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Fe₂O₃, MnO, and VCl₃-added Mg composites by reaction-involving grinding processing for hydrogen storage

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Oxide-added samples, 90 wt% Mg + 10 wt% Fe₂O₃ (named Mg-10Fe₂O₃) and 90 wt% Mg + 10 wt% MnO (named Mg-10MnO), a halide-added sample, 90 wt% Mg + 10 wt% VCl₃ (named Mg-10VCl₃), and a pure Mg sample (named Mg) were prepared by reaction-involving grinding (grinding in hydrogen). The hydriding and dehydriding properties of the prepared samples were examined and compared. For the halide-added sample, Mg-10VCl₃, the initial hydriding rate was much higher and the quantity of hydrogen absorbed for 60 min was significantly larger than those of the oxide-added samples and Mg. After activation, Mg-10VCl₃ had much higher initial hydriding and dehydriding rates, and much larger quantities of hydrogen absorbed and released for 60 min, than Mg-10Fe₂O₃, Mg-10MnO, and Mg. The activated Mg-10Fe₂O₃ and Mg-10MnO absorbed 5.16 and 3.95 wt% H, respectively, at 593 K in 12 bar H₂ for 60 min. The activation of Mg-10VCl₃ was completed after two hydriding-dehydriding cycles. Mg-10VCl₃ had an effective hydrogen-storage capacity (the quantity of hydrogen absorbed for 60 min) of 5.71 wt% at the second cycle (n = 2). At n = 2, the sample absorbed 4.58 wt% H for 5 min and 5.71 wt% H for 60 min at 593 K in 12 bar H₂. At n = 3, the sample released 1.32 wt% H for 10 min and 5.42 wt% H for 60 min at 593 K in 1.0 bar H₂. The hydrogen release equilibrium hydrogen pressure-composition-temperature (PCT) curve at 593 K showed an equilibrium plateau pressure at 2.56 bar.

Key words: Hydrogen absorbing materials, Reaction-involving grinding, Scanning electron microscopy (SEM), X-ray diffraction, MnO, Fe₂O₃, VCl₃ addition.

Introduction

Magnesium (Mg) has a high hydrogen storage capacity (7.6 wt% on the basis of magnesium hydride MgH₂ and 8.3 wt% on the basis of Mg), is relatively inexpensive, and has a great deal of reserves in the Earth's crust. The potential of magnesium hydride as a reversible hydrogen storage medium has attracted attention for improving the reaction kinetics of magnesium with hydrogen [1]. Many researchers have attempted to increase the hydrogen absorption and release rates of magnesium by alloying with magnesium transition metals [2, 3], such as Cu, Ni, Ti, and Fe, and by synthesizing compounds, such as LaMg₁₂ and CeMg₁₂ [4].

The oxides are brittle, and thus may be pulverized during mechanical grinding. The added oxides and/or the oxides pulverized during mechanical grinding may help the particles of magnesium become finer. The hydriding and dehydriding kinetics of Mg was improved by the addition to MgH_2 or Mg of V_2O_5 , VN, or VC [5], Cr₂O₃ [6], Nb₂O₅ [7-10], MgO [11], Cr₂O₃, Al₂O₃, and CeO₂ [12], CeO₂ [13], and Y₂O₃ [14]. Huang et al. [15] ball milled small amounts of the iron oxides, Fe₂O₃ and Fe₃O₄, with Mg powder in a hydrogen atmosphere (Mg to Fe atomic ratio: 20:1), using a magnetically controlled Uni-Ball-Mill. They reported that Thermogravimetry (TG) analysis combined with Differential scanning calorimetry (DSC) revealed a higher hydrogen storage capacity for the $Mg + Fe_2O_3 + H_2$ -milled product (6 wt% H), compared with 5 wt% H for Mg + $Fe_3O_4 + H_2$ and X-ray diffraction (XRD) revealed that during heating, both iron oxides were reduced to pure Fe. We were interested in Fe₂O₃ and MnO as additives. They are not expensive, their melting points are 1,838 K and 2,218 K, and their densities are 5.242 and 5.43 and g/cm³, respectively [16, 17].

Malka et al. [18] milled various halides with MgH₂, and studied the optimum amount of halide additive and milling conditions. They also investigated the influences of these additives on the decomposition temperature of MgH₂, compared the catalytic efficiencies of the chlorides and fluorides of the various metals studied were compared. They reported that among the studied

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halides, the best catalysts for magnesium hydride decomposition were ZrF₄, TaF₅, NbF₅, VCl₃, and TiCl₃.

In this work, Fe_2O_3 , MnO, and VCl₃ were chosen as additives to enhance the hydriding and dehydriding rates of Mg. The additive contents were 10 wt%. Oxide-added samples, 90 wt% Mg + 10 wt% Fe₂O₃ and 90 wt% Mg + 10 wt% MnO, a halide-added sample, 90 wt% Mg + 10 wt% VCl₃, and a pure Mg sample were prepared by reaction-involving grinding (grinding in hydrogen). The hydridindg and dehydriding properties of the prepared samples were examined and compared. The samples were designated as Mg-10Fe₂O₃, Mg-10MnO, Mg-10VCl₃, and Mg, respectively.

Experimental Details

The starting materials used were pure Mg powder (particle size 74-149 μ m, purity 99.6%, Alfa Aesar), Fe₂O₃ (< 5 μ m, purity 99+%, Aldrich), MnO (88-250 μ m, purity 99%, Aldrich), and VCl₃ (Vanadium (III) chloride, purity 97%, Aldrich).

Reaction-involving grinding was performed in a planetary ball mill (Planetary Mono Mill; Pulverisette 6, Fritsch). Mixtures with the desired compositions (total weight = 8 g) were mixed in a stainless steel container (with 105 hardened steel balls, total weight = 360 g) sealed hermetically. The sample-to-ball weight ratio was 1/45. In order to prevent oxidation, all sample handling was performed in a glove box in Ar. The disc revolution speed was 250 rpm. The mill container (volume of 250 ml) was then filled with high purity hydrogen gas (\approx 12 bar). The reaction-involving grinding was performed for 6 h by repeating 15 min grinding and 5 min rest. Hydrogen was refilled every two hours.

The absorbed or released hydrogen quantity was measured as a function of time by a volumetric method, using a Sievert's type hydriding and dehydriding apparatus described previously [19-21]. During the measurements, the hydrogen pressures were maintained nearly constant by compensating the absorbed hydrogen from a small reservoir of known volume during hydriding or removing the released hydrogen to the small reservoir during dehydriding. 0.5 g of the samples was used for the measurement of the absorbed or desorbed hydrogen quantity as a function of time. After the absorbed and then desorbed hydrogen quantities were measured at 593 K under 12 and 1.0 bar H_2 for 1 h, respectively, the sample was then dehydrided at 623 K in vacuum for 2 h. The equilibrium hydrogen pressure-compositiontemperature (PCT) curve was obtained by repeating the following steps: waiting for equilibrium, measuring equilibrium hydrogen pressure, taking some hydrogen out of the reactor, and measuring the taken hydrogen quantity.

Samples after reaction-involving grinding and samples after hydriding-dehydriding cycling were characterized by X-ray diffraction (XRD) with Cu K α radiation, using a

Rigaku D/MAX 2500 powder diffractometer. The microstructures of the powders were observed by a JSM-5900 scanning electron microscope (SEM) operated at 15 kV.

Results and Discussions

The percentage of absorbed hydrogen, H_a , was defined as 100 × the weight of absorbed hydrogen / the sample weight.

Fig. 1 shows the H_a vs. time t curves at 593 K in 12 bar H₂ at the cycle number, n, of one (n = 1) for Mg [20], Mg-10MnO [21], Mg-10Fe₂O₃ [21], and Mg-10VCl₃. Mg absorbed hydrogen extremely slowly [20]. Mg-10VCl₃ had a higher initial hydriding rate than Mg-10Fe₂O₃, but Mg-10VCl₃ had a slightly smaller quantity of hydrogen absorbed for 60 min, H_a (60 min), than Mg-10Fe₂O₃. Mg-10VCl₃ had a higher initial hydriding rate and a larger H_a (60 min) than Mg-10MnO. Mg absorbed 0.08 wt% H for 2.5 min, and 0.14 wt% H for 60 min [20]. Mg-10VCl₃ absorbed 2.75 wt% H for 5 min, 4.59 wt% H for 10 min, and



Fig. 1. H_a vs. t curves at 593 K in 12 bar H_2 at n = 1 for Mg, Mg-10MnO, Mg-10Fe₂O₃, and Mg-10VCl₃.



Fig. 2. H_a vs. t curves at 593 K in 12 bar H_2 for activated Mg, Mg-10MnO, Mg-10Fe₂O₃, and Mg-10VCl₃.

Table 1. Variations in the absorbed hydrogen quantity (wt% H) with time at 593 K in 12 bar H_2 at n = 1 for Mg, Mg-10MnO, Mg-10Fe₂O₃, and Mg-10VCl₃.

	2.5 min	5 min	10 min	30 min	60 min
Mg	0.00	0.00	0.00	0.00	0.14
Mg-10MnO	2.35	2.74	3.12	3.58	3.95
Mg-10Fe ₂ O ₃	1.95	2.58	3.52	5.05	5.56
Mg-10VCl ₃	2.75	3.71	4.59	5.20	5.43

Table 2. Variations in the absorbed hydrogen quantity (wt% H) with time at 593 K in 12 bar H_2 for the activated Mg, Mg-10MnO, Mg-10Fe₂O₃, and Mg-10VCl₃.

	2.5 min	5 min	10 min	30 min	60 min
Mg	1.69	2.61	3.24	3.81	4.15
Mg-10MnO	2.36	2.73	3.12	3.57	3.95
Mg-10Fe ₂ O ₃	2.41	3.52	4.26	4.84	5.16
Mg-10VCl ₃	3.24	4.58	5.25	5.57	5.71

5.43 wt% H for 60 min. Meanwhile, Mg-10Fe₂O₃ absorbed 2.58 wt% H for 5 min, 3.52 wt% H for 10 min, and 5.56 wt% H for 60 min [21]. Table 1 summarizes the variations in the absorbed hydrogen quantity (wt% H) with time at 593 K in 12 bar H₂ at n = 1 for these samples.

The H_a vs. t curves at 593 K in 12 bar H_2 for activated Mg, Mg-10MnO, Mg-10Fe₂O₃, and Mg-10VCl₃ are shown in Fig. 2. The activation of Mg-10MnO was not required. Mg-10Fe2O3 was activated after two hydriding-dehydriding cycles. The activation of Mg was completed after 8 hydriding-dehydriding cycles [20], and the H_a vs. t curve of Mg at n = 8 is given. The activation of Mg-10VCl₃ was completed after n = 2, as shown in Fig. 5. Mg-10VCl₃ had the highest initial hydriding rate, followed in descending order by Mg-10Fe₂O₃, Mg-10MnO, and Mg. Mg- $10VCl_3$ had the largest H_a (60 min), followed in descending order by Mg-10Fe₂O₃, Mg, and Mg-10MnO. Mg absorbed 2.61 wt% H for 5 min, 3.24 wt% H for 10 min, and 4.15 wt% H for 60 min [20]. Mg-10VCl₃ absorbed 4.58 wt% H for 5 min, 5.25 wt% H for 10 min, and 5.71 wt% H for 60 min. Meanwhile, Mg-10Fe₂O₃ absorbed 3.52 wt% H for 5 min, 4.26 wt% H for 10 min, and 5.16 wt% H for 60 min [21]. Table 2 summarizes the variations in the absorbed hydrogen quantity (wt% H) with time at 593 K in 12 bar H_2 for the activated samples.

The amount of released hydrogen, H_d , was also defined as 100 × the weight of desorbed hydrogen / the sample weight.

Fig. 3 shows the H_d vs. t curves at 593 K in 1.0 bar H_2 for activated Mg, Mg-10MnO, Mg-10Fe₂O₃, and Mg-10VCl₃. The Mg after reaction-involving grinding did not release hydrogen [20]. Mg-10VCl₃ had the highest initial dehydriding rate and the largest H_d (60 min), followed in descending order by Mg-10MnO,



Fig. 3. H_d vs. t curves at 593 K in 1.0 bar H_2 for activated Mg, Mg-10MnO, Mg-10Fe₂O₃, and Mg-10VCl₃.

Table 3. Variations in the released hydrogen quantity (wt% H) with time at 593 K in 1.0 bar H_2 for the activated Mg, Mg-10MnO, Mg-10Fe₂O₃, and Mg-10VCl₃.

	2.5 min	5 min	10 min	30 min	60 min
Mg	0	0	0	0	0
Mg-10MnO	0.18	0.28	0.45	1.35	1.94
Mg-10Fe ₂ O ₃	0.12	0.15	0.25	0.48	0.88
Mg-10VCl ₃	0.27	0.61	1.41	4.58	5.46

Mg-10Fe₂O₃, and Mg. Mg-10Fe₂O₃ released 0.25 wt% H, 0.48 wt% H, and 0.88 wt% H after 10, 30, and 60 min, respectively [21]. Mg-10MnO released 0.45 wt% H, 1.35 wt% H, and 1.94 wt% H after 10, 30, and 60 min, respectively [21]. Mg-10VCl₃ released 1.41 wt% H, 4.58 wt% H, and 5.46 wt% H after 10, 30, and 60 min, respectively. Table 3 shows the variations in the released hydrogen quantity (wt% H) with time at 593 K in 1.0 bar H₂ for the activated Mg, Mg-10MnO, Mg-10Fe₂O₃, and Mg-10VCl₃.

Fig. 4 shows the variations in the initial hydriding rate, the initial dehydriding rate, and H_a (60 min) and H_d (60 min), which are the quantities of hydrogen absorbed in 12 bar H₂ and released in 1.0 bar H₂ at 593 K for 60 min, with the activated samples: Mg, Mg-10MnO, Mg-10Fe₂O₃, and Mg-10VCl₃. The initial hydriding rates were calculated from the quantities of hydrogen absorbed for 2.5 min and the initial dehydriding rates were calculated from the quantities of hydrogen released for 10 min. Mg-10VCl₃ had the highest initial hydriding rate, followed in descending order by Mg-10Fe₂O₃, Mg-10MnO, and Mg. Mg-10VCl₃ had the highest initial dehydriding rate, followed in descending order by Mg-10MnO, Mg-10Fe₂O₃, and Mg. Mg-10VCl₃ had the largest H_a (60 min), followed in descending order by Mg-10Fe₂O₃, Mg, and Mg-10MnO. Mg-10VCl₃ had the largest H_d (60 min), followed in descending order by Mg-10MnO, Mg-10Fe₂O₃, and Mg. Mg-10VCl₃ had the highest initial hydriding and dehydriding rates, and the largest H_a (60 min) and H_d (60 min). In particular,



Fig. 4. Variations in (a) the initial hydriding rate and the initial dehydriding rate and (b) H_a (60 min) and H_d (60 min), the quantities of hydrogen absorbed in 12 bar H_2 and released in 1.0 bar H_2 at 593 K for 60 min with the activated samples: Mg, Mg-10MnO, Mg-10Fe₂O₃, and Mg-10VCl₃.

Table 4. Variations in the initial hydriding rate, the initial dehydriding rate, H_a (60 min) in 12 bar H_2 , and H_d (60 min) in 1.0 bar H_2 at 593 K with activated Mg, Mg-10MnO, Mg-10Fe₂O₃, and Mg-10VCl₃.

	Mg	Mg- 10MnO	Mg- 10Fe ₂ O ₃	Mg- 10VCl ₃
Initial hydriding rate (wt% H/min)	0.676	0.944	0.964	1.296
Initial dehydriding rate (wt% H/min)	0.000	0.045	0.025	0.141
H _a (60 min) (wt% H)	4.15	3.95	5.16	5.71
H _d (60 min) (wt% H)	0.00	1.94	0.88	5.45

Mg-10VCl₃ had much larger H_d (60 min) than the other samples. Table 4 shows the variations in the initial hydriding rate, the initial dehydriding rate, H_a (60 min) in 12 bar H_2 , and H_d (60 min) in 1.0 bar H_2 at 593 K with the activated samples: Mg, Mg-10MnO, Mg-10Fe₂O₃, and Mg-10VCl₃.

Fig. 5 shows the variations in H_a vs. t curve in 12 bar H_2 and H_d vs. t curve in 1.0 bar H_2 at 593 K with number of cycles, n, for Mg-10VCl₃. At the first cycle, the hydriding rate was quite high from the beginning to



Fig. 5. Variations in (a) H_a vs. t curve in 12 bar H_2 and (b) H_d vs. t curve in 1.0 bar H_2 at 593 K with number of cycles n for Mg-10VCl₃.

Table 5. Variations in H_a with time at 593 K in 12 bar H_2 at n = 1-3 for Mg-10VCl₃.

	2.5 min	5 min	10 min	30 min	60 min
n = 1	2.75	3.71	4.59	5.20	5.43
n = 2	3.24	4.58	5.25	5.57	5.71
n = 3	3.16	4.46	5.15	5.46	5.56

about 5 min, and then very low after 15 min. As the number of cycles increased from one to two, the initial hydriding rate and the quantity of hydrogen absorbed for 60 min, H_a (60 min), increased. From n = 2 to n = 3, the initial hydriding rate and H_a (60 min) decreased. At n = 3 and n = 4, the initial hydriding rate and H_a (60 min) were very similar. At n = 2, the sample absorbed 4.58 wt% H for 5 min, 5.25 wt% H for 10 min, and 5.71 wt% H for 60 min at 593 K in 12 bar H_2 . The effective hydrogen absorbed for 60 min. Mg-10VCl₃

Table 6. Variations in H_d with time at 593K in 1.0 bar H_2 at n = 1-3 for Mg-10VCl₃.

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	2.5 min	5 min	10 min	30 min	60 min
n = 1	0.00	0.15	0.50	2.92	5.25
n = 2	0.13	0.38	1.03	3.99	5.48
n = 3	0.21	0.53	1.32	4.47	5.42



Fig. 6. XRD patterns of Mg-10VCl₃ (a) after reaction-involving grinding and (b) dehydrided at the 4th hydriding-dehydriding cycle.

had an effective hydrogen-storage capacity of about 5.71 wt% at n = 2. Table 5 shows the variation of H_a with time at 593K in 12 bar H_2 at n = 1-3 for Mg-10VCl₃. At n = 1, the dehydriding rate was low from the beginning to about 5 min and then increased gradually. The dehydriding rate was the highest at about 25 min and then decreased gradually at n = 1. The initial dehydriding rate and the maximum dehydriding rate (appearing at 20-25 min) increased from n = 1 to n = 4. The quantity of hydrogen released for 60 min, H_d (60 min), increased from n = 1 to n = 2 and then decreased from n = 2 to n = 3. The H_d versus t curves at n = 3 and n = 4 were very close to each other. At n = 3, the sample released 0.21 wt% H for 2.5 min, 4.47 wt% H for 30 min, and 5.42 wt% H for 60 min at



Fig. 7. Microstructures of Mg-10VCl₃ (a, b) after reactioninvolving grinding and (c, d) Mg-10VCl₃ dehydrided at the 4^{th} hydriding-dehydriding cycle.

593 K in 1.0 bar H₂. At n = 3, the quantity of hydrogen released for 60 min was 97.4% of that absorbed for 60 min. Table 6 shows the variations in H_d with time at 593 K in 1.0 bar H₂ at n = 1-3 for Mg-10VCl₃. Fig. 5 shows that the activation of Mg-10VCl₃ was completed after two hydriding-dehydriding cycles.

The XRD patterns of Mg-10VCl₃ after reactioninvolving grinding and Mg-10VCl₃ dehydrided at the 4th hydriding-dehydriding cycle are shown in Fig. 6. The sample after reaction-involving grinding contained Mg and β -MgH₂. β -MgH₂ was formed by the reaction of Mg with hydrogen during reaction-involving grinding. β -MgH₂ is a low-pressure form of MgH₂ that has a tetragonal structure. The XRD pattern of Mg-10VCl₃ dehydrided at the 4th hydriding-dehydriding cycle showed that the sample contained Mg, β -MgH₂, and MgO. This XRD pattern exhibited very slightly narrower peaks and a lower background than the XRD pattern of Mg-10VCl₃ after reaction-involving grinding. This suggests that this sample had slightly better crystallinity than the sample after reaction-involving grinding.

Fig. 7 shows the microstructures of Mg-10VCl₃ after reaction-involving grinding and Mg-10VCl₃ dehydrided at the 4th hydriding-dehydriding cycle. The SEM micrographs of Mg-10VCl₃ after reaction-involving grinding show that the particle sizes were not homogeneous, and the shapes of particles were irregular. Some large particles had flat surfaces. The SEM micrographs of Mg-10VCl₃ dehydrided at the 4th hydriding-dehydriding cycle show that the particles of Mg-10VCl₃ after reaction-involving grinding became agglomerates consisting of fine particles. The fine particles are believed to have been formed due to the expansion and contraction of particles with the hydriding-dehydriding cycling.

The microstructures of Mg-10Fe₂O₃ and Mg-10MnO



Fig. 8. Microstructure of (a) $Mg-10Fe_2O_3$ and (b) Mg-10MnO after reaction-involving grinding.



Fig. 9. Hydrogen release Pressure-Composition-Temperature (PCT) curve at 593 K for Mg-10VCl₃.

after reaction-involving grinding are shown in Fig. 8. The particles of Mg-10Fe₂O₃ were in the form of agglomerates consisting of fine particles. Mg-10MnO had relatively large particles, in the surfaces of which fine particles were embedded. The particles of Mg-10Fe₂O₃ were smaller than those of Mg-10VCl₃ after reaction-involving grinding.

Fig. 9 shows the hydrogen release Pressure-Composition-Temperature (PCT) curve at 593 K for activated Mg-10VCl₃. The hydrogen pressure decreased abruptly from a hydrogen pressure of about 11.7 bar to about 2.4 bar, then increased slightly, and remained almost constant at 2.56 bar, and finally began to decrease slowly. The equilibrium plateau pressure was found in the H_d range of 4.8-1.0 wt% H. The reported data showed that the equilibrium plateau pressure in the Mg-H system at 593 K is 2.77 bar [22]. The hydrogen-storage capacity of the sample was about 5.35 wt%. This sample had an effective hydrogen-storage capacity (the quantity of hydrogen absorbed for 60 min) of 5.71 wt%. The hydrogen-storage capacity of the sample is believed to be smaller than the effective hydrogen-storage capacity, because the sample was stored for about two months in a glove box, becoming slightly contaminated.

In our other work, the VCl₃-added Mg sample exhibited VH_{0.81} phase after reaction-involving grinding and after hydriding-dehydriding cycling [23]. The TiH_{1.924} phase was observed in as-milled 95 wt% Mg+5 wt% TiCl₃ and 90 wt% Mg+10 wt% TiCl₃

samples [24]. During milling under hydrogen of the 90 wt% Mg + 10 wt% VCl₃ mixture, the following reaction is believed to produce $VH_{0.81}$:

$$Mg + VCl_3 + 1.405H_2 \rightarrow MgH_2 + VH_{0.81} + 1.5Cl_2.$$
(1)

The produced Cl_2 is considered to be taken out during pumping before the first hydriding measurement. During hydriding-dehydriding cycling, $VH_{0.81}$ remains undecomposed and the following reaction occurs:

$$Mg + VH_{0.81} + H_2 \leftrightarrow MgH_2 + VH_{0.81}.$$
 (2)

Song [25] reviewed the kinetic studies of the hydrogen absorption and release reactions of Mg. Many works do not agree with one another on the ratecontrolling step(s) for the hydriding or dehydriding of magnesium. However, there is no contradiction in the points that the hydrogen absorption and release reactions of Mg are nucleation-controlled under certain conditions, and progress by a mechanism of nucleation and growth, and that the hydriding rates of Mg are controlled by the diffusion of hydrogen through a growing Mg hydride layer. Fig. 1 shows that Mg absorbs hydrogen extremely slowly. It is considered that nucleation of the magnesium hydride and the diffusion of hydrogen through a growing Mg hydride layer control the hydriding rate of Mg. The VCl₃-added Mg sample showed a much higher initial dehydriding rate and a much larger quantity of hydrogen released for 60 min than Mg. The reactive mechanical grinding of Mg with VCl₃, which forms β -MgH₂ and VH_{0.81}, is thought to create defects on the surface and in the interior of Mg particle, to produce clean surfaces, and to reduce the particle size of Mg. Creation of defects facilitates the nucleation of magnesium hydride, production of clean surfaces increases the reactivity of particles with hydrogen, and decrease in the Mg particle size leads to the diminution of diffusion distances for hydrogen atoms [26-30]. These effects are believed to increase the initial hydriding and dehydriding rates and the quantity of hydrogen absorbed and released for 60 min of Mg-10VCl₃. The β -MgH₂ and VH_{0.81} formed in the as-milled Mg-10VCl₃ are believed to make these effects stronger.

On the other hand, the XRD patterns of as-milled 90 wt% Mg + 10 wt% oxide (oxide = Fe_2O_3 or MnO) showed that a small amount of MgH₂ was formed in the samples and the samples also contained Mg and oxide (Fe_2O_3 or MnO) [21]. While Fe_2O_3 and MnO remain unchanged in phases, the change in phase of VCl₃ to form VH_{0.81} during milling of Mg with VCl₃ is thought to effects of reactive mechanical grinding stronger.

da Conceição et al. [31] studied the MgH₂-based composites processed by mechanical alloying with the

addition of 5 wt% of V, VC and VCl₃. They reported that the MgH₂-5 wt% VCl₃ composite, which absorbed 6.0 wt% H in 7.5 min at 623 K, showed faster absorption kinetics than V or VC-added MgH₂. The MgH₂-5 wt% VCl₃ composite has a slightly higher hydrogen-storage capacity than Mg-10VCl₃. This is probably due to using MgH₂ instead of Mg as a starting material, and measuring the hydrogen-storage capacity at a higher temperature.

Conclusions

A halide-added sample, Mg-10VCl₃, had a much higher initial hydriding rate and a significantly larger quantity of hydrogen absorbed for 60 min than oxideadded samples, Mg-10Fe₂O₃ and Mg-10MnO, and Mg. After activation, Mg-10VCl₃ had much higher initial hydriding and dehydriding rates, and significantly larger quantities of hydrogen absorbed and released for 60 min, than Mg-10Fe₂O₃, Mg-10MnO, and Mg. The activated Mg-10Fe₂O₃ and Mg-10MnO absorbed 5.16 and 3.95 wt% H, respectively, at 593 K in 12 bar H₂ for 60 min. The activation of Mg-10VCl3 was completed after two hydriding-dehydriding cycles. Mg-10VCl₃ had an effective hydrogen-storage capacity (the quantity of hydrogen absorbed for 60 min) of 5.71 wt% at the second cycle (n=2). At n=2, the sample absorbed 4.58 wt% H for 5 min and 5.71 wt% H for 60 min at 593 K in 12 bar H₂. At n=3, the sample released 1.32 wt% H for 10 min and 5.42 wt% H for 60 min at 593 K in 1.0 bar H₂. The hydrogen release P (equilibrium hydrogen pressure) -C (composition) -T (temperature) curve at 593 K showed an equilibrium plateau pressure at 2.56 bar. The reactioninvolving grinding of Mg with VCl₃ is believed to increase the initial hydriding and dehydriding rates and the quantities of hydrogen absorbed and released for 60 min of Mg, by facilitating nucleation (of magnesium hydride for absorption, and of Mg-H solid solution for release), increasing the reactivity of particle surfaces, and decreasing the diffusion distances of hydrogen atoms.

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