as-milled 95Mg + 5NbF5 and the as-milled 90Mg + 10NbF5 were 10.33 and 10.50 m²/cm³, respectively.

The SEM images of 95Mg + 5NbF5 and 90Mg + 10NbF5 dehydrogenated at Cn = 3 are shown in Fig. 7. Pure Mg had large particles, the surfaces of which were quite flat. The particles had more imperfections and cracks than those of the Pure Mg sample after planetary ball milling in hydrogen [20,21]. During hydrogenation, the material expands, and during dehydrogenation, it contracts. The increase and decrease in the volumes of Mg particles with hydrogenation and dehydrogenation are considered to induce the formation of imperfections and cracks on the particles. The formation of more imperfections and cracks explains why the Pure Mg specimen at Cn = 3 had a higher hydrogenation rate than the Pure Mg specimen after planetary ball milling in hydrogen.

95Mg + 5NbF5 had small particles and large particles, but had quite a homogeneous particle size distribution, with fine particles on the particle surfaces. 90Mg + 10NbF5 had small particles, large particles, and very large particles with fine particles on the particle surfaces. The very large particles had flat surfaces. 95Mg + 5NbF5 had the smallest particle sizes, followed in order by 90Mg + 10NbF5 and Pure Mg. This agrees well with the result that 95Mg + 5NbF5 had the highest hydrogenation and dehydrogenation rates, followed in order by 90Mg + 10NbF5 and Pure Mg. 95Mg + 5NbF5 and 90Mg + 10NbF5 had generally larger particles than 95Mg + 5NbF5 and 90Mg + 10NbF5 after planetary ball milling in hydrogen, explaining why they had lower hydrogenation and dehydrogenation rates than after planetary ball milling in hydrogen. It is believed that this resulted from the coalescence of particles because the samples were maintained at a relatively high temperature of 593 K during hydrogenation-dehydrogenation cycling.

The powder XRD patterns of Pure Mg, 95Mg + 5NbF5, and 90Mg + 10NbF5 after planetary ball milling in hydrogen were investigated [2,22,25]. The powder XRD pattern of Pure Mg after planetary ball milling in hydrogen exhibited Mg and a very small amount of β-MgH2, which was formed by the reaction of Mg with hydrogen during planetary ball milling in hydrogen. The powder XRD patterns of 95Mg + 5NbF5 and 90Mg + 10NbF5 after planetary ball milling in hydrogen had quite a high background, indicating that the samples were somewhat amorphous. 95Mg + 5NbF5 and 90Mg + 10NbF5 after planetary ball milling in hydrogen included Mg, β-MgH2, and small amounts of γ-MgH2, NbH2, MgF2, and NbF3. β-MgH2 and γ-MgH2 were formed by the reaction of Mg with the hydrogen during planetary ball milling in hydrogen. β-MgH2 is a tetragonal MgH2 which can be synthesized in a low hydrogen pressure. γ-MgH2 is an orthorhombic MgH2, which is a form of the high-pressure MgH2. The reaction among Mg, NbF5, and H2 generated MgF2, NbH2, and NbF3.

The power XRD patterns of Pure Mg from which hydrogen was released at Cn = 9, and 95Mg + 5NbF5 and 90Mg + 10NbF5 from which hydrogen was released at Cn = 3 were examined [22,25]. The powder XRD pattern of Mg from which hydrogen was released at Cn = 9 showed that the specimen included Mg and a very small amount of β-MgH2. The powder XRD pattern of 95Mg + 5NbF5 from which hydrogen was released at Cn = 3 showed that the specimen included Mg, small amounts of β-MgH2 and MgO, and very small amounts of MgF2 and NbH2. The powder XRD pattern of 90Mg + 10NbF5 from which hydrogen was released at Cn = 3 showed Mg, β-MgH2, a small amount of MgO, and very small amounts of MgF2 and NbH2. In the 95Mg + 5NbF5 and 90Mg + 10NbF5 specimens, MgF2 and NbH2 stayed changeless after dehydrogenation.
Ball milling was performed in a hydrogen atmosphere. The sample may be contaminated from the hardened steel balls. The prepared sample may contain Fe. However, it is believed that this Fe does not have negative effects on hydrogenation and dehydrogenation of the samples. Residual stress is considered to be released during heating for hydrogenation and dehydrogenation and during hydrogenation-dehydrogenation cycling.

The planetary ball milling of Mg with NbF₅ in hydrogen, which formed MgF₂, NbH₂, and NbF₅ by reaction with hydrogen, is believed to have produced imperfections both on the surface and in the interior of the Mg particles, created clean surfaces, and diminished the Mg particle size. The particles have defects which are believed to be dislocations and interfaces between Mg and the other phases. Fecht et al. [26] reported that at a high strain rate, a dense network of dislocations (shear bands) forms which then deforms the material, leading to the reduction in particle size. The production of imperfections is believed to have promoted nucleation, the creation of clean surfaces is thought to have improved reactivity of particles with hydrogen, and the diminution in the Mg particle size is believed to have decreased the diffusion distances of hydrogen atoms. These influences heightened the hydrogenation and dehydrogenation rates of Mg. The formed MgF₂, NbH₂, and NbF₅ are considered to have enhanced these influences.

The average particle size of the as-milled 95Mg + 5NbF₅ was slightly smaller than that of the as-milled 90Mg + 10NbF₅, showing that the effects of milling (production of imperfections, creation of clean surfaces, and diminution in the Mg particle size) with 5 wt% NbF₅ are slightly stronger than those of milling with 10 wt% NbF₅. The larger content of NbF₅ in the 90Mg + 10NbF₅ specimen as compared with the 95Mg + 5NbF₅ specimen decreased the fraction of Mg which could store and release hydrogen in the 90Mg + 10NbF₅ specimen. These two points explain why 95Mg + 5NbF₅ had a higher initial hydrogenation rate, a larger quantity of hydrogen stored for 30 min, a higher initial dehydrogenation rate, and a larger quantity of hydrogen released in 60 min than 90Mg + 10NbF₅.

Figure 8 shows the Hₘ vs. t curves at Cₙ = 1 for Pure Mg [19], 95Mg + 5NbF₅, 90 wt% Mg + 10 wt% MnO [27], and 90 wt% Mg + 10 wt% Fe₂O₃ [27] at 593K in 12 bar hydrogen, for 98 mol% MgH₂ + 2 mol% NaOH at 593K in an initial pressure of 17 bar hydrogen [29], and for 98 mol% MgH₂ + 2 mol% FeF₃ at 573K in 10 bar hydrogen [13]. Pure Mg stored hydrogen very slowly. 95Mg + 5NbF₅ had a larger quantity of hydrogen stored in 10 min than 98 mol% MgH₂ + 2 mol% FeF₃, 90 wt% Mg + 10 wt% MnO, 90 wt% Mg + 10 wt% Fe₂O₃, and Pure Mg but a smaller quantity of hydrogen stored in 10 min than 95 wt% MgH₂ + 5 wt% NaOH and 98 mol% MgH₂ + 2 mol% NaOH. 98 mol% MgH₂ + 2 mol% NaOH had the highest initial hydrogenation rate, followed in order by 95 wt% MgH₂ + 5 wt% NaOH, 98 mol% MgH₂ + 2 mol% FeF₃, 95Mg + 5NbF₅, 90 wt% Mg + 10 wt% MnO, 90 wt% Mg + 10 wt% Fe₂O₃, and Pure Mg. 98 mol% MgH₂ + 2 mol% NaOH stored 4.00 wt% hydrogen in 0.42 min, 6.40 wt% hydrogen in 1.88 min, and 6.45 wt% hydrogen in 8.33 min. 95Mg + 5NbF₅ stored 3.17 wt% hydrogen in 2.5 min, 4.37 wt% hydrogen in 5 min, 5.10 wt% hydrogen in 2.5 min, 4.37 wt% hydrogen in 5 min, 5.10 wt% hydrogen in 2.5 min, 4.37 wt% hydrogen in 5 min.
hydrogen in 10 min, and 5.50 wt% hydrogen in 30 min. 90 wt% Mg + 10 wt% MnO stored 2.74 wt% hydrogen in 5 min, 3.12 wt% hydrogen in 10 min, 3.58 wt% hydrogen in 30 min, and 3.95 wt% hydrogen in 60 min. Pure Mg stored 0.08 wt% hydrogen in 2.5 min, and 0.14 wt% hydrogen in 60 min. The use of Mg instead of MgH₂ is considered to have led to the smaller quantity of hydrogen stored in 30 min by 95Mg + 5NbF₅ than by 95 wt% MgH₂ + 5 wt% NaOH and 98 mol% MgH₂ + 2 mol% Nb₂O₅. In order to increase the hydrogenation and dehydrogenation rates and the effective hydrogen-storage capacity of NbF₅-added Mg samples, we suggest adding nano-sized NbF₅, decreasing the content of NbF₅, or using MgH₂ as a starting material instead of Mg.

4. CONCLUSIONS

In the current work, NbF₅ was selected as an additive to heighten the hydrogenation and dehydrogenation rates of Mg in the current work. Specimens with compositions of Pure Mg, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ were prepared by planetary ball milling in hydrogen. The hydrogenation and dehydrogenation properties of the specimens were then examined. At 593 K in 12 bar hydrogen at the first cycle, 95Mg + 5NbF₅ absorbed 4.37 wt% hydrogen in 5 min and 5.50 wt% hydrogen in 30 min. At 593 K in 1.0 bar hydrogen at the first cycle, 95Mg + 5NbF₅ released 2.11 wt% hydrogen in 10 min and 5.43 wt% hydrogen in 60 min. Activations of 95Mg + 5NbF₅ and 90Mg + 10NbF₅ were not needed. The planetary ball milling in hydrogen of Mg with NbF₅, which generated MgF₂, NbH₂, and NbF₃, is believed to have produced imperfections, created clean surfaces, and diminished the Mg particle size. The average particle size of the as-milled 95Mg + 5NbF₅ was slightly smaller than that of the as-milled 90Mg + 10NbF₅, showing that the effects of milling with 5 wt% NbF₃ are slightly stronger than those of milling with 10 wt% NbF₅. The larger content of NbF₅ in the 90Mg + 10NbF₅ specimen than in the 95Mg + 5NbF₅ specimen decreased the fraction of Mg which could store and release hydrogen in the 90Mg + 10NbF₅ specimen. These two points explain why 95Mg + 5NbF₅ had a larger quantity of hydrogen stored in 30 min and a larger quantity of hydrogen released in 60 min than 90Mg + 10NbF₅.

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