ELSEVIER

Journal of Alloys and Compounds 446–447 (2007) 306–309

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Thermal analysis on the Li–Mg–B–H systems

Tessui Nakagawa[a], Takayuki Ichikawa[b,*], Nobuko Hanada[b,1],
Yoshitsugu Kojima[b], Hironobu Fujii[b]

[a] *Department of Quantum Matter, ADSM, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan*
[b] *Institute for Advanced Materials Research, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan*

Received 28 October 2006; received in revised form 3 February 2007; accepted 14 February 2007
Available online 23 February 2007

Abstract

Thermal analyses of the mixture of MgH_2 and $LiBH_4$ doped with $TiCl_3$, and each element MgH_2 or $LiBH_4$ doped with $TiCl_3$ were performed under an inert gas flow and 0.5 MPa H_2-gas conditions. It was indicated that the hydrogen desorption reaction of $MgH_2 + 2LiBH_4$ to $MgB_2 + 2LiH + 4H_2$ phases proceeded at temperature above 400 °C under 0.5 MPa hydrogen, whereas, under an inert gas atmosphere, the reaction of the same mixture was transformed into $Mg + 2B + 2LiH + 4H_2$ phases in a temperature range from 350 to 430 °C. Before these reactions, the dehydrogenation of MgH_2 and the melting of $LiBH_4$ took place under both hydrogen and the inert gas atmospheres with increasing temperature. In addition, the molten $LiBH_4$ did not decompose into LiH, B and H_2 below 450 °C under 1 MPa H_2, while the $LiBH_4$ decomposed even below 450 °C under an inert gas atmosphere. From these results, it is deduced that the reaction producing MgB_2 is a solid–liquid reaction between solid Mg and liquid $LiBH_4$ above 400 °C without decomposition of molten $LiBH_4$ under a hydrogen atmosphere, while MgH_2 dehydrogenate. A characteristic solid–liquid reaction is realized under a hydrogen atmosphere for proceeding of the MgB_2 producing reaction in this system.

Keywords: Hydrogen storage materials; Liquid–solid reactions; X-ray diffraction; Thermal analysis

1. Introduction

Lithium borohydride ($LiBH_4$) is one of the most attractive candidates for hydrogen storage because of its high gravimetric and volumetric hydrogen densities; about ∼18 mass% and 121 kg H_2/m^3, respectively [1]. The synthesis of pure $LiBH_4$ was firstly performed in 1940 by Schlesinger and Brown [2] and the thermal analysis of $LiBH_4$ was performed in 1964 by Fedneva et al. [3]. However, this material had not been paid attention as a hydrogen storage material until 21st Century. The first investigation of $LiBH_4$ as a hydrogen storage material was reported by Züttel et al. [4,5] in which thermal decomposition properties were examined. They reported that $LiBH_4$ desorbed hydrogen up to ∼13.5 mass% according to the following reaction:

$$LiBH_4 \rightarrow LiH + B + 1.5H_2. \quad (1)$$

However, the dehydrogenating temperature of $LiBH_4$ was too high for practical use and the reversibility was not realized because of its quite slow kinetics. At the next step, they reported that the thermal decomposition of SiO_2-doped $LiBH_4$ has three dehydrogenation steps on $LiBH_4$ with increasing temperature as follows:

$$LiBH_4 \rightarrow LiBH_{4-\varepsilon} + 1/2(\varepsilon)H_2 \quad (2)$$

$$LiBH_{4-\varepsilon} \rightarrow \text{“}LiBH_2\text{''} + 1/2(1-\varepsilon)H_2 \quad (3)$$

$$\text{“}LiBH_2\text{''} \rightarrow LiH + B + 1/2H_2. \quad (4)$$

Recently, many researchers have focused on this system [6–8]. Among them, Orimo et al. reported that the rehydrogenation reaction of LiH and B proceeded to form $LiBH_4$ under 35 MPa H_2-gas pressures at 600 °C [9].

In 2004, two independent groups developed a new hydrogen storage system composed of $LiBH_4$ and magnesium hydride (MgH_2), which exhibited a much better reversibility than $LiBH_4$ itself [10–12]. The reaction is expressed as follows:

$$2LiBH_4 + MgH_2 \leftrightarrow 2LiH + MgB_2 + 4H_2. \quad (5)$$

---

[*] Corresponding author. Tel.: +81 82 424 5744; fax: +81 82 424 5744.
E-mail address: tichi@hiroshima-u.ac.jp (T. Ichikawa).

[1] Current address: Karlsruhe Research Center, Institute for Nanotechnology, D-76021 Karlsruhe, Germany.

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.02.097

It is noteworthy that a finite hydrogen pressure is necessary for the reaction of Mg with $LiBH_4$ to yield MgB_2. In contrast, the Mg and B phases instead of the MgB_2 phase are produced after dehydrogenation under vacuum. This reaction is expressed as follows:

$$2LiBH_4 + MgH_2 \rightarrow 2LiH + Mg + 2B + 4H_2. \quad (6)$$

At present, it is not yet clear which role the hydrogen atmosphere does play in the reaction (5). Therefore, in this paper, we report on the results of thermal analysis for the mixture of MgH_2 and $LiBH_4$ under different atmospheric conditions. And finally, we try to clarify the role of hydrogen in this system.

2. Experimental

In this work, MgH_2 powder (95 mass% purity, Gelest Inc.), $LiBH_4$ powder (95 mass% purity, Sigma–Aldrich) and titanium chloride powder ($TiCl_3$, 99.999 mass% purity, Sigma–Aldrich) were used as starting materials. Thermal analyses were performed for MgH_2, $LiBH_4$ and a mixture of MgH_2 and $2LiBH_4$, in which 3 mol% $TiCl_3$ was added as a catalyst. Prior to thermal analyses, all the samples were ball-milled by a planetary ball-mill apparatus (Fritsch P7) for 2 h at 400 rpm under 1.0 MPa highly pure hydrogen gas (7 N). Mixed powders of ∼300 mg and 20 pieces of steel balls with a diameter of 7 mm were loaded into the milling container (Cr–steel pot with an internal volume of ∼30 ml). The thermal analyses were examined by a pressurized differential scanning calorimetry (p-DSC) (TA Instruments, DSC Q10P) and a thermogravimetry with differential thermal analysis equipment (TG-DTA) (Rigku, TG8120). The measurement of p-DSC was operated under ∼0.3 MPa Ar gas flow, or under 0.5 MPa H_2 gas as initial pressure (final pressure at 450 °C was ∼0.7 MPa) in a closed system, while the TG-DTA measurement was operated under a He gas flow condition. The heating rate was fixed at 5 °C/min for both measurements. The identification of the products was carried out by X-ray powder diffraction (XRD) measurements (Rigaku, RINT-2500, Cu Kα). All the processes from the sample preparation to the thermal analyses were performed in Ar-filled gloveboxes with a recycling purification system (MP-P60W, Miwa MFG Co., LTD) to avoid the sample pollutions by water vapor and oxygen (the dew point of water was lower than −80 °C and the oxygen concentration was below 1 ppm).

3. Result and discussion

The thermal analyses for the $TiCl_3$-doped MgH_2 and the $TiCl_3$-doped $LiBH_4$ are shown in Figs. 1 and 2, respectively. The thermal analyses were performed by TG-DTA under a He gas flow, p-DSC under ∼0.3 MPa Ar gas flow and 0.5 MPa H_2-gas in the closed system. It can be seen that the decomposition temperature of the $TiCl_3$-doped MgH_2 is ∼280 °C under the He-gas flow (Fig. 1(a)), which is almost the same as that of under the Ar flow condition (Fig. 1(b)), irrespective of sorts of inert gases. This result indicates that an inert gas gives no influence on the dehydrogenation properties of MgH_2. On the other hand, in the p-DSC profile under 0.5 MPa H_2 gas pressure (Fig. 1(c)), an endothermic peak corresponding to decomposition of MgH_2 is observed at higher temperature (∼370 °C) than that under the inert gas flow, where the pressure rises to ∼0.6 MPa at this temperature. This indicates that the hydrogen dissociation pressure is about 0.6 MPa at ∼370 °C, suppressing the dehydrogenation of MgH_2 by a reverse reaction.

For $LiBH_4$ doped with a small amount of $TiCl_3$, three endothermic reactions are observed in the DTA profile under a He gas flow (Fig. 2(a)), which is almost the same as under an Ar flow condition as shown in Fig. 2(b). Therefore, the inert gases do not show any differences on the dehydrogenation properties of $LiBH_4$. Here, it should be noted that the measuring temperature was limited up to 450 °C, because the sample pan of the Al metal was used in this work. For this reason, unfortunately, the third reaction peak could not be clearly observed in the DTA or DSC profiles under the inert gases, but the endothermic reactions could be recognized above 400 °C since the DSC signals are lower than the base lines. Comparing with the results reported by Fedneva et al. [3] and Soulié et al. [13], three endothermic reactions in Fig. 2(a) and (b) correspond to the phase transition (∼105 °C, orthorhombic to hexagonal), the melting phenomenon (∼280 °C) and the decomposition into LiH, B and H_2 (above 400 °C). On the other hand, under 0.5 MPa H_2 gas pressure in Fig. 2(c), two endothermic peaks are observed below 300 °C, but there is no other reaction above 300 °C. These two peaks are recognized at the same temperatures as those under the inert gas conditions, indicating that the hydrogen pressure does not affect both the temperatures of phase transition and melt of $LiBH_4$. However, the third reaction above 300 °C disappears in the DSC profile under 0.5 MPa H_2 gas pressure, where

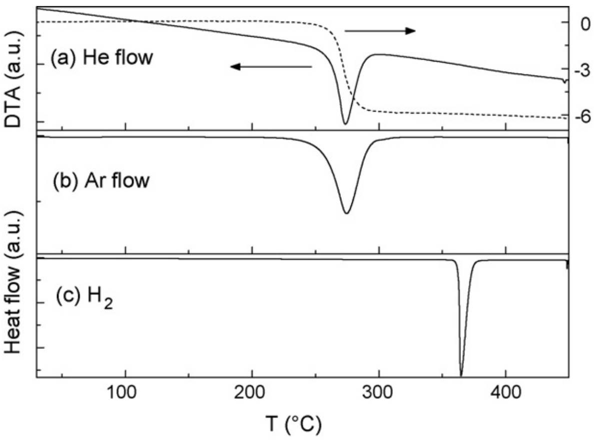

Fig. 1. TG-DTA and DSC profiles of $TiCl_3$-doped MgH_2. (a) TG-DTA profile under a He flow, (b) DSC profile under an Ar flow and (c) DSC profile under 0.5 MPa H_2 (initial pressure).

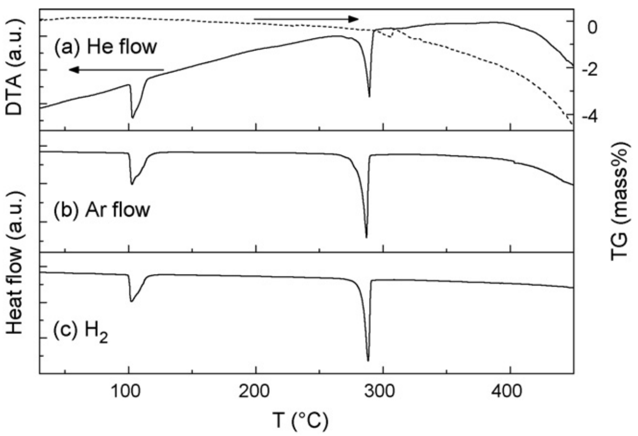

Fig. 2. TG-DTA and DSC profiles of $TiCl_3$-doped $LiBH_4$. (a) TG-DTA profile under a He flow, (b) DSC profile under an Ar flow and (c) DSC profile under 0.5 MPa H_2 (initial pressure).

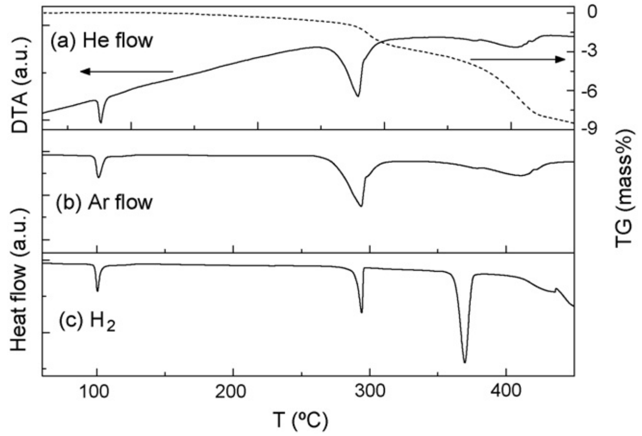

Fig. 3. TG-DTA and DSC profiles of $TiCl_3$-doped mixture of MgH_2 and $2LiBH_4$. (a) TG-DTA profile under a He flow, (b) DSC profile under an Ar flow and (c) DSC profile under 0.5 MPa H_2 (initial pressure).

the pressure rises to ~0.7 MPa at 450 °C. These results indicate that the hydrogen dissociation pressure of $LiBH_4$ is lower than 0.7 MPa at 450 °C, suppressing the dehydrogenation of $LiBH_4$ by the H_2 absorption process.

Fig. 3 shows a TG-DTA profile under a He gas flow and p-DSC profiles under ~0.3 MPa Ar gas flow and 0.5 MPa H_2 gas pressure for the $TiCl_3$-doped mixture of MgH_2 and $2LiBH_4$. Under an inert gas conditions in Fig. 3(a) and (b), there are three endothermic peaks at ~105, ~280 and ~410 °C, respectively. The two peaks below 350 °C are identified with similarity to above results as the phase transition of $LiBH_4$ (~105 °C) and superposition of the melt of $LiBH_4$ and dehydrogenation of MgH_2 (~280 °C), whereas, the endothermic peak at ~410 °C is due to the dehydrogenation of $LiBH_4$. Actually, LiH and Mg phases were confirmed in the X-ray profile (Fig. 4(b)) of the product after the DSC measurement at 450 °C under the Ar gas flow condition. Under 0.5 MPa H_2 gas pressure in Fig. 3(c), four endothermic reactions were observed around ~105, ~280, ~370 and above 400 °C. The first and the second reactions (the peaks at ~105 and ~280 °C) are due to the phase transition and melt of $LiBH_4$ because these peak temperatures are almost the same as those in Fig. 2(c). The third peak temperature at ~370 °C is similar to that of the peak in Fig. 1(c), so that the third reaction is due to the decomposition of MgH_2. Actually, the Mg phase is observed in the XRD profile as shown in Fig. 4(d) later, which was examined after heating the product up to 380 °C under 0.5 MPa H_2 gas pressure. Here, it should be noted that the most important point is appearance of the fourth endothermic peak above 400 °C. This peak was neither observed in the case of DSC measurement of MgH_2 nor $LiBH_4$ under 0.5 MPa H_2 pressure. This indicates that the dehydrogenation reaction depends on the difference whether hydrogen pressure is applied or not on the dehydrogenation process.

Fig. 4 shows XRD patterns of $TiCl_3$-doped mixture of MgH_2 and $2LiBH_4$. When a hydrogen pressure of 0.5 MPa was applied in a dehydrogenation process, the two phases of MgB_2 and LiH were produced (Fig. 4(c)). On the other hand, when no hydrogen pressure, such as an inert gas atmosphere, is applied, three phases of Mg, B and LiH were produced (Fig. 4(b)). Unfortunately, we could not find any peaks originated from B related phases, because the B peaks corresponding to single phase are too weak to be observed in our experiment. Therefore, it was clarified that the MgB_2 was generated in the forth reaction (above 400 °C).

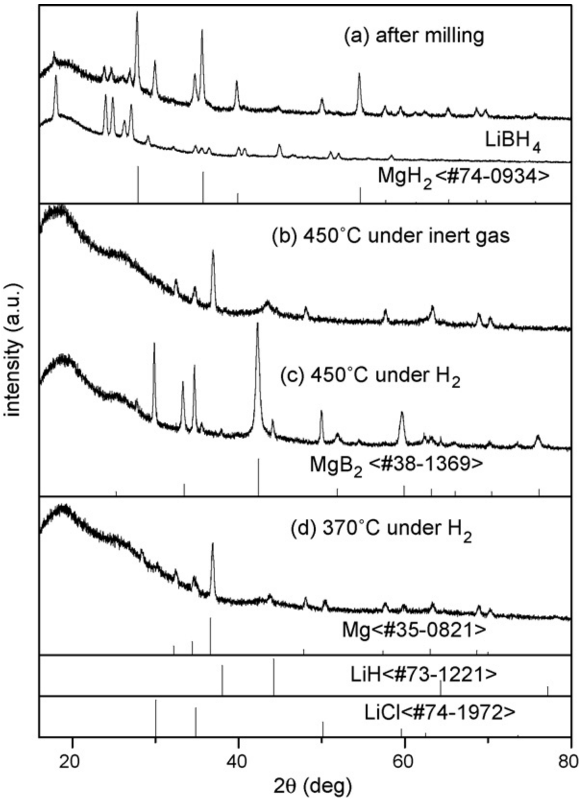

Fig. 4. XRD patterns of $TiCl_3$-doped mixture of MgH_2 and $2LiBH_4$. (a) After milling, (b) after heat treatment under an inert gas flow at 450 °C, (c) after heat treatment under 0.5 MPa H_2 (initial pressure) at 380 °C and (d) after heat treatment under 0.5 MPa H_2 (initial pressure) at 450 °C.

From the above results, we conclude that the reaction (5) proceeds in hydrogen pressure without the decomposition of $LiBH_4$, though $LiBH_4$ is under the molten phase at the temperature above 400 °C with Mg. This result indicates that the suppression of the $LiBH_4$ decomposition by hydrogen pressure plays the important role in the proceeding of the reaction (5). In addition, the reaction (5) proceeds by a solid–liquid reaction between the solid Mg phase and molten $LiBH_4$ phase, where the liquid phase of $LiBH_4$ leads to a much better contact with Mg and the Li^+ and $(BH_4)^-$ ions than a solid–solid reaction. This reaction is different from other typical hydrogen storage systems, so that this system may exhibit a characteristic reaction. In addition, hydrogen gas atmosphere could bring another contribution for proceeding of a direct reaction between condensed materials just like Mg and $LiBH_4$. As suggested by Hayashi et al., hydrogen in materials introduces some defects and reduces activation barriers for the mobility of atoms [14]. Similarly, some defects in the composite mixture of Mg and $LiBH_4$ could be introduced by exchanging hydrogen between the gas phase and condensed phase, and the activation barriers for the mobility of atoms in the composite mixture of Mg and $LiBH_4$ might be reduced, possibly yielding MgB_2 and LiH in this system.

4. Summary

In this work, we performed the thermal analyses of the $TiCl_3$-doped mixture of MgH_2 and $LiBH_4$, and each element MgH_2 or $LiBH_4$ doped with $TiCl_3$ under an inert gas flow and 0.5 MPa H_2-gas conditions. The results indicated that the reaction $[2LiBH_4 + MgH_2 \rightarrow 2LiH + MgB_2 + 4H_2]$ proceeded at 450 °C under hydrogen atmosphere of 0.5 MPa, whereas, the reaction $[2LiBH_4 + MgH_2 \rightarrow Mg + 2B + 2LiH + 4H_2]$ was induced under the inert gas atmosphere. This indicated that MgB_2 was produced by the solid–liquid reaction between solid Mg and liquid $LiBH_4$ at temperature above 400 °C, where the molten $LiBH_4$ phase remained without the dehydrogenation into $B + LiH + 1.5H_2$ under hydrogen atmosphere, while MgH_2 was dehydrogenated. Probably, a characteristic reaction between Mg metal and $(BH_4)^-$ ion was realized in this solid–liquid reaction system.

Acknowledgement

This work was supported by the project “Development for Safe Utilization and Infrastructure of Hydrogen Industrial Technology” of NEDO, Japan.

References

[1] L. Schlapbach, A. Züttel, Nature 414 (2001) 353.
[2] H.J. Schlesinger, H.C. Brown, J. Am. Chem. Soc. 62 (1940) 3429.
[3] E.M. Fedneva, V.L. Alpatova, V.I. Mikheeva, Russ. J. Inorg. Chem. 9 (6) (1964) 826.
[4] A. Züttel, P. Wenger, S. Rentsch, P. Sudan, Ph. Mauron, Ch. Emmenegger, J. Power Sources 118 (2003) 1.
[5] A. Züttel, S. Rentsch, P. Fischer, P. Wenger, P. Sudan, Ph. Mauron, Ch. Emmenegger, J. Alloys Comp. 356 (2003) 515.
[6] K. Miwa, N. Ohba, S. Towata, Y. Nakamori, S. Orimo, Phys. Rev. B 69 (2004) 245120.
[7] Y. Nakamori, S. Orimo, J. Alloys. Comp. 370 (2004) 271.
[8] J.K. Kang, S.Y. Kim, Y.S. Han, R.P. Muller, W.A. Goddard III, Appl. Phys. Lett. 87 (2005) 111904.
[9] S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, S. Towata, A. Züttel, J. Alloys. Comp. 404–406 (2005) 427.
[10] J.J. Vajo, S.L. Skeith, F. Mertens, J. Phys. Chem. B 109 (2005) 3719.
[11] J.J. Vajo, F.O. Mertens, S.L. Skeith, M.P. Balogh, International Patent pending, Publication number: WO2005/097671 A2.
[12] G. Barkhordarian, T. Klassen, R. Bormann, International Patent pending, Publication number: WO 2006/063627 A1, 2007.
[13] J-Ph. Soulié, G. Renaudin, R. Č ernỳ, K. Yvon, J. Alloys. Comp. 346 (2002) 205.
[14] E. Hayashi, Y. Kurokawa, Y. Fukai, Phys. Rev. Lett. 80 (1998) 5589.