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# Oxide or halide and nickel-added Mg by phase transition-accompanying high-energy ball milling processing

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Fe<sub>2</sub>O<sub>3</sub>, Ti, Fe, and TiCl<sub>3</sub> were chosen as additives to increase the hydrogen absorption and release rates of Mg. Samples with compositions of 80 wt% Mg + 14 wt% Ni + 6 wt% Fe<sub>2</sub>O<sub>3</sub> (named Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>), 80 wt% Mg + 14 wt% Ni + 3 wt% Fe<sub>2</sub>O<sub>3</sub> + 3 wt% Ti (named Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti), 80 wt% Mg + 14 wt% Ni + 2 wt% Fe<sub>2</sub>O<sub>3</sub> + 2 wt% Ti + 2 wt% Fe (named Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe), and 80 wt% Mg + 14 wt% Ni + 6 wt% TiCl<sub>3</sub> (named Mg-14Ni-6TiCl<sub>3</sub>) were prepared by high-energy ball milling in hydrogen. The hydrogen absorption and release properties of the prepared samples were investigated and compared. The halide and nickel-added Mg, Mg-14Ni-6TiCl<sub>3</sub>, had larger quantities of hydrogen absorbed and released for 60 min and a larger initial dehydriding rate than the oxide and nickel-added Mg samples. In particular, the hydrogen absorption and release properties of Mg-14Ni-6TiCl<sub>3</sub> was completed after two hydriding-dehydriding cycles (cycling between hydriding under 12 bar H<sub>2</sub> at 593 K and dehydriding in vacuum at 623 K). Mg-14Ni-6TiCl<sub>3</sub> had an effective hydrogen-storage capacity of about 5.2 wt%. At the third cycle, the sample released 1.05 wt% H for 2.5 min, 2.82 wt% H for 10 min, and 4.88 wt% H for 60 min.

Key words: Hydrogen absorbing materials, Phase transition-accompanying milling, Phase transition of Fe<sub>2</sub>O<sub>3</sub>, Microstructure, Fe<sub>2</sub>O<sub>3</sub>, TiCl<sub>3</sub>, and Ni 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. To release hydrogen from metal hydrides, waste heat can be used. In addition, highpurity hydrogen can be produced by using metal hydrides, which selectively absorb and release hydrogen [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 with magnesium 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 CeMg<sub>12</sub> [10], and by making composites such as Mg-20 wt%

Fe<sub>23</sub>Y<sub>8</sub> [11], Mg with more than 5 wt% FeTiO<sub>3</sub> [12], and MgH<sub>2</sub> with 5 wt%  $ZrO_2 + 5$  wt% single-walled carbon nanotubes [13].

Song [14] reviewed the kinetic studies of the hydrogen absorption and release reactions of Mg. Many studies do not agree with one another on the rate-controlling step(s) for 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. The hydrogen absorption and release kinetics of Mg can be improved, therefore, 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.

Oxides, halides, and transition metals may be pulverized during mechanical grinding. The added oxides, halides, transition metals, and/or their pulverization during mechanical milling may help the particles of magnesium become finer.

Ni-added Mg alloys [5, 6] and mechanically-alloyed Mg with Ni under an Ar atmosphere [14-17] increased the hydriding and dehydriding rates of Mg. According

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to Bobet et al. [18], the hydrogen storage properties of pure Mg and 10 wt% Co, Ni, or Fe-Mg mixtures were improved by milling in a planetary ball mill under  $H_2$  for a relatively short time of 2 h. Addition of Ti is also reported to increase the hydriding and dehydriding rates of Mg [19].

Oxides such as  $Sc_2O_3$ ,  $TiO_2$ ,  $V_2O_5$ ,  $Cr_2O_3$ ,  $Mn_2O_3$ ,  $Fe_3O_4$ , CuO [20, 21], Nb<sub>2</sub>O<sub>3</sub> [22-25], and MgO [26] were added to MgH<sub>2</sub> or Mg to improve the hydriding and dehydriding kinetics of Mg.

Song et al. [27-29] tried to improve the hydriding and dehydriding kinetics of Mg by adding oxides such as  $Al_2O_3$ ,  $SiO_2$ ,  $CeO_2$ ,  $Fe_2O_3$ ,  $Cr_2O_3$ ,  $SiO_2$ , and MnO. The  $Fe_2O_3$ -added Mg sample showed quite high hydriding rates.

Malka et al. [30] milled magnesium hydride (MgH<sub>2</sub>) 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 MgH<sub>2</sub> decomposition temperature were also studied. They reported that the best catalysts for magnesium hydride decomposition, among the halides added, were ZrF<sub>4</sub>, TaF<sub>5</sub>, NbF<sub>5</sub>, VCl<sub>3</sub>, and TiCl<sub>3</sub>. Seven wt% of various metal halide additives (ZrF4,  $TaF_5$ , NbF<sub>5</sub> and TiCl<sub>3</sub>) 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 [31]. They reported that partial and full disproportionation reactions occurred with TaF<sub>5</sub>, NbF<sub>5</sub>, and TiCl<sub>3</sub> 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 MgF<sub>2</sub> phase.

Ma et al. [32] investigated hydrogen absorption and desorption kinetics of MgH<sub>2</sub> catalyzed with 4 mol% titanium compounds (TiF<sub>3</sub>, TiCl<sub>3</sub>, TiO<sub>2</sub>, TiN, and TiH<sub>2</sub>). MgH<sub>2</sub>-4 mol% TiCl<sub>3</sub> absorbed about 3.7 wt% H at 423 K under an initial hydrogen pressure of 20 bar H<sub>2</sub> and released about 3.85 wt% H at 553 K in an initial hydrogen pressure of 0.1 bar H<sub>2</sub>. In our previous work [33], the hydrogen absorption and release properties of Mg were improved by adding TiCl<sub>3</sub> via high-energy ball milling in hydrogen.

In some studies, magnesium hydride was employed as a starting material in order to increase the hydriding and dehydriding rates of magnesium by milling in a planetary mill with metal, compound, or oxide [34, 21, 22]. In this work, we used Mg instead of  $MgH_2$  as one of the starting materials.

The magnesium prepared by mechanical grinding under  $H_2$  (reactive mechanical grinding) with transition elements or oxides showed relatively high hydriding and dehydriding rates when the content of additives was about 20 wt%.

In this work, Ni, Fe<sub>2</sub>O<sub>3</sub>, Ti, Fe, and TiCl<sub>3</sub> were chosen as additives to increase the hydrogen absorption and release rates of Mg. Samples with compositions of 80 wt% Mg + 14 wt% Ni + 6 wt% Fe<sub>2</sub>O<sub>3</sub>, 80 wt% Mg + 14 wt% Ni + 3 wt% Fe<sub>2</sub>O<sub>3</sub> + 3 wt% Ti, 80 wt% Mg + 14 wt% Ni + 2 wt% Fe<sub>2</sub>O<sub>3</sub> + 2 wt% Ti + 2 wt% Fe, and 80 wt% Mg + 14 wt% Ni + 6 wt% TiCl<sub>3</sub> were prepared by high-energy ball milling in hydrogen. The previously studied optimum conditions for high-energy ball milling in hydrogen, which is called phase transitionaccompanying milling, were used for the sample preparation. The samples were designated as Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>, Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti, Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe, and Mg-14Ni-6TiCl<sub>3</sub>, respectively. The hydrogen absorption and release properties of the prepared samples were investigated and compared. In particular, the hydrogen absorption and release properties of Mg-14Ni-6TiCl<sub>3</sub> were examined in more detail.

### **Experimental Details**

Pure Mg powder (particle size 74-149  $\mu$ m, purity 99.6%, Alfa Aesar), Fe<sub>2</sub>O<sub>3</sub> (average particle size  $< 5 \,\mu$ m, purity  $\ge 99\%$ , Aldrich), TiCl<sub>3</sub> (Titanium(III) chloride, Aldrich), Ni (average particle size 2.2-3.0  $\mu$ m, purity 99.9%, Alfa Aesar), Ti (~44  $\mu$ m, purity 99.9%, Aldrich), and Fe (spherical, particle size  $< 10 \,\mu$ m, purity 99.5%, Alfa Aesar GmbH ) 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 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, sealed hermetically, with a volume of 250 ml, was filled with high purity hydrogen gas ( $\approx$  12 bar). Milling was performed for 6 h, with hydrogen being refilled every two hours.

The absorbed or released hydrogen quantity was measured as a function of time under nearly constant hydrogen pressures (12 bar  $H_2$  for absorption and 1.0 bar  $H_2$  for release), using a Sieverts' type hydrogen absorption and release apparatus described previously [35]. 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 K $\alpha$  radiation in a Rigaku D/MAX 2500 powder diffractometer. Scanning electron microscope (SEM) micrographs of the samples were obtained by a JSM-6400 SEM operated at 20 kV.



**Fig. 1.** Variations of  $H_a$  (10 min) and  $H_a$  (60 min) at 593 K under 12 bar  $H_2$  at n = 3 with the sample Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>, Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe, Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti, and Mg-14Ni-6TiCl<sub>3</sub>.



**Fig. 2.** Variations of  $H_d$  (10 min) and  $H_d$  (30 min) at 593 K under 1.0 bar  $H_2$  at n = 3 with the sample Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>, Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe, Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti, and Mg-14Ni-6TiCl<sub>3</sub>.

#### **Results and Discussion**

The percentage of absorbed hydrogen,  $H_a$ , is expressed with respect to the sample weight. The value of  $H_a$  for x min is expressed by  $H_a$  (x min). Fig. 1 shows the variations of  $H_a$  (10 min) and  $H_a$  (60 min) at 593 K under 12 bar  $H_2$  at n = 3 with the sample Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>, Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe, Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti, and Mg-14Ni-6TiCl<sub>3</sub>. Mg-14Ni-6TiCl<sub>3</sub> has the largest  $H_a$  (10 min) and  $H_a$  (60 min), followed in a descending order by Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe, Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti, and Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>. The values of  $H_a$  (10 min) and  $H_a$  (60 min) for Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe are very similar to those for Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti.

The percentage of desorbed hydrogen,  $H_d$ , is also expressed with respect to the sample weight. The value of  $H_d$  for x min is expressed by  $H_d$  (x min). Fig. 2 shows the variations of  $H_d$  (10 min) and  $H_d$  (30 min) at 593 K under 1.0 bar  $H_2$  at n = 3 with the sample Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>, Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe, Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti, and Mg-14Ni-6TiCl<sub>3</sub>. Mg-14Ni-6TiCl<sub>3</sub> has the largest  $H_d$  (10 min) and  $H_d$  (30 min), followed in a descending order by Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti, Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-



**Fig. 3.** SEM micrographs of Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub> after phase transition-accompanying milling.



Fig. 4. SEM micrographs of Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub> after hydriding-dehydriding cycling (n = 4).

2Fe, and Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>.

The XRD pattern of Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub> after phase transition-accompanying milling showed that the sample contained Ni, Mg, β-MgH<sub>2</sub>, Mg(OH)<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub> [36]. A part of Mg is transformed into β-MgH<sub>2</sub> during phase transition-accompanying milling. Mg(OH)2 is believed to be formed by the reaction of MgO, which is formed by the reaction of Mg with oxygen, with water vapor in The XRD pattern of Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub> after air. hydriding-dehydriding cycling (n = 4) showed that XRD pattern reveals Mg, Mg<sub>2</sub>Ni, β-MgH<sub>2</sub>, MgO, Mg(OH)<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Fe phases [36, 37]. The Mg<sub>2</sub>Ni phase which is not observed in the XRD pattern of the as-milled sample appears. Fe is believed to appear by the reaction of  $Fe_2O_3$  with Mg,  $Fe_2O_3 + 3Mg \rightarrow 3MgO + 2Fe$ , leading to formation of MgO.

Fig. 3 shows the SEM micrographs of Mg-14Ni- $6Fe_2O_3$  after phase transition-accompanying milling. Particles are spherical. The particle size is not homogeneous. Fine particles form agglomerates.

The SEM micrographs of Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub> after hydriding-dehydriding cycling (n = 4) are presented in Fig. 4. Particle size is not homogeneous. Some large agglomerates formed with fine particles are observed. The particles are much smaller than those of the asmilled sample.

The addition of Ni and  $Fe_2O_3$  is believed to increase the hydriding and dehydriding rates of Mg by creating defects, decreasing the particle size, and forming the Mg<sub>2</sub>Ni phase with higher hydriding and dehydriding rates than Mg.

Fig. 1 shows that the halide and nickel-added Mg, Mg-14Ni-6TiCl<sub>3</sub>, has a larger  $H_a$  (60 min) than the oxide and nickel-added Mg samples, Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe, Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti, and Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>.



Fig. 5. Variation of the  $H_a$  versus t curve at 593 K under 12 bar  $H_2$  with the number of cycles, n, for Mg-14Ni-6TiCl<sub>3</sub>.

Fig. 2 shows that the halide and nickel-added Mg, Mg-14Ni-6TiCl<sub>3</sub> has a larger initial dehydriding rate and a larger  $H_d$  (60 min) than the oxide and nickel-added Mg samples, Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe, Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti, and Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>. By considering these results, the hydrogen-storage properties of Mg-14Ni-6TiCl<sub>3</sub> are studied in more detail.

Fig. 5 shows the variation of the  $H_a$  versus t curve at 593 K under 12 bar  $H_2$  with the number of cycles, n, for Mg-14Ni-6TiCl<sub>3</sub>. At the first cycle, the hydriding rate is very high from the beginning to about 5 min, and then extremely low after 15 min. The  $H_a$  versus t curves from n = 1 to n = 4 are abut against one another. As the number of cycles increases from n = 1 to n = 3, the initial hydriding rate and the quantity of hydrogen absorbed for 60 min increase, but decrease from n = 3 to n = 4. At n = 1, the sample absorbs 3.96 wt% H for 5 min, 4.51 wt% H for 10 min, 4.95 wt% H for 30 min, and 5.03 wt% H for 60 min. At n = 3, the sample

**Table 1.** Variations of  $H_a$  (wt% H) at 593 K under 12 bar  $H_2$  with time at n = 3 for Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>, Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti, Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe, and Mg-14Ni-6TiCl<sub>3</sub>.

	2.5 min	5 min	10 min	60 min
Mg-14Ni-6Fe <sub>2</sub> O <sub>3</sub>	2.60	3.25	3.39	3.67
Mg-14Ni-3Fe <sub>2</sub> O <sub>3</sub> -3Ti	3.42	4.05	4.17	4.40
Mg-14Ni-2Fe <sub>2</sub> O <sub>3</sub> -2Ti-2Fe	3.39	4.14	4.27	4.43
Mg-14Ni-6TiCl <sub>3</sub>	3.00	4.07	4.70	5.20

**Table 2.** Variations of  $H_d$  (wt% H) at 593 K under 1.0 bar  $H_2$  with time at n = 3 for Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>, Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti, Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe, and Mg-14Ni-6TiCl<sub>3</sub>.

	2.5 min	5 min	10 min	30 min
Mg-14Ni-6Fe <sub>2</sub> O <sub>3</sub>	0.12	0.39	0.93	2.39
Mg-14Ni-3Fe <sub>2</sub> O <sub>3</sub> -3Ti	0.06	1.26	2.56	4.03
Mg-14Ni-2Fe <sub>2</sub> O <sub>3</sub> -2Ti-2Fe	0.44	0.66	1.14	2.67
Mg-14Ni-6TiCl <sub>3</sub>	1.05	1.71	2.82	4.84

**Table 3.** Variations of  $H_a$  (wt% H) at 593 K under 12 bar  $H_2$  at n = 1 and n = 3 for Mg-14Ni-6TiCl<sub>3</sub>.

	2.5 min	5 min	10 min	20 min	60 min
n = 1	2.83	3.96	4.51	4.86	5.03
n=3	3.00	4.07	4.70	5.03	5.20

Table 4. Variations of  $H_d$  (wt% H) at 593 K under 1.0 bar  $H_2$  at n=1 and n=3 for Mg-14Ni-6TiCl<sub>3</sub>.

	2.5 min	5 min	10 min	20 min	60 min
n = 1	0.97	1.66	2.69	4.41	4.81
n = 3	1.05	1.71	2.82	4.61	4.88



Fig. 6. Variation of the  $H_d$  versus t curve at 593 K under 1.0 bar  $H_2$  with the number of cycles for Mg-14Ni-6TiCl<sub>3</sub>.

absorbs 4.07 wt% H for 5 min, 4.70 wt% H for 10 min, 5.11 wt% H for 30 min, and 5.20 wt% H for 60 min. The effective hydrogen-storage capacity is defined as the quantity of hydrogen absorbed for 60 min. Mg-14Ni-6TiCl<sub>3</sub> has an effective hydrogen-storage capacity of about 5.2 wt%. Table 3 presents the variations of H<sub>a</sub> at 593 K under 12 bar H<sub>2</sub> at n = 1 and n = 3 for Mg-14Ni-6TiCl<sub>3</sub>.

The variation of the H<sub>d</sub> versus t curve at 593 K under 1.0 bar H<sub>2</sub> with the number of cycles, n, for Mg-14Ni-6TiCl<sub>3</sub> is shown in Fig. 6. At the first cycle, the H<sub>d</sub> versus t curve exhibit three stages; the dehydriding rate is very high from the beginning to 2.5 min, quite high from 2.5 min to about 20 min, and then very low after 25 min. The  $H_d$  versus t curves from n = 1 to n = 4 are very close to one another. As the number of cycles increases from n = 1 to n = 2, the initial dehydriding rate and the quantity of hydrogen released for 60 min increase while they decrease from n = 2 to n = 4. At n = 1, the sample releases 0.97 wt% H for 2.5 min, 2.69 wt% H for 10 min, 4.41 wt% H for 20 min, and 4.81 wt% H for 60 min. At n = 3, the sample releases 1.05 wt% H for 2.5 min, 2.82 wt% H for 10 min, 4.61 wt% H for 20 min, and 4.88 wt% H for 60 min. Table 4 shows the variations of H<sub>d</sub> at 593 K under 1.0 bar  $H_2$  at n = 1 and n = 3 for Mg-14Ni-6TiCl<sub>3</sub>.



**Fig. 7.** XRD pattern of Mg-14Ni-6TiCl<sub>3</sub> after phase transitionaccompanying milling.



**Fig. 8.** XRD pattern of Mg-14Ni-6TiCl<sub>3</sub> dehydrided at the 4th hydriding–dehydriding cycle.

Fig. 5 and Fig. 6 show that the activation of Mg-14Ni-6TiCl<sub>3</sub> is completed after two hydriding-dehydriding cycles (cycling between hydriding under 12 bar  $H_2$  at 593 K and dehydriding in vacuum at 623 K).

The XRD pattern of Mg-14Ni-6TiCl<sub>3</sub> after phase transition-accompanying milling is shown in Fig. 7. The sample contains Mg, Ni,  $\beta$ -MgH<sub>2</sub>, and small amounts of  $\gamma$ -MgH<sub>2</sub> and TiH<sub>1.924</sub>.  $\beta$ -MgH<sub>2</sub> and  $\gamma$ -MgH<sub>2</sub> are formed by the reaction of Mg with hydrogen during ball milling in hydrogen.  $\beta$ -MgH<sub>2</sub>, with a tetragonal structure, is a low-pressure form of MgH<sub>2</sub>, and  $\gamma$ -MgH<sub>2</sub>, having an orthorhombic structure, is one of the high-pressure forms of MgH<sub>2</sub>. TiH<sub>1.924</sub> is also formed by the reaction of Ti with hydrogen during ball milling in hydrogen. The formation of  $\beta$ -MgH<sub>2</sub>,  $\gamma$ -MgH<sub>2</sub>, and TiH<sub>1.924</sub>, which are brittle, in Mg-14Ni-6TiCl<sub>3</sub> is believed to help particles pulverize more effectively. The reaction among Mg, TiCl<sub>3</sub>, and H<sub>2</sub> during ball milling in hydrogen can be expressed by the following reaction:

$$Mg + 2TiCl_3 + 2.924H_2 \rightarrow MgH_2 + 2TiH_{1.924} + 3Cl_2.$$
(1)



**Fig. 9.** SEM micrographs of Mg-14Ni-6TiCl<sub>3</sub> after phase transition-accompanying milling.



**Fig. 10.** SEM micrographs of Mg-14Ni-6TiCl<sub>3</sub> dehydrided at the  $4^{th}$  hydriding-dehydriding cycle.

Fig. 8 presents the XRD pattern of Mg-14Ni-6TiCl<sub>3</sub> dehydrided at the 4th hydriding–dehydriding cycle. The sample contains Mg, Mg<sub>2</sub>Ni, MgO,  $\beta$ -MgH<sub>2</sub>, and a small amount of TiH<sub>1.924</sub>. The Mg<sub>2</sub>Ni phase, which was not observed after milling, is observed in the sample dehydrided after cycling. The Mg<sub>2</sub>Ni phase forms its hydride (Mg<sub>2</sub>NiH<sub>4</sub>) under similar conditions for the hydriding reaction of Mg, and Mg<sub>2</sub>NiH<sub>4</sub> releases hydrogen under similar conditions for the dehydriding reaction of MgH<sub>2</sub>. Mg<sub>2</sub>Ni has higher hydriding and dehydriding rates than Mg. TiH<sub>1.924</sub> observed in the sample after phase transition-accompanying milling remains undecomposed. During hydriding-dehydriding cycling, the hydriding and dehydriding reactions of Mg and Mg<sub>2</sub>Ni occur, which can be expressed by the following:

$$Mg + Mg_2Ni + MgO + TiH_{1.924} + 3H_2 \leftrightarrow MgH_2 + Mg_2NiH_4 + MgO + TiH_{1.924}.$$
 (2)

The SEM micrographs of Mg-14Ni-6TiCl<sub>3</sub> after phase transition-accompanying milling is presented in Fig. 9. The particles do not have a homogeneous particle size. The particles are agglomerated, and their surfaces are quite flat.

Fig. 10 exhibits the SEM micrographs of Mg-14Ni-6TiCl<sub>3</sub> dehydrided at the 4<sup>th</sup> hydriding-dehydriding cycle. This sample has small particles and large particles with fine particles on their surfaces. The small particles on the large particles became finer. Expansion during the hydriding reaction and contraction during the dehydriding reaction make the small particles become finer. The particles are agglomerated.

The reactive mechanical grinding of Mg with Ni and TiCl<sub>3</sub> increases the hydriding and dehydriding rates. The addition of Ni and TiCl<sub>3</sub> is considered to create defects on the surface and the interior of Mg, leading to facilitation of nucleation, and to reduce the particle size of Mg, leading to diminution of diffusion distances for

the hydrogen atoms [38, 39]. The  $Mg_2NiH_4$  phase formed in the Mg-14Ni-6TiCl<sub>3</sub> sample during hydridingdehydriding cycling.  $Mg_2Ni$  has higher hydriding and dehydriding rates than Mg. The addition of Ni increases the hydriding rate of Mg as well as the dehydriding rate of  $MgH_2$  by the formation of  $Mg_2NiH_4$  from the reaction of Ni with Mg during hydriding-dehydriding cycling.

Comparison of Fig. 4 and Fig. 10 shows that after hydriding-dehydriding cycling, Mg-14Ni-6TiCl<sub>3</sub> has a little larger particle size but the particles of Mg-14Ni-6TiCl<sub>3</sub> have more hydrogen paths to the insides of particles than Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>.

As mentioned above, the Mg<sub>2</sub>Ni phase, which was not observed after milling, is observed in the sample dehydrided after hydriding-dehydriding cycling, as shown in Fig. 8. The Mg<sub>2</sub>Ni phase forms its hydride (Mg<sub>2</sub>NiH<sub>4</sub>) under similar conditions for the hydriding reaction of Mg, and Mg<sub>2</sub>NiH<sub>4</sub> releases hydrogen under similar conditions for the dehydriding reaction of MgH<sub>2</sub>. Mg<sub>2</sub>Ni has higher hydriding and dehydriding rates than Mg. The very high initial dehydriding rate observed in Fig. 6 is believed to be due to the dehydriding reaction of the Mg<sub>2</sub>NiH<sub>4</sub> phase in Mg-14Ni-6 TiCl<sub>3</sub>. The quantities of hydrogen released for 2.5 min (at the stage of the very high dehydriding rate) are 0.97 and 1.07 wt% H at n = 1 and n = 3, respectively. These values are very similar to that of 0.96 wt% H, which is calculated on the assumption that all the Ni in the sample forms the Mg<sub>2</sub>Ni phase, and the formed Mg<sub>2</sub>Ni phase release all the hydrogen. This indicates that at the stage of the very high dehydriding rate, the Mg<sub>2</sub>Ni phase decomposes.

Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe [40], Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti [40], and Mg-14Ni-6TiCl<sub>3</sub> (as shown in Fig. 8 and Fig. 9), before and after hydriding-dehydriding cycling, contained the TiH<sub>1.924</sub> phase. Fig. 1 and Fig. 2 show H<sub>a</sub> (10 min), H<sub>a</sub> (60 min), H<sub>d</sub> (10 min), and H<sub>d</sub> (30 min) increase generally as the content of Ti increases. It is believed that the formed TiH<sub>1.924</sub> has strong positive effects on the improvements of the hydriding and dehydriding rates of Mg.

#### Conclusions

The halide and nickel-added Mg, Mg-14Ni-6TiCl<sub>3</sub>, had a larger H<sub>a</sub> (60 min), a larger initial dehydriding rate, and a larger H<sub>d</sub> (60 min) than the oxide and nickeladded Mg samples, Mg-14Ni-2Fe<sub>2</sub>O<sub>3</sub>-2Ti-2Fe, Mg-14Ni-3Fe<sub>2</sub>O<sub>3</sub>-3Ti, and Mg-14Ni-6Fe<sub>2</sub>O<sub>3</sub>. H<sub>a</sub> (10 min), H<sub>a</sub> (60 min), H<sub>d</sub> (10 min), and H<sub>d</sub> (30 min) increased generally as the content of Ti, which forms TiH<sub>1.924</sub>, increased. It is believed that the formed TiH<sub>1.924</sub> has strong positive effects on the improvements of the hydriding and dehydriding rates of Mg. Considering these results, the hydrogen-storage properties of Mg-14Ni-6TiCl<sub>3</sub> are studied in more detail. The activation of Mg-14Ni-6TiCl<sub>3</sub> was completed after n = 2 (cycling between hydriding under 12 bar  $H_2$  at 593 K and dehydriding in vacuum at 623 K). At n=3, the sample absorbed 4.07 wt% H for 5 min, 4.70 wt% H for 10 min, and 5.20 wt% H for 60 min. Mg-14Ni-6TiCl<sub>3</sub> had an effective hydrogen-storage capacity of about 5.2 wt%. At n=3, the sample released 1.05 wt% H for 2.5 min, 2.82 wt% H for 10 min, and 4.88 wt% H for 60 min. The added Ni in Mg-14Ni-6TiCl<sub>3</sub> formed the Mg<sub>2</sub>Ni phase after hydriding-dehydriding cycling. The H<sub>d</sub> versus t curves exhibited three stages; at the first stage (the stage of the very high dehydriding rate), it is believed that the Mg<sub>2</sub>Ni phase decomposes.

#### Acknowledgments

This research was supported by "Research Base Construction Fund Support Program" funded by Chonbuk National University in 2017.

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