A Process for Synthesizing the Li-Mg-N-H Hydrogen Storage System from Mg and LiNH$_2$

Keisuke Okamoto[1], Kazuhiko Tokoyoda[1], *Takayuki Ichikawa[2] and Hironobu Fujii[2]

1) R&D Center, Taiheiyo Cement Corporation, 2-4-2 Osaku, Sakura 285-8655, Japan

2) Materials Science Center, N-BARD, Hiroshima University, 1-3-1 Kagamiyama,

Higashi-Hiroshima 739-8526, Japan

ABSTRACT

We successfully established a method to synthesize the Li-Mg-N-H hydrogen storage system composed of Mg(NH$_2$)$_2$ and LiH from Mg and LiNH$_2$ as starting materials. First of all, Mg and Li$_2$NH were homogeneously mixed by ball-milling for 2 h under 1 MPa argon atmosphere. After that, the mixture was heat-treated at 250 °C for 16 h under vacuum condition to be transformed into Mg$_3$N$_2$ and Li$_2$NH. Target materials, Mg(NH$_2$)$_2$ and LiH, were synthesized by a further heat-treatment for Mg$_3$N$_2$ and Li$_2$NH at 200 °C under 10 MPa hydrogen atmosphere for 12 h. The phases in the sample at each processing stage were examined by X-ray diffraction and Fourier transformation infra-red absorption measurements and confirmed to be the expected ones. From experimental results of a thermal desorption mass spectroscopy, the final hydrogenated sample indicated that ~7 mass% hydrogen was desorbed starting from about 150 °C and peaked around 230 °C under helium flow condition at 5 °C/min heating rate without ammonia emission in our experimental accuracy.

Keywords: hydrogen storage materials, mechanochemical synthesis, X-ray diffraction, thermal analysis

*corresponding author (T. Ichikawa), E-mail:tichi@hiroshima-u.ac.jp, FAX: +81-(0)82-424-5744

1. Introduction

The lease sales of the fuel-cell electric vehicles (FCEVs) were begun in the United States and Japan from a few car manufacturers in recent years. Because the fuel of the FCEVs is hydrogen and oxygen and the exhaust is only water, the spread of that vehicle is expected from the viewpoint of global environmental problems. However, these FCEVs still need some further innovations. Particularly, hydrogen storage is one of the key issues to a hydrogen economy. Because hydrogen is gaseous under standard conditions, it is difficult to store it compactly and safely. In fact, hydrogen storage systems examined so far are compressed H_2, liquefied H_2 or absorption in lightweight materials such as carbon based materials[1,2], magnesium hydride[3], sodium alanate[4] and so on.

Recently, Chen et al.[5] have reported the Li-N-H hydrogen storage system, which can absorb/desorb a large amount of hydrogen (10.4mass% in theory). This system is expressed by the following 2-step reactions;

$$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH \qquad (1)$$
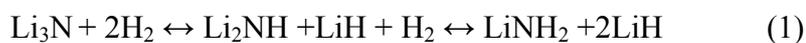
Ichikawa et al.[6] have focused on this second reaction and have reported that a large amount of hydrogen (5.5-6.0mass%) can be reversibly absorbed/desorbed at 150-250 °C for the ball-milled mixture of lithium amide ($LiNH_2$) and lithium hydride (LiH) with 1 mol% titanium chloride ($TiCl_3$) as a catalyst. This reaction is a system to be classified

into the Li-N-H system as well. Moreover, Ichikawa *et al.*[7] experimentally confirmed that this reaction contains two elementary reactions as follows,

$$2LiNH_2 \rightarrow Li_2NH + NH_3 \qquad (2)$$

$$LiH + NH_3 \rightarrow LiNH_2 + H_2 \qquad (3)$$

The reactions (2) and (3) are, respectively, the decomposition of $LiNH_2$ and the conversion from generated NH_3 and LiH to $LiNH_2$ and gaseous H_2. The reaction (2) mainly controls the second reaction of reaction (1) as the rate-determining step. Therefore, if there were some metal amide compounds that can take place the decomposition and can generate NH_3 at a lower temperature than that of $LiNH_2$, the H_2 desorption would proceed at a lower temperature by mixing with LiH as well.

Luo[8], Leng *et al.*[9], Nakamori *et al.*[10] and Xiong *et al.*[11] have independently reported the hydrogen storage characteristics in Li-Mg-N-H systems at almost the same time. This system consists of $Mg(NH_2)_2$ and LiH as the hydrogenated state. Because $Mg(NH_2)_2$ is expected to decompose at a lower temperature than $LiNH_2$ due to the larger electronegativity, this system has been considered to be able to desorb H_2 below 200 °C under a He flow atmosphere with zero partial pressure of H_2. The reaction of the Li-Mg-N-H system reported by Leng *et al.* can be described as follows;[9]

$$3Mg(NH_2)_2 + 8LiH \leftrightarrow Mg_3N_2 + 4Li_2NH + 8H_2 \qquad (4)$$
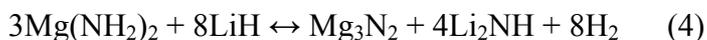
This Li-Mg-N-H hydrogen storage system is very attractive because it desorbs hydrogen below 200°C. However, $Mg(NH_2)_2$ was not commercially available. Furthermore, it is not so easy to be synthesized from MgH_2 by ball-milling MgH_2 under NH_3 atmosphere[12]. In addition, MgH_2 is commercially available, but it is so expensive. Therefore, it is quite important to establish a new method to more easily synthesize the Li-Mg-N-H system. In this work, a direct synthesis of the Li-Mg-N-H system from $LiNH_2$ and Mg, which can easily be obtained, was successfully established.

2. Experimental Section

Starting material Mg powder with 3N purity, under 180 μm grain size, was purchased from Kojundo Chemical Laboratory Co., Ltd; also starting material $LiNH_2$ with 95% purity was from Sigma-Aldrich. The samples were handled in a glovebox filled with purified argon to minimize oxidation and water adsorption by the gas recycling purification system (DBO-1NKH, Miwa Mfg. Co., Ltd).

The powder of Mg and $LiNH_2$ with 3:8 molar ratio was milled by a mechanical ball-milling method (Fritsch P-5). In the milling process, the mixed powders of 1.3 g and 60 pieces of Cr steel balls with a diameter of 10 mm were brought into a Cr steel vial with 250 ml inner volume, and milled with 250 rpm under 1 MPa argon gas at room temperature for 2 hrs, which was thought to be long enough in our milling condition.

The thermal gas desorption properties were examined by thermal desorption mass spectroscopy (TDMS, PFEIFFER, QME200) combined with thermogravimetry (TG) and differential thermal analysis (DTA) (Seiko Nano Technology Inc., TG/DTA6300) in a heating rate of 5 °C/min up to 400 °C under a highly pure helium (purity > 99.9999%) flow. TG/DTA was set up in the glovebox filled with purified argon. The TG-DTA-TDMS measurements could simultaneously be performed without any exposure of the samples to air at all.

The identification of phases in the samples was carried out by X-ray powder diffraction (XRD) with Cu-Kα radiation (Rigaku, RINT 2500), and FT-IR spectrometer (JASCO, FT/IR-6100) with Diffuse Reflection spectrum measurement cell (JASCO, DR PRO410-M), which was modified to keep Ar atmosphere in the cell without contacting the samples to air at all.

3. Results and Discussions

As described in the Introduction, we tried to synthesize the Li-Mg-N-H system with raw materials of Mg and $LiNH_2$. We assumed that the following reaction progresses by a heat-treatment for the mixed powder of Mg and $LiNH_2$ under vacuum, down to ~ 10 Pa.

$$3Mg + 8LiNH_2 \rightarrow Mg_3N_2 + 4Li_2NH + 3H_2\uparrow + 2NH_3\uparrow \quad (5)$$

If this reaction takes place under the vacuum at suitable temperature, only the mixed phase of Mg_3N_2 and $4Li_2NH$ would remain after the heat-treatment. These materials correspond to the fully dehydrogenated products of the Li-Mg-N-H system as shown in the reaction (4). As a result of the hydrogenation for the product, target materials would be expected to be generated.

First of all, we performed mechanical milling for the mixture of $3Mg$ and $8LiNH_2$ under 1 MPa Ar gas for 2 hrs at room temperature. After that, we measured TG-DTA-TDMS for this mixture to understand the thermal gas desorption properties against the programmed temperature, the result of which is shown in Fig.1. According to the DTA curve, the reaction contains two endothermic thermal reactions. Comparing with TDMS and DTA curves, it is understood that the first thermal reaction mainly consists of H_2 desorption, and the second one mainly corresponds to NH_3 generation. From these results, we decided that the heat-treatment would be done at 250 °C which was around the second peak top temperature corresponding to the ammonia desorption.

Figure 2 shows the XRD profiles at each stage in the synthesizing processes for the products after milling, heat-treatment and hydrogenation. The heat-treatment was performed at 250 °C under a vacuum condition for 16 hrs to obtain fully dehydrogenated state, and the hydrogenation was at 200 °C under 10 MPa hydrogen gas

for 12 hrs, which was the same condition as our previous report[13]. As shown in Fig.2, the raw materials of Mg and $LiNH_2$ are confirmed in the XRD profile for the product after the milling, which indicates that the materials remain their own structures even after milling. After the heat-treatment at 250 °C under the vacuum, the Li_2NH phase was assigned as the main phase. However, the Mg_3N_2 phase could not be found in this XRD profile, similar to that in the dehydrogenated product of the mixture of $3Mg(NH_2)_2$ and $8LiH$ in the previous report[14]. The reason is because the Mg_3N_2 phase produced after gas desorptions by heat treatment at 250 °C is composed of a nano-crystalline or an amorphous structure phases irrespective of difference in the starting materials. In addition, we can find an unknown peak around 18°, which was thought to be a part of the peaks corresponding to the $Li_2Mg(NH)_2$ phase as mentioned in Xiong et al.'s report[11]. With respect to the profile after hydrogenation, the target products, $Mg(NH_2)_2$ and LiH, were successfully identified in the XRD profile, indicating the establishment of a new method to synthesize the Li-Mg-N-H system.

In order to identify whether the products after the heat-treatment for releasing gases and the successive hydrogenation are expected ones or not, we have examined those samples by FT-IR spectroscopy. Figure 3 shows the FT-IR profiles of the products after heat-treatment and further hydrogenation, in which the x-axis of the profile specially

takes an enlarged light wave in the range from 2850 to 3650 cm^{-1}. For the product after the heat-treatment at 250 °C, only Li$_2$NH is recognized in the profiles, indicating that the Li$_2$Mg(NH)$_2$ phase mentioned above doesn't exist as a main phase. These results are almost consistent with the results of the XRD experiment.

It is quite interesting to examine the hydrogen storage properties of the product synthesized by this method. The hydrogen desorption properties of the hydrogenated product in this work were measured by the TG/DTA and TDMS experiments which is shown in Figure 4. The results indicated that a large amount of hydrogen starts to be desorbed from about 150 °C and takes a peak around 230 °C under a helium flow condition at a 5 °C/min heating rate. Total weight loss reached about 8 mass% by heating up to 400 °C, which was chiefly due to the release of hydrogen and ammonia gases. However, the ammonia gas was really below the detection limit in our experiments, indicating that the ammonia was difficult to be detected. Moreover, it should be noted that the hydrogen desorption profile is quite similar to that of the ballmilled mixture of 8LiH and 3Mg(NH$_2$)$_2$ reported in the previous paper[9].

4. Conclusion

We have developed a new method for synthesizing the Li-Mg-N-H hydrogen storage system. Because the starting materials of LiNH$_2$ and Mg are easy to be commercially

obtained, this method should be of great advantage compared with other methods. The final hydrogenated product composed of $Mg(NH_2)_2$ and LiH could be synthesized by the following two steps. Firstly, the ballmilled mixture of 3Mg and $8LiNH_2$ is heat-treated at 250°C under vacuum condition, which leads to the generation of the mixed phase composed of mainly Li_2NH and nano- or amorphous-structured Mg_3N_2. Secondly, this dehydrogenated product is hydrogenated at 200 °C under 10MPa hydrogen gas. As a result, the desired mixture of $3Mg(NH_2)_2$ and 8LiH could be synthesized as expected. The hydrogen desorption properties were quite similar to those of the direct ballmilled mixture of $3Mg(NH_2)_2$ and 8LiH as the starting materials.

Acknowledgement

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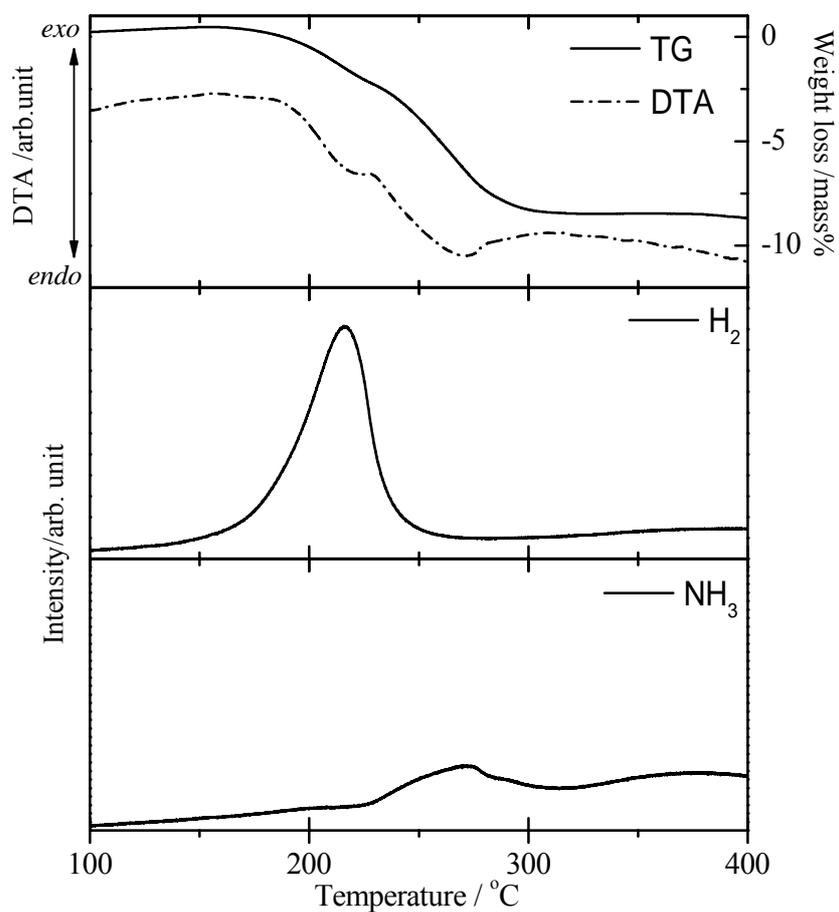
Figure 1. TG/DTA(upper), H_2 TDMS(middle), NH_3 TDMS(lower) profiles of the mixture of 3Mg and $8LiNH_2$ prepared by ball-milling. The examinations were performed under a purified He flow and a 5 °C/min heating rate.
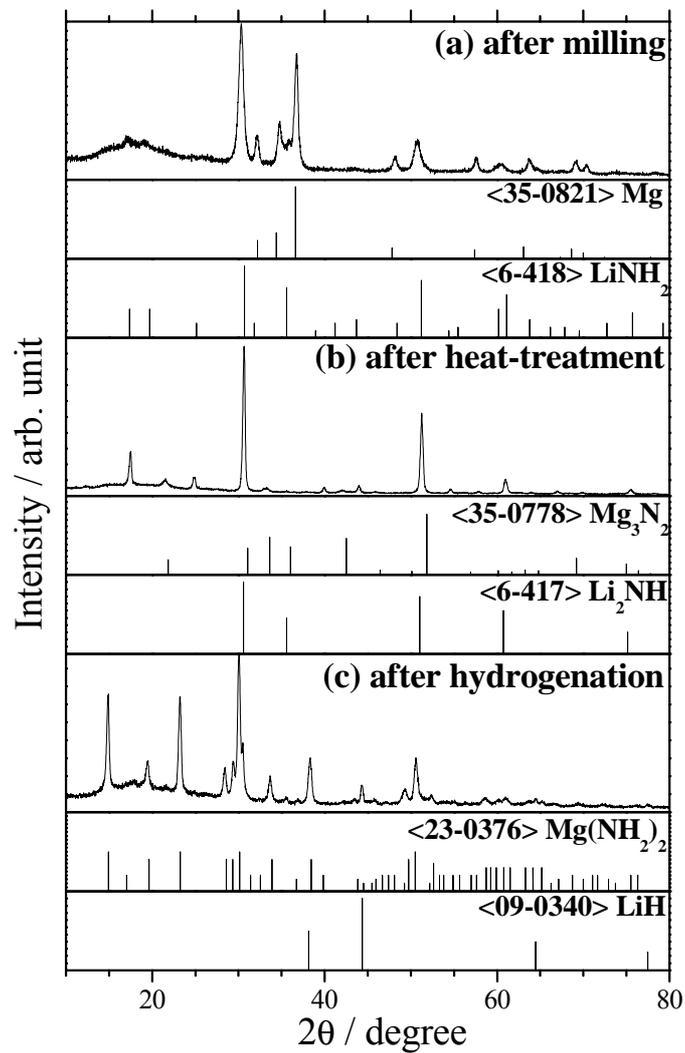
Figure 2. XRD patterns at each processing stage for the products after (a) milling for 2 h, (b) heat treatment at 250 °C under a vacuum for 16 h, and (c) hydrogenation at 200 °C under 10 MPa H₂ gas.
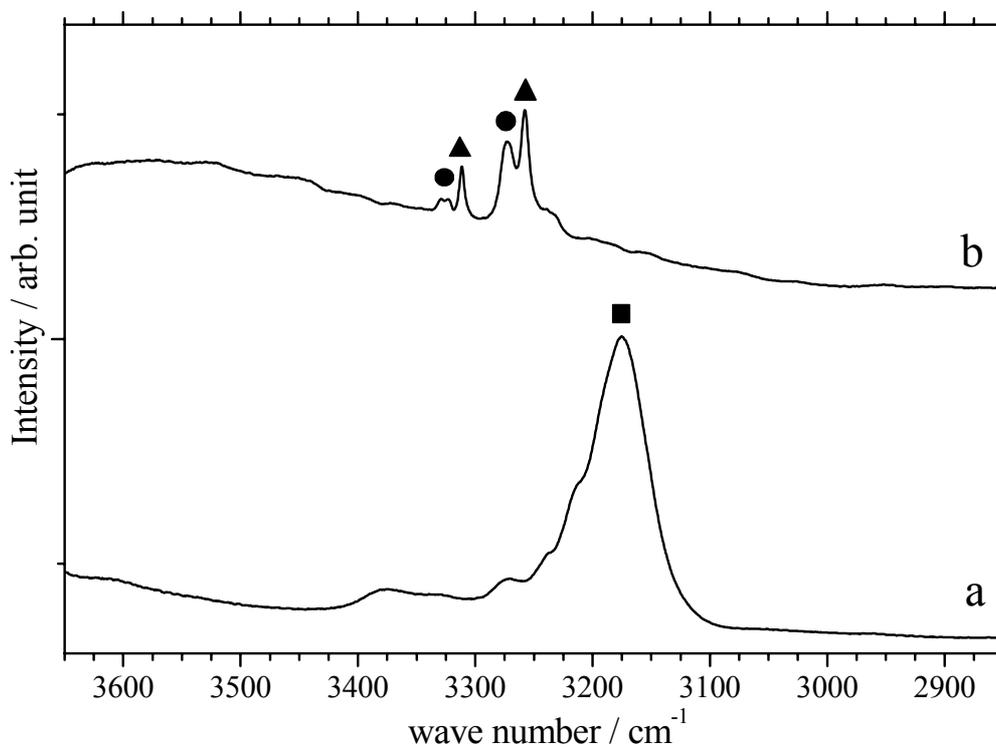
Figure 3. FT-IR profiles in the range of 2850–3650 cm^{-1} for the mixture of 3Mg and 8LiNH$_2$ prepared by ball-milling. (a) after heat-treatment at 250 °C, (b) after hydrogenation at 200 °C under 10 MPa H$_2$. Peaks marked with ■ (3177 cm^{-1}) correspond to Li$_2$NH, ▲(3260 cm^{-1} and 3313 cm^{-1}) correspond to LiNH$_2$, ●(3275cm^{-1} and 3327 cm^{-1}) indicate Mg(NH$_2$)$_2$.
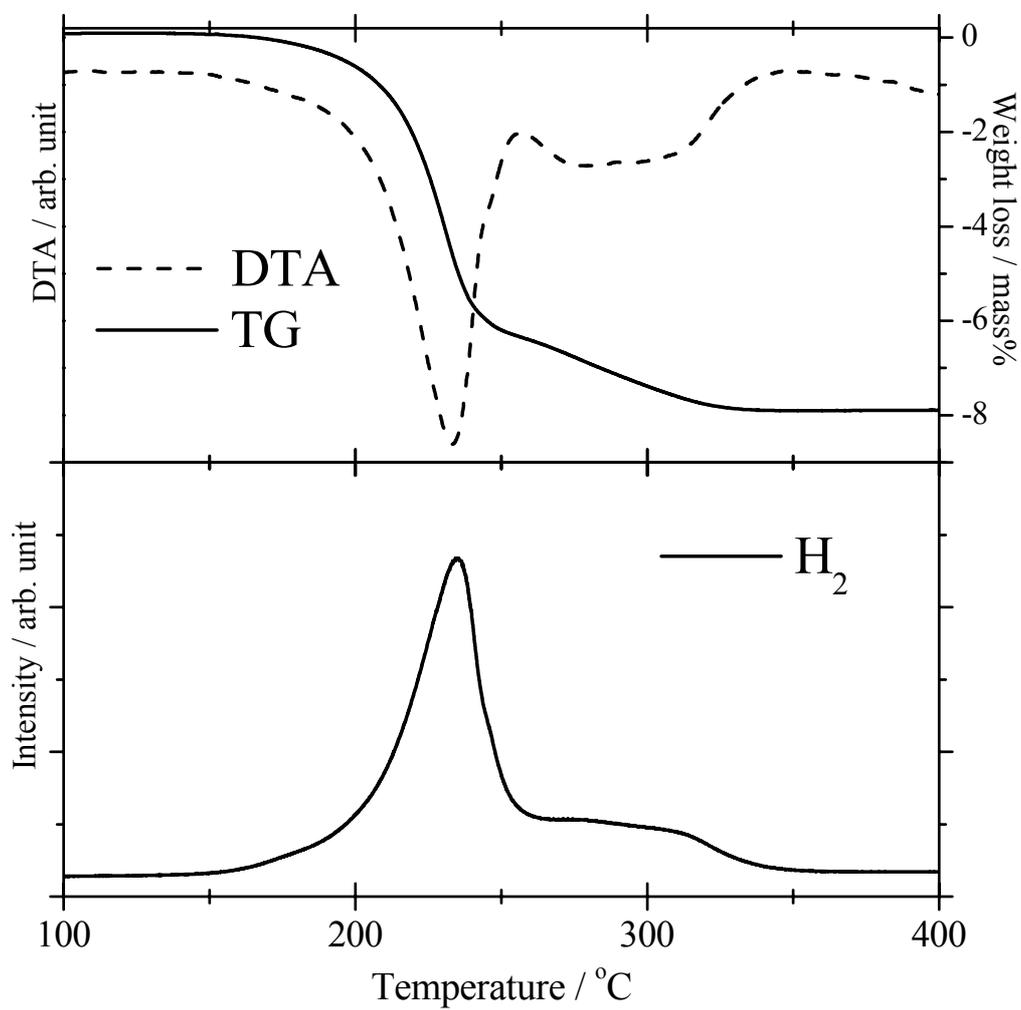
Figure 4. TG/DTA (upper) and TDMS (lower) profiles of the Li-Mg-N-H hydrogen storage system synthesized from $3Mg-8LiNH_2$ products.