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 ($C_n = 1$), 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 $C_n = 1$, 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.

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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 TiF₃ [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.

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Table 1. Variations in H_h with t at 593 K in 12 bar hydrogen for Pure Mg, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ at $C_n = 1$.

	Stored hydrogen quantity (wt% hydrogen)			
	2.5 min	5 min	10 min	30 min
Pure Mg	0.08			0.11
95Mg + 5NbF ₅	3.17	4.37	5.10	5.50
90Mg + 10NbF ₅	3.11	3.55	3.86	4.23

Fig. 1. Variations in H_h with t at 593 K in 12 bar hydrogen for Pure Mg, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ 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% NbF₅, and 90 wt% Mg + 10 wt% NbF₅ were prepared by planetary ball milling in hydrogen. The hydrogen sorption properties of the specimens were then examined. The pure Mg, 95 wt% Mg + 5 wt% NbF₅, and 90 wt% Mg + 10 wt% NbF₅ samples were named Pure Mg, 95Mg + 5NbF₅, and 90Mg + 10NbF₅, respectively.

2. EXPERIMENTAL DETAILS

We employed pure Mg powder (particle size 74-149 μm , purity 99.6%, Alfa Aesar) and NbF₅ (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-dehydrogenation cycling were analyzed by obtaining powder X-ray diffraction (XRD) patterns with Cu K α 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 + 5NbF₅, and 90Mg + 10NbF₅ 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 + 5NbF₅ and 90Mg + 10NbF₅ had quite high hydrogenation rates, with 95Mg + 5NbF₅ having a higher hydrogenation rate than 90Mg + 10NbF₅ [20,21]. 95Mg + 5NbF₅ stored 4.37

Table 2. Variations in H_r with t at 593 K in 1.0 bar hydrogen for Pure Mg, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ at $C_n = 1$.

	Released hydrogen quantity (wt% hydrogen)				
	2.5 min	5 min	10 min	30 min	60 min
Pure Mg	0.00				0.00
95Mg + 5NbF ₅	0.36	1.03	2.11	4.66	5.43
90Mg + 10NbF ₅	0.00	0.17	0.74	2.03	2.81

Fig. 2. Variations in H_r with t at 593 K in 1.0 bar hydrogen for Pure Mg, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ at $C_n = 1$.

wt% hydrogen in 5 min and 5.50 wt% hydrogen in 30 min. 90Mg + 10NbF₅ stored 3.55 wt% hydrogen in 5 min and 4.23 wt% hydrogen in 30 min [22]. Table 1 presents the variations in H_h with t at 593 K in 12 bar hydrogen for Pure Mg, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ at $C_n = 1$. It is believed that Pure Mg stored very slowly because the nucleation rate of MgH₂ was very low. Milling with NbF₅ in hydrogen atmosphere is believed to have facilitated the nucleation rate of MgH₂ and increased the hydrogenation rate of Mg.

We define an effective hydrogen-storage capacity as the quantity of hydrogen stored by hydrogenation in 60 min. 95Mg + 5NbF₅ showed an effective hydrogen-storage capacity of about 5.5 wt%.

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, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ at $C_n = 1$ are shown in Fig. 2. The dehydrogenation rate of Pure Mg was zero [19]. 90Mg + 10NbF₅ had an incubation period of 2.5 min. 95Mg + 5NbF₅, and 90Mg + 10NbF₅ (after

the incubation period) had quite high dehydrogenation rates, with 95Mg + 5NbF₅ having a higher dehydrogenation rate than 90Mg + 10NbF₅ [20,21]. 95Mg + 5NbF₅ released 2.11 wt% hydrogen in 10 min and 5.43 wt% hydrogen in 60 min. 90Mg + 10NbF₅ 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, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ at $C_n = 1$. Milling with NbF₅ in hydrogen atmosphere is believed to have facilitated the nucleation rate of Mg and increased the dehydrogenation rate of MgH₂.

The variation in H_r with t according to the number of cycles, C_n , for 90Mg + 10NbF₅ 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:

$$\ln P_{eq} (\text{bar}) = 17.65 - 9,844/T \quad (1)$$

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 90Mg + 10NbF₅ at 593 K in 1.0 bar hydrogen.

	Released hydrogen quantity (wt% hydrogen)				
	2.5 min	5 min	10 min	30 min	60 min
$C_n=1$	0.00	0.17	0.74	2.03	2.81
$C_n=3$	0.00	0.42	1.03	2.34	3.08

Fig. 3. Variations in H_h with t at 593 K in 12 bar hydrogen for Pure Mg, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ at $C_n = 3$.

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 90Mg + 10NbF₅ 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 + 5NbF₅, and 90Mg + 10NbF₅ at $C_n = 3$. Table 3 shows the variation in H_r with t at $C_n = 1$ and $C_n = 3$ for 90Mg + 10NbF₅ 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 + 5NbF₅, and 90Mg + 10NbF₅ 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 + 5NbF₅ had the highest initial hydrogenation rate and the largest quantity of hydrogen stored for 30 min, followed in order by 90Mg + 10NbF₅ 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

Table 4. Variations in H_h with t at 593 K in 12 bar hydrogen for Pure Mg, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ at $C_n = 3$.

	Stored hydrogen quantity (wt% hydrogen)			
	2.5 min	5 min	10 min	30 min
Pure Mg	0.41	0.71	1.05	2.00
95Mg+5NbF ₅	2.92	3.99	4.59	5.16
90Mg+10NbF ₅	3.19	3.54	3.83	4.21

Fig. 4. Variations in H_r with t at 593 K in 1.0 bar hydrogen for Pure Mg, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ at $C_n = 3$.

30 min. 95Mg + 5NbF₅ stored 3.99 wt% hydrogen in 5 min and 5.16 wt% hydrogen in 30 min. 90Mg + 10NbF₅ 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 + 5NbF₅, and 90Mg + 10NbF₅ 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_r with t at 593 K in 1.0 bar hydrogen for Pure Mg, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ at $C_n = 3$. Mg did not release hydrogen [19]. This is believed to be due to the small driving force for dehydrogenation. 90Mg + 10NbF₅ had an incubation period of 2.5 min. 95Mg + 5NbF₅ and 90Mg + 10NbF₅ (after the incubation period) had quite high dehydrogenation rates, with 95Mg + 5NbF₅ having a higher dehydrogenation rate than

Table 5. Variations in H_t with t at 593 K in 1.0 bar hydrogen for Pure Mg, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ at $C_n=3$.

	Released hydrogen quantity (wt% hydrogen)				
	2.5 min	5 min	10 min	30 min	60 min
Pure Mg	0.00				0.00
95Mg + 5NbF ₅	0.21	0.91	1.92	4.53	5.14
90Mg + 10NbF ₅	0.00	0.42	1.03	2.34	3.08

Fig. 5. SEM images of (a) 95Mg + 5NbF₅ and (b) 90Mg + 10NbF₅ after planetary ball milling in hydrogen.

90Mg + 10NbF₅ [20,21]. 95Mg + 5NbF₅ released 1.92 wt% hydrogen in 10 min and 5.14 wt% hydrogen in 60 min. 90Mg+10NbF₅ released 1.03 wt% hydrogen in 10 min and 3.08 wt% hydrogen in 60 min [22]. Table 5 presents the variations in H_t with t at 593 K in 1.0 bar hydrogen for Pure Mg, 95Mg + 5NbF₅, and 90Mg + 10NbF₅ 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 + 5NbF₅ decreased. As the number of cycles for 90Mg + 10NbF₅ 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 + 5NbF₅ decreased. As the number of cycles for 90Mg + 10NbF₅ 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 + 5NbF₅ and 90Mg + 10NbF₅ was not required.

Figure 5 shows the SEM images of 95Mg+5NbF₅ and 90Mg+10NbF₅ after planetary ball milling in hydrogen. 95Mg + 5NbF₅ and 90Mg + 10NbF₅ had a wide range of

Fig. 6. Particle size distributions of (a) 95Mg + 5NbF₅ and (b) 90Mg + 10NbF₅ after planetary ball milling in hydrogen.

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 + 5NbF₅ had the largest number of fine particles, followed in order by 90Mg + 10NbF₅ and Pure Mg. This agrees well with the results that Pure Mg absorbed hydrogen very slowly, Pure Mg did not release hydrogen, and 95Mg + 5NbF₅ and 90Mg + 10NbF₅ had quite high hydrogenation and dehydrogenation rates, with 95Mg + 5NbF₅ having higher hydrogenation and dehydrogenation rates than 90Mg + 10NbF₅.

Figure 6 shows the particle size distributions of 95Mg + 5NbF₅ and 90Mg + 10NbF₅ 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 + 5NbF₅ had the strongest peak at 0.5 μm and the second strongest peak at 1.2 μm. 90Mg + 10NbF₅ had the strongest peak at 1.0 μm and the second strongest peak at 0.3

Fig. 7. SEM images of (a) 95Mg + 5NbF₅ and (b) 90Mg + 10NbF₅ from which hydrogen was released at $C_n = 3$.

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 $C_n = 3$ 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 $C_n = 3$ 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 powder XRD patterns of Pure Mg from which hydrogen was released at $C_n = 9$, and 95Mg + 5NbF₅ and 90Mg + 10NbF₅ from which hydrogen was released at $C_n = 3$ were examined [22,25]. The powder XRD pattern of Mg from which hydrogen was released at $C_n = 9$ 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 $C_n = 3$ 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 $C_n = 3$ 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.

Fig. 8. H_h vs. t curves at $C_n = 1$ 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% Nb₂O₅ at 573K in 10 bar hydrogen [28], for 95 wt% MgH₂ + 5 wt% NaOH at 573K in an initial pressure of 17 bar hydrogen [29], and for 98 mol% MgH₂ + 2 mol% FeF₃ at 573K in 10 bar hydrogen [13].

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 NbF₃ 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 NbF₃ 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 H_h vs. t curves at $C_n = 1$ 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% Nb₂O₅ at 573K in 10 bar hydrogen [28], for 95 wt% MgH₂ + 5 wt% NaOH at 573K 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% Nb₂O₅. 98 mol% MgH₂ + 2 mol% Nb₂O₅ 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% Nb₂O₅ 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. 95 wt% MgH₂ + 5 wt% NaOH stored 4.00 wt% hydrogen in 0.63 min, 5.50 wt% hydrogen in 1.17 min, and 5.76 wt% hydrogen in 10 min. 98 mol% MgH₂ + 2 mol% FeF₃ stored 3.00 wt% hydrogen in 0.67 min, 4.60 wt% hydrogen in 2.8 min, and 5.32 wt% hydrogen in 16.67 min. 95Mg + 5NbF₅ stored 3.17 wt% hydrogen in 2.5 min, 4.37 wt% hydrogen in 5 min, 5.10 wt%

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 MgH_2 is considered to have led to the smaller quantity of hydrogen stored in 30 min by 95Mg + 5NbF₅ than by 95 wt% MgH_2 + 5 wt% NaOH and 98 mol% MgH_2 + 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 MgH_2 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 MgF_2 , 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% NbF₅ 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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