

## A study on thermal analysis of $\text{MgH}_2$ powder made by hydriding chemical vapor deposition method

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**Abstract**—The desorption kinetics of Mg hydride made by the HCVD method was assessed by thermal analysis in order to study desorption behavior. Desorption kinetics was analyzed by the theoretical equation which was derived on the basis of a continuous moving boundary model. At various initial hydride wt% from 1.65 to 7.42, the sample was heated to 573 K at a rate of 1.0 K/min. The starting temperature of evolution of hydrogen rises higher as the initial hydride wt% increases. The number of thermal desorption peaks corresponds to the occupation sites of hydrogen. As the heating rate was increased, the peak temperatures increased; the peak temperatures for heating rates 1, 2, 3 and 4 K/min were 667, 683, 690 and 698 K, respectively. The pressure range is 0.1 to 0.2 atm for measuring. The activation energy for the decomposition of Mg hydride made by HCVD method was 166 kJ/mol.

**Key words:** Hydrogen Storage, HCVD, Thermal Desorption

### INTRODUCTION

Magnesium hydride,  $\text{MgH}_2$ , is attractive from an engineering perspective because its raw materials are abundant and it has a great hydrogen storage capacity of 7.6 mass%. However, it usually requires activation treatments of at least ten times, which are quite time- and energy-intensive [1]. Even after the activation treatments, magnesium is not hydrided completely. Because of these problems Mg is realistically difficult to use. The gas-solid reaction between magnesium and hydrogen includes a reaction step of hydrogen diffusion in solid magnesium, which is sufficiently slow. This accounts for the rate-limiting step of the reaction. Therefore, to overcome this problem many studies are currently underway.

Synthesizing metal hydride in the gas phase is expected to alleviate the problems mentioned above. For this reason, chemical vapor deposition (CVD) under highly pressurized hydrogen, known as hydriding CVD (HCVD) [2-5], was used to synthesize magnesium hydride from the mixture of high-pressure  $\text{H}_2$  and magnesium vapor, and a highly pure product of  $\text{MgH}_2$  was obtained.

The dehydriding reaction of  $\text{MgH}_2$  under an isothermal condition has been investigated by Konstanchuk [6]. The property of  $\text{MgH}_2$  made by HCVD method is summarized below.

First, the  $\text{MgH}_2$  made by HCVD method did not require activation treatment. It reversibly stored hydrogen of as much as 7.6 mass%, which corresponds to the hydrogen capacity of  $\text{MgH}_2$  [4]. The value of plateau pressure was lower than that of the reported one. Second, the hydrogen sorption rate was great because of the short reaction pathway through the radial direction of the fiber [4].

However, in spite of its importance, the hydrogen storage property of  $\text{MgH}_2$  made by HCVD method has not been evaluated precisely.

Therefore, we evaluated the hydrogen storage property through thermal analysis of the  $\text{MgH}_2$  made by HCVD method [7-13]. Also,

we investigated the activation energy and the hydrogen occupation site of Mg alloy.

### THEORETICAL REACTION RATE EQUATION

The reaction temperature will change over linear heating time. Therefore, the equation used in the thermal analysis method was derived in the following. For simplicity, the alloy particles were assumed to be spherical with a uniform diameter.

#### 1. Interfacial Reaction [14]

When the rate-controlling step is an interfacial reaction, the equation is written as follows:

$$\ln\left(\frac{b}{T^2}\right) = \ln\left[\frac{kAP_0^{1/2}}{Er_0(C_\beta - C_\alpha)}\{1 - (1-F)^{-1/3}\}^{-1}\right] - \frac{E}{T} \quad (1)$$

Where  $b$  is the heating rate,  $T$  is the temperature,  $K$ ,  $A$ ,  $P_0$  are constant,  $r_0$  is the radius of the particle,  $C_\beta$  is hydrogen concentration of  $\beta$  phase formed parallel to the  $\alpha$  phase,  $C_\alpha$  is hydrogen concentration of  $\alpha$  phase formed parallel to the  $\beta$  phase.  $E$  is expressed as follows:

$$E = (\Delta H/2 + \Delta \bar{H}_H + Q_c)/R$$

$\Delta H$  is the heat of reaction ( $\beta \rightarrow \alpha$ ),  $\Delta \bar{H}_H$  is the partial molar heat of solution of hydrogen,  $R$  is a constant,  $Q_c$  is activation energy which is needed for interfacial reaction. Eq. (1) shows the relation of the heating rate to the reacted fraction,  $F$ , and peak temperature.  $E$  can be obtained from the slope of the plot of  $\ln(b/T^2)$  vs.  $1/T$  (termed as Han plot).

#### 2. Diffusion of Hydrogen through $\alpha$ Phase [14]

When the rate-controlling step for desorption of hydrided system is the diffusion of hydrogen through  $\alpha$  phase, the equation is written as follows:

$$\ln\left(\frac{b}{T^2}\right) = \ln\left[\frac{6AD_0P_0^{1/2}R^2}{Er_0^2(C_\beta - C_\alpha)}\{3 - 2F - 3(1-F)^{2/3}\}^{-1}\right] - \frac{E}{RT} \quad (2)$$

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Where  $D_0$  is the diffusion coefficient,  $E$  is expressed as follows:

$$E = Q_D + \Delta H_f - \Delta H/2$$

$Q_D$  is the activation energy for the diffusion of hydrogen through the  $\alpha$  phase. Eq. (2) shows the relation of the heating rate to the reacted fraction and peak temperature. Incidentally, the form of Eq. (2) is the same type of Eq. (1). Only the relationship of a constant term and reacted fraction term can find a difference. Therefore, at a constantly reacted fraction,  $E$  can be also obtained from the slope of the plot of  $\ln(b/T^2)$  vs.  $1/T$ . Because of the same type of the equations that were derived, even if the rate-controlling step for the desorption of the system is not known, the equations can be adapted to analyze a desorption peak.

## EXPERIMENTAL SECTION

$\text{MgH}_2$  used in this study was prepared by the hydriding chemical vapor deposition (HCVD) method.  $\text{MgH}_2$  particles of smaller than  $1\ \mu\text{m}$  size were made by HCVD. To prevent oxidation,  $\text{MgH}_2$  was kept in a vacuum. To analyze the change of the sample, the microstructures of the  $\text{MgH}_2$  made by the HCVD method were examined by XRD and SEM. The apparatus used in the experiment is the Sievert's type apparatus. The thermal desorption of hydrogen from the hydride was measured by a volumetric apparatus based on Sievert's method. Therefore, this thermal desorption technique was termed as volumetric thermal analysis (VTA). To activate the specimen the reactor was evacuated at 643 K for 1 hour. And the hydrogenation was performed at 643 K and hydrogen pressure of 35 atm. After equilibrium was reached, dehydrogenation was performed for 1 hour in vacuum. The above process was repeated until the specimen was fully activated. After full activation, the VTA were performed.

After the hydrogen of wanted capacity was absorbed in the sample, the reactor was cooled slowly to 523 K, which was the VTA starting temperature. While the temperature was lowered to 523 K, hydrogen was continually absorbed. Therefore, the total amount absorbed in the sample was added to the initial amount of hydrogen absorbed and the amount of hydrogen absorbed during the lowering temperature. The amount of hydrogen absorbed was converted to the wt% of the hydride, which was called as the initial wt%.

### 1. Specimen Preparation

The starting material, Mg from Hananics Co., was used as received without any further purification. All the material handling was carried out in a glove box filled with argon gas (99.999%) in the presence of an oxygen scavenger and a drying agent to prevent samples and starting materials from being oxidized or forming a hydroxide.

HCVD reactor was used in study, which consists of a vertical type reactor, alumina ( $\text{Al}_2\text{O}_3$ ) bowl, Cu gasket, and reactor cover housing flowing coolant. An Inconel 601 tube with an inside length of 100 mm and inner diameter of 40 mm was used as the reactor and placed into the tube furnace, which was uniformly heated to 1,473 K. One gram of raw Mg powders was placed at the bottom of the alumina bowl without any pretreatment, and after five iterations of a repeating cycle of vacuuming and charging of argon gas (99.999%) for removal of air and oxygen from the system, hydrogen gas (99.999%) was charged up to 40 atm for HCVD. Each sam-

ple was then uniformly heated to 873 K with a heating rate of 373 K/h using the tube furnace. The furnace was kept at the final temperature given above for 24 h and then slowly cooled to room temperature while high hydrogen pressure was maintained. After the HCVD process, the products were observed at two deposition locations: the cover substrate cooled by coolant and the bottom of the alumina bowl.

### 2. Control the Initial Hydrogen Absorption

According to the amount of hydrogen absorbed, the impact was different on the occupation site. Also, the released temperature and rate had changed. Therefore, the amount of hydrogen absorbed in the sample had to be changed. We controlled the hydrogen capacity through change in absorption time. This method is necessary when a large amount of hydrogen absorption is used. However, when one wants to lower the amount of hydrogen absorbed, it is difficult to control the amount of absorbed hydrogen only through change in absorption time, because a large amount of hydrogen is absorbed in Mg during the lowering of the VTA starting temperature. Therefore, in this case, the temperature and pressure were adjusted to lower the absorption of hydrogen.

### 3. Thermal Analysis Method

Fig. 1 shows a schematic diagram of the automatic apparatus. It consists of valve and pressure transducer. All operations are done through computers.

After the desired amount of hydrogen was absorbed, the temperature of the reactor was lowered to the starting temperature of thermal analysis through natural cooling. V6, V7, V9 and solenoid valves of Fig. 1 were opened until hydrogen pressure 1.2 atm and solenoid valves were closed. And reservoir was open. Then, the pressure decreases from 1.2 atm to 0.08 atm. The reactor was heated to a various constant heating rate. The samples were linearly heated from 523 K to 710 K. As the desorption of hydrogen from the hydride started, the hydrogen pressure of the system was increased. When the pressure of the system with a volume of  $118.9\ \text{cm}^3$  reached 0.15 atm, the system opened to the vacuum until the hydrogen pressure of the system returned to 0.1 atm. These procedures were repeated. The evolution rate was defined as the amount of hydrogen desorbed from 0.1 to 0.15 atm divided by the reaction time in the pressure range.

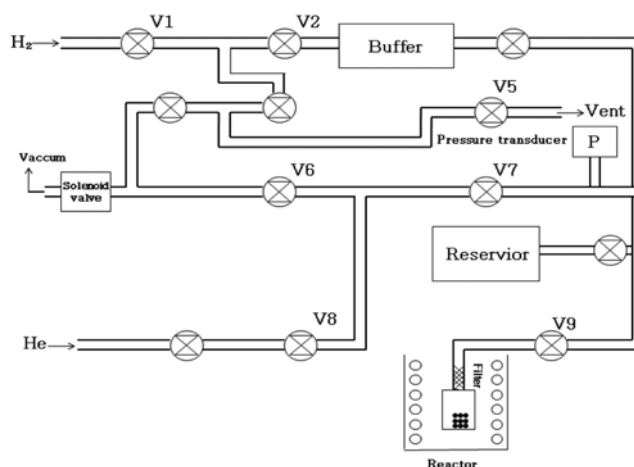


Fig. 1. Schematic diagram of automatic apparatus.

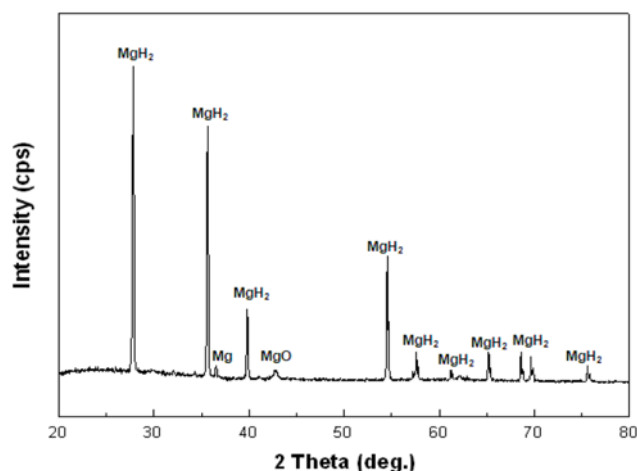


Fig. 2. X-ray diffraction of  $\text{MgH}_2$  made by HVCD process.

## RESULTS AND DISCUSSION

### 1. XRD and SEM Analysis

$\text{MgH}_2$  made by the HCVD process was examined by XRD and SEM. Fig. 2 shows the XRD patterns of  $\text{MgH}_2$  prepared by the HCVD process.

The major phase was  $\text{MgH}_2$  and a small amount of  $\text{MgO}$  and  $\text{Mg}$  existed. Some of  $\text{Mg}$  did not react with hydrogen. So, the com-

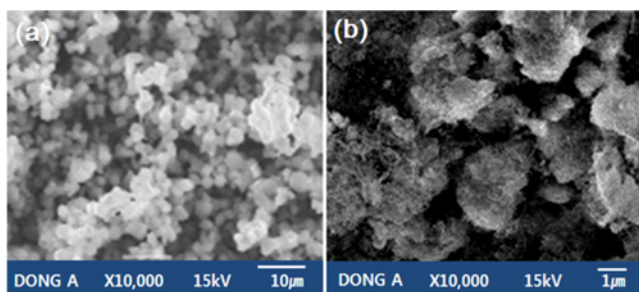


Fig. 3. SEM image of  $\text{MgH}_2$  made by HCVD: (a) before thermal analysis, (b) after thermal analysis.

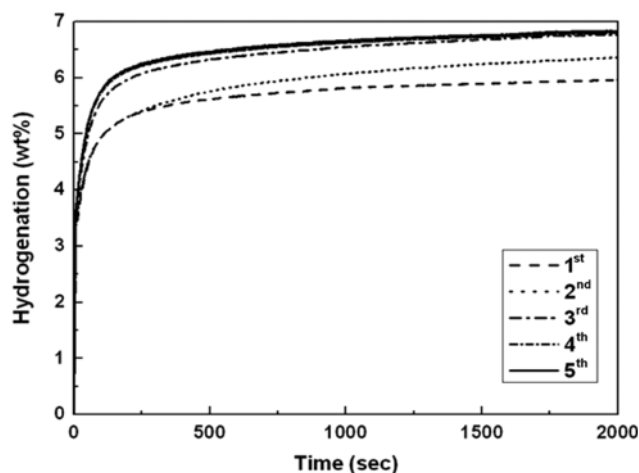


Fig. 4. Activation process of  $\text{MgH}_2$  made by HCVD method.

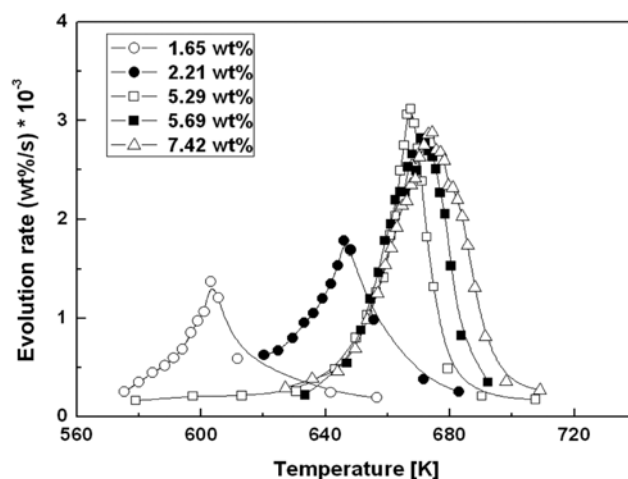


Fig. 5. The desorption spectra of  $\text{Mg}$  hydride for various initial wt% hydride at a constant heating rate.

bination of hydrogen and  $\text{Mg}$  does not make all of  $\text{MgH}_2$ . Therefore,  $\text{Mg}$  was detected through SEM.  $\text{Mg}$  was oxidized in air when the powder was put into the SEM equipment. So, an  $\text{MgO}$  peak was detected.

The SEM images of  $\text{MgH}_2$  powder before and after the experiment are shown in Fig. 3(a) which presents the SEM images of  $\text{MgH}_2$  powder before the experiment. Particles had a size of  $1\ \mu\text{m}$ . After the thermal analysis, the particle size was  $10\ \mu\text{m}$ . It was largely increased before the experiment. In addition, cracks in the particles are shown. This was created by stress acting on the particles.

### 2. Activation Process

The activation process of general  $\text{MgH}_2$  powders was necessary several times. However, as shown in Fig. 5, the activation process of  $\text{MgH}_2$  made by the HCVD method was completed in four cycles.

The absorption experiments were conducted at  $643\ \text{K}$  and under  $35\ \text{atm}$  hydrogen for  $30\ \text{min}$  and the desorption experiments were conducted at  $673\ \text{K}$  and under vacuum atmosphere for  $30\ \text{min}$ . The storage capacity of  $\text{MgH}_2$  made by HCVD method was  $6.8\ \text{wt}\%$ . In absorption,  $\text{MgH}_2$  completed  $80\%$  of reaction in  $200\ \text{s}$ . The initial reaction rate was very fast. However, in general  $\text{MgH}_2$ ,  $80\%$  of reaction in  $800\ \text{s}$  at  $673\ \text{K}$  was completed and storage capacity was  $6.8\ \text{wt}\%$  [15]. Therefore, the storage capacity was identical but the reaction rate of  $\text{MgH}_2$  made by the HCVD method was faster than that of general  $\text{MgH}_2$ .

### 3. Thermal Analysis with Various Initial wt%

Fig. 5 shows the results of thermal desorption at a various initial hydride wt% from  $1.65$  to  $7.42$  for  $\text{Mg}$  hydride as the sample was heated to  $710\ \text{K}$  at a rate of  $1.0\ \text{K/min}$ . Fig. 5 shows only one peak even if the initial wt% hydride of the sample that is different. It means that one of the types of hydrogen occupation sites were available in  $\text{Mg}$  made by the HCVD method [16]. As the initial wt% increased, the peak temperature increased. Peak temperatures for initial wt% of  $1.65$ ,  $2.21$  and  $5.29$  are  $600$ ,  $650$  and  $673\ \text{K}$ . However, if the initial wt% was higher than initial  $5.29\ \text{wt}\%$ , the peak temperature was fixed. This phenomenon was considered related to the interface morphology of the  $\beta$  phase (hydride) and the  $\alpha$  phase (solid solution) during the hydriding reaction before the thermal desorption had started. This situation has been proven by Vigeholm, et al. [17]. Therefore,

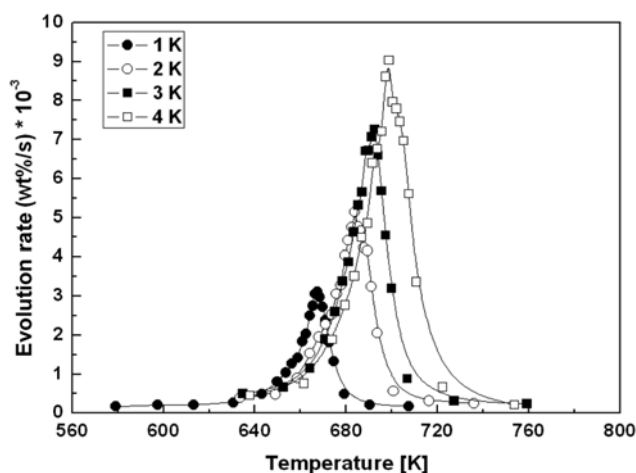


Fig. 6. Thermal desorption spectra of  $\text{MgH}_2$  hydride made by HCVD method for constant initial wt% (5.29 wt%) at various heating rates.

the results are shown in Fig. 5: a continuous  $\alpha/\beta$  interface boundary was formed in less than 5.29 wt%.

As with the Mg made by the HCVD method, a peak temperature of commercially available Mg (Sigma Aldrich Co.) was increased as the initial wt% increased. However, if the initial wt% is higher than initial 4.46 wt%, the peak temperature was fixed [18].

If the initial hydride wt% was less than 2.21 wt%, hydrogen was released at about 643 K. However, where the initial hydride wt% was more than 5.29 wt%, hydrogen was released at about 673 K. This is because of the  $\alpha$  phase on the surface of the sample; when the hydride phase surrounded outside of the sample, there was no  $\alpha$  phase on the surface of the sample. So, nuclear generation was slowed. Therefore, for high initial wt%, hydrogen was released at a high temperature. The above results showed a relation to  $\alpha/\beta$  continuous interface boundary.

#### 4. Thermal Analysis with Various Heating Rates

Fig. 6 shows the results of the thermal desorption for various heating rates using a constant initial hydride wt% (5.29 wt%). As the heating rate was increased, the peak temperature was increased. The peak temperatures for heating rates of 1, 2, 3 and 4 K/min are 667, 683, 690 and 698 K, respectively.

To obtain the activation energy using equations derived from the first term of the right-hand side, the equation should be constant, namely in the  $\ln(b/T^2)$  vs.  $1/T$  plot [14],  $T$  is the temperature at a time during the thermal decomposition when a constant initial wt% was reached. Therefore, to substitute the peak temperature obtained with various heating rates for  $T$  in Eqs. (1) and (2), an assumption is needed: although the heating rate was different, the peak temperature was formed at a constant wt% if the initial wt% was constant. In Fig. 6, the shapes of the thermal desorption curves did not change even if the heating rate was different. This result implies that the above assumption was reasonable. To obtain the activation energy for the desorption of magnesium hydride made by HCVD method,  $\ln(b/T^2)$  vs.  $1/T$  was plotted in Fig. 7.

The activation energy for the decomposition of Mg hydride made by the HCVD method was 166 kJ/mol. This value was higher than the activation energy of 120 kJ/mol reported by Huot et al. [19].

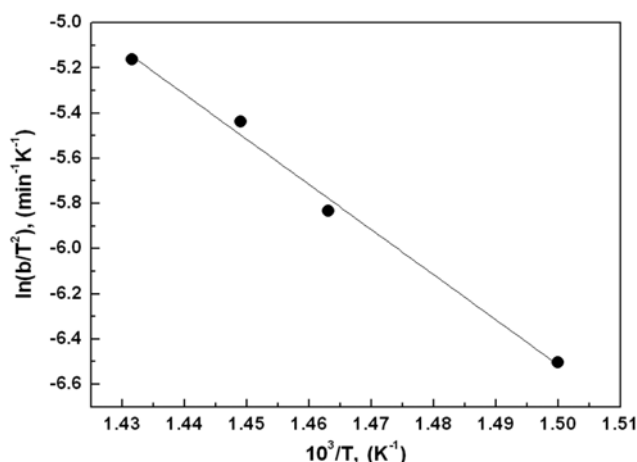


Fig. 7. The plot of  $\ln(b/T^2)$  against reciprocal temperature.

## CONCLUSIONS

$\text{MgH}_2$  made by HCVD method was evaluated through volumetric thermal analysis technique and the results were as follows.

The peak temperatures for initial wt% of 1.65, 2.21, and 5.29 were 600, 650 and 673 K, respectively. However, the peak temperature had been fixed when there was more than the initial 5.29 wt%. The reason is that the morphology of  $\alpha$ -phase and  $\beta$ -phase changes. Therefore, an  $\alpha/\beta$  continuous interface boundary was formed at the initial wt% of less than 5.29. The peak temperatures for heating rates of 1, 2, 3 and 4 K/min were 667, 683, 690 and 698 K, respectively. Also, the activation energy for the decomposition of Mg hydride made by the HCVD method was 166 kJ/mol.

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