Improvement of the Hydrogen-Storage Properties of Mg by Adding a Polymer CMC via Transformation-Involving Milling

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The addition of CMC (Carboxymethylcellulose, Sodium Salt) may improve the hydrogen uptake-release properties of Mg since it has a relatively low melting point and the melting of CMC during transformation-involving milling may make the milled samples be in the good states to absorb and release hydrogen rapidly. Samples with compositions of 95 w/o Mg + 5 w/o CMC (named Mg-5CMC) were made through transformation-involving milling. Mg-5CMC was activated in about 3 hydrogen uptake-release cycles. After activation, Mg-5CMC had a higher beginning hydrogen uptake rate and a larger amount of hydrogen absorbed in 60 min, U (60 min), than milled Mg. At the third cycle ($CN = 3$), Mg-5CMC had a very high beginning hydrogen uptake rate (1.45 w/o H/min) and a very large U (60 min) (7.18 w/o H), showing that the activated Mg-5CMC has an effective hydrogen-storage capacity of about 7.2 w/o at 593 K in hydrogen of 12 bar at $CN = 3$. Mg-5CMC after transformation-involving milling contained Mg and very small amounts of β-MgH_2 and MgO, with no evidence of the phases related to CMC. The milling in hydrogen of Mg with CMC is believed to fabricate defects and cracks and lessen the particle size. To the best of our knowledge, this study is the first one in which a polymer CMC is added to Mg by transformation-involving milling to improve the hydrogen uptake-release properties of Mg.

Keywords: hydrogen storage material, a polymer CMC (carboxymethylcellulose, sodium salt) addition, hydrogen storage capacity, activation, milling in hydrogen.

1. INTRODUCTION

A lot of work to increase the hydrogen uptake and release rates and hydrogen-storage capacity of magnesium, which is known to have excellent hydrogen uptake and release properties, has been performed [1–4] by alloying with magnesium certain metals [5–7], by synthesizing Mg-based compounds [8–13] such as $LaMg_{12}$, $CeMg_{12}$ [12], $MmMg_{12}$ (Mm-mischmetal), La_2Mg_{17} [9], γ-$Mg_{17}Al_{12}$ [13], and by adding graphite [14] and adding Nb and multi-walled carbon nanotubes to Mg-Ni alloys [15].

In our previous works, the hydrogen uptake and release properties of Mg were improved by adding halogen compounds such as NbF_5 [16], TaF_5 [17], VCl_3, and $TiCl_3$ [18, 19] by transformation-involving milling. The low decomposition temperatures of these halogen compounds are thought to contribute to the improvement of the hydrogen uptake and release properties of Mg.

CMC (Carboxymethylcellulose, Sodium Salt, $[C_6H_7O_2(OH)_x(C_2H_2O_3Na)_y]_n$) is a water-soluble anionic linear polymer, which is a cellulose derivative with carboxymethyl groups (-CH_2-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 hydrogen uptake and release properties of Mg since it has a relatively low melting point and the melting of CMC during transformation-involving milling may make the milled samples be in the good states to absorb and release hydrogen rapidly.

In this work, samples with compositions of 95 w/o Mg + 5 w/o CMC (named Mg-5CMC) were made through transformation-involving milling, and the hydrogen uptake-release properties of Mg-5CMC were examined in detail and compared with the hydrogen uptake-release properties of oxide, halide, or transition metals-added Mg samples by milling in hydrogen using conditions similar to those for the preparation of Mg-5CMC. As far as we know, this study is the first one in which a polymer CMC is added to Mg by transformation-involving milling to improve the hydrogen uptake-release 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 transformation-involving milling.

The employed planetary ball mill was a Planetary Mono Mill (Pulverisette 6) from Fritsch. The total weight of the constituents of mixtures was 8 g. The total weight of hardened steel balls was 360 g and their number was 105. Handling of samples was done in argon atmosphere. The disc rotation speed was 400 rounds per minutes (rpm). The transformation-involving milling was carried out in

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hydrogen of about 12 bar for 6 h. The periods of refilling the mill container (with a volume of 250 mL) with hydrogen was 2 h.

Changes in the absorbed or released hydrogen amount with time were measured using a Sieverts' type hydrogen uptake and release apparatus elucidated previously [20]. A half gram of the samples was used to measure changes in absorbed or released hydrogen amounts with time.

Phases in the samples after transformation-involving milling and after hydrogen uptake-release cycling were analyzed by X-ray diffraction (XRD) with Cu Kα 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

A micrograph of CMC observed by SEM is shown in Fig. 1. Particles are irregular in shape and have flat and bumpy surfaces with some cracks.
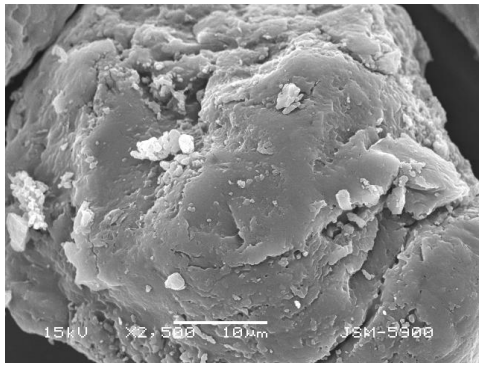

Fig. 1. Microstructure observed by SEM of CMC

The uptake hydrogen amount of the sample, U, was calculated on the basis of the sample weight, and U was given in the unit of weight percent of hydrogen (w/o H).

Mg-5CMC was activated in about 3 hydrogen uptake-release cycles, as shown in Fig. 3. Fig. 2 shows the curves of change in U as a function of time t at 593 K in hydrogen of 12 bar at cycle number of four ($CN = 4$) for Mg-5CMC, Mg-10CMC, and Mg which was milled in hydrogen. Mg-10CMC with a composition of 90 w/o Mg + 10 w/o CMC was prepared under the conditions similar to those to prepare Mg-5CMC. Mg-5CMC has a very slightly higher beginning hydrogen uptake rate and a larger quantity of hydrogen absorbed in 60 min, U (60 min), than Mg-10CMC. Mg-5CMC and Mg-10CMC have much higher beginning hydrogen uptake rates and much larger U (60 min)'s than Mg. These results show that Mg-5CMC is a better composition for hydrogen uptake than Mg-10CMC and the addition of CMC to Mg by transformation-involving milling and hydrogen uptake-release cycling increase the beginning hydrogen uptake rate and U (60 min). These results led us to study the hydrogen uptake and release properties of Mg-5CMC in detail. The Mg sample absorbs 1.20 w/o H in 2.5 min, 2.28 w/o H in 10 min, and 3.46 w/o H in 60 min. Mg-5CMC absorbs 3.62 w/o H in 2.5 min, 6.54 w/o H in 10 min, and 7.38 w/o H in 60 min. Table 1 shows the changes in U as a function of t at 593 K in hydrogen of 12 bar at $CN = 4$ for Mg and Mg-5CMC.

The curves of change in U as a function of t at 523 K in hydrogen of 12 bar at $CN = 1 - 4$ for Mg-5CMC are shown in Fig. 3. Hydrogen is absorbed even at a relatively low temperature, 523 K. The beginning hydrogen uptake rate and U (60 min) increase as CN increases. At $CN = 3$ and $CN = 4$, the curves of change in U as a function of t are very similar from the start to 35 min. This shows that Mg-5CMC is activated in about 3 hydrogen uptake-release cycles. At $CN = 1$, Mg-5CMC absorbs 0.36 w/o H in 2.5 min, 0.44 w/o H in 10 min, and 0.81 w/o H in 60 min. At $CN = 4$, Mg-5CMC absorbs 0.42 w/o H in 2.5 min, 0.79 w/o H in 10 min, and 1.48 w/o H in 60 min.
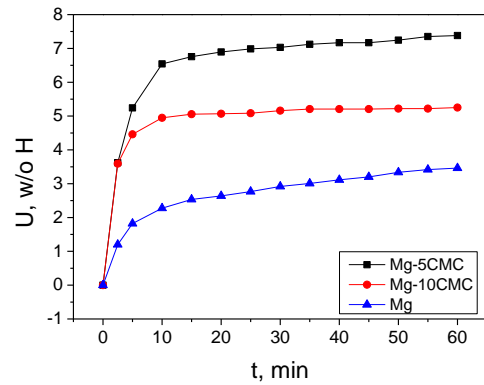

Fig. 2. Curves of change in U as a function of t at 593 K in hydrogen of 12 bar at $CN = 4$ for Mg-5CMC, Mg-10CMC, and Mg
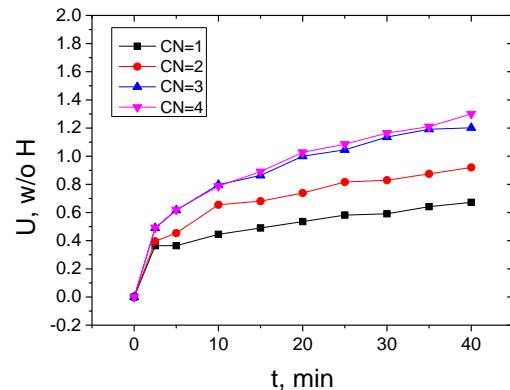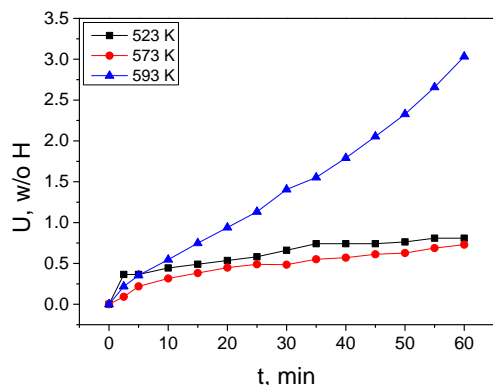

Fig. 3. Curves of change in U as a function of t at 523 K in hydrogen of 12 bar at $CN = 1 - 4$ for Mg-5CMC

Table 1. Changes in U (w/o H) as a function of t at 593 K in hydrogen of 12 bar at $CN = 4$ for Mg and Mg-5CMC
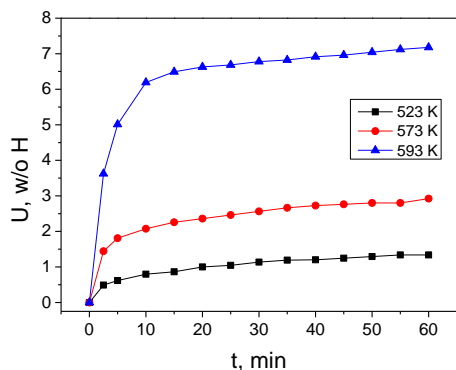
	2.5 min	5 min	10 min	30 min	60 min
Mg	1.20	1.82	2.28	2.92	3.46
Mg-5CMC	3.62	5.24	6.54	7.03	7.38

Fig. 4 depicts the curves of change in U as a function of t at 523 K, 573 K, and 593 K in hydrogen of 12 bar at $CN = 1$ for Mg-5CMC. The curves of change in U as a function of t at 523 K and 573 K are similar. After 10 min, U values at 593 K are higher than those at 523 K and 573 K. The U (60 min) at 593 K is much larger than those at 573 K and 523 K. At 523 K, Mg-5CMC absorbs 0.36 w/o H in 2.5 min, 0.44 w/o H in 10 min, and 0.81 w/o H in 60 min. At 593 K, Mg-5CMC absorbs 0.21 w/o H in 2.5 min, 0.55 w/o H in 10 min, and
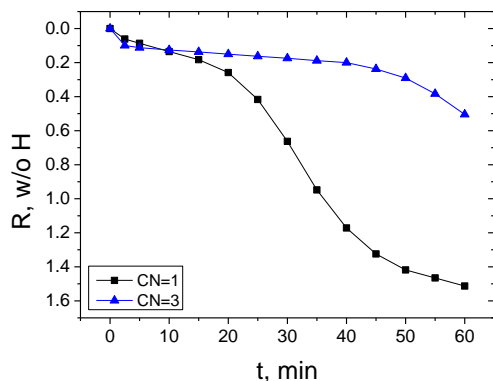
3.03 w/o H in 60 min.

Fig. 4. Curves of change in U as a function of t at 523 K, 573 K, and 593 K in hydrogen of 12 bar at $CN = 1$ for Mg-5CMC

Fig. 5. Curves of change in U as a function of t at 523 K, 573 K, and 593 K in hydrogen of 12 bar at CN=3 for Mg-5CMC

Fig. 6. Curves of change in R as a function of t at 593 K in hydrogen of 1.0 bar at $CN = 1$ and $CN = 3$ for Mg-5CMC

Table 2. Changes in U (w/o H) as a function of t at 523 K, 573 K, and 593 K in hydrogen of 12 bar at $CN = 3$ for Mg-5CMC

	2.5 min	5 min	10 min	30 min	60 min
523 K	0.49	0.62	0.80	1.14	1.34
573 K	1.44	1.81	2.07	2.56	2.92
593 K	3.62	5.01	6.19	6.78	7.18

The curves of change in U as a function of t at 523 K, 573 K, and 593 K in hydrogen of 12 bar at $CN = 3$ for Mg-5CMC are shown in Fig. 5. The beginning hydrogen uptake rate and U (60 min) increase rapidly as the temperature increases. At 593 K, the beginning hydrogen uptake rate is very high (1.45 w/o H/min) and U (60 min)

is very large (7.18 w/o H). At 523 K, Mg-5CMC absorbs 0.49 w/o H in 2.5 min, 0.80 w/o H in 10 min, and 1.34 w/o H in 60 min. At 593 K, Mg-5CMC absorbs 3.62 w/o H in 2.5 min, 6.19 w/o H in 10 min, and 7.18 w/o H in 60 min.

Table 3. Changes in R (w/o H) as a function of t at 593 K in hydrogen of 1.0 bar at $CN = 1$ and $CN = 3$ 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=3	0.10	0.11	0.13	0.17	0.50

Table 2 shows the changes in U as a function of t at 523 K, 573 K, and 593 K in hydrogen of 12 bar at $CN = 3$ for Mg-5CMC.

We define an effective hydrogen-storage capacity as the amount of the hydrogen absorbed in 60 min, U (60 min). Mg-5CMC has an effective hydrogen-storage capacity of about 7.4 w/o at 593 K in hydrogen of 12 bar at $CN = 4$. An effective hydrogen-storage capacity of about 7.4 w/o is a very high one of Mg-based alloy.

The amount of the hydrogen released from the sample, R, was also calculated on the basis of the sample weight, and R was also given in the unit of weight percent of hydrogen (w/o H).

Fig. 6 shows the curves of change in R as a function of t at 593 K in hydrogen of 1.0 bar at $CN = 1$ and $CN = 3$ for Mg-5CMC. The beginning hydrogen release rates at $CN = 1$ and $CN = 3$ are similar and the amount of the hydrogen released in 60 min, R (60 min), decreases very rapidly from $CN = 1$ to $CN = 3$. At $CN = 1$, the hydrogen release rate is low in the beginning, increasing slowly and reaching the maximum rate in about 30 min, and then decreasing again. At $CN = 1$, Mg-5CMC releases 0.06 w/o H in 2.5 min, 0.66 w/o H in 30 min, and 1.51 w/o H in 60 min. At $CN = 3$, Mg-5CMC releases 0.10 w/o H in 2.5 min, 0.17 w/o H in 30 min, and 0.50 w/o H in 60 min. Table 3 shows the changes in R as a function of t at 593 K in hydrogen of 1.0 bar at $CN = 1$ and $CN = 3$ for Mg-5CMC. This result shows that the hydrogen release rates of Mg-5CMC are low and the cycling performance in the hydrogen release reaction of Mg-5CMC is poor. To increase the hydrogen release rates and R (60 min) and to improve the cycling performance of Mg-5CMC, we will study the hydrogen uptake-release properties of the samples prepared by adding transition elements such as Ni and Ti in the future.

Transformation-involving milling of Mg-5CMC yielded the particles depicted in Fig. 7. The particle sizes are not homogeneous. The particles are slightly spherical and have quite flat surfaces. Fine particles are embedded in the large particles.

Fig. 8 shows the micrograph observed by SEM of Mg-5CMC dehydrogenated (a, b) at 593 K after hydrogen uptake-release cycling at 593 K and (c, d) at 523 K after hydrogen uptake-release cycling at 523 K, in hydrogen of 1.0 bar at the 4th cycle. The particle sizes of the sample after cycling at 593 K are not homogeneous. The particles of the sample after hydrogen uptake-release cycling are smaller than those of the sample after transformation-involving milling.
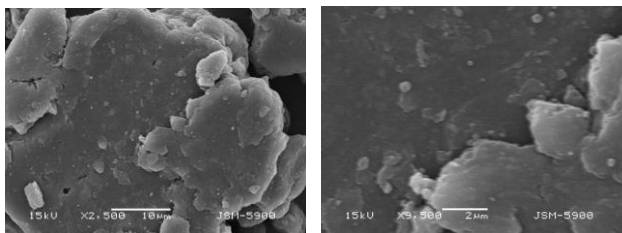
Fig. 7. Micrographs observed by SEM of Mg-5CMC after transformation-involving milling

The particles of the sample after transformation-involving milling have quite flat surfaces, but those of the sample after hydrogen uptake-release cycling are covered with fine particles. The particles of the sample after cycling at 523 K are similar to those of Mg-5CMC after cycling at 593 K, but the particles covering the large particles are slightly finer than those of the sample after cycling at 593 K. The lower beginning hydrogen uptake rate and smaller U (60 min) at 523 K, compared with those at 593 K, are believed to have led to this result.
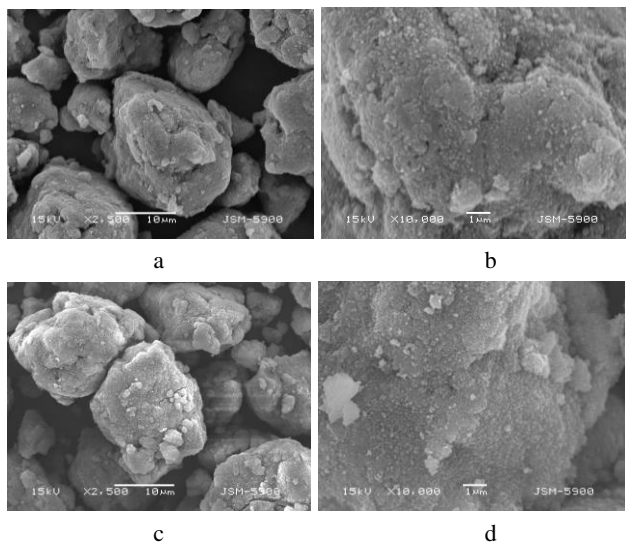

Fig. 8. Micrographs observed by SEM of Mg-5CMC dehydrogenated (a, b) at 593 K after hydrogen uptake-release cycling at 593 K and (c, d) at 523 K after hydrogen uptake-release cycling at 523 K, in hydrogen of 1.0 bar at the 4th cycle

The XRD (X-ray diffraction) diagram of Mg-5CMC before and after transformation-involving milling is shown in Fig. 9. The sample before transformation-involving milling contains only Mg and has a slightly high background, which is caused by the presence of CMC in the sample. The sample after transformation-involving milling contains Mg and very small amounts of β-MgH$_2$ and MgO, with no evidence of the phases related to CMC. This indicates that β-MgH$_2$, which is known as a low-pressure form of magnesium hydride with a tetragonal structure, is formed by the reaction of Mg with H$_2$ during milling in hydrogen.

A very small amount of MgO was formed by the reaction of Mg with the oxygen adsorbed on the particle surfaces exposed to air probably during treating the sample to obtain XRD diagram. The XRD diagram of Mg-5CMC dehydrogenated at 593 K in hydrogen of 1.0 bar at the 4th cycle after hydrogen uptake-release cycling at 593 K

showed that the sample contained Mg and tiny amounts of β-MgH$_2$ and MgO, with no evidence of the phases related to CMC, showing that a tiny amount of β-MgH$_2$ was not decomposed, even after the hydrogen release reaction at 593 K in hydrogen of 1.0 bar.
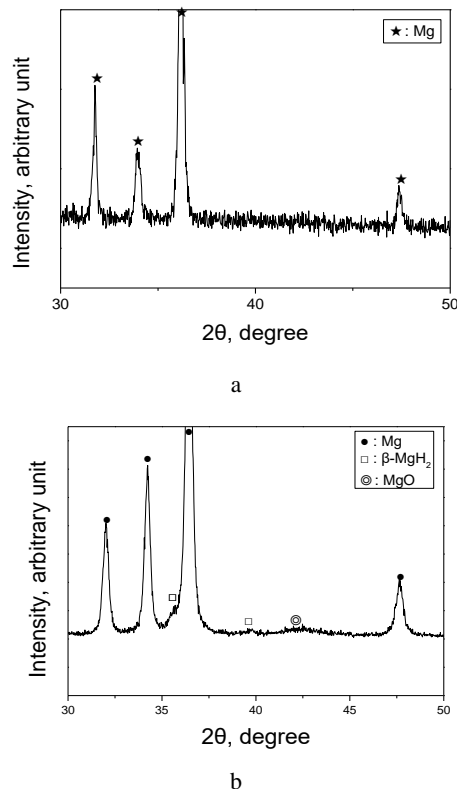
Fig. 9. XRD diagram of Mg-5CMC (a) before and (b) after transformation-involving milling
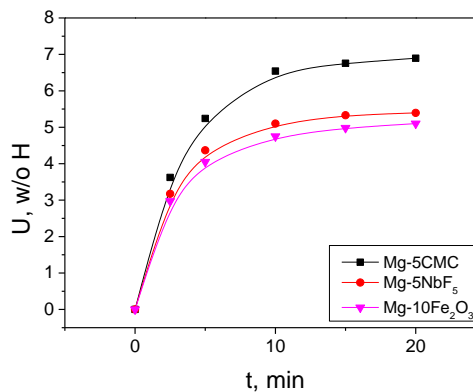
Fig. 10. Curves of change in U as a function of t at 593 K in hydrogen of 12 bar for activated Mg-5CMC, Mg-5NbF$_5$, and Mg-10Fe$_2$O$_3$

In our previous works, the hydrogen uptake-release properties of Mg-5NbF$_5$ [16], and Mg-10Fe$_2$O$_3$ [21] were investigated. These materials were prepared by transformation-involving milling under conditions similar to those for the preparation of Mg-5CMC. Mg-5NbF$_5$ as one of halide-added Mg alloys [16] and Mg-10Fe$_2$O$_3$ as one of oxide-added Mg alloys [21] showed relatively good hydrogen uptake-release properties. The curves of change of U as a function of t at 593 K in hydrogen of 12 bar for activated Mg-5CMC, Mg-5NbF$_5$, and Mg-10Fe$_2$O$_3$ are presented in Fig. 10. The beginning hydrogen uptake rate

of Mg-5CMC is the highest, trailed in descending order by those of Mg-5NbF$_5$ and Mg-10Fe$_2$O$_3$. The U (60 min) of Mg-5CMC is the largest, trailed in a descending order by those of Mg-10Fe$_2$O$_3$ and Mg-5NbF$_5$. This shows that the addition of 5 w/o CMC has the strongest effects on the beginning hydrogen uptake rate and the U (60 min) compared with the additions of NbF$_5$ or Fe$_2$O$_3$.

Fig. 2 shows that the addition of CMC to Mg by transformation-involving milling increases the beginning hydrogen uptake rate and U (60 min). The particle of the pure Mg has a few cracks, with quite a flat surface [22]. Mg-5CMC after transformation-involving milling has smaller particles and more cracks than the pure Mg.

The milling in hydrogen of Mg with CMC 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 increase in the reactivity of particles with hydrogen. Decreasing the particle size is believed to increase the flux of diffusing hydrogen atoms [23-25].

The XRD diagrams of other samples after transformation-involving milling exhibited peak broadening and increases in the background [16 – 18]. 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. This suggests that the transformation-involving milling of Mg-5CMC induces very small strain.

It was reported that the hydrogen uptake rates of Mg are determined by nucleation in hydrogen pressures which exert a small driving force for hydrogen uptake reaction (the difference between an 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 [26]. The hydrogen release rates of MgH$_2$ are determined by nucleation in hydrogen pressures which exert a small driving force for hydrogen release reaction (the difference between the equilibrium plateau pressure at a given temperature and an applied hydrogen pressure) [26]. Therefore, the hydrogen uptake and hydrogen release rates can be increased by easing nucleation, and the hydrogen uptake rate of Mg can be raised by lessening the particle size of Mg.

The result in Fig. 3 shows that hydrogen uptake-release cycling increases the beginning hydrogen uptake rate and U (60 min) until the completion of activation, probably due to the repetition of the expansion (by hydrogen uptake) and contraction (by hydrogen release) of the material. The expansion and contraction is thought to cause defects, produce cracks, and lessen the particle sizes [27-29].

The particles of the pure Mg had a few cracks, with quite a flat surface [22]. The particles of Mg-5NbF$_5$ [16], and Mg-10Fe$_2$O$_3$ [21] were agglomerated.

4. CONCLUSIONS

Samples with compositions of 95 w/o Mg + 5 w/o CMC (named Mg-5CMC) were made by adding CMC with a low melting point to Mg via transformation-involving milling. Mg-5CMC was activated in about 3 hydrogen uptake-release cycles. After activation, Mg-5CMC had a larger amount of hydrogen absorbed in 60 min, U (60 min), than milled Mg. At $CN = 3$, Mg-5CMC had a very high beginning hydrogen uptake rate (1.45 w/o H/min) and a very large U (60 min) (7.18 w/o H), showing that the activated Mg-5CMC has an effective hydrogen-storage capacity of about 7.2 w/o at 593 K in hydrogen of 12 bar at $CN = 3$. Mg-5CMC after transformation-involving milling contained Mg and very small amounts of β-MgH$_2$ and MgO, with no evidence of the phases related to CMC. The milling in hydrogen of Mg with CMC is believed to fabricate defects and cracks and lessen the particle size. The addition of 5 w/o CMC was more effective on the initial hydrogen uptake rate and the U (60 min) compared with the additions of NbF$_5$ or Fe$_2$O$_3$. To increase the hydrogen release rate and the amount of the hydrogen released in 60 min, R (60 min), of Mg-5CMC, the hydrogen uptake-release properties of the samples prepared by adding transition elements such as Ni and Ti will be studied in our future work.

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