

# How to Analyse Metal Hydride Decomposition Temperatures Using a Sieverts' Type Hydriding-Dehydriding Apparatus and Hydrogen-Storage Characteristics for an $\text{MgH}_2$ -Based Alloy

Young Jun KWAK, Myoung Youp SONG \*

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

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In this work, a method to analyze metal hydride decomposition temperatures (the onset temperature of the metal hydride decomposition and the temperature for the maximum ratio of released gas quantity change with temperature change), of prepared samples were investigated using a Sieverts' type hydriding-dehydriding apparatus, in which a back-pressure regulator was employed. The quantity of the gas released under 1.0 bar  $\text{H}_2$  was measured as the temperature was increased with a heating rate of 4 K/min. The variation in the ratio of released hydrogen quantity  $H_d$  change with temperature  $T$  change,  $dH_d/dT$ , as a function of temperature was obtained and from the variation in  $dH_d/dT$  with  $T$ , the metal hydride decomposition temperatures were analyzed. This analysis method can be used instead of thermal analysis methods such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) analysis, differential thermal analysis (DTA), and thermal desorption spectroscopy (TDS) analysis. For this analysis, a sample with a composition of 89 wt.%  $\text{MgH}_2$  + 4.9 wt.% Ni + 1.7 wt.%  $\text{Zn}(\text{BH}_4)_2$  + 1.0 wt.% NaCl + 1.7 wt.% Ti + 1.7 wt.% Fe (named  $\text{MgH}_2$ -Ni- $\text{Zn}(\text{BH}_4)_2$ -NaCl-Ti-Fe) sample was prepared by planetary ball milling. In the prepared  $\text{MgH}_2$ -Ni- $\text{Zn}(\text{BH}_4)_2$ -NaCl-Ti-Fe sample, it is believed that  $\text{MgH}_2$  begins to decompose at about 575 K and  $dH_d/dT$  reaches its peak at about 610 K.

**Keywords:** hydrogen absorbing materials; mechanical milling; hydrogen; thermal analysis;  $\text{MgH}_2$ -based alloy.

## 1. INTRODUCTION

To analyse the hydride decomposition temperature, the quantity of hydrogen released, and the heat involved in the hydride decomposition, thermal analysis methods such as thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) analysis, differential thermal analysis (DTA), and thermal desorption spectroscopy (TDS) analysis must be performed. By the way, it is possible to investigate the gas release properties, especially the metal hydride decomposition temperatures, of magnesium or magnesium hydride-based samples, using a Sieverts' type volumetric hydriding apparatus.

For this analysis, a sample with a composition of 89 wt.%  $\text{MgH}_2$  + 4.9 wt.% Ni + 1.7 wt.%  $\text{Zn}(\text{BH}_4)_2$  + 1.0 wt.% NaCl + 1.7 wt.% Ti + 1.7 wt.% Fe (named  $\text{MgH}_2$ -Ni- $\text{Zn}(\text{BH}_4)_2$ -NaCl-Ti-Fe) sample was prepared by ball milling.  $\text{Zn}(\text{BH}_4)_2$ , Ni, and Ti were added because they were reported to increase the dehydriding and rehydriding rates of magnesium when added. Many studies have focused on metal borohydrides  $[\text{M}(\text{BH}_4)_n]$  such as  $\text{LiBH}_4$  and  $\text{Mg}(\text{BH}_4)_2$  [1–10] as promising candidates for advanced hydrogen storage materials due to their high gravimetric hydrogen densities. The complex metal hydride  $\text{Zn}(\text{BH}_4)_2$  has also drawn attention for its high gravimetric hydrogen density (8.4 wt.%) [11] and its reportedly low decomposition temperature (323–393 K). A relatively large amount of Ni was added, compared with Ti and Fe, since the addition of Ni is known to increase

greatly the dehydriding and rehydriding rates of magnesium [12, 13]. Shahi et al. [14] compared the dehydrogenation/rehydrogenation characteristics of  $\text{MgH}_2$  with and without catalysts (Ti, Fe, and Ni). They reported that mechanical milling of  $\text{MgH}_2$  with transition metals (Ti, Fe, and Ni) led to a reduction in the decomposition temperature and a corresponding enhancement in the rehydrogenation kinetics.

In the present work, a method to analyse metal hydride decomposition temperatures using a Sieverts' type volumetric apparatus was investigated for an  $\text{MgH}_2$ -Ni- $\text{Zn}(\text{BH}_4)_2$ -NaCl-Ti-Fe sample.

## 2. EXPERIMENTAL DETAILS

Hydrogen release of  $\text{MgH}_2$ -Ni- $\text{Zn}(\text{BH}_4)_2$ -NaCl-Ti-Fe was analysed using a Sieverts' type volumetric apparatus, as described previously [15], by measuring the quantity of the hydrogen released as the temperature was increased.

To prepare the  $\text{MgH}_2$ -Ni- $\text{Zn}(\text{BH}_4)_2$ -NaCl-Ti-Fe sample, starting materials were  $\text{ZnCl}_2$  (Zinc chloride, Aldrich, purity 99.999 %),  $\text{NaBH}_4$  (Sodium borohydride, Aldrich, granular, purity 99.99 %),  $\text{MgH}_2$  (Magnesium hydride, Aldrich, hydrogen-storage grade), Ni (Nickel powder, Alfa Aesar, average particle size 2.2–3.0  $\mu\text{m}$ , 99.9 % (metals basis), C typically < 0.1 %), Ti (Titanium powder, Aldrich, -325 mesh (-0.044 mm), 99 % (metals basis)), and Fe [Iron powder, Alfa Aesar, spherical, < 10  $\mu\text{m}$ , 99.9 % (metals basis), 99.5 %). For the synthesis of  $\text{Zn}(\text{BH}_4)_2$ , milling was carried out in a planetary ball mill (Planetary Mono Mill; Pulverisette 6, Fritsch). A mixture of  $\text{ZnCl}_2$  and  $\text{NaBH}_4$  at the molar ratio of 1:2 (total

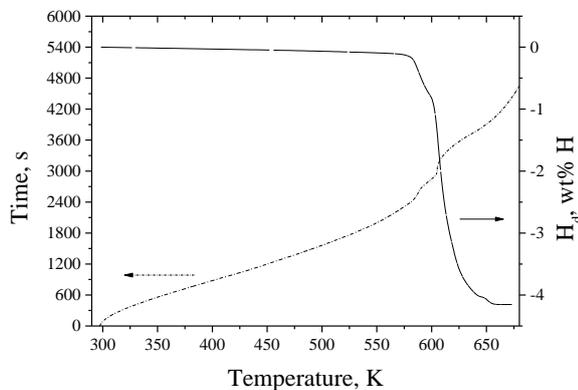
\* Corresponding author. Tel.: +82-63-270-2379; fax: +82-63-270-2386. E-mail address: [songmy@jbnu.ac.kr](mailto:songmy@jbnu.ac.kr) (M.Y. Song)

weight = 2.23 g) was mixed in a hermetically sealed stainless steel container (with 30 hardened steel balls, total weight = 102.1 g). The sample to ball weight ratio was 1:45. All sample handling was performed in a glove box under an Ar atmosphere in order to minimize oxidation. The mill container (volume of 250 ml) was then filled with high purity Ar gas (about 2 bar). Milling was performed at the disc revolution speed of 400 rpm for 4 h. The prepared  $\text{Zn}(\text{BH}_4)_2$  sample contained NaCl with the weight ratio of  $\text{NaCl}/\text{Zn}(\text{BH}_4)_2$  being 0.61:1.

A mixture of  $\text{MgH}_2$ , Ni, Ti and Fe was milled in a planetary ball mill in a hydrogen atmosphere of about 12 bar at a revolution speed of 400 rpm for 4 h. The sample to ball weight ratio was 1:45. To prepare  $\text{MgH}_2\text{-Ni-Zn}(\text{BH}_4)_2\text{-NaCl-Ti-Fe}$ ,  $\text{Zn}(\text{BH}_4)_2$  was then added by milling in a horizontal ball mill in Ar atmosphere for 24 h (with zirconia balls, total = 16 g). The revolution speed was 100 rpm and the weight ratio of the sample to ball was 1:36.

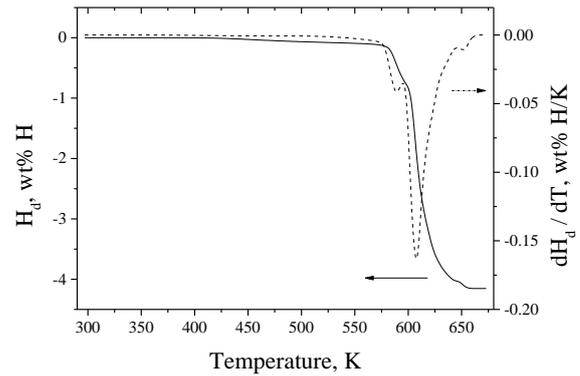
### 3. RESULTS AND DISCUSSION

Released hydrogen quantity,  $H_d$ , was defined as the percentage of hydrogen released with respect to sample weight. The synthesized samples were put into the reactor in a glove box in which the sample was synthesized. Fig. 1 shows the variation of the released hydrogen quantity,  $H_d$ , with temperature for a prepared  $\text{MgH}_2\text{-Ni-Zn}(\text{BH}_4)_2\text{-NaCl-Ti-Fe}$ . The sample was heated from room temperature to 673 K with a heating rate of 4 K/min. Time  $t$  is also given. The value of  $H_d$  increases rapidly at about 580 K. The values of  $H_d$  are 0.13 wt.% at 575 K, 0.81 wt.% at 600 K, 4.07 wt.% at 650 K, and 4.15 wt.% at 673 K.



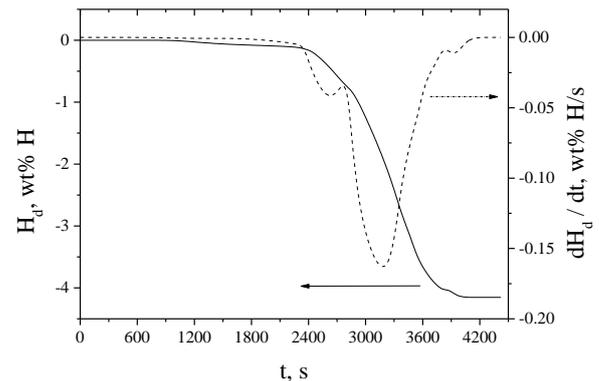
**Fig. 1.** Variation of the released hydrogen quantity,  $H_d$ , with temperature for an as-milled  $\text{MgH}_2\text{-Ni-Zn}(\text{BH}_4)_2\text{-NaCl-Ti-Fe}$ . The sample was heated from room temperature to 673 K with a heating rate of 4 K/min

At different temperatures, the ratio of  $H_d$  change with temperature  $T$  change,  $dH_d/dT$ , were obtained. The variations with temperature of the released hydrogen quantity,  $H_d$ , and the ratio of  $H_d$  change with temperature  $T$  change,  $dH_d/dT$ , for a prepared  $\text{MgH}_2\text{-Ni-Zn}(\text{BH}_4)_2\text{-NaCl-Ti-Fe}$  are shown in Fig. 2. A metal hydride begins to decompose at about 575 K. An absorption peak appears at about 610 K. It is believed that  $\text{MgH}_2$  begins to decompose at about 575 K and the ratio of  $H_d$  change with temperature  $T$  change,  $dH_d/dT$ , reaches its peak at about 610 K.



**Fig. 2.** Variations with temperature of the released gas quantity,  $H_d$ , and the ratio of  $H_d$  change with temperature  $T$  change,  $dH_d/dT$ , for an as-milled  $\text{MgH}_2\text{-Ni-Zn}(\text{BH}_4)_2\text{-NaCl-Ti-Fe}$

At different times, the rates of  $H_d$  change,  $dH_d/dt$ , were obtained. Fig. 3 shows the variations with time of the released gas quantity,  $H_d$ , and the rate of  $H_d$  change,  $dH_d/dt$ , for an as-milled  $\text{MgH}_2\text{-Ni-Zn}(\text{BH}_4)_2\text{-NaCl-Ti-Fe}$ . A metal hydride begins to decompose at about 2300 s. An absorption peak appears at about 3200 s. It is believed that  $\text{MgH}_2$  begins to decompose at about 2300 s and the rate of  $H_d$  change,  $dH_d/dt$ , reaches its peak at about 3200 s.



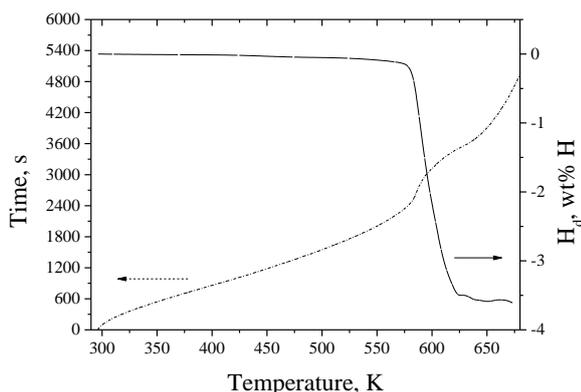
**Fig. 3.** Variations with time of the released gas quantity,  $H_d$ , and the rate of  $H_d$  change,  $dH_d/dt$ , for an as-milled  $\text{MgH}_2\text{-Ni-Zn}(\text{BH}_4)_2\text{-NaCl-Ti-Fe}$

Nakagawa et al. [11] reported that  $\text{Zn}(\text{BH}_4)_2$  releases hydrogen with toxic diborane ( $\text{B}_2\text{H}_6$ ), after melting with increasing temperature, and this reaction can be described as  $\text{Zn}(\text{BH}_4)_2 \rightarrow \text{Zn} + \text{B}_2\text{H}_6 + \text{H}_2$ . When the as-milled  $\text{MgH}_2\text{-Ni-Zn}(\text{BH}_4)_2\text{-NaCl-Ti-Fe}$  is heated, the released gas is believed to contain hydrogen and a very small quantity of diborane.

From the first cycle, decomposition temperatures of hydrides can be determined without exposing the samples under oxidation conditions because the analysis can be carried out in the same apparatus after hydriding reaction.

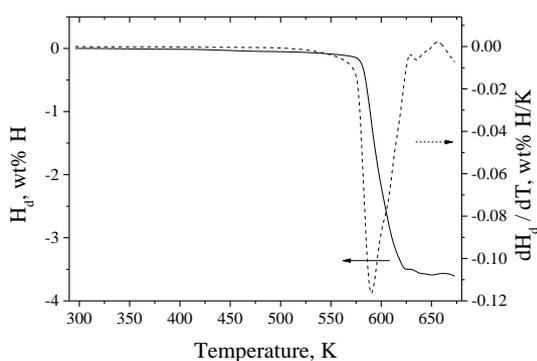
The variation of the released hydrogen quantity,  $H_d$ , with temperature for  $\text{MgH}_2\text{-Ni-Zn}(\text{BH}_4)_2\text{-NaCl-Ti-Fe}$  at the number of cycles,  $C_n$ , of 2 ( $C_n = 2$ ) is presented in Fig. 4. The sample was heated from room temperature to 673 K with a heating rate of 4 K/min after hydrogen absorption at 593 K under 12 bar  $\text{H}_2$  for 30 min. The value of  $H_d$  increases rapidly at about 575 K. The values of  $H_d$  are 0.14 wt.% at 575 K, 2.18 wt.% at 600 K, 3.49 wt.% at

625 K, and 3.61 wt.% at 673 K.



**Fig. 4.** Variation of the released hydrogen quantity,  $H_d$ , with temperature for  $\text{MgH}_2\text{-Ni-Zn(BH}_4)_2\text{-NaCl-Ti-Fe}$  at  $C_n=2$ . The sample was heated from room temperature to 673 K with a heating rate of 4 K/min after hydrogen absorption at 593 K under 12 bar  $\text{H}_2$  for 30 min

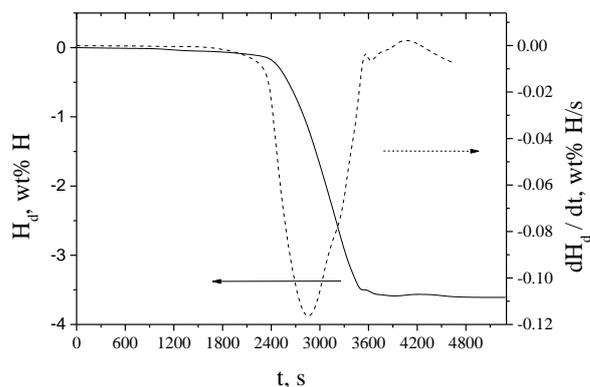
The variations with temperature of the released hydrogen quantity,  $H_d$ , and the ratio of  $H_d$  change with temperature  $T$  change,  $dH_d/dT$ , for  $\text{MgH}_2\text{-Ni-Zn(BH}_4)_2\text{-NaCl-Ti-Fe}$  at  $C_n=2$  are shown in Fig. 5. The sample was heated from room temperature to 673 K with a heating rate of 4 K/min after hydrogen absorption at 593 K under 12 bar  $\text{H}_2$  for 30 min. A metal hydride begins to decompose at about 550 K. An absorption peak appears at about 590 K. It is believed that  $\text{MgH}_2$  begins to decompose at about 550 K and the rate of  $H_d$  change with temperature  $T$  change,  $dH_d/dT$ , reaches its peak at about 590 K. After the decomposition reaction of the as-milled sample,  $\text{Zn(BH}_4)_2$  is decomposed into Zn, and the main phase which absorbs hydrogen is Mg. From the first cycle, the released gas is thus believed to contain only hydrogen.



**Fig. 5.** Variations with temperature of the released gas quantity,  $H_d$ , and the ratio of  $H_d$  change with temperature  $T$  change,  $dH_d/dT$ , for  $\text{MgH}_2\text{-Ni-Zn(BH}_4)_2\text{-NaCl-Ti-Fe}$  at  $C_n=2$ . The sample was heated from room temperature to 673 K with a heating rate of 4 K/min after hydrogen absorption at 593 K under 12 bar  $\text{H}_2$  for 30 min

Fig. 6 shows the variations with time of the released gas quantity,  $H_d$ , and the rate of  $H_d$  change,  $dH_d/dt$ , for  $\text{MgH}_2\text{-Ni-Zn(BH}_4)_2\text{-NaCl-Ti-Fe}$  at  $C_n=2$ . The sample was heated from room temperature to 673 K with a heating rate of 4 K/min after hydrogen absorption at 593 K under 12 bar  $\text{H}_2$  for 30 min. A metal hydride begins to decompose at about 2100 s. An absorption peak appears at

about 2850 s. It is believed that  $\text{MgH}_2$  begins to decompose at about 2100 s and the rate of  $H_d$  change,  $dH_d/dt$ , reaches its peak at about 2850 s.



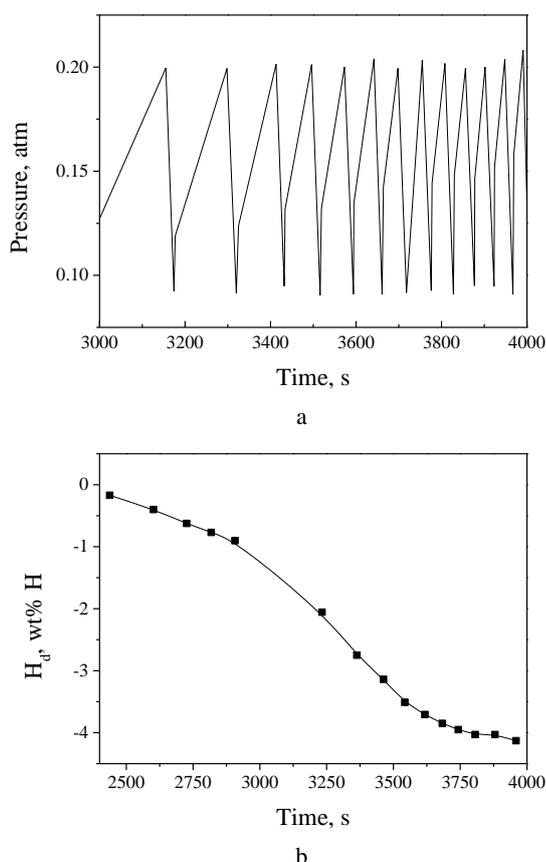
**Fig. 6.** Variations with time of the released gas quantity,  $H_d$ , and the rate of  $H_d$  change,  $dH_d/dt$ , for  $\text{MgH}_2\text{-Ni-Zn(BH}_4)_2\text{-NaCl-Ti-Fe}$  at  $C_n=2$ . The sample was heated from room temperature to 673 K with a heating rate of 4 K/min after hydrogen absorption at 593 K under 12 bar  $\text{H}_2$  for 30 min

Tanniru et al. [16] investigated the dehydrogenation behavior of magnesium hydride. They measured the hydrogen release temperature by thermogravimetric analysis (TGA). The onset temperature of hydrogen release from the partially hydrogenated sample (54 min) was 492 K, while that of the sample hydrogenated to saturation (5 h) was 563 K for similar conditions used in the TGA. Yang et al. [17] studied site density effect of Ni particles on hydrogen desorption of  $\text{MgH}_2$ . They determined the hydrogen desorption temperature of  $\text{MgH}_2$  by differential scanning calorimetry (DSC) analysis. Increasing the content of Ni to 4 at.%, or a combined (2 at.% Ni + 2 at.% Fe), led to hydrogen desorption starting from 433 K. Kyoj et al. [18] studied magnesium manganese hydrides prepared by high pressure technique. The hydrogen-storage capacity was analysed as 2.4 wt.% by thermogravimetry analysis (TGA) and differential thermal analysis (DTA) showed that the hydrogen desorption temperature was 603 K. Ershova et al. [19] studied hydrogen-sorption and thermodynamic characteristics of mechanically grinded  $\text{TiH}_{1.9}$  using thermal desorption spectrometer (TDS). They analyzed the temperature of the  $\gamma \rightarrow \beta$  phase transition and the enthalpy of the formation of the  $\gamma$ -titanium hydride and measured released hydrogen quantities and hydrogen release rates.

For the thermal analysis methods [20] such as TGA [16], DSC analysis [17], DTA [18], and TDS analysis [19], it is necessary to move the samples from a hydriding apparatus to other analysis equipment. During this process, the samples can be contaminated. On the other hand, by using the method of this work, the oxidation of samples during analysis can be avoided because the synthesized samples can be put into a reactor in a glove box in which the sample was synthesized. From the first cycle, decomposition temperatures of hydrides can be determined without exposing the samples under oxidation conditions because the analysis can be carried out in the same apparatus after hydriding reaction. For the thermal analysis methods mentioned above, sensing parts may be

contaminated or oxidized due to reactions with hydrogen or other gases and in order to prevent some reactions in air, additional systems must be attached which require space and cost. For TDS analysis, a mass spectrometer in high vacuum is necessary, which is connected to the thermal desorption part [19]. In the other thermal analysis methods mentioned above, decomposition of hydrides was performed in vacuum. In this work, hydrides were decomposed under 1 bar  $H_2$ , which is an important atmosphere pressure to apply the metal hydrides to practical hydrogen storage.

Han et al. [20–22] investigated the dehydrogenation of the Mg-H system in order to apply the Sievert's type automatic apparatus to thermal analysis hydrogen absorbing materials. Fig. 7 a shows change in the system hydrogen pressure with time in their automatic apparatus.



**Fig. 7.** a—change in the system pressure with time in an automatic apparatus by Han et al. [20]; b—change in released hydrogen quantity,  $H_d$ , with time in this work

High pressure valves (pneumatic actuators) are open when the hydrogen pressure reaches 0.2 atm (for example, a point c in Fig. 7 a) due to the increase in hydrogen pressure by dehydrogenation and close when the hydrogen pressure reaches 0.1 atm (for example, a point d in Fig. 7 a). Computer monitors and stores hydrogen pressure, time, and temperature during this process. Hydrogen evolution rates were calculated by dividing the released hydrogen quantity by reaction time. In this work, to release hydrogen under a constant pressure (1 bar), a back-pressure regulator was used, and the change in released hydrogen quantity,  $H_d$ , was obtained as a function of temperature and time, as shown in Fig. 7 b. Han et al.'s

results [20–22] are given by the variation in evolution rate as a function of temperature. On the other hand, our results are expressed by the variation in the ratio of  $H_d$  change with temperature  $T$  change,  $dH_d/dT$ , as a function of temperature, as shown in Fig. 2 and Fig. 5. Our results can also be expressed by the variation in the rate of  $H_d$  change,  $dH_d/dt$ , as a function of time, as shown in Fig. 3 and Fig. 6.

When the as-milled  $MgH_2$ -Ni-Zn(BH<sub>4</sub>)<sub>2</sub>-NaCl-Ti-Fe is heated, as shown in Fig. 1, Zn(BH<sub>4</sub>)<sub>2</sub> is believed to decompose into Zn, diborane, and hydrogen. The released gas is thus considered to contain hydrogen and a very small quantity of diborane. From the first cycle the phase which absorbs hydrogen is Mg, and the released gas is thus believed to contain only hydrogen.

## 4. CONCLUSIONS

Hydrogen release of  $MgH_2$ -Ni-Zn(BH<sub>4</sub>)<sub>2</sub>-NaCl-Ti-Fe prepared via ball milling was analysed using a Sievert's type volumetric apparatus, in which a back-pressure regulator was employed, by measuring the quantity of the hydrogen released under 1.0 bar as the temperature was increased with a heating rate of 4 K/min and obtaining the variation of the ratio of released hydrogen quantity  $H_d$  change with temperature  $T$  change,  $dH_d/dT$ , according to temperature. By using this method, decomposition temperatures of hydrides can be determined without exposing the samples under oxidation conditions because the analysis can be carried out in the same apparatus after hydriding reaction. This analysis method can be used instead of thermal analysis methods such as TGA, DSC analysis, DTA, and TDS analysis. In the as-milled  $MgH_2$ -Ni-Zn(BH<sub>4</sub>)<sub>2</sub>-NaCl-Ti-Fe, it is believed that  $MgH_2$  begins to decompose at about 575 K and the ratio of  $H_d$  change with temperature  $T$  change,  $dH_d/dT$ , reaches its peak at about 610 K. At the second cycle,  $MgH_2$ -Ni-Zn(BH<sub>4</sub>)<sub>2</sub>-NaCl-Ti-Fe released 1.32 wt.% H for 10 min, 3.22 wt.% H for 30 min, and 3.41 wt.% H for 40 min at 593 K under 1.0 bar  $H_2$ .

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