

Hydrogen storage property of MgH_2 synthesized by hydriding chemical vapor deposition

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Abstract

As reported previously, MgH_2 synthesized by hydriding chemical vapor deposition (HCVD) was made of single crystals with nano-fibrous figures. Therefore, the hydrogen storage property of the HCVDed MgH_2 is expected to reflect its structural character. In this study, we examined the hydrogen storage property of MgH_2 synthesized by HCVD. Results of pressure-composition-isotherm (PCT) measurement showed that the HCVDed MgH_2 reversibly absorbed and desorbed hydrogen as much as 7.6 mass% without any activation treatment retaining the fiber shape. Each hydrogenation/dehydrogenation rate was great because hydrogen diffused through a short pathway in a radial direction of the fiber.

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1. Introduction

Magnesium hydride, MgH_2 , is attractive from the viewpoint of an engineering perspective because its raw materials are abundant and it has great hydrogen density of 7.6 mass%. However, it usually requires at least ten times or more activation treatments, which are quite time and energy intensive [1]; such treatments include both hydriding and dehydriding treatments under control of temperature and hydrogen pressure. Even after the activation treatments, magnesium is not hydrided completely because of the low reaction rate of hydrogenation and the only-slightly-recoverable poisoned part. For marketed products, the product purity of MgH_2 is 98% at most. The activation difficulty of MgH_2 remains as a practical obstacle against its use as a hydrogen storage material.

The problem of activation difficulty occurs because of the low rate of hydrogen diffusion and its unrecoverable poisoned part. The gas–solid reaction between magnesium and hydrogen includes a reaction step of hydrogen diffusion in solid magnesium, which is sufficiently slow that it is the rate-limiting step of the reaction. Therefore, synthesizing metal hydride in

gas phase is expected to alleviate those problems. For that reason, chemical vapor deposition (CVD) under highly pressurized hydrogen, known as hydriding CVD (HCVD), was used to synthesize magnesium hydride from the mixture of high-pressure H_2 and magnesium vapor, and obtained the highly pure product of MgH_2 [2]. The HCVD method indicates the attractive advantage that both the activation treatment and the rate-limiting step in the solid–gas reaction are removed completely because large collision frequency between gaseous metals and hydrogen molecules quickly synthesizes metal hydrides and because as-synthesized metal hydride deposits quickly on the cool substrate. However, in spite of its importance, the hydrogen storage property of HCVDed product of MgH_2 has not been evaluated precisely. Therefore, in this study, we evaluated the hydrogen storage property of the HCVDed MgH_2 . From the viewpoint of the structural character of HCVDed MgH_2 , which was made of single crystals with fibrous shapes, the hydrogen storage property is expected to differ from that of the current product, which inherently becomes polycrystalline because of large strain stress during the hydrogenation and dehydrogenation.

2. Experiment

A sample of MgH_2 was prepared by HCVD as reported elsewhere [2]. Commercial magnesium (99.9% purity) was heated to 870 K to vaporize in hydrogen

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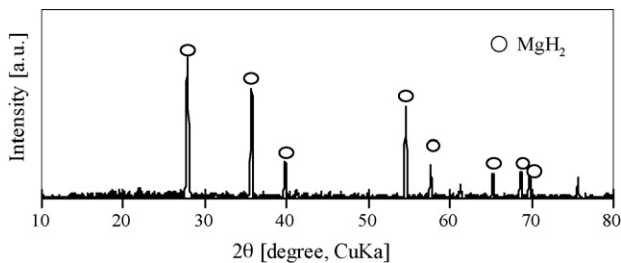


Fig. 1. XRD pattern of the product.

atmosphere at a pressure of 4 MPa. The product of the hydrogen and the magnesium vapor was deposited on the substrate of cooled Inconel. The deposited product was collected and investigated using X-ray diffractometry (XRD) and scanning electron microscopy (SEM). Both the hydrogen storage and release behavior and the pressure-composition-isotherm (PCT) were measured using a PCT measurement apparatus (Suzuki Shokan Co., Ltd., Japan).

3. Results and discussion

Fig. 1 shows the XRD pattern of the product. The XRD pattern was measured shortly after the product was removed from the HCVD apparatus to alleviate oxidization of the product in air because the HCVDed product is readily oxidized in air and forms oxidized phase [2]. Consequently, all peaks were identified with MgH_2 , indicating high purity of HCVDed MgH_2 ; in addition, expected impurities, as observed in a previous report [2], were not detected in this study.

Fig. 2 shows an SEM image of the as-HCVDed MgH_2 . The product showed two shapes: curved fibers; straight, needle-like fibers, which a previous study [2] has identified as single crystals of MgH_2 . The curved fibers were also revealed as MgH_2 according to the XRD results. Each fiber had less than $1 \mu\text{m}$ diameter and each was ten or more micrometers long.

Fig. 3 shows the PCT of the product measured at 578 K. It is noteworthy that the product was not treated in any process but was evacuated for 2 h at a temperature of 578 K before the measurement. The product reversibly absorbed hydrogen approximately 7.6 mass%, as much as the theoretical maximum

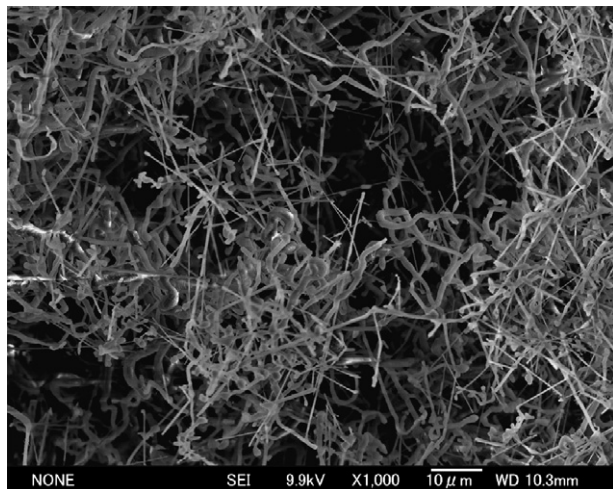


Fig. 2. SEM image of as-HCVDed MgH_2 .

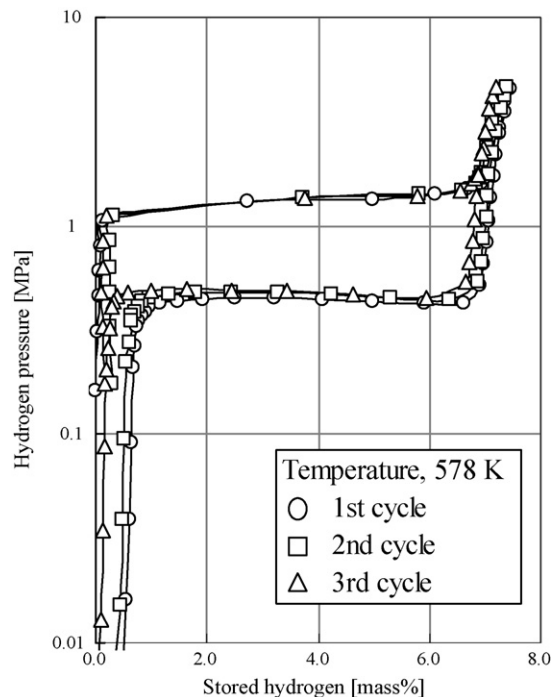


Fig. 3. PCT of HCVDed MgH_2 at 578 K.

capacity of magnesium, even without activation treatment. The measurement finished in 1 and 2 h, respectively, for hydrogenation and dehydrogenation. The reaction rates were much faster than that of conventional Mg, which is only slightly activated by the current activation treatment. The results revealed that the HCVDed MgH_2 was not poisoned in air, thereby had great activity for hydrogen storage.

The plateau pressure in hydrogen absorption and desorption was slightly lower than the reported value; that is, HCVDed MgH_2 was stable in comparison to the conventional product of MgH_2 . That stability was considered to be attributable to the great crystallinity of the HCVDed MgH_2 because hysteresis is usually affected by the irreversible loss during hydrogenation and dehydrogenation. The difference of plateau pressures was more apparent at temperatures lower than 578 K. Fig. 4 shows the PCT of HCVDed MgH_2 at temperatures of 560 and 543 K. Hydrogen desorption pressure of MgH_2 at 560 K is reported to be 0.1 MPa. However, HCVDed MgH_2 desorbed hydrogen at a pressure less than 0.1 MPa. In addition, the pressure showed a remarkable super-decrease (see the blank square under the dotted line in Fig. 4). The HCVDed MgH_2 did not desorb hydrogen until the pressure decreased to 0.04 MPa, but it recovered at pressure greater than 0.06 MPa and started desorption. The same phenomenon was observed at 543 K: the HCVDed product did not desorb hydrogen, even at a pressure of less than 0.01 MPa.

It is difficult to determine equilibrium pressures in hydrogen desorption. Therefore, those in absorption were used for the van't Hoff's plot. Fig. 5 shows the result. Although the pressures were slightly smaller than the reported value, the slope of the line was well fitted (the correlation coefficient in least square method was 99.99%) and was almost parallel to the

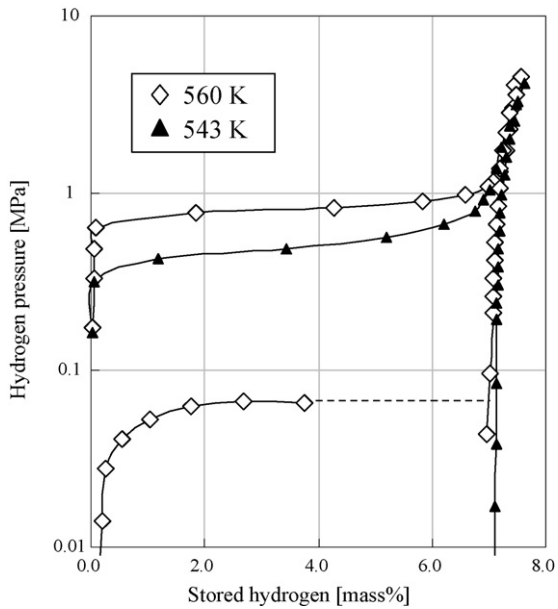


Fig. 4. PCT of HCVDed MgH₂ at 560 and 543 K.

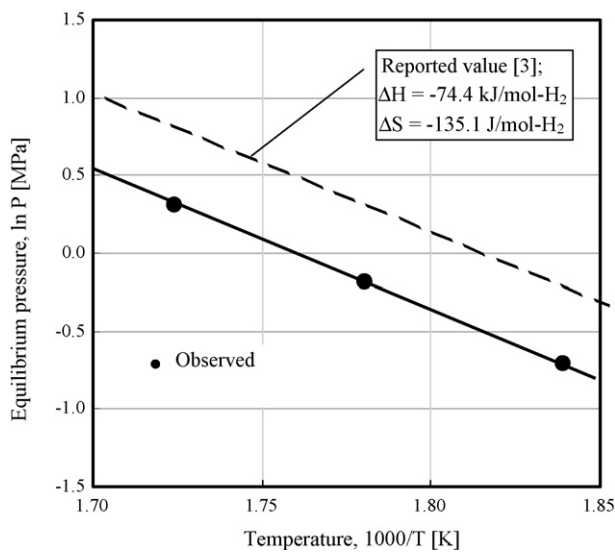


Fig. 5. van't Hoff plot.

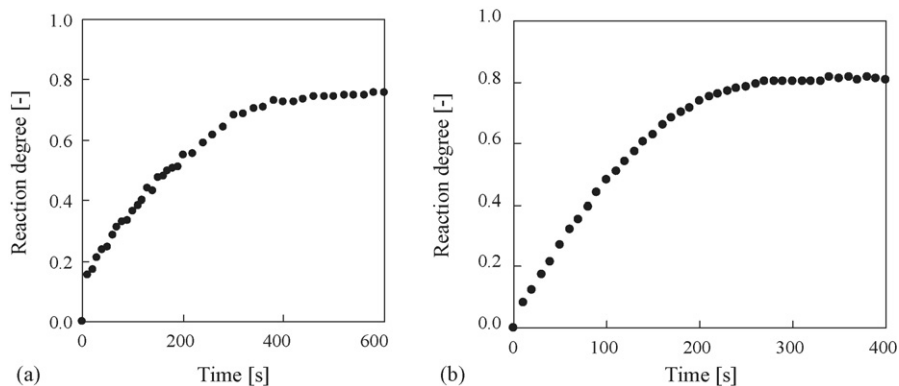


Fig. 6. Hydrogen absorption and desorption behavior of HCVDed MgH₂ at a temperature of 615 K. (a) Hydrogen absorption at a pressure of 4 MPa; (b) hydrogen desorption at a pressure of 0.6 MPa.

reported one. The enthalpy change and entropy change of the reaction, ΔH and ΔS , were as much as -73.4 kJ/mol H₂ and -129.0 J/mol H₂, respectively. The differences in comparison to reported values ($\Delta H = -74.4$ kJ/mol H₂, $\Delta S = -135.1$ J/mol H₂ [3]) were, respectively, within 1.5% and 4.5%.

Fig. 6 shows hydrogen sorption behavior of HCVDed MgH₂. In absorption, HCVDed product completed 80% of the reaction in 600 s at a pressure of 4 MPa H₂. In desorption, it completed 80% of the reaction in 300 s at a pressure of 0.6 MPa H₂. Each reaction rate was greater than those of previous reports [4], which examined the magnesium particles of approximately 10 μm . Regarding the dimensions of the samples, the HCVDed MgH₂ remained at original fiber lengths greater than 10 μm , even after the evaluation of hydrogen storage properties, as described later. Therefore, the greater reaction rate of HCVDed MgH₂ was considered to result from the reaction through the radial pathway of the fibers. The reaction rate of the HCVDed MgH₂ was even large compared to the other reports [5–23] on modified magnesium such as catalyzed magnesium, ball milled one, film-shaped one, and the complex of them, in which ball milled magnesium records the fastest hydrogenation completing 95% of hydrogenation in 400 s. Most of those ball milling and catalyst addition use high-energy mill and produce nano-ordered magnesium or magnesium composites. However, the nano-ordered materials are not stable in air and easily lose those effects. Film structured magnesium is relatively stable, but not so reactive. Therefore, the HCVDed MgH₂, which actively reacted even after being treated in air, is useful from the viewpoint of engineering perspective.

Fig. 7 shows an SEM image of the HCVDed MgH₂ after evaluation of hydrogen storage properties. The sample remained in its original fibrous shape. Neither cracks nor fissures were observed; moreover, the fiber length did not change. Metal hydrides usually generate some cracks to release strain during hydrogen storage cycles. Therefore, the morphological stability of MgH₂ fiber might have imparted great stress during hydrogen absorption and desorption, but that remains a matter of speculation. The fibrous shape is a clue for studying the difference of plateau pressures between conventional MgH₂ and HCVDed MgH₂, as shown in Figs. 3 and 4.

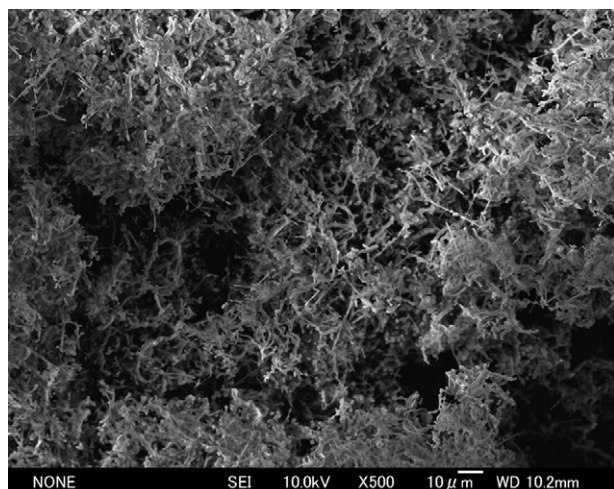


Fig. 7. SEM image of HCVDed MgH_2 after the measurements of hydrogen storage properties.

4. Conclusion

Highly pure MgH_2 was produced using HCVD method; it was then evaluated for its hydrogen storage properties. Although similar whisker-like products were observed in bulk hydrided magnesium powders [24,25], it is difficult to evaluate hydrogen storage properties of the whisker-like products independently of the bulk magnesium. Therefore, the results reported here are believed to be the first information about hydrogen storage properties of the MgH_2 whiskers themselves. Salient results are summarized as described below.

- (A) The HCVDed MgH_2 did not require activation treatment. It reversibly stored hydrogen of as much as 7.6 mass%, which corresponds to the hydrogen capacity of MgH_2 . The plateau pressure was lower than the reported value.
- (B) The hydrogen sorption rate was great because of the short reaction pathway through the radial direction of the fiber.
- (C) The fibers retained their shapes after hydriding and dehydriding. Therefore, those hydrogen storage properties of HCVDed MgH_2 was considered as the effects of structural characteristics.

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