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Synthesis of Mg-based composite material with *in-situ* formed LaH₃ and its hydrogen storage characteristics[☆]

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ABSTRACT

In this work, a Mg-based composite material with *in-situ* formed LaH₃, Mg₂NiH₄-LiBH₄ + 20 wt% LaH₃, was prepared by ball milling LiBH₄ and hydrogenated LaMg₂Ni and Mg₂Ni powder mixture, followed by heat treatment at 573 K. The onset dehydrogenation temperature of the composite is reduced by 50 K compared with that of Mg₂NiH₄-LiBH₄. The LaH₃-doped composite shows faster kinetics, absorbing 1.43 wt% hydrogen within 100 s at 423 K, which is 6.5 times faster than Mg₂NiH₄-LiBH₄. Moreover, the composite releases 1.24 wt% hydrogen within 500 s at 573 K, 0.69 wt% higher than Mg₂NiH₄-LiBH₄. The activation energy of the composite is reduced by 8.2 and 80 kJ/mol compared with that of Mg₂NiH₄-LiBH₄ and commercial MgH₂, respectively. The improvement in hydrogen storage properties is attributed to the fact that LaH₃ promotes the generation of nano-sized spongy Mg structure, which has good catalytic activity during the subsequent hydrogenation/dehydrogenation process.

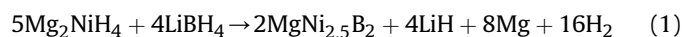
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1. Introduction

Hydrogen is considered to be a very promising energy carrier due to its high combustion heat and clean burning. Hydrogen storage, especially a high capacity storage under moderate conditions, is the key for utilization of hydrogen energy. Thus, it is important to develop a material which is able to absorb/desorb hydrogen efficiently. Among different kinds of materials, metal/intermetallic hydride storage materials are considered as promising candidates.^{1–4} Magnesium is widely investigated for on-board hydrogen storage, especially for vehicular applications, due to its high hydrogen storage capacity (up to 7.6 wt%), light weight and low cost.^{5,6} However, the sluggish hydrogen absorbing/desorbing kinetics and high hydride stability prevent practical applications of Mg-based hydrogen storage materials. To improve the kinetics and destabilize Mg hydride, various metals

have been used to form alloys with Mg.^{7–10} Among these alloys, Mg₂Ni has been considered a potential choice for hydrogen storage applications because of its lower hydriding/dehydriding temperature around 573 K^{11–13} and high hydrogen storage capacity of 3.6 wt%.¹⁴ For further improvement in hydrogen storage ability of Mg₂Ni, partial or complete substitution of nickel by other suitable elements has been attempted. Substitution with Co¹⁵ and Cu¹⁶ has been carried out on Mg₂Ni alloy, and it was found that the presence of Co and Cu weakened the interactions between magnesium and nickel, as well as interactions between nickel and hydrogen. Consequently, the alloy was destabilized and the materials showed a remarkable decrease of the onset dehydrogenation temperature.

Rare earth elements have been doped into Mg₂Ni alloy as hydrogen absorbing elements and found to be effective in improving hydrogen storage properties due to their role as reactive destabilizer.^{17,18} The addition of La into Mg₂Ni alloy created a new ternary Mg-based compound, LaMg₂Ni,^{19–21} which showed significant improvement in its dehydriding properties at low temperature. Previous reports have shown that LiBH₄ and Mg₂NiH₄ undergo the following reaction (1), providing an easy dehydrogenation process.



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The decomposition products were identified as LiH, Mg, $\text{MgNi}_{2.5}\text{B}_2$, and H_2 . The dehydrogenation reaction of the composite began at 550 K, which was a lower onset dehydrogenation temperature compared with that of Mg_2NiH_4 . Moreover, the hydrogenation/dehydrogenation rate of the composite was faster than that of Mg_2NiH_4 . This improvement makes the composite a potential candidate as a hydrogen storage material.

In our previous work, LaH_3 was demonstrated to be effective in catalyzing the dehydrogenation of Mg-based alloys by expanding/contracting the lattices.^{22,23} Here, we have prepared a Mg-based composite material, $\text{Mg}_2\text{NiH}_4\text{-LiBH}_4 + 20 \text{ wt\% LaH}_3$, by a solid state reaction in which LaH_3 is formed *in-situ* in the system. Subsequently, the microstructures and reversible hydrogen storage properties of the $\text{Mg}_2\text{NiH}_4\text{-LiBH}_4/\text{LaH}_3$ composite were investigated.

2. Experimental

Commercial LiBH_4 (95%, Alfa Aesar) powder was used as-received. The Mg_2Ni and LaMg_2Ni alloys were prepared by induction melting of the components, metallic La, Mg and Ni (99.9% purity) under protection of highly pure argon atmosphere (99.9% purity). The as-cast Mg_2Ni and LaMg_2Ni alloys were mechanically crushed into 100 mesh powders. A mixture of Mg_2Ni (2.417 g) and LaMg_2Ni (1.000 g) alloys was then hydrogenated under 3 MPa hydrogen pressure at 673 K for 8 h to ensure complete transformation into Mg_2NiH_4 and LaH_3 (*in-situ* reaction). The mixture of LiBH_4 (0.27 g)/ $\text{Mg}_2\text{NiH}_4\text{-LaH}_3$ (2.13 g) hydride system was prepared by ball-milling the as-received LiBH_4 powder and as-prepared Mg_2NiH_4 powder in a molar ratio of 4:5, and the weight percentage of LaH_3 was 20 wt% of the total material weight. The ball-milling process was performed in a stainless steel vial with a ball-to-powder weight ratio of 20:1 using a QM-ISP2 planetary mill at 500 r/min for 2 h. The composite was then heated to 573 K for 2 h under a dynamic vacuum environment to generate Mg. To avoid air-exposure, all handlings were carried out in an Ar-filled glove box equipped with a purification system, in which the typical $\text{O}_2/\text{H}_2\text{O}$ levels were below 1 ppm.

The curves of hydrogen absorption/desorption quantity of the samples were measured on a pressure-composition-temperature characteristic measurement equipment. The temperature programmed desorption (TPD) properties were determined by heating the sample from ambient temperature to 500 °C at a heating rate of 5 °C/min under a hydrogen back pressure below 0.0001 MPa. Before the TPD measurement, the composite was placed under vacuum for 10 min to remove hydrogen atoms physically adsorbed onto the composite surface. For the hydrogen absorption/desorption tests, the composite was firstly dehydrogenated at 623 K for 2 h to get completely dehydrogenated species. The phase composition of the samples was characterized by X-ray diffraction (XRD, D/MAX-2500/PC, Cu K α radiation). The hydrogen thermodynamic performance was studied by a simultaneous thermal analyzer (DTG-60A) under an Ar flow rate of 100 mL/min from the room temperature to 773 K with the heating rates of 5, 10, 15 and 20 K/min, respectively.

3. Results and discussion

3.1. Hydrogenation characteristics and morphology of LaMg_2Ni and Mg_2Ni alloys

Fig. 1 presents the XRD patterns of the fully hydrogenated $\text{LaMg}_2\text{Ni-Mg}_2\text{Ni}$ mixture. In the patterns, only diffraction peaks corresponding to Mg_2NiH_4 phase and LaH_3 phase are observed. It

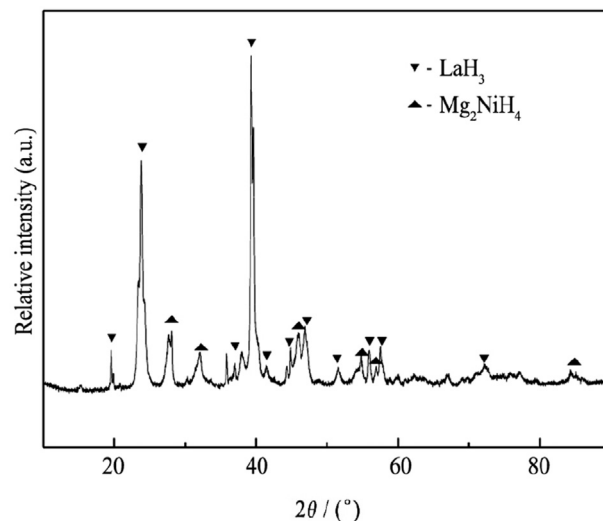


Fig. 1. XRD patterns of the LaMg_2Ni and Mg_2Ni alloys hydride.

indicates that the following reactions (2) and (3) occur during the hydrogenation process.



In the hydrogenated samples, no $\text{LaMg}_2\text{NiH}_7$ phase is detected. It has been suggested by Renaudin et al.²⁴ that reaction of LaMg_2Ni in hydrogen atmosphere is generally affected by temperature, and the compound LaMg_2Ni will decompose into LaH_3 and an amorphous phase when the temperature is higher than 573 K. The phase transformation here is similar to that reported by Ouyang et al.²⁵

Through the above solid-state reaction of LaMg_2Ni in hydrogen atmosphere, a composite consisting of Mg_2NiH_4 and LaH_3 can be obtained. However, LaH_3 is a stable hydride and it is difficult to release hydrogen from this hydride. Therefore, too much LaH_3 hydride will lead to a low reversible capacity for the system. Thus, the ratio of Mg_2Ni to LaMg_2Ni was adjusted to obtain a composite with an appropriate amount of LaH_3 , and LiBH_4 was added to achieve a high capacity and reversible hydrogen absorbing/desorbing system by accomplishing reaction (1) according to a previous report.²⁶ Fig. 2 presents the decomposition behaviors of $\text{Mg}_2\text{NiH}_4\text{-LiBH}_4$ composite and $\text{Mg}_2\text{NiH}_4\text{-LaMg}_2\text{Ni-LiBH}_4$ composite. The amount of hydrogen evolution as a function of temperature was examined using a PCT apparatus. According to Fig. 2, the onset decomposition temperature of the $\text{Mg}_2\text{NiH}_4\text{-LaMg}_2\text{Ni-LiBH}_4$ composite decreases to 500 K, which is 50 K lower than that of the $\text{Mg}_2\text{NiH}_4\text{-LiBH}_4$ composite. The results indicate that the *in-situ* formed LaH_3 facilitates the hydrogen desorption process of $\text{Mg}_2\text{NiH}_4\text{-LiBH}_4$ system at a relatively low temperature (see Fig. 3).

To reveal the phase structure of the LaH_3 -containing composite and the mechanism of effect of LaH_3 in the hydrogenation/dehydrogenation process, different hydrogenation state species were collected, including as-milled powders, hydrogenated powders and dehydrogenated powders, and characterized by XRD analysis. XRD results show that the as-milled powders consist of Mg_2NiH_4 phase and LaH_3 phase, with no detection of any new phases, indicating that no chemical reactions occurred upon ball milling. Moreover, the diffraction peaks of LiBH_4 are not observed, which can be ascribed to its fine grain and amorphous nature after the ball milling treatment.²⁷ After ball milling, the species was subjected to dehydrogenation at 623 K, and the XRD patterns for the

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