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Analysis of the Metal Hydride Decomposition Temperatures of MgH_2 – $Zn(BH_4)_2$ –NaCl – Tm (Tm = Ni or Ti) Using a Sievert's Type Volumetric Apparatus

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In this work, $Zn(BH_4)_2$, Ni, or Ti were selected as additives to improve the hydriding and dehydriding rates of magnesium. $Zn(BH_4)_2$ was prepared by milling $ZnCl_2$ and $NaBH_4$ in a planetary ball mill under an Ar atmosphere. The prepared $Zn(BH_4)_2$ sample contained NaCl. 13.6 wt.% MgH_2+49.1 wt.% $Zn(BH_4)_2$+30.2 wt.% NaCl+7.0 wt.% Ni (named $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ni$) and 13.6 wt.% MgH_2+49.1 wt.% $Zn(BH_4)_2$+30.2 wt.% NaCl+7.0 wt.% Ti (named $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$) samples were prepared by horizontal ball milling. The gas release properties, especially the metal hydride decomposition temperatures (the onset temperature of the metal hydride decomposition and the maximum rate of released gas quantity change with temperature change), of the prepared samples were investigated using a Sievert's type volumetric apparatus. The quantity of the gas released under 1.0 bar H_2 was measured as the temperature was increased and the variation in the rate of released gas quantity G_r change with temperature T change, dG_r/dT, as a function of temperature was obtained. This analysis method can be used instead of thermal analysis methods such as thermogravimetric analysis (TGA), differential scanning calorimeter (DSC), and differential thermal analysis (DTA). The investigated properties of the samples were then compared. In the as-milled $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ni$, it is believed that $Zn(BH_4)_2$ begins to decompose at about 350 K and the rate of G_r change with T change, dG_r/dT, reaches its peak at about 390 K, and that MgH_2 begins to decompose at about 670 K and dG_r/dT reaches its peak at about 698 K.

Keywords: hydrogen absorbing materials, ball milling, scanning electron microscopy (SEM), X-ray diffraction, $Zn(BH_4)_2$-added MgH_2-based alloy.

1. INTRODUCTION

Among many metal hydrides, magnesium hydride has been intensively studied [1] since it has many advantages as a hydrogen storage material, from the viewpoints of gravimetric hydrogen density, price, and reserves in the earth's crust [2]. However, its reaction rate with hydrogen is very low. A great deal of effort has been made toward increasing the hydriding and dehydriding rates of magnesium [3 – 8] by alloying it with certain metals [9, 10] such as Cu, Ni, Co, Fe, and Ni and Y and by synthesizing compounds such as $CeMg_{12}$ [11].

Many studies have focused on metal borohydrides [$M(BH_4)_n$] such as $LiBH_4$ and $Mg(BH_4)_2$ [12 – 21] as promising candidates for advanced hydrogen storage materials due to their high gravimetric hydrogen densities. The complex metal hydride $Zn(BH_4)_2$ has also drawn attention for its high gravimetric hydrogen density (8.4 wt.%) [22] and its reportedly low decomposition temperature (323 – 393 K). In addition, it is possible to synthesize $Zn(BH_4)_2$ easily by the reaction between $ZnCl_2$ and $NaBH_4$ in a solvent [22], or by milling them [23 – 27]. According to Nakagawa et al. [22], $Zn(BH_4)_2$ is formed by milling $ZnCl_2$ and $NaBH_4$, which is expressed as follows:

$$ZnCl_2 + 2NaBH_4 \rightarrow Zn(BH_4)_2 + NaCl. \quad (1)$$

Bobet et al. [9] reported that mechanical grinding in H_2 (reactive mechanical grinding (RMG)) of magnesium powder enabled partial conversion of Mg to MgH_2. The ratio MgH_2/Mg could be improved by increasing the milling time or by adding a 3d-element (with the same initial particle size). Shahi et al. [28] compared the dehydrogenation/rehydrogenation characteristics of MgH_2 with and without catalysts (Ti, Fe, and Ni). They reported that mechanical milling of 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 this work, $Zn(BH_4)_2$, Ni, or Ti were selected as additives to improve the hydriding and dehydriding rates of magnesium. A $Zn(BH_4)_2$ sample was prepared by milling $ZnCl_2$ and $NaBH_4$ in a planetary ball mill under an Ar atmosphere. Samples with a large fraction of $Zn(BH_4)_2$, 13.6 wt.% MgH_2 + 49.1 wt.% $Zn(BH_4)_2$ + 30.2 wt.% NaCl + 7.0 wt.% Ni (named $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ni$) and 13.6 wt.% MgH_2+49.1 wt.% $Zn(BH_4)_2$+30.2 wt.% NaCl+7.0 wt.% Ti (named $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$) were prepared by horizontal ball milling. The gas release properties, especially the metal hydride decomposition temperatures, of the prepared samples were investigated

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using a Sievert's type volumetric apparatus. By using the method studied in the present work to find the metal hydride decomposition temperatures, the oxidation of samples during analysis can be avoided because the analysis can be carried out in the same apparatus after the hydriding reaction; it is not necessary to move the samples to other analysis equipment. This analysis method can be used instead of thermal analysis methods such as thermogravimetric analysis (TGA), differential scanning calorimeter (DSC), and differential thermal analysis (DTA). The investigated properties of the samples were then compared.

2. EXPERIMENTAL DETAILS

The starting materials were $ZnCl_2$ (Zinc chloride, Aldrich, purity 99.999 %), $NaBH_4$ (Sodium borohydride, Aldrich, granular, purity 99.99 %), MgH_2 (Magnesium hydride, Aldrich, hydrogen-storage grade), Ni (Nickel powder, Alfa Aesar, average particle size 2.2 – 3.0 μm, 99.9 % (metals basis), C typically < 0.1 %), and Ti (Titanium powder, Aldrich, -325 mesh (-0.044 mm), 99 % (metals basis)).

For the synthesis of $Zn(BH_4)_2$, milling was carried out in a planetary ball mill (Planetary Mono Mill; Pulverisette 6, Fritsch). A mixture of $ZnCl_2$ and $NaBH_4$ at the molar ratio of 1 : 2 (total 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 $Zn(BH_4)_2$ sample contained NaCl with the weight ratio of NaCl/$Zn(BH_4)_2$ being 0.61/1.

$14MgH_2 + 49Zn(BH_4)_2 + 30NaCl + 7Ni$ and $14MgH_2 + 49Zn(BH_4)_2 + 30NaCl + 7Ti$ were prepared 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. Gas release of MgH_2–$Zn(BH_4)_2$–NaCl–Tm(Tm = Ni or Ti) prepared via horizontal ball milling was analysed using a Sievert's type volumetric apparatus, as described previously [29], by measuring the quantity of the gas released G_r under 1.0 bar H_2 as the temperature was increased with a heating rate of 3 – 4 K/min and obtaining the variation in the rate of G_r change with T change, dG_r/dT, as a function of temperature. This enabled us to determine the decomposition temperatures of the formed hydrides. The synthesized samples were characterized using Fourier transform infrared (FT-IR) spectroscopy (Frontier, PerkinElmer). The microstructures of the samples were observed using a JSM-5900 scanning electron microscope (SEM) operated at 20 kV, equipped with EDS (energy dispersive X-ray spectroscopy).

3. RESULTS AND DISCUSSION

Fig. 1 presents the XRD pattern of $Zn(BH_4)_2$ powder synthesized by milling for 2 h. The sample contains $Zn(BH_4)_2$, NaCl, $NaBH_4$, and $ZnCl_2$. This shows that NaCl was formed during the synthesis of $Zn(BH_4)_2$ and $NaBH_4$ and $ZnCl_2$ are remaining [25, 26].

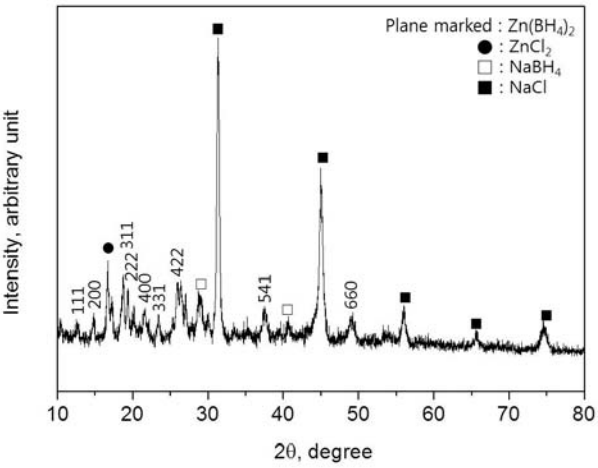

Fig. 1. XRD pattern of synthesized $Zn(BH_4)_2$ powder

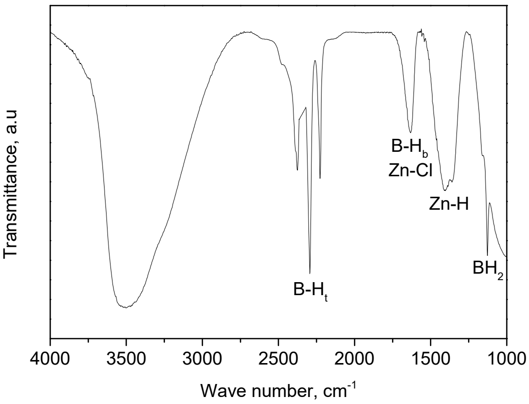

Fig. 2. FT-IR spectrum of $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ni$ prepared by horizontal ball milling under Ar at 100 rpm for 24 h

Fig. 2 shows the FT-IR spectrum of $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ni$ prepared by horizontal ball milling under Ar at 100 rpm for 24 h. Strong bands due to B-H_t (terminal B-H) stretching between 2227 and 2377 cm^{-1} are observed. In addition, two bands from B-H_b (bridge B-H) stretching at 2134 and 1630 cm^{-1} are observed. These are typical bands that can be detected in metal borohydrides [23]. Quite a strong band due to Zn-Cl is observed at 1630 cm^{-1}. A Zn-H band is observed between 1358 and 1409 cm^{-1}, and a BH_2 band is observed at 1131 cm^{-1}. This result shows that $Zn(BH_4)_2$ is formed in the sample. The band at about 3513 cm^{-1} corresponds to that of H_2O, which is believed to be adsorbed during treatment. $Zn(BH_4)_2$ is known to have strong deliquescence [24].

The SEM micrographs of $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ni$ prepared by horizontal ball milling under Ar at 100 rpm for 24 h are shown in Fig. 3. The shape of the particles is very irregular and particle sizes are not homogeneous. Some particles are separated and agglomerates are also observed. At the high magnification, some fine particles and agglomerates with various sizes are found. Some agglomerates with a size of about 15 μm have smooth surfaces with fine particles embedded on the surface.

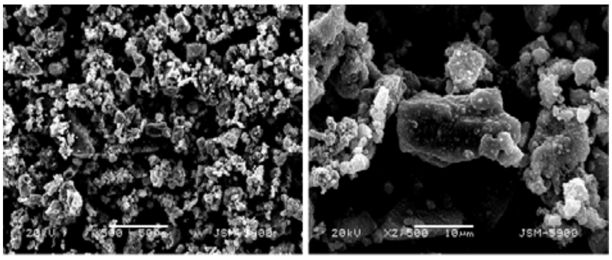

Fig. 3. SEM micrographs of $14MgH_2$+$49Zn(BH_4)_2$+30NaCl+7Ni prepared by horizontal ball milling under Ar at 100 rpm for 24 h

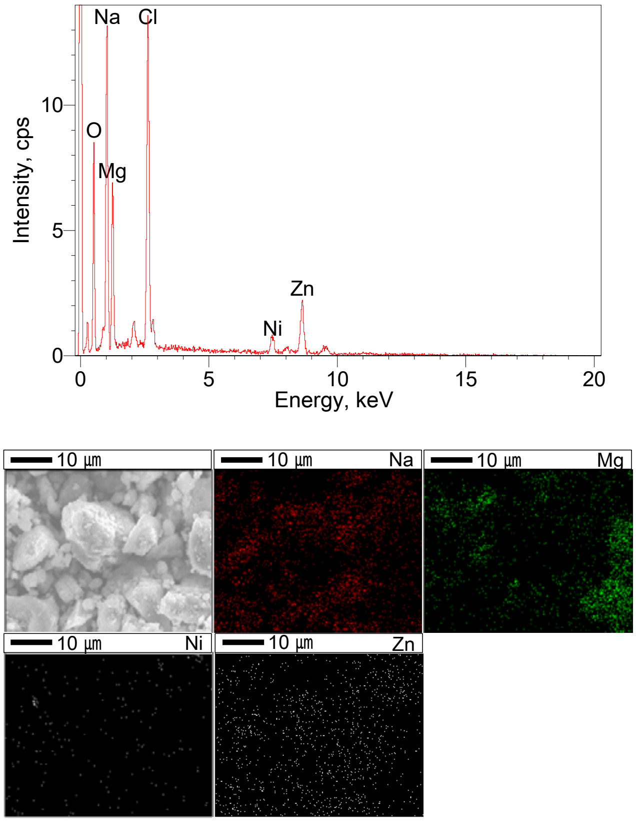

Fig. 4. EDS spectrum, SEM image, and Na, Mg, Ni, and Zn mapping for $14MgH_2$+$49Zn(BH_4)_2$+30NaCl+7Ni prepared by horizontal ball milling under Ar at 100 rpm for 24 h

Fig. 4 shows EDS (energy dispersive X-ray spectroscopy) spectrum, SEM image, and Na, Mg, Ni, and Zn mapping for $14MgH_2$+$49Zn(BH_4)_2$+30NaCl+7Ni. The sample contains Mg, Ni, Zn, Na, Cl, and O. Oxygen is believed to have been adsorbed from air during treatment. Their atomic percentages are 12.0, 1.6, 7.7, 15.4, 12.1, and 51.3, respectively. The particle size is not homogeneous. N a, Ni, and Zn are distributed quite homogeneously. Large particles contain large fraction of Mg.

Fig. 5 shows the XRD pattern of $14MgH_2$+ +$49Zn(BH_4)_2$+30NaCl+7Ni prepared by horizontal ball milling under Ar at 100 rpm for 24 h. The sample contains β-MgH_2, Mg, Ni, $Zn(BH_4)_2$, NaCl, $NaBH_4$, and $ZnCl_2$. The NaCl formed during the synthesis of $Zn(BH_4)_2$ is contained and remaining $NaBH_4$ and $ZnCl_2$ are also contained.

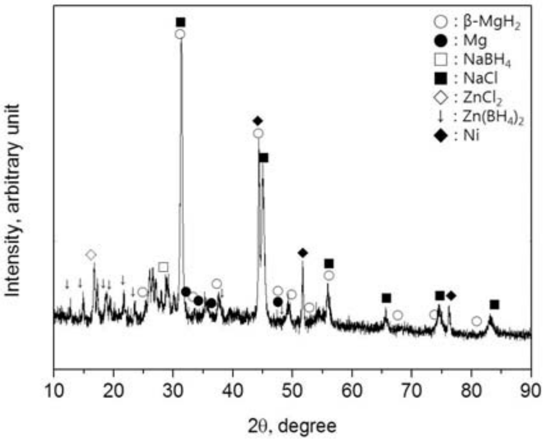

Fig. 5. XRD pattern of $14MgH_2$+$49Zn(BH_4)_2$+30NaCl+7Ni prepared by horizontal ball milling under Ar at 100 rpm for 24 h

The released gas quantity, G_r, was given as the weight percentage of the released gas with respect to the sample weight. The variation in the released gas quantity, Gr, with temperature for as-milled $14MgH_2$+$49Zn(BH_4)_2$+30NaCl+ +7Ni was examined. The sample was heated from room temperature to 698 K with a heating rate of 3 K/min under 1.0 bar H_2. At about 375 K and 680 K, the value of G_r decreased rapidly. The values of G_r were 0.22 wt.% at 379 K, 0.92 wt.% at 473 K, and 1.56 wt.% at 698 K.

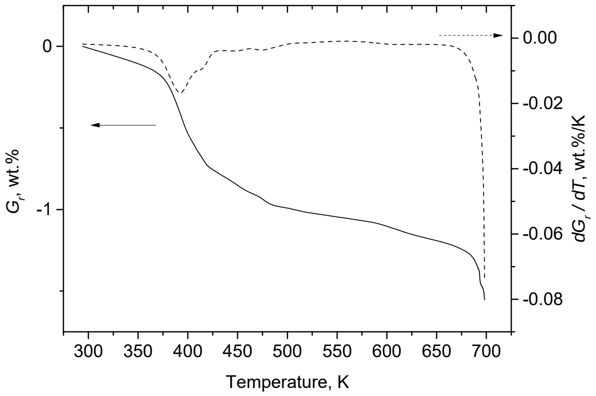

Fig. 6. Changes with temperature of the released gas quantity, G_r, and the rate of G_r change with temperature T change, dG_r/dT, for as-milled $14MgH_2$+$49Zn(BH_4)_2$+30NaCl+7Ni

The changes with temperature of the released gas quantity, G_r, and the rate of G_r change with temperature T change, dG_r/dT, for as-milled $14MgH_2$+$49Zn(BH_4)_2$ +30NaCl+7Ni are shown in Fig. 6. Metal hydrides begin to decompose at about 350 K and 670 K. Peaks at the dG_r/dT versus T curve are observed at about 390 K and about 698 K. It is believed that $Zn(BH_4)_2$ begins to decompose at about 350 K and the rate of G_r change with temperature T change, dG_r/dT, reaches its peak at about 390 K. It is also believed that MgH_2 begins to decompose at about 670 K and dG_r/dT reaches its peak at about 698 K.

Fig. 7 shows the FT-IR spectrum of $14MgH_2$ +$49Zn(BH_4)_2$+30NaCl+7Ti prepared by horizontal ball milling under Ar at 100 rpm for 24 h. Strong bands due to B-H_t (terminal B-H) stretching between 2229 and 2369 cm^{-1} are observed. In addition, two bands from B-H_b

(bridge B-H) stretching at 2133 and 1636 cm^{-1} are observed. These are typical bands that can be detected in metal borohydrides [23]. Quite a strong band due to Zn-Cl is observed at 1636 cm^{-1}. A Zn-H band is observed between 1356 and 1406 cm^{-1}, and a BH_2 band is observed at 1129 cm^{-1}. This result shows that $Zn(BH_4)_2$ is formed in the sample. The band at about 3508 cm^{-1} corresponds to that of H_2O, which is believed to be adsorbed during treatment. $Zn(BH_4)_2$ is known to have strong deliquescence [24].

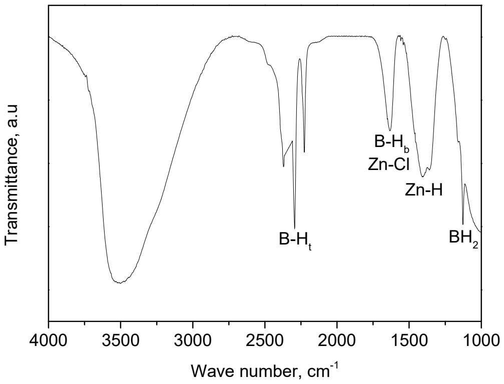

Fig. 7. FT-IR spectrum of $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$ prepared by horizontal ball milling under Ar at 100 rpm for 24 h

The SEM micrographs of $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$ prepared by horizontal ball milling under Ar at 100 rpm for 24 h are shown in Fig. 8.

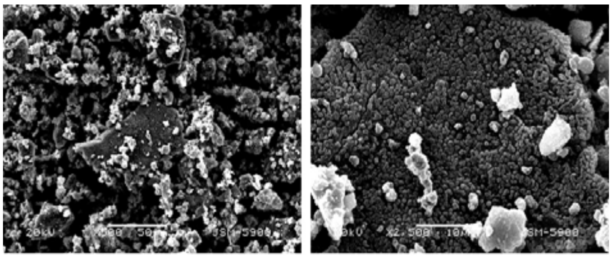

Fig. 8. SEM micrographs of $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$ prepared by horizontal ball milling under Ar at 100 rpm for 24 h

Fig. 9 shows EDS spectrum, SEM image, and Na, Mg, Ti, and Zn mapping for $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$. The sample contains Mg, Ti, Zn, Na, Cl, and O. Oxygen is believed to have been adsorbed from air during treatment. Their atomic percentages are 15.4, 0.3, 8.2, 10.5, 16.8, and 48.9, respectively. The particle size is not homogeneous. Some particles are very large. Na, Ti, and Zn are distributed quite homogeneously. Large particles contain large fraction of Mg.

The shape of the particles is very irregular and particle sizes are not homogeneous. Some particles are separated and agglomerates are also observed. An agglomerate with a size of about 60 μm is found. At a low magnification, the microstructure of $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$ is very similar to that of $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ni$. In contrast to $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ni$, $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$ has agglomerates consisting of small spherical particles with a relatively homogeneous particle size.

Fig. 10 shows the XRD pattern of $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$ prepared by horizontal ball milling under Ar at 100 rpm for 24 h. The sample contains β-MgH_2, Mg, Ti, $Zn(BH_4)_2$, NaCl, $NaBH_4$, and $ZnCl_2$. The NaCl formed during the synthesis of $Zn(BH_4)_2$is contained and remaining $NaBH_4$ and $ZnCl_2$ are also contained.

The variation in the released gas quantity, G_r, with temperature for as-milled $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$ was examined. The sample was heated from room temperature to 703 K with a heating rate of 4 K/min under 1.0 bar H_2. At about 400 K and 690 K, the value of G_r decreased rapidly. The values of G_r were 0.01 wt.% at 373 K, 0.58 wt.% at 573 K, and 0.93 wt.% at 703 K.

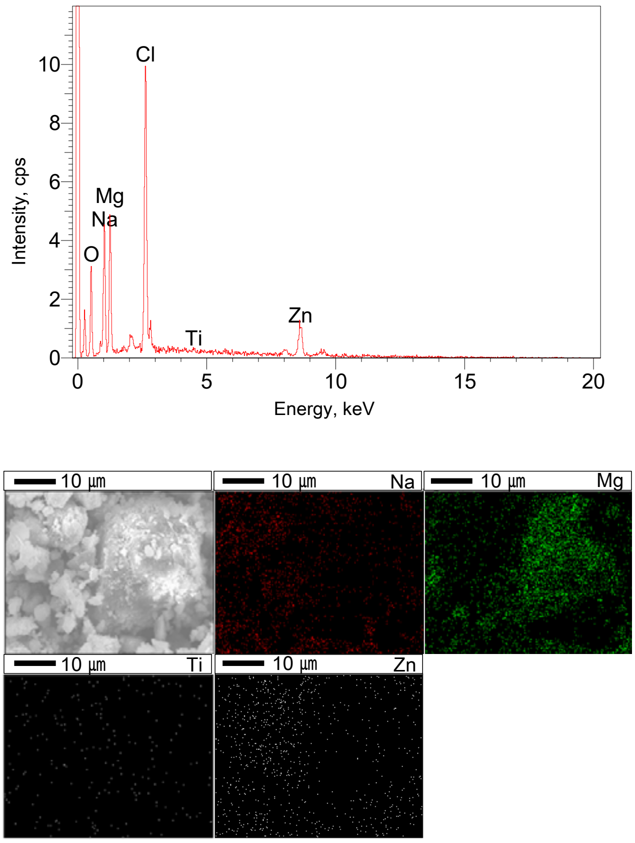

Fig. 9. EDS spectrum, SEM image, and Na, Mg, Ti, and Zn mapping for $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$ prepared by horizontal ball milling under Ar at 100 rpm for 24 h

The changes with temperature of the released gas quantity, G_r, and the rate of G_r change with temperature T change, dG_r/dT, for as-milled $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$ are shown in Fig. 11. Metal hydrides begin to decompose at about 320 K and 620 K. Peaks at the dG_r/dT versus T curve are observed at about 460 K and 703 K. It is believed that $Zn(BH_4)_2$ begins to decompose at about 320 K and the rate of G_r change with temperature T change, dG_r/dT, reaches its peak at about 460 K. It is also believed that MgH_2 begins to decompose at about 620 K and dG_r/dT reaches its peak at about 703 K. As-milled $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ni$ releases a larger amount of gas (1.56 wt.%) than as-milled $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$ (0.93 wt.%).

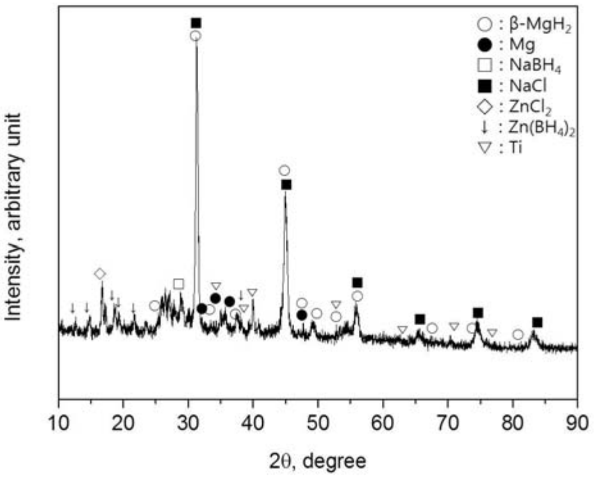

Fig. 10. XRD pattern of $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$ prepared by horizontal ball milling under Ar at 100 rpm for 24 h

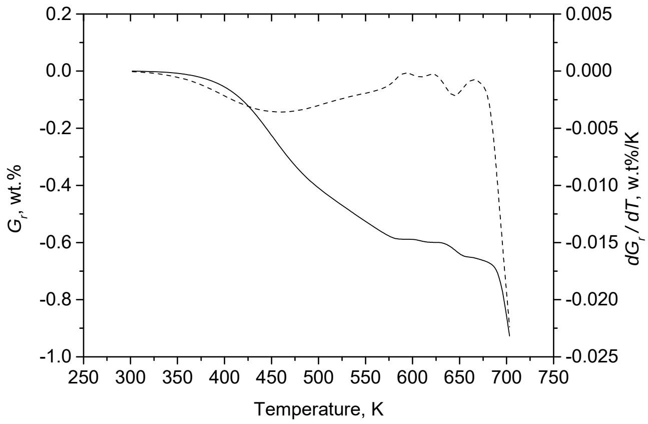

Fig. 11. Changes with temperature of the released gas quantity, G_r, and the rate of G_r change with temperature T change, dG_r/dT, for as-milled $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$

Nakagawa et al. [22] reported that $Zn(BH_4)_2$ releases hydrogen with toxic diborane (B_2H_6), after melting with increasing temperature, and this reaction can be described as follows:

$$Zn(BH_4)_2 \rightarrow Zn + B_2H_6 + H_2. \qquad (2)$$

When the as-milled $14MgH_2+49Zn(BH_4)_2+$ $+30NaCl+7Ni$ and $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ti$ were heated for the measurements of decomposition, the released gas is believed to contain diborane and hydrogen.

4. CONCLUSIONS

Gas release of $Zn(BH_4)_2$–MgH_2–NaCl–Tm (Tm = Ni or Ti) prepared via horizontal ball milling was analysed using a Sievert's type volumetric apparatus by measuring the quantity of the gas released under 1.0 bar as the temperature was increased with a heating rate of 3 – 4 K/min and obtaining the variation in the rate of released gas quantity G_r change with temperature T change, dG_r/dT, as a function of 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, and DTA. In the as-milled $14MgH_2$ $+49Zn(BH_4)_2+30NaCl+7Ni$, it is believed that $Zn(BH_4)_2$ begins to decompose at about 350 K and dG_r/dT reaches its peak at about 390 K, and that MgH_2 begins to decompose at about 670 K and dG_r/dT reaches its peak at about 698 K. As-milled $14MgH_2+49Zn(BH_4)_2+30NaCl+7Ni$ releases a larger amount of gas (1.56 wt.%) than as-milled $14MgH_2$ $+49Zn(BH_4)_2+30NaCl+7Ti$ (0.93 wt.%).

Acknowledgments

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