

## Development of a Mg-Based Alloy with a Hydrogen-Storage Capacity of 7 wt% by Adding a Polymer CMC via Transformation-Involving Milling

Myoung Youp Song<sup>1,\*</sup>, Eunho Choi<sup>2</sup>, and Young Jun Kwak<sup>1</sup>

<sup>1</sup>*Division of Advanced Materials Engineering, Hydrogen & Fuel Cell Research Center, Engineering Research Institute, Chonbuk National University, 567 Baekje-daero Deokjin-gu Jeonju, 54896, Republic of Korea*

<sup>2</sup>*Department of Materials Engineering, Graduate School, Chonbuk National University, 567 Baekje-daero Deokjin-gu Jeonju, 54896, Republic of Korea*

**Abstract:** The addition of CMC (Carboxymethylcellulose, Sodium Salt) may improve the hydriding and dehydriding properties of Mg since it has a relatively low melting point and the melting of CMC during transformation-involving milling may put the milled samples in good states to absorb and release hydrogen rapidly. Samples with compositions of 95 wt% Mg + 5 wt% CMC (named Mg-5CMC) and 90 wt% Mg + 10 wt% CMC (named Mg-10CMC) were made using transformation-involving milling. Mg-5CMC was activated in about 3 hydriding-dehydriding cycles. After activation, Mg-5CMC had a larger amount of hydrogen absorbed in 60 min,  $H_a$  (60 min), than Mg-10CMC and milled Mg. At the fourth cycle (CN=4), Mg-5CMC had a very high beginning hydriding rate (1.45 wt% H/min) and  $H_a$  (60 min) (7.38 wt% H), showing that the activated Mg-5CMC has an effective hydrogen-storage capacity of about 7.4 wt% at 593 K in hydrogen of 12 bar at CN=4. Mg-5CMC after transformation-involving milling contained Mg and very small amounts of  $\beta$ -MgH<sub>2</sub> and MgO, and Mg-5CMC dehydrogenated at 593 K in hydrogen of 1.0 bar at the 4<sup>th</sup> cycle contained Mg and tiny amounts of  $\beta$ -MgH<sub>2</sub> and MgO, with no evidence of the phases related to CMC. The milling of Mg with CMC in hydrogen is believed to introduce defects and cracks and lessen the particle size. To the best of our knowledge, this study is the first in which a polymer CMC is added to Mg by transformation-involving milling to improve the hydriding and dehydriding properties of Mg.

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**Keywords:** hydrogen absorbing materials, mechanical milling scanning electron microscopy (SEM), X-ray diffraction, a polymer CMC (Carboxymethylcellulose, Sodium Salt) addition.

### 1. INTRODUCTION

A considerable amount of research has been conducted to increase the hydriding and dehydriding rates and hydrogen-storage capacity of magnesium, which is known to have excellent hydriding and dehydriding properties. Approaches include alloying magnesium with certain metals [1-3], synthesizing Mg-based compounds [4-9] such as LaMg<sub>12</sub>, CeMg<sub>12</sub> [8], MmMg<sub>12</sub> (Mm-mischmetal), La<sub>2</sub>Mg<sub>17</sub> [5],  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> [9], and adding graphite [10] and adding Nb and multi-walled carbon nanotubes to Mg-Ni alloys [11].

In our previous works, the hydriding and dehydriding

properties of Mg were improved by adding halogen compounds such as NbF<sub>5</sub> [12], TaF<sub>5</sub> [13], VCl<sub>3</sub>, and TiCl<sub>3</sub> [14,15] by transformation-involving milling. The low decomposition temperatures of these halogen compounds are thought to contribute to the improvement of the hydriding and dehydriding properties of Mg.

CMC (Carboxymethylcellulose, Sodium Salt, [C<sub>6</sub>H<sub>7</sub>O<sub>2</sub>(OH)<sub>x</sub>(C<sub>2</sub>H<sub>2</sub>O<sub>3</sub>Na)<sub>y</sub>]<sub>n</sub>) is a water-soluble anionic linear polymer, which is a cellulose derivative with carboxymethyl groups (-CH<sub>2</sub>-COOH). The melting point of CMC is relatively low (547 K). CMC has high viscosity and is non-toxic. CMC is used as a viscosity modifier or thickener, and to stabilize emulsions in various products.

We thought that the addition of CMC might improve the hydriding and dehydriding properties of

\*Corresponding Author: Myoung Youp Song

[Tel: +82-63-270-2379, E-mail: songmy@jbnu.ac.kr]

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Mg since it has a relatively low melting point and the melting of CMC during transformation-involving milling may put the milled samples in good states to absorb and release hydrogen rapidly.

In this work, samples with compositions of 95 wt% Mg + 5 wt% CMC (named Mg-5CMC) and 90 wt% Mg + 10 wt% CMC (named Mg-10CMC) were made through transformation-involving milling, and the hydriding properties of the prepared samples were compared with Mg milled under hydrogen. The hydriding and dehydriding properties of Mg-5CMC were examined in detail and compared with those of oxide, halide, or transition metals-added Mg samples by milling in hydrogen using similar conditions to those employed to prepare Mg-5CMC and Mg-10CMC. As far as we know, this study is the first in which a polymer CMC is added to Mg by transformation-involving milling to improve the hydriding and dehydriding properties of Mg.

## 2. EXPERIMENTAL DETAILS

Pure Mg powder (-20 +100 mesh, 99.8%, metals basis, Alfa Aesar) and CMC (Carboxymethylcellulose, Sodium Salt, Aldrich) were the constituents of mixtures for the transformation-involving milling.

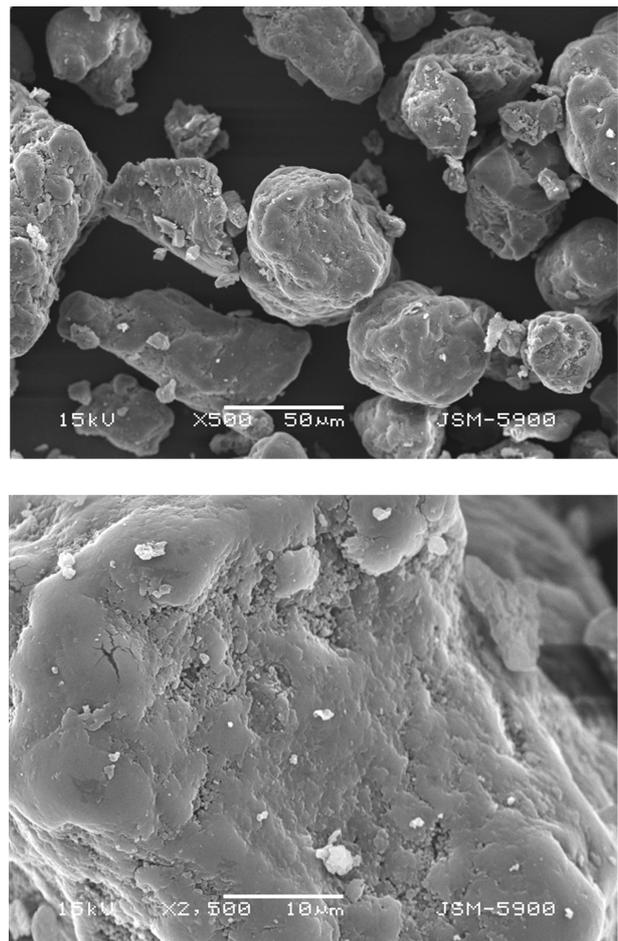
The employed planetary ball mill was a Planetary Mono Mill (Pulverisette 6) from Fritsch. The total weight of the constituents of the mixtures was 8 g. The total weight of hardened steel balls was 360 g and 105 balls were used. Handling of samples was done in argon atmosphere. The disc rotation speed was 400 rounds per minute (rpm). The transformation-involving milling was carried out in hydrogen of about 12 bar for 6 h. The periods of refilling the mill container (with a volume of 250 mL) with hydrogen were 2 h.

Changes in the amounts of absorbed and released hydrogen with time were measured using a Sieverts' type hydriding and dehydriding apparatus elucidated previously [16]. A half gram of the samples was used to measure changes in the amounts of absorbed and released hydrogen with time.

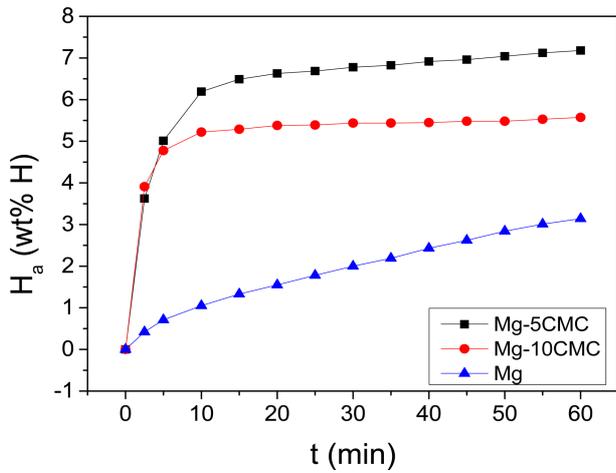
Phases in the samples after transformation-involving milling and after hydriding-dehydriding cycling were analyzed by X-ray diffraction (XRD) with Cu K $\alpha$  radiation, using a Rigaku D/MAX 2500 powder diffractometer. The scanning electron microscope (SEM) to observe the microstructures of the powders was a JSM-5900, which was operated at 15 kV.

## 3. RESULTS AND DISCUSSION

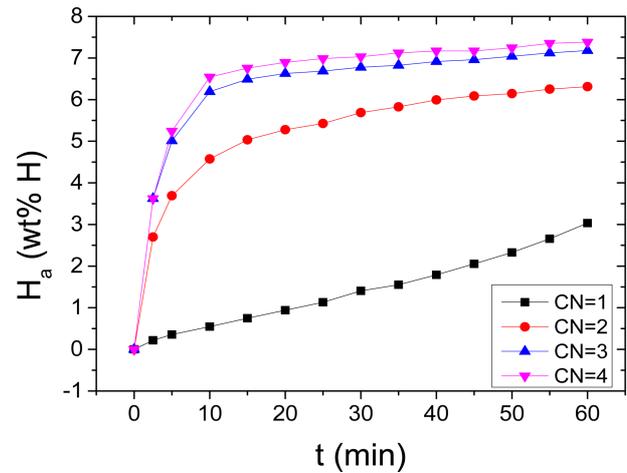
Microstructures of the CMC were observed by SEM at different magnifications and are shown in Fig. 1. The particles of CMC are irregular in shape with some cracks on the surfaces and particle sizes are not homogeneous. The XRD diagram of CMC exhibited two broad peaks, showing that the used CMC was



**Fig. 1.** Microstructures observed by SEM of CMC at different magnifications.



**Fig. 2.** Curves of change in  $H_a$  as a function of  $t$  at 593 K in hydrogen of 12 bar at CN=3 for Mg, Mg-5CMC, and Mg-10CMC.



**Fig. 3.** Curves of change in  $H_a$  as a function of  $t$  at 593 K in hydrogen of 12 bar at CN=1-4 for Mg-5CMC

amorphous.

The amount of hydrogen absorbed by the sample,  $H_a$ , was calculated on the basis of sample weight, and  $H_a$  was given in the unit of weight percent of hydrogen (wt% H).

Mg-5CMC and Mg-10CMC were activated in about 3 hydriding-dehydriding cycles. Figure 2 shows the curves of change in  $H_a$  as a function of  $t$  at 593 K in hydrogen of 12 bar at cycle number three (CN=3) for Mg, Mg-5CMC, and Mg-10CMC. The beginning hydriding rate of Mg-10CMC is the highest, trailed in descending order by those of Mg-5CMC and Mg. Mg-5CMC has a very slightly lower beginning hydriding rate than Mg-10CMC. The amount of the hydrogen absorbed in 60 min,  $H_a$  (60 min), of Mg-5CMC is the largest, trailed in descending order by those of Mg-10CMC and Mg. These results show that the addition of CMC to Mg by transformation-involving milling and hydriding-dehydriding cycling increases the beginning hydriding rate and  $H_a$  (60 min). The Mg sample absorbs 0.41 wt% H in

2.5 min, 1.05 wt% H in 10 min, and 3.14 wt% H in 60 min. Mg-5CMC absorbs 3.62 wt% H in 2.5 min, 6.19 wt% H in 10 min, and 7.18 wt% H in 60 min. Table 1 shows the changes in  $H_a$  as a function of  $t$  at 593 K in hydrogen of 12 bar at CN=3 for Mg, Mg-5CMC, and Mg-10CMC. The hydriding and dehydriding properties of Mg-5CMC were examined in detail.

Figure 3 shows the curves of change in  $H_a$  as a function of  $t$  at 593 K in hydrogen of 12 bar at CN=1-4 for Mg-5CMC. The beginning hydriding rate and  $H_a$  (60 min) increase rapidly with a rise in CN. The curves of change in  $H_a$  as a function of  $t$  at CN=3 and CN=4 are similar. At CN=4, the beginning hydriding rate is very high (1.45 wt% H/min) and  $H_a$  (60 min) is very large (7.38 wt% H). At CN=1, Mg-5CMC absorbs 0.22 wt% H in 2.5 min, 0.55 wt% H in 10 min, and 3.03 wt% H in 60 min. At CN=4, Mg-5CMC absorbs 3.62 wt% H in 2.5 min, 6.54 wt% H in 10 min, and 7.38 wt% H in 60 min. Table 2 shows the changes in  $H_a$  as a function of  $t$  at 593

**Table 1.** Changes in  $H_a$  (wt% H) as a function of  $t$  at 593 K in hydrogen of 12 bar at CN=3 for Mg, Mg-5CMC, and Mg-10CMC.

	2.5 min	5 min	10 min	30 min	60 min
Mg	0.41	0.71	1.05	2.00	3.14
Mg-5CMC	3.62	5.01	6.19	6.78	7.18
Mg-10CMC	3.91	4.78	5.22	5.44	5.57

**Table 2.** Changes in  $H_a$  (wt% H) as a function of  $t$  at 593 K in hydrogen of 12 bar at CN=1-4 for Mg-5CMC.

	2.5 min	5 min	10 min	30 min	60 min
CN=1	0.21	0.35	0.55	1.41	3.03
CN=2	2.70	3.69	4.58	5.69	6.31
CN=3	3.62	5.01	6.19	6.78	7.18
CN=4	3.62	5.24	6.54	7.03	7.38

K in hydrogen of 12 bar at CN=1-4 for Mg-5CMC.

Figure 4 shows the curves of change in  $H_a$  as a function of  $t$  at 593 K in hydrogen of 12 bar at CN=1-7 for Mg-5CMC after being stored in a glove box for about 12 months. The beginning hydriding rate is the highest at CN=5. At CN=5, from the beginning to 15 min, the hydriding rates are the highest. At CN=4, from the beginning to 10 min, the hydriding rates are second highest, absorbing 2.97 wt% H in 2.5 min, 4.92 wt% H in 10 min, and 5.67 wt% H in 60 min.  $H_a$  (60 min) is the largest at CN=2 and decreases in general from CN=2 to CN=7. Mg-5CMC stored in a glove box for about 12 months has higher hydriding rates and larger  $H_a$  (60 min)'s at CN=1 and CN=2 but lower hydriding rates and smaller  $H_a$  (60 min)'s at CN=3 and CN=4 than Mg-5CMC. We found that even if we increased CN after the fourth cycle, the beginning hydriding rate and  $H_a$  (60 min) increased very slightly. It is considered that storing for a relatively long period made the sample less reactive, having led to a smaller effective hydrogen-storage capacity of 6.45 wt% at CN=2, compared with that of 7.38 wt% for Mg-5CMC (studied just after transformation-involving milling) at CN=4.

The results in Figs. 3 and 4 show that Mg-5CMC is activated in about 3 hydriding-dehydriding cycles.

We define an effective hydrogen-storage capacity as the amount of the hydrogen absorbed in 60 min,  $H_a$  (60 min). Mg-5CMC has an effective hydrogen-storage capacity of about 7.4 wt% at 593 K in hydrogen of 12 bar at CN=4.

The amount of hydrogen released from the sample,  $H_d$ , was also calculated on the basis of sample weight, and  $H_d$  was also given in the unit of weight percent of hydrogen (wt% H).

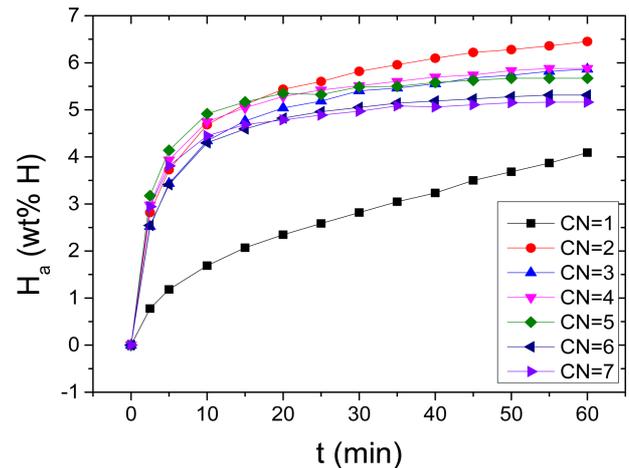
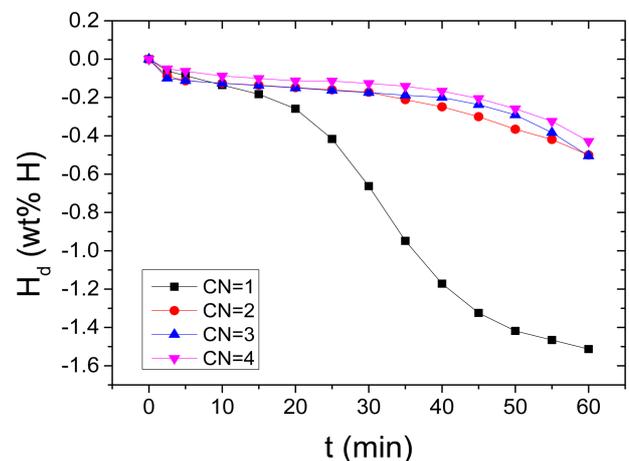
**Fig. 4.** Curves of change in  $H_a$  as a function of  $t$  at 593 K in hydrogen of 12 bar at CN=1-7 for Mg-5CMC stored in a glove box for about 12 months.**Fig. 5.** Curves of change in  $H_d$  as a function of  $t$  at 593 K in hydrogen of 1.0 bar at CN=1-4 for Mg-5CMC.

Figure 5 shows the curves of change in  $H_d$  as a function of  $t$  at 593 K in hydrogen of 1.0 bar at CN=1-4 for Mg-5CMC. The amount of the hydrogen released in 60 min,  $H_d$  (60 min), decreases rapidly from CN=1 to CN=2, and they are similar from CN=2 to CN=4. The curves of change in  $H_d$  as a

**Table 3.** Changes in  $H_d$  (wt% H) as a function of  $t$  at 593 K in hydrogen of 1.0 bar at CN=1-4 for Mg-5CMC.

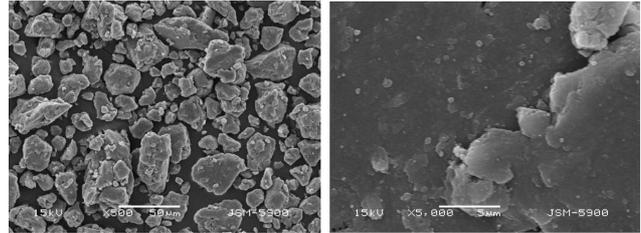
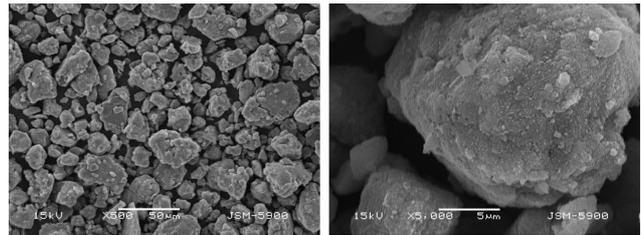
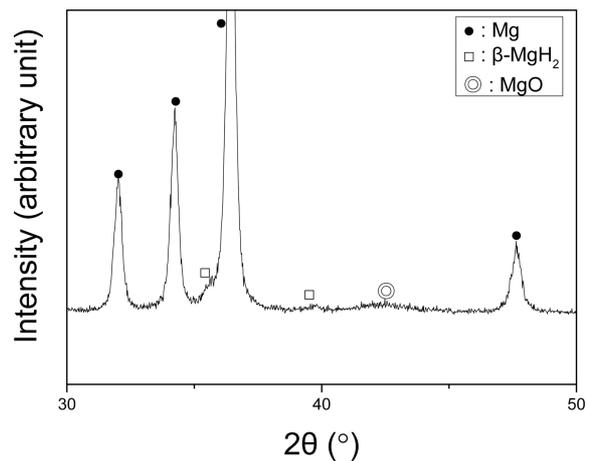
	2.5 min	5 min	10 min	30 min	60 min
CN=1	0.06	0.09	0.14	0.66	1.51
CN=2	0.09	0.11	0.13	0.17	0.50
CN=3	0.10	0.11	0.13	0.17	0.50
CN=4	0.05	0.06	0.09	0.13	0.43

function of  $t$  at CN=2-4 are similar, but the beginning dehydrogenating rate is the lowest and the value of  $H_d$  (60 min) is the smallest at CN=4. At CN=1, the dehydrogenating rate is low in the beginning, increases slowly and reaches the maximum rate in about 30 min, and then decreases again. At CN=1, Mg-5CMC releases 0.06 wt% H in 2.5 min, 0.66 wt% H in 30 min, and 1.51 wt% H in 60 min. At CN=4, Mg-5CMC releases 0.05 wt% H in 2.5 min, 0.13 wt% H in 30 min, and 0.43 wt% H in 60 min. Table 3 shows the changes in  $H_d$  as a function of  $t$  at 593 K in hydrogen of 1.0 bar at CN=1-4 for Mg-5CMC. These results show that the dehydrogenating rates of Mg-5CMC are low and the cycling performance in the hydrogen release reaction of Mg-5CMC is poor. To increase the dehydrogenating rate and  $H_d$  (60 min) of Mg-5CMC, we will add transition elements such as Ni and Ti and study the hydriding and dehydrogenating properties of the prepared samples in the future.

Transformation-involving milling of Mg-5CMC yielded the particles depicted in Fig. 6. The particle sizes are not homogeneous. The particles are slightly spherical and have quite flat surfaces. Fine particles are embedded in the large particles.

Figure 7 shows the microstructures observed by SEM of Mg-5CMC dehydrogenated at 593 K in hydrogen of 1.0 bar at the 4<sup>th</sup> cycle after hydriding-dehydrogenating cycling at 593 K. The particle sizes of the sample are not homogeneous. The particles of the sample after hydriding-dehydrogenating cycling are smaller than those of the sample after transformation-involving milling. The particles of the sample after transformation-involving milling have quite flat surfaces, but those of the sample after hydriding-dehydrogenating cycling are covered with fine particles.

The XRD (X-ray diffraction) diagram of Mg-5CMC

**Fig. 6.** Microstructures observed by SEM of Mg-5CMC after transformation-involving milling.**Fig. 7.** Microstructures observed by SEM of Mg-5CMC dehydrogenated at 593 K in hydrogen of 1.0 bar at the 4<sup>th</sup> cycle after hydriding-dehydrogenating cycling at 593 K.**Fig. 8.** XRD diagram of Mg-5CMC after transformation-involving milling.

after transformation-involving milling is shown in Fig. 8. The sample contains Mg and very small amounts

of  $\beta$ -MgH<sub>2</sub> and MgO, with no evidence of the phases related to CMC. This indicates that  $\beta$ -MgH<sub>2</sub>, which is known as a low-pressure form of magnesium hydride with a tetragonal structure, is formed by the reaction of Mg with H<sub>2</sub> during milling in hydrogen. A very small amount of MgO was formed by the reaction of Mg probably with the oxygen adsorbed on the surfaces of particles when the sample was treated to obtain the XRD diagram.

The XRD diagram of Mg-5CMC dehydrogenated at 593 K in hydrogen of 1.0 bar at the 4<sup>th</sup> cycle after hydriding-dehydriding cycling at 593 K showed that the sample contained Mg and tiny amounts of  $\beta$ -MgH<sub>2</sub> and MgO, with no evidence of the phases related to CMC. This showed that a tiny amount of  $\beta$ -MgH<sub>2</sub> was not decomposed, even after the dehydriding reaction at 593 K in hydrogen of 1.0 bar.

In our previous works, we investigated the hydriding and dehydriding properties of Mg-5NbF<sub>5</sub> [12], Mg-10Fe<sub>2</sub>O<sub>3</sub> [17], and Mg-5Ni-2.5Fe-2.5Ti [18]. These materials were prepared by transformation-involving milling under similar conditions to those used here to prepare Mg-5CMC. These alloys showed relatively good hydriding and dehydriding properties. The curves of change of H<sub>a</sub> as a function of t at 593 K in hydrogen of 12 bar for activated Mg-5CMC, Mg-5NbF<sub>5</sub>, Mg-10Fe<sub>2</sub>O<sub>3</sub>, and Mg-5Ni-2.5Fe-2.5Ti are presented in Fig. 9. The beginning hydriding rate of Mg-5CMC is the highest, trailed in descending order by those of Mg-5NbF<sub>5</sub>, Mg-5Ni-2.5Fe-2.5Ti, and Mg-10Fe<sub>2</sub>O<sub>3</sub>. The H<sub>a</sub> (60 min) of Mg-5CMC is the largest, trailed in a descending order by those of Mg-10Fe<sub>2</sub>O<sub>3</sub>, Mg-5NbF<sub>5</sub>, and Mg-5Ni-2.5Fe-2.5Ti. These show that the addition of 5 wt% CMC has the strongest effects on the beginning hydriding rate and the H<sub>a</sub> (60 min) compared with the additions of NbF<sub>5</sub> or Fe<sub>2</sub>O<sub>3</sub> and the simultaneous addition of Ni, Fe, and Ti.

Figure 2 shows that the addition of CMC to Mg by transformation-involving milling increases the beginning hydriding rate and H<sub>a</sub> (60 min). The particle of pure Mg had a few cracks, with quite a flat surface [19]. Mg-5CMC after transformation-involving milling has smaller particles and more

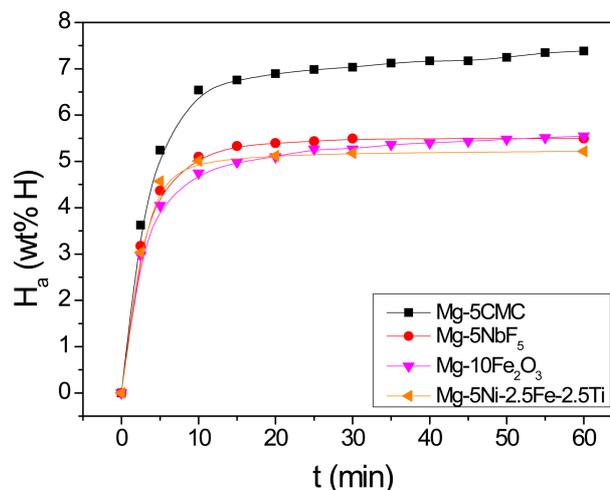


Fig. 9. Curves of change in H<sub>a</sub> as a function of t at 593 K in hydrogen of 12 bar for activated Mg-5CMC, Mg-5NbF<sub>5</sub>, Mg-10Fe<sub>2</sub>O<sub>3</sub>, and Mg-5Ni-2.5Fe-2.5Ti.

cracks than the pure Mg.

The milling of Mg with CMC in hydrogen is believed to fabricate defects and cracks and lessen the particle size. Fabrication of defects is considered to ease nucleation. Fabrication of cracks and decreasing the particle size is thought to expose fresh surfaces, resulting in an increase in the reactivity of particles with hydrogen. Decreasing the particle size is believed to increase the flux of diffusing hydrogen atoms [20-23].

Figure 2 shows that the amount of the hydrogen absorbed in 60 min, H<sub>a</sub> (60 min), of Mg-5CMC is larger than that of Mg-10CMC. Under the conditions used to prepare Mg-5CMC and Mg-10CMC, it is believed that the milling effects are stronger in Mg-5CMC than in Mg-10CMC and it is also believed the larger fraction of Mg in Mg-5CMC than in Mg-10CMC makes Mg-5CMC have the larger H<sub>a</sub> (60 min) than Mg-10CMC.

The XRD diagrams of other samples after transformation-involving milling exhibited peak broadening and increases in the background [12-14]. However, the XRD diagram of the Mg-5CMC after transformation-involving milling shows a very small peak-broadening and a very small increase in the background. The XRD diagram of the Mg-5CMC dehydrogenated at 593 K in hydrogen of 1.0 bar at the 4<sup>th</sup> cycle was very similar to that of the Mg-

5CMC after transformation-involving milling. These results suggest that the transformation-involving milling of Mg-5CMC induces very small strain.

It was reported that the hydriding rates of Mg are determined by nucleation in hydrogen pressure which exerts a small driving force for the hydriding reaction (the difference between the applied hydrogen pressure and the equilibrium plateau pressure at a given temperature) and the diffusion of hydrogen atoms through a thickening layer of magnesium hydride [24]. The dehydriding rates of MgH<sub>2</sub> are determined by nucleation in hydrogen pressure which exerts a small driving force for the dehydriding reaction (the difference between the equilibrium plateau pressure at a given temperature and the applied hydrogen pressure) [24]. Therefore, the hydriding and dehydriding rates can be increased by easing nucleation, and the hydriding rate of Mg can be raised by lessening the Mg particle size.

The result in Fig. 3 shows that hydriding-dehydriding cycling increases the beginning hydriding rate and H<sub>a</sub> (60 min) until the completion of activation, probably due to the repeated expansion (by hydrogen absorption) and contraction (by hydrogen release) of the material. The expansion and contraction is thought to cause defects, produce cracks, and lessen the particle sizes.

The particles of pure Mg had a few cracks, with quite a flat surface [19]. The particles of Mg-5NbF<sub>5</sub> [12] and Mg-10Fe<sub>2</sub>O<sub>3</sub> [17] were agglomerated. The particles of Mg-5Ni-2.5Fe-2.5Ti [18] and Mg-5CMC were separated, and the particles of Mg-5CMC were smaller than those of Mg-5Ni-2.5Fe-2.5Ti.

#### 4. CONCLUSIONS

Samples with compositions of 95 wt% Mg + 5 wt% CMC (named Mg-5CMC) and 90 wt% Mg + 10 wt% CMC (named Mg-10CMC) were made by adding CMC with a low melting point to Mg via transformation-involving milling. Mg-5CMC was activated in about 3 hydriding-dehydriding cycles. After activation, Mg-5CMC had a larger amount of hydrogen absorbed in

60 min, H<sub>a</sub> (60 min), than Mg-10CMC and milled Mg. At CN=4, Mg-5CMC had a very high beginning hydriding rate (1.45 wt% H/min) and a very large H<sub>a</sub> (60 min) (7.38 wt% H), showing that the activated Mg-5CMC has an effective hydrogen-storage capacity of about 7.4 wt% at 593 K in hydrogen of 12 bar at CN=4. Mg-5CMC after transformation-involving milling contained Mg and very small amounts of β-MgH<sub>2</sub> and MgO, and Mg-5CMC dehydrogenated at 593 K in hydrogen of 1.0 bar at the 4<sup>th</sup> cycle contained Mg and tiny amounts of β-MgH<sub>2</sub> and MgO, with no evidence of the phases related to CMC. The milling of Mg with CMC in hydrogen is believed to introduce defects and cracks and lessen the particle size. The addition of 5 wt% CMC was more effective on the beginning hydriding rate and the H<sub>a</sub> (60 min) compared with the additions of NbF<sub>5</sub> or Fe<sub>2</sub>O<sub>3</sub> and the simultaneous addition of Ni, Fe, and Ti. To increase the dehydriding rate and the amount of the hydrogen released in 60 min, H<sub>d</sub> (60 min), of Mg-5CMC, transition elements such as Ni and Ti will be added and the hydriding and dehydriding properties of the prepared samples will be studied in the future.

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