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Short communication

Effect of La_2O_3-CaO composite additive on the hydrogen storage properties of Mg_2Ni alloy

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ABSTRACT

La_2O_3-CaO composite additive is employed to accelerate the hydrogen absorption/desorption rate of the Mg_2Ni alloy. The composite additive was ball milled with Mg_2Ni hydride to produce Mg_2Ni–5 wt.% La_2O_3–5 wt.% CaO composite. The composite additive significantly reduces the thermal stability of Mg_2NiH_4. The onset decomposition temperature of the hydrogenated composite is 470 K, 21 K lower than that of the pure Mg_2NiH_4. Meanwhile, the composite presents accelerated hydriding/dehydriding kinetic properties. It absorbs 1.61 wt.% H at 373 K in 2 h and releases 2.44 wt.% H at 573 K in 1200 s, while the absorbed and desorbed hydrogen by the Mg_2NiH_4 is only 0.78 wt.% H and 1.32 wt.% H, respectively. The improvement in the hydrogen storage properties of the Mg_2Ni alloy by the adoption of La_2O_3-CaO additive is ascribed to the modified catalytic effects of La_2O_3 and CaO in the composite.

1. Introduction

Since the hydrogen storage property of Mg_2Ni alloy was first presented by Reilly in 1968 [1], it has been extensively investigated by researches due to its relatively large hydrogen capacity, light weight and low cost [2–4]. In the past decades, with the development of the full cell technology, Mg_2Ni hydride is considered as a potential H carrier in full cell system. However, relative high thermal stability and poor hydrogen desorption kinetic property restrict its applications. To overcome the defects, mechanical milling (MM) is employed to decrease the particle size and increase the active surfaces of the powder [5,6]. The modifications brought by MM result in dramatic improvements in the hydriding/dehydriding kinetics of the samples.

Moreover, additional improvement in the hydrogen storage performances of the Mg_2Ni is also observed upon the introduction of catalytic additives. It was found that small amount of Pd catalyst could enhance the hydrogen absorption/desorption kinetics of Mg_2Ni at 200 °C. Moreover, nanocrystalline Pd doped Mg_2Ni absorbed hydrogen even at room temperature without activation, and with relatively good kinetics [7]. Additionally, the nanocrystalline $Mg_{1.9}Ti_{0.1}Ni$ showed better kinetics compared to the nanocrystalline Mg_2Ni, with more than 3 wt.% H_2 absorbed in 2000 s at 423 K and also destabilizes the hydride [8]. Grigorova et al. [9] reported that 90% Mg_2Ni + 10% V composite showed positive effect on the hydrogenation/dehydrogenation kinetics and hydrogen absorption capacity as compared with those of the pure Mg_2Ni. Ru [10], Zr [11], Cu [12], Cr [13] etc. have also been proved to have catalytic effect on the development of the hydrogen storage properties of Mg_2Ni. Also, rare earth elements like Y, Ce, La and Nd were reported to improve the reversible hydriding/dehydriding process of the Mg_2Ni alloy [14]. Zhao et al. [15] showed that the Mg_2Ni–20 wt.% $LaMg_2Ni$ hydride composite exhibited complete reversible dehydrogenation of over 3 wt.% H_2 at 473 K. The improvement was ascribed to the existence of La hydride. Moreover, a composite additive named LaH_3-TiH_2 was introduced into Mg_2Ni alloy to ameliorate its hydrogen storage properties [16]. It was reported that the interactions between the components of the additive could accelerate their hydrogenation/dehydrogenation rate. Additionally, metal oxides also present remarkable catalytic effects on improving hydrogen kinetic properties of Mg-Ni based alloys. Fe_2O_3 [17] and Nb_2O_5 [18] were found to have positive effects on the hydrogenation/dehydrogenation kinetic properties of Mg-Ni based alloys. However, the improvements on the thermodynamic properties of the Mg-Ni based alloys has been rarely reported.

In previous investigations, CaO has hardly been applied for the improvement of the hydrogen storage properties of Mg-based alloys. La_2O_3 [19] was proved to have accelerating effect on the hydriding/dehydriding rate of Mg-Ni based alloys, but its effect on the thermodynamic properties was not reported. Herein, La_2O_3-CaO are employed as a composite additive to prepare Mg_2Ni–5 wt.%

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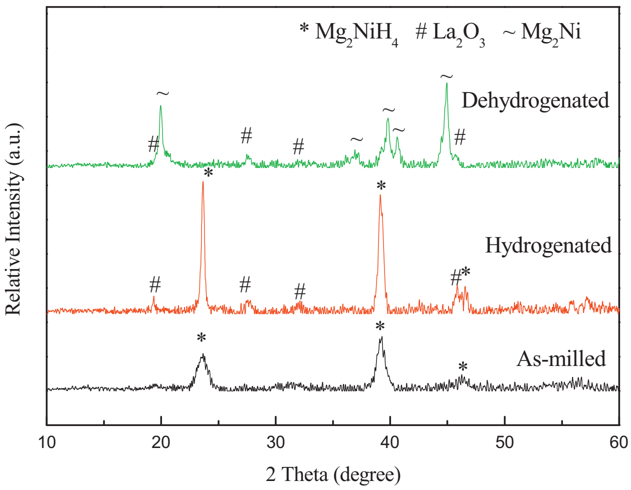

Fig. 1. XRD patterns of ball milled and hydrogenated/dehydrogenated Mg_2Ni–5 wt.% La_2O_3–5 wt.% CaO composites.

La_2O_3–5 wt.% CaO composite by ball milling. The structure, morphology and hydrogen storage properties of the composite are explored.

2. Experimental

The powder of La_2O_3 and CaO (99% purity, mean grain size of 50 μm) were purchased from Aladdin. Powders of La_2O_3 and CaO were mixed together at a 1:1 weight ratio and subsequently ball milled for 3 h to produce La_2O_3-CaO composite additive. The ball milling process was performed in a 65 ml vial using a SPEX 8000 ball milling machine with ball (10 mm in diameter)-to-powder ratio of 10:1 at 1000 rpm. The original Mg_2Ni hydride matrix was obtained from hydrogenated Mg_2Ni powder, which produced by inductive melting and air crushed [15], under a 5 MPa hydrogen atmosphere at 673 K for 3 h. The Mg_2Ni hydride and La_2O_3-CaO composite additive were ball milled at a 9:0.5:0.5 weight ratio to obtain the Mg_2Ni–5 wt.% La_2O_3–5 wt.% CaO composite. The duration of the ball milling treatment was 2 h, and the ball-to-powder ratio was 10:1 at 1000 rpm. For comparison, Mg_2Ni–10 wt.% CaO and Mg_2Ni–10 wt.% La_2O_3 composites and pure Mg_2Ni alloy were also produced under the same conditions. All handing of the powders were performed in a glove box under purified argon atmosphere (with concentrations of both oxygen and water at less than 1 ppm).

The hydrogen storage 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 with the PCI device, which was equipped with a homemade programmed heater, and the heating rate was 2°/min. Before the measurements, each sample was dehydrogenated for 2 h at 623 K, and then went through one hydrogen absorption/desorption cycle at 573 K to activate the sample. The microstructure was determined via X-ray diffraction (XRD) with Cu Kα radiation and scanning electron microscope (SEM) (HITACHI S3400N).

3. Results and discussion

Fig. 1 shows XRD patterns of as-milled and hydrogenated/dehydrogenated Mg_2Ni–5 wt.% La_2O_3–5 wt.% CaO composites. The as-milled composite presents considerably broad peaks at 23.5°, 39.2° and 46.3°, all of which belong to Mg_2NiH_4 phase. The broad diffraction peaks were resulted from the ball milling process during which the particles were ground and deformed, leading to the increase of amorphization. For both the hydrogenated and dehydrogenated composites, the La_2O_3 phase remains without transformation while CaO phase disappears. There are some tiny peaks in the patterns, which belong to the strong background of diffraction. This is caused by the amorphization for as-milled sample and the crystal pulverization of the sample in hydrogen absorb/desorb processes.

However, CaO is clearly observed in Mg_2Ni–10 wt.% CaO composite (Fig. 2). In the above two composites, Mg_2Ni phase transforms to Mg_2NiH_4 phase in the hydrogenation process and reversely decomposes into Mg_2Ni and H_2 in the dehydrogenation process. The XRD patterns of Mg_2Ni–10 wt.% La_2O_3 composite (Fig. 3) present the stable La_2O_3 phase in hydrogen absorb/desorb processes of the composite. The diffraction intensity of La_2O_3 peaks in Fig. 3 are higher than that in Fig. 1, which is caused by the different content of La_2O_3 in the composites. The peaks of Mg_2Ni phase and those of its hydride phase become sharper and higher, which indicates that the crystalline structure of the Mg_2Ni phase is refined in the hydrogenation cycles.

Table 1 shows the cell parameters of the Mg_2Ni phase in the composite and those of the pure Mg_2Ni phase. A slight expansion in cell volume of the Mg_2Ni phase in the composite is detected,

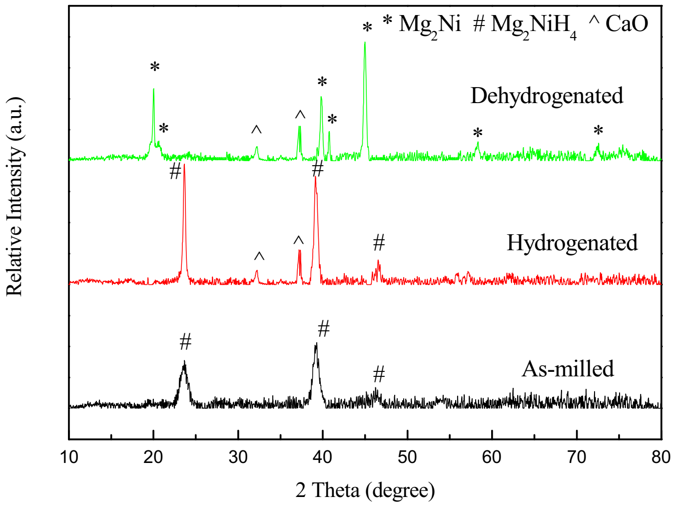

Fig. 2. XRD patterns of as-milled and hydrogenated/dehydrogenated Mg_2Ni–10 wt.% CaO composites.

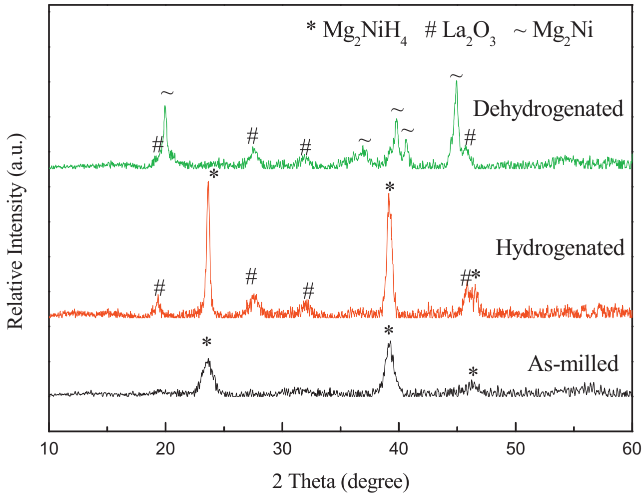

Fig. 3. XRD patterns of as-milled and hydrogenated/dehydrogenated Mg_2Ni–10 wt.% La_2O_3 composites.