Promotional Effect of Aluminum on $\text{MgH}_2+\text{LiBH}_4$ Hydrogen Storage Materials

Young Li, Toshihisa Izuhara^{*1} and Hiroyuki T. Takeshita^{*2}

Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita 564-8680, Japan

The effect of Al addition on the reversibility of a $\text{MgH}_2+2\text{LiBH}_4$ hydrogen storage mixture was examined in order to improve the mixture's requirement for a hydrogen atmosphere even in dehydrogenation. The experiments using high pressure differential scanning calorimetry and X-ray powder diffraction confirmed that a $\text{MgH}_2+\text{Al}+4\text{LiBH}_4$ mixture can reversibly dehydrogenate and rehydrogenate below 773 K under mild conditions of 0.1 MPa H_2 for dehydrogenation and 4.0 MPa H_2 for rehydrogenation. Moreover, thermogravimetry tests revealed that this mixture starts hydrogen desorption at about 530 K, which is 80 K lower than the corresponding temperature for the $\text{MgH}_2+2\text{LiBH}_4$ mixture, and desorbs 9.5 mass% of hydrogen below 773 K. Thus, the addition of Al improves not only the reversibility of the reaction but also dehydrogenation kinetics. The hydrogen desorption of the mixture occurs by three steps, which includes the formation of Mg-Al alloys by the reaction of MgH_2 and metallic Al followed by the formation of $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ by the reaction of the Mg-Al alloys and LiBH_4 . Al in this mixture suppresses the formation of metallic Mg and accelerates the formation of $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ from B produced by dehydrogenation of LiBH_4 . $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ is derived from partial substitution of Al for Mg in MgB_2 , which contributes to reversible hydrogenation and dehydrogenation of $\text{MgH}_2+2\text{LiBH}_4$. [doi:10.2320/matertrans.MA201005]

(Received September 30, 2010; Accepted November 4, 2010; Published January 13, 2011)

Keywords: complex hydride, magnesium hydride, aluminum, reversibility

1. Introduction

Among complex hydride materials, LiBH_4 , with the highest hydrogen content of 18.5%, is regarded as one of the most promising materials for hydrogen storage.¹⁻⁴⁾ Unfortunately, on heating above 673 K, after melting at ca. 550 K, LiBH_4 begins to release ca. 13.5 mass% hydrogen, forming LiH and amorphous B.⁵⁾ Subsequently, rehydrogenation to form LiBH_4 from LiH and B can only proceed under 35 MPa H_2 pressure at 873 K⁶⁾ or 15 MPa H_2 pressure at 973 K,⁷⁾ conditions which are too harsh for practical application. Therefore, although much more progress on the properties of LiBH_4 has been reported in recent years,⁸⁻¹¹⁾ its dehydrogenation/rehydrogenation still poses a big challenge to its use as hydrogen storage material.

Generally, LiBH_4 can be destabilized in either of the following three. One is to substitute a metal ion, such as Mg^{2+} , Ca^{2+} , or Zn^{2+} , for Li^+ forming $\text{Mg}(\text{BH}_4)_2$,¹²⁻¹⁶⁾ $\text{Ca}(\text{BH}_4)_2$,¹⁷⁻¹⁹⁾ or $\text{Zn}(\text{BH}_4)_2$,^{20,21)} respectively. In this way, the strength of the B-H bonds is weakened by the formation of new borohydride compounds. The hydrogen desorption temperature of these borohydride compounds is indeed less than that of LiBH_4 by several hundred degrees, but reversible hydrogen absorption is very difficult owing to the formation of B, which is very inert during the rehydriding process.²²⁻²⁴⁾ Moreover, in the case of $\text{Zn}(\text{BH}_4)_2$, decomposition leads to the formation of B_2H_6 , which makes reversibility impossible.^{20,21)}

Since the pioneering work on TiCl_3 -doped NaAlH_4 as a reversible hydrogen storage material by Bogdanović,²⁵⁾ many different metal oxides and metal chlorides, such as SiO_2 ,²⁶⁾ TiO_2 ,²⁷⁾ $\text{MgCl}_2+\text{TiCl}_3$,^{28,29)} and $\text{SiO}_2+\text{TiF}_3$ ³⁰⁾ have been employed to improve the dehydrogenation/hydrogenation kinetics of LiBH_4 . In these cases, the content of additive is about 20–30 mass%. However, this second way of destabi-

lizing LiBH_4 is not effective, because these additives may react with it to form Li_4SiO_4 , LiOH , B, etc.,²⁶⁻³⁰⁾ which make hydrogen absorption difficult.

The third way to modify the thermodynamics of LiBH_4 is using reactive hydride composites (RHCs),³¹⁾ that is, using additives with stoichiometric content, such as LiNH_2 ,^{32,33)} MgH_2 ,³⁴⁻³⁶⁾ or CaH_2 ,^{36,37)} to form the corresponding compound $\text{Li}_4\text{BN}_3\text{H}_{10}$ or alloys MgB_2 , CaB_6 in the dehydrogenated state, which are energetically favorable with respect to the products of the reaction without additives. These RHCs have been proved to be an effective way to destabilize LiBH_4 not only by experimental work but also by theoretical calculation.³⁸⁻⁴⁰⁾ More recently, even a new ternary mixture of $\text{LiNH}_2\text{-MgH}_2\text{-LiBH}_4$ has been proposed as an effective way to destabilized LiBH_4 .⁴¹⁻⁴³⁾ Among these RHCs, the mixture $\text{MgH}_2\text{-LiBH}_4$, which was proposed by Vajo³⁴⁾ and Barkhodarian³⁵⁾ independently in 2004, exhibited much better reversibility than LiBH_4 itself, because of the formation of MgB_2 . It has also been proved that the kinetic barriers to the formation of LiBH_4 are drastically reduced when MgB_2 is used instead of B as a starting material, because B in MgB_2 has a higher reactivity to form BH_4^- than elemental B.⁴⁴⁾ However, this new binary material for hydrogen storage has certain drawbacks. One is the sluggish kinetics of dehydrogenation. This mixture can release 8 mass% of hydrogen at 723 K, but even in the presence of TiCl_3 as a catalyst, the kinetics were very slow and times up to 100 h were necessary to attain equilibrium.³⁴⁾ Titanium isopropoxide exhibited better effect to improve the dehydrogenation rate but 4 h are still required for complete dehydrogenation even at 673 K.⁴⁵⁾ Some metal dopants such as Pd,⁴⁶⁾ Mn and V⁴⁷⁾ were tried by several research groups but longer time than in the case of titanium isopropoxide is required for the complete dehydrogenation. Another drawback is the requirement of an applied H_2 pressure of at least 0.3 MPa to ensure the reaction of Mg with LiBH_4 to yield MgB_2 ,⁴⁸⁾ which is necessary to absorb hydrogen for the formation of LiBH_4 under mild conditions. Otherwise, the

^{*1}Graduate Student, Kansai University

^{*2}Corresponding author, E-mail: h-take@kansai-u.ac.jp

decomposition of $\text{MgH}_2 + 2\text{LiBH}_4$ in an inert atmosphere of He, Ar, or in vacuum will result in the formation of Mg and amorphous B, which is very difficult to rehydrogenate to LiBH_4 .^{48–50)}

In this study, aluminum is found to overcome the above two drawbacks of $\text{MgH}_2\text{-LiBH}_4$ as a hydrogen storage materials. Furthermore, the decomposition mechanism and reversibility of $\text{MgH}_2\text{-Al-LiBH}_4$ are also studied by thermogravimetry (TG), high-pressure differential scanning calorimetry (HP-DSC) and X-ray powder diffraction (XRD).

2. Experimental

In this study, MgH_2 powder (98% purity, Alfa Aesar), LiBH_4 powder (95% purity, Alfa Aesar), and Al powder (99.5% purity, 53–150 μm , Wako) were used as received without further purification. For sample preparation, in a He glove box, 1.0 g mixtures of $\text{MgH}_2/\text{Al}/\text{LiBH}_4$ with different molar ratios were placed in a 40-ml hardened steel grinding bowl, containing 15 steel balls (the weight ratio of the balls to the powder was 60 : 1). The sealed grinding bowls were removed from the glove box, placed on the Fritsch P6 planetary mill machine, and ground for 36 ks (10 h) at 400 rpm. Then, about 0.3 g of the mixtures was transferred to a modified Sieverts' apparatus (Lesca Co., Japan) for the temperature-programmed desorption (TPD) measurements under vacuum.

Thermal analyses were performed by HP-DSC (Rigaku DSC8230HP) and TG (Rigaku TG8120), both of whose instruments were located in a He glove box. Typical sample quantities were ca. 13 mg. The HP-DSC measurements were carried out under initial pressures of 0.1 MPa of H_2 gas for dehydrogenation and 4.0 MPa for rehydrogenation (final pressures at 773 K were 0.14 MPa and 4.3 MPa, respectively) in a closed system. The TG studies were conducted under 100-ml/min He gas flow, and the outlet gas was analyzed by an on-line mass spectrometer (Canon Anelva M-101QA-TDM). The heating rate was fixed at 2 K/min in all runs.

Identification of phases was carried out by XRD (Rigaku, RINT-2500); the diffractometer was operated at 40 kV and 300 mA with step increments of 0.02° measured for 1.2 s with Cu $\text{K}\alpha$ radiation ($\lambda = 0.154178 \text{ nm}$). Amorphous polymer tape was used to cover the surface of the powder to avoid oxidation during the XRD test.

3. Results and Discussion

3.1 TPD screening of LiBH_4 -based materials

The mixtures of MgH_2 and LiBH_4 with different molar ratios and the mixture of MgH_2 , LiBH_4 , and Al with a 1 : 4 : 1 molar ratio (mixture hereafter referred to $\text{MgH}_2 + \text{Al} + 4\text{LiBH}_4$; other mixtures will be denoted in a similar manner) were studied by XRD after milling for 10 h (Fig. 1). In these samples, no new phases were formed during ball milling and they remained the original mixtures of MgH_2 , Al and LiBH_4 . In the TPD test of the above-mentioned samples from room temperature to 873 K, we faced some difficulties in precisely determining the amount of hydrogen desorbed at higher temperatures, so the change in hydrogen pressure was used directly to characterize the

Fig. 1 XRD profiles of LiBH_4 -based materials after ball milling for 36 ks. For reference, XRD patterns of MgH_2 and metallic Al are also shown, with their JCPDS PDF numbers, for example, 74-0934 (MgH_2).

Fig. 2 TPD profiles of LiBH_4 -based materials.

dehydrogenation kinetics, as shown in Fig. 2. Commercial LiBH_4 began to decompose at a very slow rate above 550 K, and the decomposition rate increased appreciably above 700 K. For $\text{MgH}_2 + 2\text{LiBH}_4$, although the initial temperature for hydrogen desorption shifted to a slightly higher value, hydrogen decomposition proceeded at a much faster rate than that in the case of commercial LiBH_4 , and at ca. 810 K a plateau appeared in the TPD curve. This confirmed the improvement effect of MgH_2 on the decomposition of LiBH_4 , as previously reported by Vajo³⁴⁾ and Barkhordarian.³⁵⁾ However, when the molar ratio of LiBH_4 to MgH_2 increased from 2 : 1 to 4 : 1 and from 2 : 1 to 7 : 1, further improvement was not observed and the dehydrogenation was slow, even as compared to that in the case of commercial LiBH_4 . The best dehydriding kinetics was found for $\text{MgH}_2 + \text{Al} + 4\text{LiBH}_4$; an appreciable dehydrogenation rate was found above 550 K, and the plateau of hydrogen pressure appeared at ca. 780 K, which is somewhat lower than that for $\text{MgH}_2 + 2\text{LiBH}_4$.

After TPD tests, the dehydrogenated samples were analyzed by XRD. The XRD profiles are shown in Fig. 3. For commercial LiBH_4 , only LiH could be identified, and there was no trace of any B in the XRD profiles,

Fig. 3 XRD profiles of LiBH_4 -based materials after TPD test. For reference, XRD patterns of LiAl , $\text{Mg}_{0.5}\text{Al}_{0.5}\text{B}_2$, MgB_2 , metallic Mg and Al , and LiH are also shown, with their JCPDS PDF numbers, for example, 71-0362 (LiH).

which suggests that it is in an amorphous phase. For $\text{MgH}_2+2\text{LiBH}_4$, LiH and MgB_2 formed after dehydrogenation. In addition, the dehydrogenation in this study was carried out under vacuum, so peaks ascribed to metallic Mg were also found, which is in accordance with the results obtained by Vajo.⁴⁸⁾ For $\text{MgH}_2+4\text{LiBH}_4$ and $\text{MgH}_2+7\text{LiBH}_4$, in addition to LiH , MgB_2 , and Mg , peaks corresponding to LiBH_4 also appeared in XRD profiles, which could explain why the hydrogen pressure in TPD is lower than that for $\text{MgH}_2+2\text{LiBH}_4$, despite the latter having a lower hydrogen content. It is worthwhile to note that there were no peaks ascribed to either MgB_4 or MgB_7 in the XRD profiles of $\text{MgH}_2+4\text{LiBH}_4$ and $\text{MgH}_2+7\text{LiBH}_4$. This may explain why $\text{MgH}_2+4\text{LiBH}_4$ and $\text{MgH}_2+7\text{LiBH}_4$ do not give better dehydrogenation kinetics than LiBH_4 , despite these two having been predicted to be promising binary materials for hydrogen storage.^{38,39)} For $\text{MgH}_2+\text{Al}+4\text{LiBH}_4$, the diffraction peak at 42.3° , corresponding to MgB_2 , clearly shifted to the higher degree of 43.2° , which means that Al partly substitutes for Mg , leading to the formation of $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$.⁵¹⁾ Therefore, its dehydrogenation products were composed of $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$, LiAl , and LiH , and there were no signs of metallic Mg , a pattern that is completely different from that of $\text{MgH}_2+2\text{LiBH}_4$. The absence of Mg implies that the Mg from MgH_2 was completely used in the formation of $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ and that in addition, much of the B from LiBH_4 was contained in this compound. Therefore, it would be expected that $\text{MgH}_2+\text{Al}+4\text{LiBH}_4$ after dehydrogenation would be rehydrogenated more easily than $\text{MgH}_2+2\text{LiBH}_4$.

3.2 TG study of LiBH_4 -based materials

TG-MS tests were performed to confirm the improvement effect of Al on $\text{MgH}_2\text{-LiBH}_4$, as can be seen in Fig. 4. Although all the samples underwent multiple steps for their respective weight losses, as previously reported,⁵⁰⁾ all the dehydrating temperatures of $\text{MgH}_2+\text{Al}+4\text{LiBH}_4$ shifted to much lower values than those of $\text{MgH}_2+2\text{LiBH}_4$ and $\text{MgH}_2+4\text{LiBH}_4$. For $\text{MgH}_2+\text{Al}+4\text{LiBH}_4$, the first step

Fig. 4 TG profiles of LiBH_4 -based materials.

Fig. 5 Mass spectrum profiles of thermal decomposition of $\text{MgH}_2+\text{Al}+4\text{LiBH}_4$ during TG test.

commences at around 530 K, which is ca. 80 K lower than that for $\text{MgH}_2+2\text{LiBH}_4$; the second step commences at around 560 K. (Peak assignment is analyzed in connection with the XRD results below.) No plateau of weight loss was observed in our TG test, which also differs from the results of Bösenberg.⁵⁰⁾ This perhaps results from the lower rate of temperature increase (2 K/min) in our studies. Since $\text{MgH}_2+2\text{LiBH}_4$ theoretically has 11.3 mass% of hydrogen content, considering impurity (according to the reaction equation $\text{MgH}_2+2\text{LiBH}_4 \rightarrow \text{MgB}_2+2\text{LiH}+4\text{H}_2$) and since $\text{MgH}_2+4\text{LiBH}_4$ theoretically has 12.2 mass% of hydrogen content, considering impurity (according to the reaction equation $\text{MgH}_2+4\text{LiBH}_4 \rightarrow \text{MgB}_4+4\text{LiH}+\text{H}_2$), it was expected that these two would have greater hydrogen content than $\text{MgH}_2+\text{Al}+4\text{LiBH}_4$, which theoretically only has 9.9 mass% (according to $\text{MgH}_2+\text{Al}+4\text{LiBH}_4 \rightarrow \text{Mg}_{0.5}\text{Al}_{0.5}\text{B}_2+4\text{LiH}+\text{H}_2$). However, in fact, the latter showed higher weight loss (9.5 mass%) than the former two (9.1 mass%) at the end of 773 K, and this value is very close to the theoretical hydrogen content. Mass-spectral analysis indicates that the decomposition gas stream from $\text{MgH}_2+\text{Al}+4\text{LiBH}_4$ consisted only of hydrogen, with no trace of B_2H_6 , as depicted in Fig. 5. In contrast, for LiBH_4 destabilized by TiO_2 , B_2H_6 is released, causing permanent loss of boron and resulting in a gradual decrease in hydrogen storage capacity during dehydrating/rehydrating cycling.²⁷⁾ Two

Fig. 6 XRD profiles of LiBH₄-based materials after TG test. For reference, XRD patterns of LiAl, Mg_{0.5}Al_{0.5}B₂, MgB₂, metallic Mg and Al, and LiH are also shown, with their JCPDS PDF numbers, for example, 71-0362 (LiH).

main peaks of hydrogen desorption were observed, which correspond to the weight loss in the TG test.

Figure 6 shows the XRD profiles of the samples after the TG test in a He flow. As expected, the MgH₂+2LiBH₄ and MgH₂+4LiBH₄ samples have similar phase compositions after decomposition, and both form metallic Mg, which is in accordance with the results of Ichikawa.⁴⁹⁾ MgH₂+Al+4LiBH₄, in contrast, has a similar phase to that following the TPD test. There is no trace of metallic Mg, which is completely different from previously reported results by Vajo,⁴⁸⁾ Ichikawa,⁴⁹⁾ and Bösenberg.⁵⁰⁾ In their studies, for MgH₂+2LiBH₄, only dehydrogenating under a finite H₂ pressure could prohibit the formation of metallic Mg and suppress direct decomposition of LiBH₄, which reacts with the Mg to produce LiH and MgB₂ in a fully reversible process. Therefore, the addition of Al not only improves the dehydrogenating kinetics, but also, as Mg_{1-x}Al_xB₂, accelerates the formation of MgB₂ by partial substitution of Al for Mg in MgB₂.

Therefore, the results of the TPD, TG, and XRD analyses confirm that aluminum can indeed alleviate the two aforementioned drawbacks of MgH₂-LiBH₄ mixtures as hydrogen storage materials. More recently, Al has been used to destabilize LiBH₄, with the expectation of AlB₂ formation via the reaction $\text{Al} + 2\text{LiBH}_4 \rightarrow \text{AlB}_2 + \text{LiH} + \text{H}_2$.^{38,51,52)} However, this reaction cannot reach completion and Al+2LiBH₄ also has similar shortcomings to those of MgH₂+2LiBH₄. For example, when Al+2LiBH₄ was dehydrogenated in a vacuum at 723 K, the amount of hydrogen desorbed decreased from 7 mass% to 3 mass% hydrogen in four dehydrogenation-rehydrogenation recycle tests,⁵²⁾ while dehydrogenation at a pressure of 0.3 MPa H₂ at 668 K increased the amount of hydrogen desorbed from 5.2 to 6.7 mass%.³⁶⁾

The formation of LiAl alloy means that the dehydrogenating of MgH₂+Al+4LiBH₄ does not proceed as expected, so, in an attempt to understand the reaction mechanism, the phase of dehydrogenation products at different temperatures during the TG test was studied by XRD, results of which are shown

Fig. 7 XRD profiles of MgH₂+Al+4LiBH₄ after TG test at different temperatures. For reference, XRD patterns of LiAl, Mg_{0.5}Al_{0.5}B₂, MgB₂, Mg₂Al₃, Mg₁₇Al₁₂, metallic Mg and Al, and LiH are also shown, with their JSPDS PDF numbers, for example, 71-0362 (LiH).

in Fig. 7. After heating to 573 K, the XRD peaks corresponding to MgH₂ disappeared and new peaks corresponding to Mg₁₇Al₁₂ and Mg₂Al₃ appeared, without the formation of Mg metal. At the same time, no peak due to LiH could be identified, suggesting that LiBH₄ at this temperature cannot decompose. Thus, the decomposition of MgH₂ resulted in the weight loss of the first step in the TG test. When the temperature increased to 623 K, peaks assigned to LiH and Mg_{1-x}Al_xB₂ appeared, which suggests the decomposition of LiBH₄. The peaks for LiBH₄ became almost invisible until 673 K. The peaks for Mg₁₇Al₁₂ and Mg₂Al₃ became weaker and disappeared when the temperatures increased to 673 K and 723 K, respectively. Therefore, the decomposition of LiBH₄ was responsible for the weight loss of the second step in the TG test. According to thermodynamic calculations, LiH may react with Al to form LiAl and H₂ above 600 K. However, in this study, the formation of LiAl alloy was confirmed in the XRD profiles only when the temperature increased to 773 K. Neither was formation of LiAl alloy observed by Yang,³⁶⁾ Cho,⁵²⁾ or Wang,⁵³⁾ who used Al to destabilize LiBH₄, perhaps owing to the lower dehydrogenation temperatures in their studies. On the other hand, we did not observe the peaks at 34.38° and 44.46° corresponding to AlB₂, as reported by Yang,³⁶⁾ Cho,⁵²⁾ and Wang.⁵³⁾ This means that Mg-Al alloy would react more easily with LiBH₄ than metallic Al and Mg alone would.

According to the DSC and *in situ* XRD results, the decomposition of MgH₂+2LiBH₄ takes the following reaction route: after melting of LiBH₄, first, MgH₂ decomposes to metallic Mg, then, Mg and LiBH₄ react to form MgB₂ via a solid-liquid reaction.⁴⁸⁻⁵⁰⁾ However, for 4MgH₂+LiBH₄, a different mechanism based on the formation of Li-Mg alloy is proposed.^{54,55)} In our case, from the above analyses, with increase in temperature, first LiBH₄ melts; then, MgH₂ reacts with Al to form Mg-Al alloy (this explains why the initial temperature for hydrogen desorption in the case of MgH₂+Al+4LiBH₄ is much lower than that in the case of MgH₂+2LiBH₄⁴⁹⁾ and 4MgH₂+LiBH₄^{54,55)}). Next, Mg-Al alloy reacts with LiBH₄ to form Mg_{1-x}Al_xB₂ and LiH,

Fig. 8 HP-DSC profiles of $\text{MgH}_2 + \text{Al} + 4\text{LiBH}_4$. In the figure, scan 1 and scan 2 are the heat flow profiles for dehydrogenation in 0.1 MPa of hydrogen and for rehydrogenation in 4.0 MPa of hydrogen, respectively.

and finally, LiH reacts with Al or $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ to form LiAl alloy. This mechanism can be expressed by the following equations:

In each equation, x may take a different value.

3.3 HP-DSC study of $\text{MgH}_2 + \text{Al} + 4\text{LiBH}_4$

From the above-mentioned XRD test results, we can conclude that Mg-Al alloy is much more active than metallic Mg and Al in reacting with LiBH_4 . In the dehydrogenation of $\text{MgH}_2 + \text{Al} + 4\text{LiBH}_4$, there was no evidence for metallic Mg or Al , which means that all B originated from the reaction of LiBH_4 with Mg-Al alloy to form $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$. This is indeed a great improvement for $\text{MgH}_2 + 2\text{LiBH}_4$ RHCs, and it also leads us to anticipate that $\text{MgH}_2 + \text{Al} + 4\text{LiBH}_4$ after dehydrogenation can absorb hydrogen to form LiBH_4 under much milder conditions.

Primary research on the reversibility of $\text{MgH}_2 + \text{Al} + 4\text{LiBH}_4$ was conducted by HP-DSC, and the results are shown in Fig. 8. Scan 1 shows the results of desorption reactions of this ternary material in a 0.1 MPa H_2 atmosphere. Peaks at ca. 380 K and ca. 540 K correspond to the polymorphic transformation and melting of LiBH_4 , respectively. During the cooling process, no peaks are observed for the reversible phase transition and melting, which means LiBH_4 has decomposed completely. The very wide peak at ca. 740 K is due to the decomposition of MgH_2 and LiBH_4 . Scan 2 shows results of the subsequent hydrogen absorption reaction at 4.0 MPa hydrogen pressure. Upon cooling this sample to room temperature, two exothermic peaks at ca. 380 K and ca. 540 K are observed, and they reveal the formation of LiBH_4 . After the HP-DSC test, the phase changes were studied by XRD, as shown in Fig. 9. Not only were MgH_2 and Al formed but also peaks corresponding to

Fig. 9 XRD profiles of $\text{MgH}_2 + \text{Al} + 4\text{LiBH}_4$ after HP-DSC test. For reference, XRD patterns of $\text{Mg}_{0.5}\text{Al}_{0.5}\text{B}_2$, metallic Al , and MgH_2 are also shown, with their JCPDS PDF numbers, for example, 89-3178 ($\text{Mg}_{0.5}\text{Al}_{0.5}\text{B}_2$).

LiBH_4 were visible in the XRD profiles. In addition, perhaps owing to short hydrogenation time, $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ was also present. Nevertheless, these results confirm the good reversibility of $\text{MgH}_2 + \text{Al} + 4\text{LiBH}_4$, and it can be regarded as a very promising hydrogen storage material.

4. Conclusion

As compared to $\text{MgH}_2 + 2\text{LiBH}_4$ and $\text{MgH}_2 + 4\text{LiBH}_4$, $\text{MgH}_2 + \text{Al} + 4\text{LiBH}_4$ showed pronounced improvement in the reversible dehydrogenation kinetics of LiBH_4 . Even in He flow, the presence of Al led to the formation of a new ternary compound, $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$, by the partial substitution of Al for Mg in the binary MgB_2 compound; this contributed to the reversible hydrogenation and dehydrogenation of $\text{MgH}_2 + 2\text{LiBH}_4$ and prohibited formation of Mg metal, which exists in $\text{MgH}_2 - \text{LiBH}_4$ mixtures showing slower dehydrogenation kinetics. HP-DSC and XRD analyses confirmed that $\text{MgH}_2 + \text{Al} + 4\text{LiBH}_4$ has good reversibility.

The dehydrogenation of $\text{MgH}_2 + \text{Al} + 4\text{LiBH}_4$ occurs in the following three steps: first, MgH_2 reacts with metallic Al to form hydrogen and Mg-Al alloys such as Mg_2Al_3 and $\text{Mg}_{17}\text{Al}_{12}$. In the second step, the Mg-Al alloys react with liquid LiBH_4 to form hydrogen, LiH and $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$. Finally, LiH reacts with excess Al or $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ to form LiAl , accompanied by hydrogen emission. Thus, the role of Al in this mixture is to suppress the formation of metallic Mg and to promote the presence of B from LiBH_4 after dehydrogenation in $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$, by formation of Mg-Al alloys that react with LiBH_4 more readily than metallic Mg and Al alone do, to form $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$.

As mentioned above, the reversible hydrogenation and dehydrogenation properties of $\text{MgH}_2 - \text{LiBH}_4$ mixtures are significantly improved by the addition of Al . However, several unknown features of $\text{MgH}_2 - \text{Al} - \text{LiBH}_4$ mixtures still remain, such as their thermodynamics. A more detailed study on this ternary material, particularly isothermal dehydriding/rehydriding studies, is needed.

Acknowledgment

A part of the present study was financially supported by “Strategic Project to Support the Formation of Research Bases at Private Universities (Support for Building a Research Base)” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) in Japan.

REFERENCES

- 1) F. Schüth, B. Bogdanović and M. Felderhoff: *Chem. Commun.* (2004) 2249.
- 2) W. Grochala and P. P. Edwards: *Chem. Rev.* **104** (2004) 1283.
- 3) S. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel and C. M. Jensen: *Chem. Rev.* **107** (2007) 4111.
- 4) A. Züttel, A. Borgschulte and S. Orimo: *Scr. Mater.* **56** (2007) 823.
- 5) A. Züttel, S. Rentsch, P. Fischer, P. Wenger, P. Sudan, P. Mauron and C. Emmenegger: *J. Alloy. Compd.* **356–357** (2003) 515.
- 6) S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, S. Towata and A. Züttel: *J. Alloy. Compd.* **404–406** (2005) 427.
- 7) O. Friedrichs, F. Buchter, A. Rorgschulte, A. Remhof, C. N. Zwicky, P. Mauron, M. Biemann and A. Züttel: *Acta Mater.* **56** (2008) 949.
- 8) Y. Filinchuk, D. Chernyshov, A. Nevidomskyy and V. Dmitriev: *Angew. Chem. Int. Ed.* **47** (2008) 529.
- 9) P. Mauron, F. Buchter, O. Friedrichs, A. Remhof, M. Biemann, C. N. Zwicky and A. Züttel: *J. Phys. Chem. B* **112** (2008) 906.
- 10) L. Mosegaard, B. Møller, J. E. Jørgensen, Y. Filinchuk, Y. Cerenius, J. C. Hanson, E. Dimasi, F. Besenbacher and T. R. Jensen: *J. Phys. Chem. C* **112** (2008) 1299.
- 11) L. Mosegaard, B. Møller, J. E. Jørgensen, U. Bösenberg, M. Dornheim, J. C. Hanson, Y. Cerenius, G. Walker, H. J. Jakobsen, F. Besenbacher and T. R. Jensen: *J. Alloy. Compd.* **446–447** (2007) 301.
- 12) R. Černý, Y. Filinchuk, H. Hagemann and K. Yvon: *Angew. Chem. Int. Ed.* **46** (2007) 5765.
- 13) J. H. Her, P. W. Stephens, Y. Gao, G. L. Soloveichik, J. Rijssenbeek, M. Andrus and J. C. Zhao: *Acta Cryst. B* **63** (2007) 561.
- 14) P. Zanella, L. Crociani, N. Masciocchi and G. Giunchi: *Inorg. Chem.* **46** (2007) 9039.
- 15) H. W. Li, K. Kikuchi, Y. Nakamori, K. Miwa, S. Towata and S. Orimo: *Scr. Mater.* **57** (2007) 679.
- 16) K. Chlopek, C. Frommen, A. Léon, O. Zabara and M. Fichtner: *J. Mater. Chem.* **17** (2007) 3496.
- 17) J. H. Kim, S. A. Jin, J. H. Shim and Y. W. Cho: *Scr. Mater.* **58** (2008) 481.
- 18) E. Rönnebro and E. H. Majzoub: *J. Phys. Chem. B* **111** (2007) 12045.
- 19) G. Barkhordarian, T. R. Jensen, S. Doppiu, U. Bösenberg, A. Borgschulte, R. Gremaud, Y. Cerenius, M. Dornheim, T. Klassen and R. Bormann: *J. Phys. Chem. C* **112** (2008) 2743.
- 20) E. Jeon and Y. W. Cho: *J. Alloy. Compd.* **422** (2006) 273.
- 21) S. Srinivasan, D. Escobar, M. Jurczyk, Y. Goswami and E. Stefanakos: *J. Alloy. Compd.* **462** (2008) 294.
- 22) H. W. Li, K. Kikuchi, Y. Nakamori, N. Ohba, K. Miwa, S. Towata and S. Orimo: *Acta Mater.* **56** (2008) 1342.
- 23) T. Matsunaga, F. Buchter, P. Mauron, M. Bielman, Y. Nakamori, S. Orimo, N. Ohba, K. Miwa, S. Towata and A. Züttel: *J. Alloy. Compd.* **459** (2008) 583.
- 24) M. D. Riktor, M. H. Sørby, K. Chlopek, M. Fichtner, F. Buchter, A. Züttel and B. C. Hauback: *J. Mater. Chem.* **17** (2007) 4939.
- 25) B. Bogdanović and M. Schwickardi: *J. Alloy. Compd.* **253–254** (1997) 1.
- 26) A. Züttel, P. Wenger, S. Rentsch, P. Sudan, P. Mauron and C. Emmenegger: *J. Power Sources* **118** (2003) 1.
- 27) M. Au and A. Jurgensen: *J. Phys. Chem. B* **110** (2006) 7062.
- 28) M. Au, A. Jurgensen and K. Zeigler: *J. Phys. Chem. B* **110** (2006) 26482.
- 29) M. Au, W. Spencer, A. Jurgensen and K. Zeigler: *J. Alloy. Compd.* **462** (2008) 303.
- 30) Y. Zhang, W. S. Zhang, M. Q. Fan, S. S. Liu, H. L. Chu, Y. H. Zhang, X. Y. Gao and L. X. Sun: *J. Phys. Chem. C* **112** (2008) 4005.
- 31) J. J. Vajo and G. L. Olson: *Scr. Mater.* **56** (2007) 829.
- 32) F. E. Pinkerton, G. P. Meisner, M. S. Meyer, M. P. Balogh and M. D. Kundrat: *J. Phys. Chem. B* **109** (2005) 6.
- 33) G. P. Meisner, M. L. Scullin, M. P. Balogh, F. E. Pinkerton and M. S. Meyer: *J. Phys. Chem. B* **110** (2006) 4186.
- 34) J. J. Vajo, S. L. Skeith and F. Mertens: *J. Phys. Chem. B* **109** (2005) 3719.
- 35) G. Barkhordarian, T. Klassen and R. Bormann: *WO 2006/063627*.
- 36) J. Yang, A. Sudik and C. Wolverton: *J. Phys. Chem. C* **111** (2007) 19134.
- 37) F. E. Pinkerton and M. S. Meyer: *J. Alloy. Compd.* **464** (2008) L1.
- 38) S. V. Alapati, J. K. Johnson and D. S. Sholl: *Phys. Chem. Chem. Phys.* **9** (2007) 1438.
- 39) S. V. Alapati, J. K. Johnson and D. S. Sholl: *J. Phys. Chem. B* **110** (2006) 8769.
- 40) A. R. Akbarzadeh, V. Ozoliņš and C. Wolverton: *Adv. Mater.* **19** (2007) 3233.
- 41) G. J. Lewis, J. W. A. Sachtler, J. J. Low, D. A. Lesch, S. A. Faheem, P. M. Dosek, L. M. Knight, L. Halloran, C. M. Jensen, J. Yang, A. Sudik, D. J. Siegel, C. Wolverton, V. Ozoliņš and S. Zhang: *J. Alloy. Compd.* **446–447** (2007) 355.
- 42) J. Yang, A. Sudik, D. J. Siegel, D. Halliday, A. Drews, R. O. Carter, III, C. Wolverton, G. J. Lewis, J. W. A. Sachtler, J. J. Low, S. A. Faheem, D. A. Lesch and V. Ozoliņš: *Angew. Chem. Int. Ed.* **47** (2008) 882.
- 43) A. Sudik, J. Yang, D. Halliday and C. Wolverton: *J. Phys. Chem. C* **112** (2008) 4384.
- 44) G. Barkhordarian, T. Klassen, M. Dornheim and R. Bormann: *J. Alloy. Compd.* **440** (2007) L18.
- 45) E. Deprez, A. Justo, T. C. Rojas, C. López-Cartés, C. Bonatto Minella, U. Bösenberg, M. Dornheim, R. Bormann and A. Fernández: *Acta Mater.* **58** (2010) 5683.
- 46) B. C. Weng, X. B. Yu, Z. Wu, Z. L. Li, T. S. Huang, N. X. Xu and J. Ni: *J. Alloy. Compd.* **503** (2010) 345.
- 47) K. Crosby, X. Wan and L. L. Shaw: *J. Power Sources* **195** (2010) 7380.
- 48) F. E. Pinkerton, M. S. Meyer, G. P. Meisner, M. P. Balogh and J. J. Vajo: *J. Phys. Chem. C* **111** (2007) 12881.
- 49) T. Nakagawa, T. Ichikawa, N. Hanada, Y. Kojima and H. Fujii: *J. Alloy. Compd.* **446–447** (2007) 306.
- 50) U. Bösenberg, S. Doppiu, L. Mosegaard, G. Barkhordarian, N. Eigen, A. Borgschulte, T. R. Jensen, Y. Cerenius, O. Gutfleisch, T. Klassen, M. Dornheim and R. Bormann: *Acta Mater.* **55** (2007) 3951.
- 51) M. Mudgel, V. P. S. Awana, H. Kishan and G. L. Bhalla: *Phys. C* **467** (2007) 31.
- 52) S. A. Jin, J. H. Shim, Y. W. Cho, K. W. Yi, O. Zabara and M. Fichtner: *Scr. Mater.* **58** (2008) 963.
- 53) X. D. Kang, P. Wang, L. P. Ma and H. M. Cheng: *Appl. Phys. A* **89** (2007) 963.
- 54) X. B. Yu, D. M. Grant and G. S. Walker: *Chem. Commun.* (2006) 3906.
- 55) J. F. Mao, Z. Wu, T. J. Chen, B. C. Weng, N. X. Xu, T. S. Huang, Z. P. Guo, H. K. Liu, D. M. Grant, G. S. Walker and X. B. Yu: *J. Phys. Chem. C* **111** (2007) 12495.