Effect of CeH$_{2.29}$ on the microstructures and hydrogen properties of LiBH$_4$–Mg$_2$NiH$_4$ composites

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Abstract: A composite of LiBH$_4$–Mg$_2$NiH$_4$ doped with 10wt% CeH$_{2.29}$ was prepared by ball milling followed by dynamic interspace vacuum treatment at 573 K. The introduction of CeH$_{2.29}$ caused a transformation in the morphology of Mg from complex spongy and lamellar to uniformly spongy, resulting in refined particle size and abundant H diffusion pathways. This LiBH$_4$–Mg$_2$NiH$_4$ + 10wt% CeH$_{2.29}$ composite exhibited excellent hydrogen storage properties. The starting temperature of rapid H absorption decreased to 375 K in the doped composite from 452 K for the unmodified material, and the onset decomposition temperature of its hydride was reduced from 536 K to 517 K. In addition, the time required for a hydrogen release of 1.5wt% (at 598 K) was 87 s less than that of the un-doped composite.

Keywords: hydrogen storage materials; cerium hydride; mechanical alloying; microstructure

1. Introduction

The challenges of global warming and finite fossil fuel resources have made hydrogen a promising alternative energy source. Hence novel approaches have been focused on metal/intermetallic hydride storage materials. Magnesium is considered as a promising hydrogen storage material for onboard hydrogen storage, especially for vehicular application due to its high hydrogen storage capacity (up to 7.6wt%), light weight and low cost [1]. Nevertheless, its relatively slow hydrogen absorption-desorption kinetic properties and high thermodynamic stability are still key obstacles preventing its practical application [2]. To move this technology forward, researchers have developed several preparation methods such as high-energy ball milling [3], hydriding combustion synthesis (HCS) [4], and arc plasma methods [5]. The grain sizes of MgH$_2$ ball milled for up to several hours are known to be reduced to nanometer dimensions ranging from 10 to 30 nm [6–8]. As a result, the H-sorption kinetics is substantially accelerated, and the hydrogen desorption temperature is decreased by about 100 K [9]. Since HCS was first developed for the synthesis of Mg$_2$Ni hydride, it has been also applied to prepare some other Mg-based hydrogen storage materials such as Mg–Ni–Cu alloys [10], Mg–Ni–Fe [11] alloys, and Mg–30wt%LaNi$_5$ composites [12], which presented significantly improved hydrogenation kinetic properties compared to pure MgH$_2$ powder. Moreover, rare earth elements have also been shown to have positive effects on the hydrogen storage properties of Mg [13]. Long et al. [14] reported that an Mg–Ce nanocomposite prepared by arc plasma could absorb 4.07wt% hydrogen at 323 K. The above improvements in hydrogen storage properties generally result from the refined grain size and increased interface between the Mg matrix and additives caused by different preparation methods.

Recently, a new reversible solid-phase reaction involving LiBH$_4$–Mg$_2$NiH$_4$ composite was reported [15]. The decomposition products from the original reactants were identified as LiH, MgH$_2$, MgNi$_{2.5}$B$_2$, and H$_2$. Moreover, the dehydrogenation reaction began at 523 K, which was lower than that of the single LiBH$_4$ or Mg$_2$NiH$_4$. This improvement makes the composite a potential candidate as a hydro-
gen storage material. In order to further improve the hydrogen storage properties of the LiBH$_4$–Mg$_2$NiH$_4$ composite, Ce hydride was chosen as an additive to accelerate the hydrogen storage kinetics of the composite. The phase transformations and microstructures have been investigated in detail as well as the hydrogen absorption/desorption properties.

2. Experimental

The original Mg$_2$Ni alloy was prepared by induction melting under the protection of pure argon atmosphere using Mg and Ni ingots (99.9% pure) [16]. The Mg$_2$Ni alloys were then hydrogenated under a hydrogen pressure of 5 MPa at 673 K for 3 h to ensure complete transformation with respect to Mg$_2$NiH$_4$. LiBH$_4$ powder was purchased from Alfa Aesar, and the CeH$_{2.29}$ powder was prepared by hydrogenating Ce metal under a hydrogen pressure of 10 MPa at 773 K. A hydride mixture was prepared by mixing the as-received LiBH$_4$ and Mg$_2$NiH$_4$ powders in a mole ratio of 4:5. The mixture was mechanically ball-milled in a stainless steel vial with a ball-to-powder weight ratio of 10:1 using an SPEX 8000 ball milling machine at a speed of 1000 r/min for 2 h. The composite was then heated to 573 K for 2 h under a dynamic interspace vacuum environment to generate Mg. For comparison, a LiBH$_4$–Mg$_2$NiH$_4$ + 10wt% CeH$_{2.29}$ composite was prepared by the same ball milling process. In the CeH$_{2.29}$-doped composite, the molar ratio of LiBH$_4$ and Mg$_2$NiH$_4$ remained unchanged, and the percentage of CeH$_{2.29}$ was 10wt%. All handing procedures in this work were performed in a glove box filled with purified nitrogen (the concentrations of both oxygen and water were less than 1 × 10$^{-6}$) in order to minimize sample contamination.

The hydrogen absorption/desorption properties were measured on a pressure–composition–isotherm (PCI) automatically controlled device (manufactured by Suzuki Shokan in Japan). The temperature programmed desorption (TPD) properties were measured by the PCI device, which was equipped with a homemade programmed heater at a heating rate of 2°/min. In the TPD test, samples were first vacuumed for 10 min to avoid effects of physically absorbed H. Before measurements were performed, each sample was dehydrogenated for 2 h at 623 K and then went through one hydrogen absorption/desorption cycle to be activated. The microstructure was determined via X-ray diffraction (XRD) with Cu K$_{a}$ radiation and scanning electron microscopy (SEM; HITACHI S3400N). In addition, a high-resolution scanning transmission electron microscope (Cs-corrected STEM; Hitachi H–800) equipped with scanning electron (SE)/bright field (BF)/dark field (DF) was used with an accelerating voltage of 200 kV. The hydrogenated samples were processed in a 3-MPa hydrogen atmosphere at 573 K. The dehydrogenated samples were decomposed in a 0.001-MPa hydrogen atmosphere at 573 K. All the hydrogenated/dehydrogenated samples were collected after hydrogenation characteristic tests.

3. Results and discussion

The XRD patterns in Fig. 1 show the phase transition of the LiBH$_4$–Mg$_2$NiH$_4$ composite under different hydrogenation conditions. The XRD pattern of the ball-milled composite shows the obvious broad peaks of Mg$_2$NiH$_4$. It is worth mentioning that the Mg$_2$NiH$_4$ and LiBH$_4$ mixture was only ground and smashed without chemical reaction during the mechanical ball-milling process. This causes the absence of the LiBH$_4$ diffraction peaks due to their significant grain refinement and amorphous tendency. After the thermal treatment process at 598 K in a dynamic interspace vacuum environment, the Mg$_2$NiH$_4$ phase disappears accompanied by the appearance of Mg and MgNi$_{2.5}$B$_2$ phases (Fig. 1(c)). This transformation is attributed to the reaction between Mg$_2$NiH$_4$ and LiBH$_4$, consistent with the results reported by Vajo et al. [15]. In the present study, the reaction can be described by reaction (1):

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4\text{LiBH}_4 + 5\text{Mg}_2\text{NiH}_4 \xrightarrow{573 \text{K}} 2\text{MgNi}_{2.5}\text{B}_2 + 4\text{LiH} + 8\text{Mg} + 16\text{H}_2
$$

The existence of undecomposed LiH is mainly due to its high thermal stability; its decomposition temperature is over 973 K [17]. The amount of LiH generated by reaction (1) is close to the detection limit of the XRD technique, therefore,