

EFFECT OF MECHANICAL ALLOYING ON HYDROGEN CYCLING OF MAGNESIUM HYDRIDE (MgH₂) AT ELEVATED TEMPERATURES

A. Miizan, T. Ashida, A. Takasaki

Graduate School of Engineering and Science, Shibaura Institute of Technology

md15075@shibaura-it.ac.jp

ABSTRACT

In this study, we investigated the effect of mechanical milling on hydrogen cycling of Magnesium Hydride (MgH₂) powder, through the evolution of its microstructures upon hydrogenation/dehydrogenation cycling at elevated temperatures of higher than 300°C. Several samples of MgH₂ crystalline powder were milled mechanically for 20 hours at 300 rpm under an argon atmosphere by using a high-energy planetary ball mill (MM). By using Sievert's apparatus (PCT), the samples underwent hydrogenation/dehydrogenation cycling for 20 cycles at elevated temperatures of higher than 300°C. Then, the samples were also tested by using Differential Scanning Calorimetry (DSC) to analyze temperatures of endothermic reaction and its energy of the reaction. The effects of both hydrogen cycling and the mechanical milling on the crystalline structure of MgH₂ were investigated by using an X-Ray Diffraction (XRD) instrument and a Scanning Electron Microscope (SEM). Both of the samples before and after hydrogen cycling were analyzed and compared. The result of this analyses showed that as the cycling temperature increased, the hydrogen release kinetics were also increased. However, at the same time, the maximum gravimetric capacity of MgH₂ continued to drop slightly as the cycle number of 20 was achieved. We concluded that deterioration of the gravimetric capacity was mainly due to the agglomeration of the MgH₂ particles, which resulted in a decrease of the specific surface area and thus, reduced the hydrogen gravimetric capacity of the samples. These results were also supported by the DSC measurement results which showed that the activation energy increased after the samples underwent the hydrogen cycling. Therefore, XRD peak analysis also showed that the crystalline structure of the MgH₂ became more stable as the hydrogen cycling temperature increased due to the recrystallization phenomenon of the MgH₂ particles caused by the

hydrogenation reaction itself.

1. INTRODUCTION

The Hydrogen energy is now considered by many, to be one of the most reliable candidate for clean energy source since it only produces water as its waste product. It also can replace the fossil fuel, which is almost depleted in these days, and also possible to be considered as a main energy source in the future. For a safer use and a higher efficiency of hydrogen storage, developments of hydrogen storage materials are now currently being researched, in order to produce the most promising storage materials for future use.

Magnesium hydride (MgH₂) particularly, is considered to be as one of the most reliable candidates for the reversible hydrogen storage materials since it has a relatively high storage capacity of 7.6 wt.% and has a very stable molecule compound at standard temperature and pressure. It also comes with the benefit of the low cost and still has a high abundant available from many source on earth.

Unfortunately, MgH₂ itself still has some limitations. Even though possessing a very stable molecule compound is considered as its advantages, however, it also means that MgH₂ possesses a relatively high thermodynamic stability. Possessing a high thermodynamic stability of MgH₂ means that it has a relatively high desorption enthalpy ($\Delta H = -74.5$ kJ/mol) which is corresponds to the undesirable desorption temperature higher than 300°C at 1 bar H₂. Also, the hydrogen desorption kinetics is still sluggish and slow. Due to these reasons, these disadvantages become the main barriers for pure MgH₂ to be directly utilized in its applications.

In recent studies, there are many efforts such as the fabrication of nanocrystalline MgH₂ by the method of mechanical milling. Using mechanical milling or ball mill, the MgH₂ crystal undergo a uniform deformation on its

microstructure and its surface, which is grinding MgH_2 particle further into a smaller size and thus, significantly increases the total effective surface area of the MgH_2 particle for the hydrogenation. As a result, nanocrystalline MgH_2 that produced by the milling exhibits a remarkable improvement on its absorption and desorption kinetics. [1] On the other hand, few studies were further developed from the same laboratory by the matter of using some additive material in order to significantly improve the sorption kinetics of the MgH_2 . The outcome of this development are mostly applicable for the low temperature MgH_2 sorption property, which is below 300°C . However, the studies regarding MgH_2 performance and characteristic at an elevated temperature of 300°C and above, are still few. So, all the information regarding this topic must be acquired before making any implementation of its suitable applications.

In this paper, we present results of the investigation for hydrogen sorption performance and properties of MgH_2 at an elevated temperature of 300°C and above.

2. EXPERIMENTAL

MgH_2 powder with a mean particle size of approximately $60\ \mu\text{m}$ was purchased from Biocoke Lab. Co., Ltd. and used to make samples. The MgH_2 powder was mechanically milled using a planetary ball mill with a stainless steel vial and 10 stainless steel balls (10 mm diameter), and the ball-to-powder ratio was 10:1. MgH_2 was mechanically milled for a total of 20 h at a rotational speed of 300 rpm under a high-purity argon atmosphere. Hydrogen storage capacity and cycle stability of the samples were examined at three different temperatures using an automatic Sievert-type apparatus manufactured (PCT; Japan Metals and Chemical Ltd.), where the data for pressure and temperature were recorded automatically and simultaneously. Prior to every measurement, each of the sample were dehydrated for 20 h at 300°C in a vacuum atmosphere. Approximately 200 mg of sample was performed at three different temperatures with a hydrogen pressure of 1 MPa for absorption and 1 kPa for desorption. Crystallographic characterization was conducted using an X-Ray Diffraction (XRD; Rigaku Ultima IV) with $\text{Cu K}\alpha$ radiation. The hydrogenation performance of each sample was analyzed using a Differential Scanning Calorimetry (DSC; Shimadzu DSC-60) under an argon gas flow (50 mL/min) with different heating rates. The morphology of each samples was analyzed using a scanning electron microscope (SEM; JEOL-1060LV).

3. RESULT AND DISCUSSION

Fig.1 shows the XRD patterns of MgH_2 before and after milling, as well as MgH_2 after cycling at 300°C , 400°C and 450°C respectively. The XRD pattern for after milling MgH_2 shows a lower intensity and broad diffraction lines, indicating a grain refinement and deformation of the crystal structure due to high energy ball milling. However, the milled samples that underwent

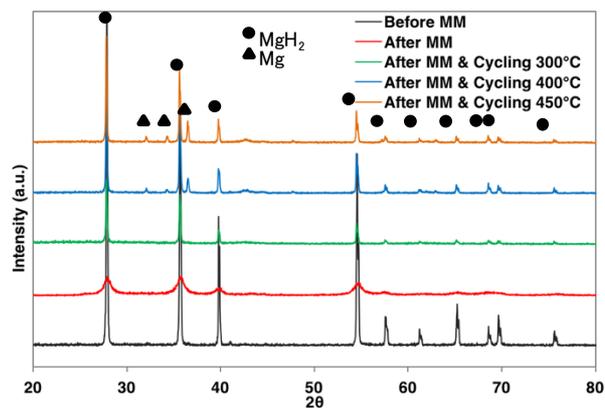


Fig.1 XRD result of each samples examined.

hydrogenation/dehydrogenation cycling shows a higher intensity and sharper peaks again. One of the possibility is that the milled crystal structure of MgH_2 started to recrystallized and formed a more stable crystal structure compared to one after milling, due to the exposition towards heating. [2]

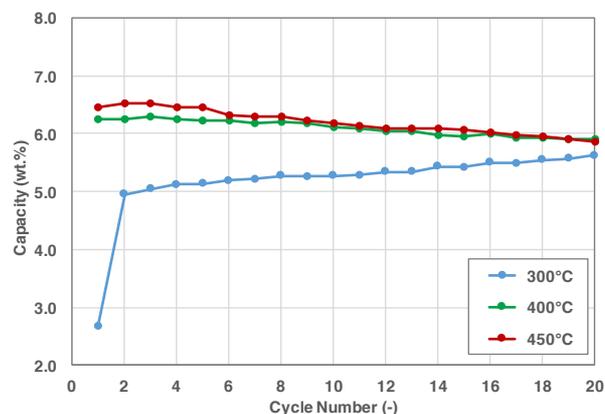


Fig.2 Cycle stability test for MgH_2 at different desorption temperatures.

Fig.2 illustrates the results for the hydrogen desorption capacity of all MgH_2 samples during the hydrogenation/dehydrogenation cycling at three different desorption temperatures of 300°C , 400°C , and 450°C . During the hydrogen cycling at 300°C , the result shows a steep increase in the desorption capacity from cycle 1 to cycle 2. This occurrence is probably due to the MgH_2 samples already oxidized during the sample handling processes, and thus the sample also was unable to absorb the hydrogen gas completely. However, starting from cycle 2, the desorption capacity gradually increases as the cycle number increases, due to the activation effect on the samples.

On the other hand, for the samples that underwent a hydrogen cycling at 400°C and 450°C , the result shows a quite similar behavior between both of them. As the hydrogenation/dehydrogenation cycle number increases, the desorption capacity of the MgH_2 started to decreases starting from the first cycle, indicating the deterioration of the desorption capacity. [3][4]

Fig.3 shows a compiled DSC curves for five of the investigated samples obtained without any activation

treatment. The DSC curve of as-received MgH_2 showed a strongest endothermic peak at approximately 460°C . Meanwhile, the curve for after-milled MgH_2 displayed double endothermic peaks overlapping together at approximately 370°C and 380°C . The appearance of the double peaks in the DSC curve is possibly due to the decomposition of the high-pressure phase of MgH_2 or usually known as $\gamma\text{-MgH}_2$. This phase usually appears after mechanical milling process, particularly in a high energy ball milling process. Compared to the $\beta\text{-MgH}_2$ phase, $\gamma\text{-MgH}_2$ phase is metastable and able to transform to the $\beta\text{-MgH}_2$ easily, especially during the hydrogenation/dehydrogenation cycling at the higher temperature. Fig.3 clearly shows that the occurrence of the double peaks only appeared in the after-milled MgH_2 and the double peaks completely disappeared after the cycling at higher temperatures. Because of the $\gamma\text{-MgH}_2$ phase is metastable, the hydrogen desorption temperature for this phase appeared to be lower than that for $\beta\text{-MgH}_2$ phase. [5]

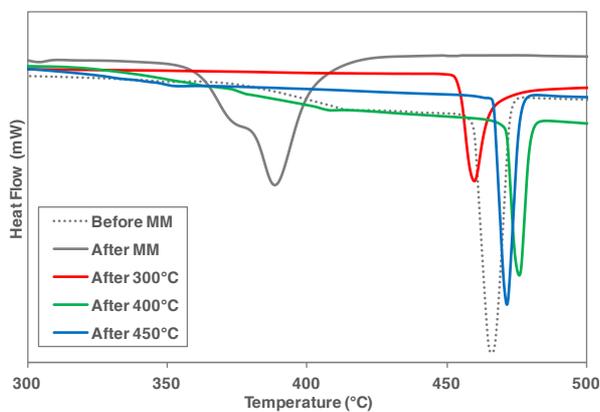


Fig.3 DSC curves of each samples.

The activation energy (E_A) for dehydrogenation of each of all samples can be calculated using the Kissinger plot, where according to the Eq.3 as shown below.

$$\ln \frac{\beta}{T_P} = -\frac{E_A}{RT_P} + \ln \frac{k_0 R}{E_A} \quad \text{Eq.3}$$

The estimated activation energy of each samples were 245 kJ/mol for before milled MgH_2 , 200 kJ/mol for after milled MgH_2 , 266 kJ/mol for MgH_2 after cycling at 300°C , 277 kJ/mol for MgH_2 after cycling at 400°C , 354 kJ/mol for MgH_2 after cycling at 450°C respectively. The result clearly showed that the activation energy is the lowest for after milled MgH_2 , which is corresponds to the particle confinement due to mechanical milling, and then the activation energy gradually increases after cycling at 300°C , 400°C , and 450°C . The decrease of the activation energy as the cycling temperature increases could be attributed to the particle agglomeration or particle recrystallization due to heat treatment during the cycling. [6]

As shown in Fig.4(a)-(c), SEM micrographs exhibit the change of grain size and particle of the samples. The initial size of MgH_2 was as shown in Fig.4(a) and Fig.4(b) shows the particle size after milling. These two images

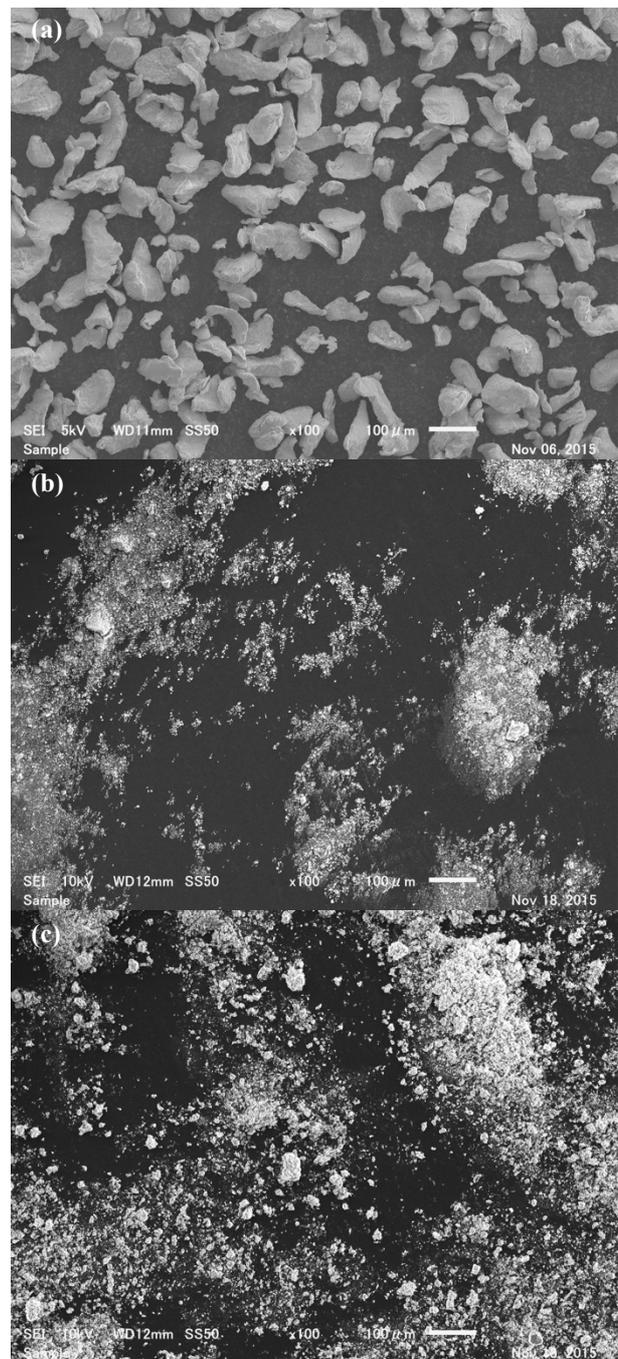


Fig.4 SEM micrographs of the (a) MgH_2 as-received, (b) MgH_2 after milling and (c) MgH_2 after cycling at 450°C respectively.

show the particle size is significantly reduced after underwent high energy ball mill. On the other hand, Fig.4(c) shows MgH_2 that underwent the hydrogen cycling at 450°C . This results indicates that the particle agglomeration occurred intensely in this high temperature situation. Base on this results, we can also validate other results regarding the particle agglomeration occurrence during high temperature hydrogen cycling.

CONCLUSION

From our experiments, the hydrogen desorption capacity of MgH_2 at high temperature gradually decreases

as the number of cycle increases. We can conclude that the main factor for this phenomenon is particle agglomerations which occurred inside of the sample itself. This result is also supported by the activation energy of each samples. In further study, we will consider to improve the cycling stability of the MgH_2 at high temperatures.

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Akito Takasaki, received D.Eng. (1988) and D.Sc. (1996) degrees from Tokyo Institute of Technology and Hiroshima University respectively. He is a professor, Department of Engineering Science and Mechanics, Shibaura Institute of Technology. His current interests include hydrogen storage materials, hydrogen embrittlement of advanced engineering materials and thin films.



Ahmad Miizan, received the B.Sc (2015) degrees in Naval Architecture and Ocean Engineering from Tokai University. He presently is a Master's degree student in Shibaura Institute of Technology and now currently researching on topics regarding hydrogen storage materials technologies and renewable energies.