

Comparison of the hydrogenation and dehydrogenation properties of oxide and halide-added Mg composites prepared by reactive mechanical grinding and characterization of an Mg-TiCl₃ composite

Hye Ryoung Park^a, Seong Ho Lee^b and Myoung Youp Song^{c,*}

^aSchool of Chemical Engineering, Chonnam National University, 77 Yongbong-ro Buk-gu, Gwangju 61186, Korea

^bDepartment of Materials Engineering, Graduate School, Chonbuk National University, 567 Baekje-daero Deokjin-gu, Jeonju 54896, Korea

^cDivision of Advanced Materials Engineering, Hydrogen & Fuel Cell Research Center, Engineering Research Institute, Chonbuk National University, 567 Baekje-daero Deokjin-gu, Jeonju 54896, Korea

The hydrogen absorption and release properties of oxide-added alloys (90Mg + 10Fe₂O₃ and 90Mg + 10MnO) and halide-added alloys (90Mg + 10TiCl₃ and 90Mg + 10TaF₅), which were prepared by high-energy ball milling in hydrogen (reactive mechanical grinding), were compared after activation. In addition, the hydrogen absorption and release properties of 95Mg + 5TiCl₃, which had high hydrogen absorption and release rates, were investigated in detail. A halide-added Mg alloy, 90Mg + 10TiCl₃, had better hydrogen absorption and release properties than the oxide-added Mg alloys, 90Mg + 10Fe₂O₃ and 90Mg + 10MnO. 95Mg + 5TiCl₃ had a relatively high effective hydrogen-storage capacity of about 6.3 wt% and a relatively high hydrogen release rate. At the first cycle ($n = 1$), the sample absorbed 4.84 wt% H for 5 min, 5.86 wt% H for 10 min, and 6.27 wt% H for 60 min at 593 K in 12 bar H₂. The activation of the sample was completed after three hydrogen absorption-release cycles. At the third cycle ($n = 3$), the sample released 1.26 wt% H for 10 min, 3.52 wt% H for 30 min, and 5.32 wt% H for 60 min at 593 K in 1.0 bar H₂. The XRD pattern of 95Mg + 5TiCl₃ dehydrided at $n = 4$ revealed Mg, β -MgH₂, and small amounts of MgO and TiH_{1.924}. The formation of titanium hydride (TiH_{1.924}) in 95Mg + 5TiCl₃ is believed to have contributed to the improvement of hydrogen absorption and release properties of 95Mg + 5TiCl₃.

Key words: Hydrogen absorbing materials, Reactive mechanical grinding, Microstructure, Phase transformation, Oxide and halide addition to Mg.

Introduction

Compared with other hydrogen storage methods, such as pressure storage, cryogenic storage, and carbon nanotube storage, metal hydride storage has several advantages: storage of a large amount of hydrogen per unit volume and higher safety than pressure storage and cryogenic storage. Waste heat can be used to release hydrogen from metal hydrides. In addition, high-purity hydrogen can be produced using metal hydrides due to selective absorption and release of hydrogen by metal hydrides [1].

Magnesium has a high hydrogen storage capacity (7.6 wt%), is of low cost, and is abundant in the earth's crust. However, it absorbs and releases hydrogen very slowly. A lot of work to improve the reaction kinetics with hydrogen of magnesium has been performed by alloying magnesium with certain metals [2, 3], such as Cu [4], Ni [5, 6], Ti [7], Ni and Y [8], and Ti, Fe, and Ni [9], by synthesizing compounds such as CeMg₁₂

[10], and by making composites, such as Mg-20 wt% Fe₂₃Y₈ [11], Mg with more than 5 wt% FeTiO₃ [12], and MgH₂ with 5 wt% ZrO₂ + 5 wt% single-walled carbon nanotubes [13].

Song [14] reviewed the kinetic studies of the hydrogen absorption and release reactions of Mg. Many works disagree one another on the rate-controlling step(s) for the hydriding or dehydriding of magnesium. However, there is no contradiction on 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. The hydrogen absorption and release kinetics of Mg can thus be improved by a treatment such as high-energy ball milling, which can create defects on the surface and/or in the interior of Mg and reduce the particle size of Mg.

The oxides or halides may be pulverized during mechanical grinding. The added oxides or halides and/or their pulverization during mechanical grinding may help the particles of magnesium become finer. The hydrogen absorption and release kinetics of Mg was also improved by the addition to MgH₂ or Mg of Sc₂O₃,

*Corresponding author:
Tel : +82-63-270-2379
Fax: +82-63-270-2386
E-mail: songmy@jbnu.ac.kr

TiO₂, V₂O₅, Cr₂O₃, Mn₂O₃, Fe₃O₄, CuO, Al₂O₃, SiO₂ [15], V₂O₅, VN or VC [16], Cr₂O₃ [17], Nb₂O₅ [18-21], MgO [22], Cr₂O₃, Al₂O₃ and CeO₂ [23], CeO₂ [24], and Y₂O₃ [25]. Oelerich et al. [15] reported that the transition-metal oxides act as catalysts for the magnesium-hydrogen reaction, after investigating high energy ball-milled MgH₂ / Metal oxide-nanocomposites with respect to hydrogen sorption kinetics.

In our previous work [26], the hydrogen absorption and release properties were studied for 90Mg + 10Fe₂O₃, 90Mg + 10Fe₂O₃ prepared by spray conversion, 90Mg + 10MnO, and 90Mg + 10SiO₂ samples, which were prepared by ball milling in hydrogen for 2 h under the conditions similar to those for the preparation of halide-added Mg alloys. 90Mg + 10Fe₂O₃ and 90Mg + 10MnO had relatively high hydrogen absorption or release rates.

Malka et al. [27] milled magnesium hydride (MgH₂) with various halides to study their effects on the optimum content of halide additive and milling conditions. The effects of oxidation state, valence, and periods and groups of added halides on MgH₂ decomposition temperature were also studied. They reported that among the halides added, the best catalysts for magnesium hydride decomposition were ZrF₄, TaF₅, NbF₅, VCl₃ and TiCl₃. Seven wt% of various metal halide additives (ZrF₄, TaF₅, NbF₅ and TiCl₃) were added to magnesium hydride by ball milling, and the effects of these additives on the hydrogen absorption and release kinetics were investigated by Sieverts' apparatus [28]. They reported that partial and full disproportionation reactions occurred with TaF₅, NbF₅, and TiCl₃ involved directly after milling and the first hydrogen release-absorption cycle. The catalytic effect of metal halides on the Mg hydrogen absorption and release process resulted from the formation of pure transition metal and/or the MgF₂ phase.

Ma et al. [29] investigated the hydrogen absorption and desorption kinetics of MgH₂ catalyzed with 4 mol% titanium compounds (TiF₃, TiCl₃, TiO₂, TiN, and TiH₂). MgH₂-4 mol% TiCl₃ absorbed about 3.7 wt% H at 423 K in an initial hydrogen pressure of 20 bar H₂ and released about 3.85 wt% H at 553 K in an initial hydrogen pressure of 0.1 bar H₂.

In another previous work of our group [30], the hydrogen absorption and release properties were studied for TaF₅, NbF₅, TiCl₃, or VCl₃-added Mg samples prepared by ball milling in hydrogen. Among these samples TiCl₃ or TaF₅-added Mg samples showed quite high hydrogen absorption and release rates.

In this work, TiCl₃ was chosen as an additive to enhance the hydrogen absorption and release rates of Mg. Samples with compositions of Mg-x wt% TiCl₃ (x = 5 and 10), which had additive contents equal or less than 10 wt%, were prepared by ball milling in hydrogen. The previously studied optimum conditions for ball milling in hydrogen, which is called reactive mechanical grinding or reaction-involved milling, were used for the sample preparation. The samples were

designated as 95Mg + 5TiCl₃ and 90Mg + 10TiCl₃, respectively. The hydrogen absorption and release properties of the oxide-added Mg samples (90Mg + 10Fe₂O₃ and 90Mg + 10MnO) and halide-added samples (90Mg + 10TiCl₃ and 90Mg + 10TaF₅) were compared and those of 95Mg + 5TiCl₃, which had high hydrogen absorption and release rates, were investigated in detail.

Experimental Details

Pure Mg powder (particle size 74-149 μm, purity 99.6%, Alfa Aesar) and TiCl₃ (Titanium (III) chloride, Aldrich) were used as the starting materials to prepare samples.

All sample handling was performed in a glove box under Ar in order to prevent oxidation. Mixtures with the desired compositions (total weight = 8 g) were milled in a stainless steel container (with 105 hardened steel balls, total weight = 360 g) of a planetary ball mill (Planetary Mono Mill; Pulverisette 6, Fritsch). The disc revolution speed was 250 rpm. The mill container with a volume of 250 ml, sealed hermetically, was filled with high purity hydrogen gas (≈ 12 bar). 15 min milling and 5 min rest were repeated 24 times, resulting in 6 h milling. Hydrogen was refilled every two hours.

The absorbed or released hydrogen quantity was measured as a function of time in nearly constant hydrogen pressures (12 bar H₂ for absorption and 1.0 bar H₂ for release), using a Sievert's type hydrogen absorption and release apparatus described previously [31]. 0.5 g of the samples was used for these measurements. After the absorbed and then released hydrogen quantities were measured for 1 h, respectively, the sample was then dehydrided at 623 K in vacuum for 2 h. X-ray diffraction (XRD) patterns of the samples after ball milling in hydrogen and after hydrogen absorption-release cycling were obtained with Cu Kα radiation in a Rigaku D/MAX 2500 powder diffractometer. Scanning electron microscope (SEM) micrographs of the samples were obtained by JSM-6400 SEM operated at 20 kV. Particle size distributions of the samples after ball milling in hydrogen and after hydrogen absorption-release cycling were analyzed by dynamic light scattering incorporating the patented controlled reference method for advanced power spectrum analysis of Doppler shifts under Brownian motion, using Microtac UPA150.

Results and Discussion

The percentage of absorbed hydrogen, H_a, is expressed with respect to the sample weight. The percentage of desorbed hydrogen, H_d, is also expressed with respect to the sample weight.

Fig. 1 shows the H_a versus t curves at 593 K under 12 bar H₂ for activated 90Mg + 10Fe₂O₃ [26], 90Mg + 10MnO [26], 90Mg + 10TiCl₃, and 90Mg + 10TaF₅ [32]. Fe₂O₃ (< 5 μm, purity 99+%, Aldrich) and MnO (88-

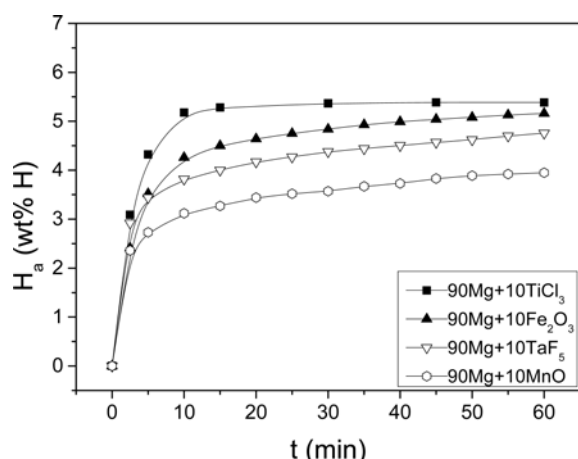


Fig. 1. H_a versus t curves at 593 K in 12 bar H_2 for activated 90Mg + 10Fe₂O₃, 90Mg + 10MnO, 90Mg + 10TiCl₃, and 90Mg + 10TaF₅.

250 μ m, purity 99%, Aldrich) were used for the preparation of 90Mg + 10Fe₂O₃ and 90Mg + 10MnO, respectively. 90Mg + 10TiCl₃ has a higher initial hydrogen absorption rate and a larger quantity of hydrogen absorbed for 60 min than 90Mg + 10TaF₅, 90Mg + 10Fe₂O₃, and 90Mg + 10MnO. 90Mg + 10TiCl₃ has the highest initial hydrogen absorption rate, followed in order by 90Mg + 10TaF₅, 90Mg + 10Fe₂O₃, and 90Mg + 10MnO. 90Mg + 10TiCl₃ has the largest quantity of hydrogen absorbed for 60 min, followed in order by 90Mg + 10Fe₂O₃, 90Mg + 10TaF₅, and 90Mg + 10MnO. 90Mg + 10TiCl₃ absorbs 4.32 wt% H for 5 min, 5.18 wt% H for 10 min, 5.37 wt% H for 30 min, and 5.38 wt% H for 60 min.

The H_d versus t curves at 593 K in 1.0 bar H_2 for activated 90Mg + 10Fe₂O₃ [26], 90Mg + 10MnO [26], 90Mg + 10TiCl₃ [32], and 90Mg + 10TaF₅ are shown in Fig. 2. 90Mg + 10TiCl₃ has the highest initial hydrogen release rate, followed in order by 90Mg + 10MnO and 90Mg + 10Fe₂O₃. The curve for 90Mg + 10TaF₅ exhibits an incubation period of about 2.5 min. After the incubation

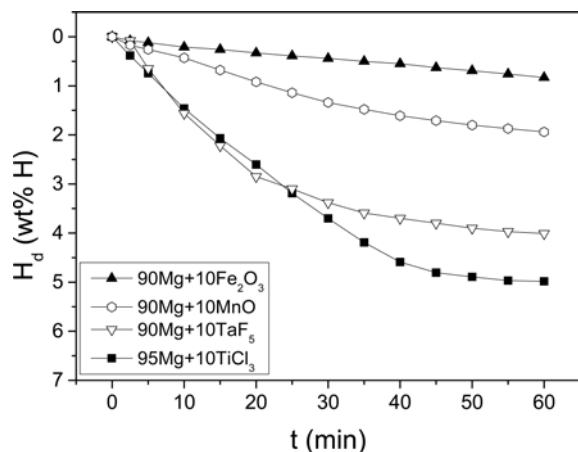


Fig. 2. H_d versus t curves at 593 K in 1.0 bar H_2 for activated 90Mg + 10Fe₂O₃, 90Mg + 10MnO, 90Mg + 10TiCl₃, and 90Mg + 10TaF₅.

period, 90Mg + 10TaF₅ has the highest hydrogen release rate, followed in order by 90Mg + 10TiCl₃, 90Mg + 10MnO, and 90Mg + 10Fe₂O₃. 90Mg + 10TiCl₃ has the largest quantity of hydrogen desorbed for 60 min, followed in order by 90Mg + 10TaF₅, 90Mg + 10MnO, and 90Mg + 10Fe₂O₃. 90Mg + 10TiCl₃ releases 0.38 wt% H for 2.5 min, 1.46 wt% H for 10 min, 3.70 wt% H for 30 min, and 4.98 wt% H for 60 min. 90Mg + 10TaF₅ desorbs 0.65 wt% H for 5 min, 1.56 wt% H for 10 min, 3.38 wt% H for 30 min, and 4.01 wt% H for 60 min.

90Mg + 10TiCl₃ has the highest initial hydrogen absorption rate and the largest quantity of hydrogen absorbed for 60 min among the oxide-added samples (90Mg + 10Fe₂O₃ and 90Mg + 10MnO) and the halide-added samples (90Mg + 10TiCl₃ and 90Mg + 10TaF₅). 90Mg + 10TiCl₃ has the highest initial hydrogen release rate and the largest quantity of hydrogen desorbed for 60 min among these samples.

The X-ray (Cu K α) powder diffraction patterns of 90Mg + 10Fe₂O₃ and 90Mg + 10MnO dehydrided after hydrogen absorption-release cycling showed that peaks for Fe existed in the XRD (X-ray diffraction) pattern of 90Mg + 10Fe₂O₃ and Mn was found in 90Mg + 10MnO. Fe and Mn were formed due to the reduction of each oxide during hydrogen absorption-release cycling. MgO was found in both of the samples. 90Mg + 10Fe₂O₃ contained a very small amount of β -MgH₂, a low pressure form of MgH₂ with a tetragonal structure [26]. The SEM micrographs of 90Mg + 10Fe₂O₃ dehydrided at the 5th hydrogen absorption-release cycle showed that the particle size was not homogeneous and the shapes of particles were irregular. The particles were agglomerated and small particles were on the surfaces of large particles [33].

For 90Mg + 10TiCl₃ and 95Mg + 5TiCl₃, the initial hydrogen absorption rate and the quantity of hydrogen absorbed for 60 min from the first cycle ($n = 1$) to the third cycle ($n = 3$) were similar, while the initial hydrogen release rate and the quantity of hydrogen released for 60 min at $n = 1-3$ were the largest at $n = 2$ or 3. H_a versus time

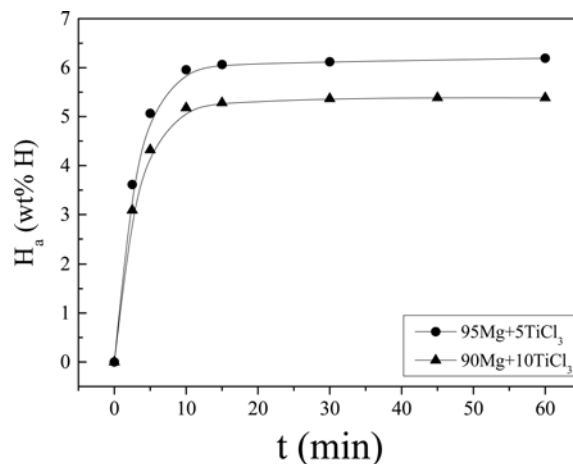


Fig. 3. H_a versus t curves at the 3rd cycle at 593 K in 12 bar H_2 for 95Mg + 5TiCl₃ and 90Mg + 10TiCl₃.

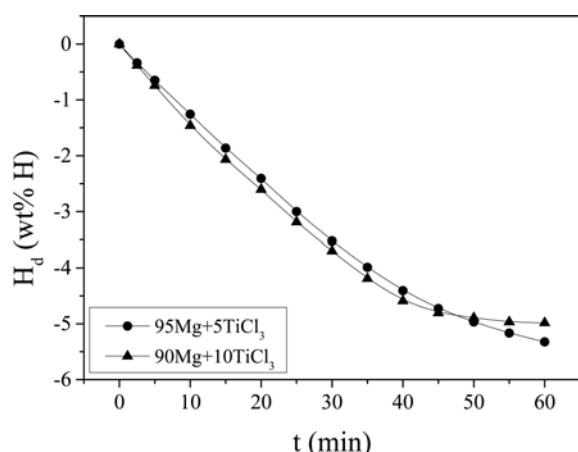


Fig. 4. H_d versus t curves at the 3rd cycle at 593 K in 1.0 bar H_2 for 95Mg + 5TiCl₃ and 90Mg + 10TiCl₃.

t curves and H_d versus t curves for 95Mg + 5TiCl₃ and 90Mg + 10TiCl₃ were thus compared at $n = 3$.

Fig. 3 shows the H_a versus t curves at the 3rd cycle at 593 K in 12 bar H_2 for 95Mg + 5TiCl₃ and 90Mg + 10TiCl₃. 95Mg + 5TiCl₃ and 90Mg + 10TiCl₃ have very high hydrogen absorption rates, and 95Mg + 5TiCl₃ has a higher initial hydrogen absorption rate and a larger quantity of hydrogen absorbed for 60 min than 90Mg + 10TiCl₃. 95Mg + 5TiCl₃ absorbs 5.06 wt% H for 5 min, 5.96 wt% H for 10 min, 6.12 wt% H for 30 min, and 6.19 wt% H for 60 min. 90Mg + 10TiCl₃ absorbs 4.32 wt% H for 5 min, 5.18 wt% H for 10 min, 5.37 wt% H for 30 min, and 5.38 wt% H for 60 min.

The H_d versus t curves at the 3rd cycle at 593 K in 1.0 bar H_2 for 95Mg + 5TiCl₃ and 90Mg + 10TiCl₃ are shown in Fig. 4. 95Mg + 5TiCl₃ and 90Mg + 10TiCl₃ have quite high hydrogen release rates and 90Mg + 10TiCl₃ has a slightly higher initial hydrogen release rate than 95Mg + 5TiCl₃, but 95Mg + 5TiCl₃ has a slightly larger quantity of hydrogen released for 60 min than 90Mg + 10TiCl₃. 95Mg + 5TiCl₃ releases 0.34 wt% H for 2.5 min, 1.26 wt% H for 10 min, 3.52 wt% H for 30 min, and 5.32 wt% H for 60 min. 90Mg + 10TiCl₃

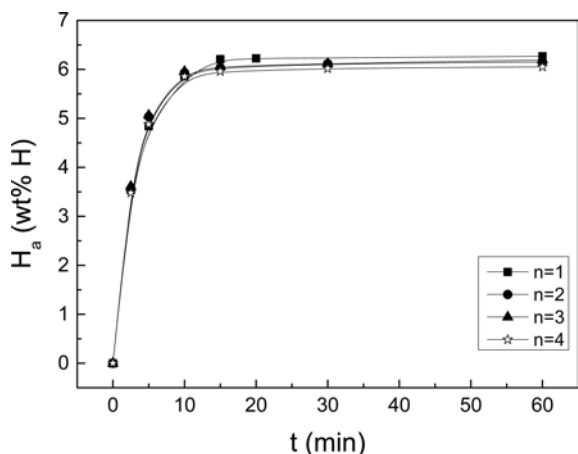


Fig. 5. Variation of the H_a versus t curve with the number of cycles, n , for 95Mg + 5TiCl₃ at 593 K in 12 bar H_2 .

releases 0.38 wt% H for 2.5 min, 1.46 wt% H for 10 min, 3.70 wt% H for 30 min, and 4.98 wt% H for 60 min.

Tanguy et al. [34] 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 follows:

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

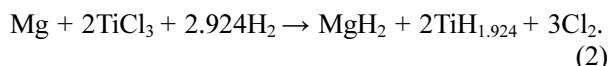
Stampfer et al. [35] also reported a similar relation between the equilibrium plateau pressure (P_{eq}) and temperature in the Mg-H system. The quantities of the hydrogen released for 60 min from 95Mg + 5TiCl₃ and 90Mg + 10TiCl₃ are smaller than those of the hydrogen absorbed for 60 min to 95Mg + 5TiCl₃ and 90Mg + 10TiCl₃, respectively. The driving force for hydrogen absorption is the difference between the applied hydrogen pressure (12 bar H_2 in the present work) and the equilibrium plateau pressure (2.87 bar H_2 at 593 K of the present work), whereas that for the driving force for hydrogen release is the difference between the equilibrium plateau pressure (2.87 bar H_2 at 593 K of the present work) and the applied hydrogen pressure (1.0 bar H_2 in the present work). For the calculation of the equilibrium plateau pressure (P_{eq}) at 593 K in the Mg-H system, the relation (1) was used. The driving force for hydrogen absorption is 9.13 bar, while that for the driving force for hydrogen release is 1.87 bar. This is believed to lead to smaller quantities of the hydrogen released for 60 min than the quantities of the hydrogen absorbed for 60 min. Release of hydrogen in 1.0 bar H_2 rather than in vacuum also leads in part to these results.

95Mg + 5TiCl₃ has a higher initial hydrogen absorption rate and a larger quantity of hydrogen absorbed for 60 min than 90Mg + 10TiCl₃, as shown in Fig. 3. Fig. 4 shows that 95Mg + 5TiCl₃ has a slightly lower initial hydrogen release rate, but a slightly larger quantity of hydrogen released for 60 min than 90Mg + 10TiCl₃. Larger content in 90Mg + 10TiCl₃, leading to a decrease in Mg content, is believed to have decreased the initial hydrogen absorption rate and the quantities of hydrogen absorbed and released for 60 min, compared with those for 95Mg + 5TiCl₃. The hydrogen absorption and release properties of 95Mg + 5TiCl₃ were investigated in detail.

SEM micrographs of 95Mg + 5TiCl₃ after ball milling in hydrogen showed that particles do not have a homogeneous particle size, with small particles and large particles coexisting. Fine particles were observed on the surfaces of particles.

The XRD pattern of 95Mg + 5TiCl₃ after ball milling in hydrogen showed that the sample contains Mg, β -MgH₂, γ -MgH₂, and TiH_{1.924}. β -MgH₂ and γ -MgH₂ are formed by the reaction of Mg with hydrogen during ball milling in hydrogen. β -MgH₂, with a tetragonal structure, is a low-pressure form of MgH₂, and γ -MgH₂, having an orthorhombic structure, is one of the high-

pressure forms of MgH_2 . $\text{TiH}_{1.924}$ is also formed by the reaction of Ti with hydrogen during ball milling in hydrogen. The reaction among Mg, TiCl_3 , and H_2 during ball milling in hydrogen can be expressed by the following reaction:



The variation of the H_a versus t curve with the number of cycles, n , for $95\text{Mg} + 5\text{TiCl}_3$ at 593 K in 12 bar H_2 is shown in Fig. 5. At the first cycle, the hydrogen absorption rate is very high from the beginning to 5 min, low from 5 min to 15 min, and then extremely low after 15 min. As the number of cycles increases from $n = 1$ to $n = 3$, the initial hydrogen absorption rate increases, and then decreases from $n = 3$ to $n = 4$. As the number of cycles increases from $n = 1$ to $n = 4$, the quantity of hydrogen absorbed for 60 min decreases on the whole. At $n = 1$, the sample absorbs 4.84 wt% H for 5 min, 5.86 wt% H for 10 min, 6.22 wt% H for 20 min, and 6.27 wt% H for 60 min. The quantity of hydrogen absorbed for 60 min is defined as the effective hydrogen-storage capacity. $95\text{Mg} + 5\text{TiCl}_3$ has a very high effective hydrogen-storage capacity of about 6.3 wt%.

The variation of the H_d versus t curve with the number of cycles, n , for $95\text{Mg} + 5\text{TiCl}_3$ at 593 K in 1.0 bar H_2 was examined. As the number of cycles increased from $n = 1$ to $n = 3$, the initial hydrogen release rate and the quantity of hydrogen released for 60 min increased, and then decreased from $n = 3$ to $n = 4$. At $n = 3$, the sample released 1.26 wt% H for 10 min, 3.52 wt% H for 30 min, and 5.32 wt% H for 60 min at 593 K in 1.0 bar H_2 . This result and that in Fig. 7 show that the activation of $95\text{Mg} + 5\text{TiCl}_3$ was completed after three hydrogen absorption (at 593 K in 12 bar H_2)-release (at 623 K in vacuum) cycles.

The variation of H_a versus t curve in 12 bar H_2 with temperature (423 K, 523 K, 573 K, and 593 K) for $95\text{Mg} + 5\text{TiCl}_3$ is shown in Fig. 6. At 423 K, the hydrogen absorption rate is nearly constant during

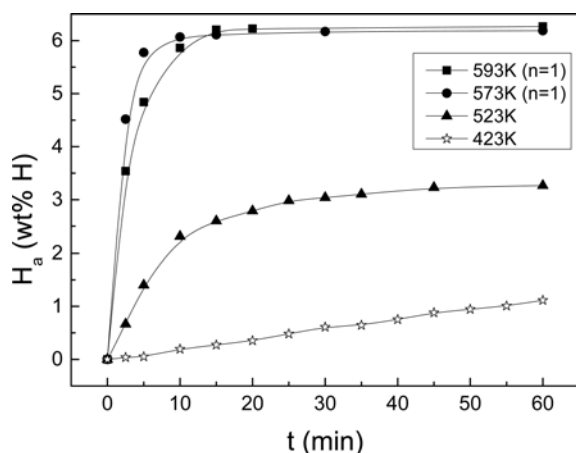


Fig. 6. Variation of H_a versus t curve in 12 bar H_2 with temperature (423 K, 523 K, 573 K, and 593 K) for $95\text{Mg} + 5\text{TiCl}_3$.

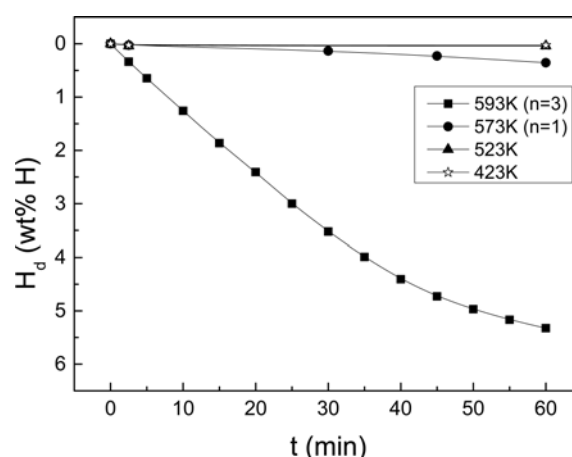


Fig. 7. Variation of H_d versus t curve in 1.0 bar H_2 with temperature (423 K, 523 K, 573 K, and 593 K) for $95\text{Mg} + 5\text{TiCl}_3$.

60 min. At 523 K, the hydrogen absorption rate is relatively high from the beginning to about 10 min and then becomes low. At 573 K and 593 K, the hydrogen absorption rate is very high from the beginning to about 5 min, low between 5 min and 10 min, and then very low after 10 min. The initial hydrogen absorption rate (for about 5 min) of the sample increases as the temperature increases from 423 K to 573 K and then decreases from 573 K to 593 K. As the temperature increases, the driving force for the hydrogen absorption reaction, which is related to the difference between the applied hydrogen pressure (12 bar H_2) and the equilibrium plateau pressure at a given temperature decreases. For the $\text{Mg}-\text{H}_2$ system, the differences between the equilibrium plateau pressure and the hydrogen pressure (12 bar H_2) at 573 K and 593 K are 10.39 and 9.13 bar, respectively [32]. The decrease in the driving force for the hydrogen absorption reaction, with the increase in temperature from 573 K to 593 K, leads to the decrease in the initial hydrogen absorption rate as the temperature increases from 573 K to 593 K. However, the quantity of hydrogen absorbed for 60 min, H_a (60 min), increases as the temperature increases from 423 K to 593 K. In the later part of the hydrogen absorption reaction, the rate is reported to be controlled by the diffusion of hydrogen atoms through a growing hydride layer [36]. The diffusion of hydrogen atoms is a thermally activated process, the rate of which increases as the temperature increases. H_a (60 min) thus increases as the temperature increases from 423 K to 593 K.

Fig. 7 shows the variation of H_d versus t curve in 1.0 bar H_2 with temperature (423 K, 523 K, 573 K, and 593 K) for $95\text{Mg} + 5\text{TiCl}_3$. The sample releases extremely small amount of hydrogen at 423 K and 523 K. At 573 K, the hydrogen release rate is very low; the sample releases 0.03 wt% H for 2.5 min, 0.13 wt% H for 30 min, and 0.35 wt% H for 60 min. At 593 K, the hydrogen release rate is quite high; the sample releases 0.34 wt% H for 2.5 min, 1.26 wt% H for 10 min, 3.52 wt% H for

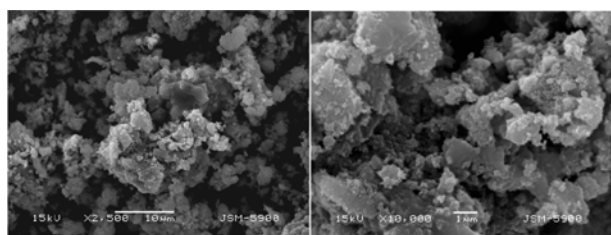


Fig. 8. SEM micrographs of 95Mg + 5TiCl₃ dehydrided at the 4th hydrogen absorption-release cycle.

30 min, and 5.32 wt% H for 60 min.

The SEM micrographs of 95Mg + 5TiCl₃ dehydrided at the 4th hydrogen absorption-release cycle are shown in Fig. 8. This sample also has small particles and large particles with fine particles on their surfaces. The fine particles on the small particles and large particles became finer. The particles are agglomerated.

Fig. 9 shows the XRD pattern of 95Mg + 5TiCl₃ dehydrided at the 4th hydrogen absorption-release cycle. The sample contains Mg, β -MgH₂, and small amounts of MgO and TiH_{1.924}. A relatively large amount of β -MgH₂ remains even after dehydriding. This partially explains the difference in the quantities of hydrogen absorbed and released for 60 min.

Fig. 10 shows the particle size analysis results for 95Mg + 5TiCl₃ after ball milling in hydrogen and after being dehydrided at the 4th hydrogen absorption-release cycle. The sample after ball milling exhibits three peaks at the particle diameters of about 0.013 μ m, 0.4 μ m, and 1.7 μ m. The sample after 4 hydrogen absorption-release cycles exhibits one peak at the particle diameter of about 0.013 μ m. The average particle sizes of the samples after ball milling and after 4 hydrogen absorption-release cycles are 0.20 μ m and 0.01 μ m, respectively. The average particle size of 95Mg + 5TiCl₃ after 4 hydrogen absorption-release cycles is smaller than those of 90Mg + 10TiCl₃ after 4 hydrogen absorption-release cycles (0.02 μ m) and Mg after 7 hydrogen absorption-release cycles (0.53 μ m).

The ball milling in hydrogen of Mg with oxides or halides is thought to produce defects on the surface and in the interior of Mg, to create clean surfaces, and to reduce the particle size of Mg. Producing defects facilitates nucleation, creation of clean surfaces enhances the reactivity of particles with hydrogen, and reduction in the particle size diminishes diffusion distances for hydrogen atoms. These effects increase the hydrogen absorption and release rates of Mg.

90Mg + 10Fe₂O₃ dehydrided at the 5th hydrogen absorption-release cycle contains Mg and small amounts of Fe, β -MgH₂, and MgO [26]. 95Mg + 5TiCl₃ dehydrided at the 4th hydrogen absorption-release cycle contains Mg, β -MgH₂, and small amounts of MgO and TiH_{1.924} (Fig. 9). The formation of titanium hydride (TiH_{1.924}) is believed to have contributed to the higher initial hydrogen absorption and release rates and the larger quantities of hydrogen

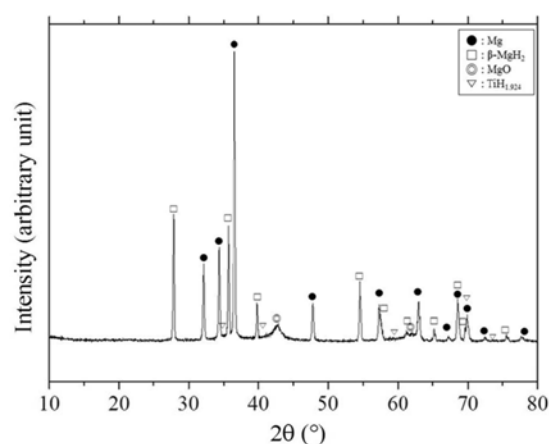


Fig. 9. X-ray (Cu K α) powder diffraction pattern of 95Mg+5TiCl₃ dehydrided at the 4th hydrogen absorption-release cycle.

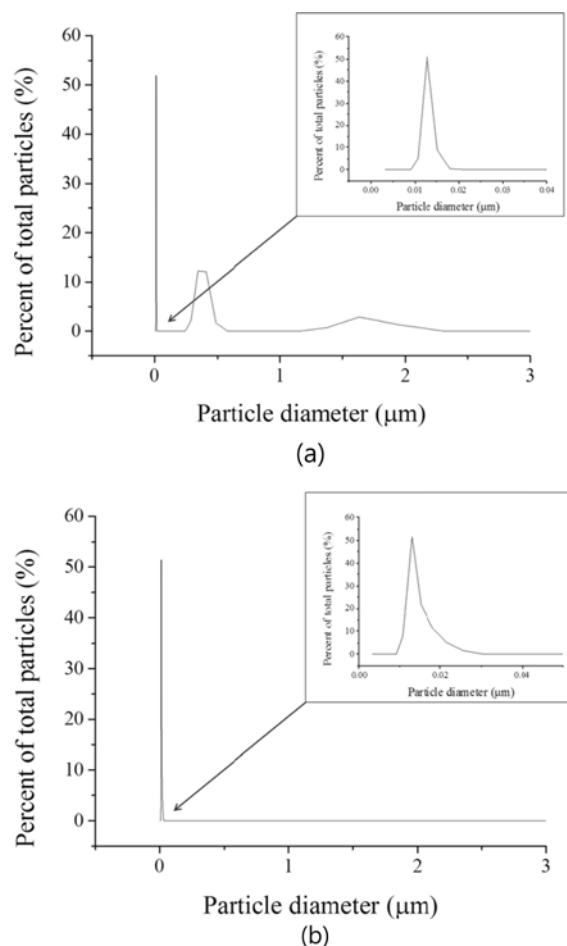


Fig. 10. Particle size distributions of 95Mg + 5TiCl₃ (a) after ball milling in hydrogen and (b) after being dehydrided at the 4th hydrogen absorption-release cycle.

absorbed and released for 60 min of 95Mg + 5TiCl₃.

Malka et al. [28] reported that it has been argued recently that metal halides often have even better catalytic activity to the hydrogen sorption kinetics of Mg than their metal or metal oxide counterparts do. Bhat et al. [37] compared the effect of Nb₂O₅ on the reaction

kinetics of Mg with hydrogen with that of its halide equivalent NbCl₅ and found a higher catalytic influence of NbCl₅ in comparison with Nb₂O₅. They insisted that the ionic character of the catalyst was important in enhancing the hydrogen sorption kinetics of Mg; we think that the ionic character of the catalyst is the kind of anions and their ionic states.

Conclusions

The hydrogen absorption and release properties of oxide-added alloys (90Mg + 10Fe₂O₃ and 90Mg + 10MnO) and halide-added alloys (90Mg + 10TiCl₃ and 90Mg + 10TaF₅) after activation were compared. 90Mg + 10TiCl₃ had higher initial hydrogen absorption and release rates and larger quantities of hydrogen absorbed and desorbed for 60 min than 90Mg + 10TaF₅, 90Mg + 10Fe₂O₃, and 90Mg + 10MnO. The hydrogen absorption and release properties of Mg-x wt% TiCl₃ (x = 5 and 10) were also compared. 95Mg + 5TiCl₃ had a quite high initial hydrogen absorption rate and a very large quantity of hydrogen absorbed for 60 min. The activation of 95Mg + 5TiCl₃ was completed after three hydrogen absorption (at 593 K in 12 bar H₂)-release (at 623 K in vacuum) cycles. 95Mg + 5TiCl₃ had a very large effective hydrogen-storage capacity of about 6.3 wt%. At n = 1, 95Mg + 5TiCl₃ absorbed 4.84 wt% H for 5 min, 5.86 wt% H for 10 min, and 6.27 wt% H for 60 min at 593 K in 12 bar H₂. At n = 3, 95Mg + 5TiCl₃ released 1.26 wt% H for 10 min, 3.52 wt% H for 30 min, and 5.32 wt% H for 60 min at 593 K in 1.0 bar H₂. The XRD pattern of 95Mg + 5TiCl₃ dehydrided at n = 4 revealed Mg, β-MgH₂, and small amounts of MgO and TiH_{1.924}. The formation of titanium hydride (TiH_{1.924}) in 95Mg + 5TiCl₃ is believed to have contributed to the higher initial hydrogen absorption and release rates and the larger quantities of hydrogen absorbed and released for 60 min of 95Mg + 5TiCl₃ than those of 90Mg + 10Fe₂O₃.

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