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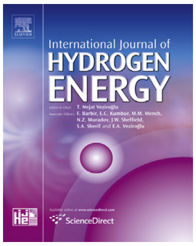

Investigations on AB_3-, A_2B_7- and A_5B_{19}-type La–Y–Ni system hydrogen storage alloys

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ABSTRACT

The structure and properties of new La–Y–Ni system alloys with high hydrogen-storing capacity were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM), solid-H_2 reactions (*P-C-I* curves) and electrochemical measurements. The $LaY_2Ni_{8.2}Mn_{0.5}Al_{0.3}$ (AB_3-type), $LaY_2Ni_{9.7}Mn_{0.5}Al_{0.3}$ (A_2B_7-type) and $LaY_2Ni_{10.6}Mn_{0.5}Al_{0.3}$ (A_5B_{19}-type) hydrogen storage alloys were prepared with the induction-melting rapid-quenching method and annealed at 1148 K for 16 h. The La–Y–Ni–Mn–Al alloys were also compared with commercial AB_5-type hydrogen storage alloy with high capacity. Similarly to La–Mg–Ni system hydrogen storage alloy, La–Y–Ni system alloys are multiphase structures and Y element in the La–Y–Ni alloys avoid or delay the hydrogen-induced amorphous (HIA) of the alloys in the hydrogenation/dehydrogenization process. The hydrogen storage capacities of the A_2B_7- and A_5B_{19}-type alloys at 313 K are 1.48 wt.% and 1.45 wt.%, respectively, which are larger than that of the AB_5-type alloy (1.38 wt.%). The maximum discharge capacities of the A_2B_7- and A_5B_{19}-type alloy electrodes at 298 K are 385.7 mAh g^{-1} and 362.1 mAh g^{-1}, respectively, which are larger than that of the AB_5-type alloy (356.1 mAh g^{-1}). The maximum discharge capacity of the A_2B_7-type alloy exceeds the theoretical capacity (372 mAh g^{-1}) of the AB_5-type alloy. The A_2B_7- and A_5B_{19}-type alloy electrodes have better cycling ability than the AB_5-type alloy.

Introduction

Hydrogen storage is one of the key technologies for hydrogen energy appliance which provides an ideal solution for the dwindling global energy crisis and ever-increasing environmental pollution [1]. Rare earth hydrogen storage alloys are the most mature hydrogen storage products, which are mainly used for the negative materials of nickel-metal hydride (Ni-MH) batteries [2,3] and gas-phase hydrogen storage devices [4,5]. AB_5-type $LaNi_5$-based alloys are currently the main commercial hydrogen storage materials. However, the theoretically electrochemical capacity (372 mAh g^{-1}) or maximal hydrogen storage amount (160 cm^3 g^{-1} or 1.43 wt.%) after optimization of this material [6] often hardly satisfies the required hydrogen storage capacity because of its restraining intrinsic structure ($CaCu_5$-type). RE-Mg-Ni (RE = Rare Metals) system $AB_{3\text{-}3.8}$-type metal hydride alloys are of special

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concern because of the higher discharge capacity (~400 mAh g^{-1}), and a series of significant developments in the study of this material has been made in the past few years [7–12].

RE-Mg-Ni hydrogen storage alloys have been widely used as negative electrode active materials for Ni-MH batteries as substitutes for conventional AB_5-type alloys [10–12]. The active Mg element is one of the main compositions in RE-Mg-Ni system alloys. The chemical composition of RE-Mg-Ni system alloys is difficult to control in the high-temperature melting manufacturing process because of the high vapor pressure of Mg. Ultra-fine magnesium powder, which is formed by Mg volatilization, becomes a safety hazard. Thus, new manufacturing techniques are investigated, such as smelting protection with helium gas [7,12,13], various sintering technologies [14,15], high-powered ball-grinding technology [16] and so on. However, the application of these techniques has either a high cost or a complicated process. So, the research and development of Mg-free hydrogen storage alloys with high hydrogen-storing capacity is of great significance.

Combining $LaNi_5$ and YNi_2 binary compounds with hydrogen storage properties, Baddour-Hadjean et al. [17] studied the La–Y–Ni ternary alloy, which is equivalent to an overall substitution of the Mg element in the La–Mg–Ni system alloy by a rare earth Y element. By studying AB_3-type $La_{1-x}Ce_xY_2Ni_9(0 \le x \le 1)$ alloys, it is found that the LaY_2Ni_9 alloy is a $PuNi_3$-type structure and forms $LaY_2Ni_9H_{12}$ after hydrogenation, which excels the hydrogen capacity of $LaMg_2Ni_9$ alloy under identical conditions. However, the maximum discharge capacity of LaY_2Ni_9 alloy electrodes is only 265 mAh g^{-1}. Belgacem et al. [18] also tested the electrochemical properties of LaY_2Ni_9 alloy electrode. The maximum discharge capacity of the alloy electrodes is 258 mAh g^{-1} within five cycles, and 54% of the capacity is maintained after 100 cycles, which is far from meeting the needs of the application. In our previous work [19–21], the reversible hydrogen storage performance of AB_3-, A_2B_7- and A_5B_{19}-type La–Y–Ni system alloys is noticeably improved by adjusting the alloy composition using the element substitution method. Importantly, La–Y–Ni system alloys can be directly prepared using the high-temperature melting method, which solves the preparation problems for Mg-based hydrogen storage alloys.

The structure and properties of the representative AB_3-, A_2B_7- and A_5B_{19}-type La–Y–Ni–Mn–Al hydrogen storage alloys were systematically investigated in this paper and compared with commercial AB_5-type hydrogen storage alloy with high capacity.

Experimental

The chemical compositions of the investigated La–Y–Ni–Mn–Al alloys are $LaY_2Ni_{8.2}Mn_{0.5}Al_{0.3}$ (AB_3-type), $LaY_2Ni_{9.7}Mn_{0.5}Al_{0.3}$ (A_2B_7-type) and $LaY_2Ni_{10.6}Mn_{0.5}Al_{0.3}$ (A_5B_{19}-type). These alloys were prepared in a 0.05 MPa argon atmosphere using a vacuum induction-quenching furnace with a rotating copper wheel. In this work, the linear velocity of the copper wheel was 4.33 m s^{-1}. The purities of the component metals were at least 99 wt.%. The prepared alloy flakes were annealed in vacuum of 10^{-2} Pa at 1148 K for 16 h. The annealed alloy flakes and commercial AB_5-type $(LaCe)Ni_{3.8}Co_{0.7}Mn_{0.4}Al_{0.2}$ hydrogen storage alloy were mechanically pulverized into powder particles of 38–74 μm in size for the electrochemical measurements.

The phases of the alloy powders were characterized by X-ray diffraction (XRD) using a Philips-PW 1700 X powder diffractometer with Cu Kα radiation at 40 kV, 200 mA in the range from 0° to 80° with 0.02° min^{-1}, and the diffraction patterns were analyzed with a Rietveld refinement (using the software MAUD). The morphologies of the alloys were examined by HITACHI S-3400N scanning electron microscope (SEM) linked with an energy dispersive X-ray spectrometer (EDS).

Pressure-composition isotherms for the H_2 absorption/desorption reactions were determined over the pressure range of 10^{-3} MPa to 2.0 MPa in a Sieverts testing device. The alloy flakes were mechanically broken into small particles of 74 μm-1.2 mm in size before testing. Alloy particles with a mass of approximately 5 g were placed in the reaction chamber, evacuated for 60 min at 343 K and then allowed to react with hydrogen gas (99.999% purity) under a pressure of 2 MPa. The chamber was then slowly cooled to room temperature and held at that temperature for 30 min. De-hydriding was performed by heating the chamber to 343 K and evacuating it for 60 min until the hydrogen pressure was below 10^{-3} MPa. Five hydriding/de-hydriding cycles were performed to ensure that the alloys were fully activated. Next, the *P-C* isotherms were measured at 298 K, 313 K, 333 K and 343 K.

MH electrodes were prepared by mixing 0.1 g alloy powder with 0.4 g carbonyl nickel powder and then cold-pressed into pellets with 15 mm in diameter under a pressure of 16 MPa. This pellet was then placed between two Ni gauze layers, and the edges were tightly spot-welded to maintain good electrochemical contact between the pellet and the Ni gauze. A Ni lead wire was then attached to the Ni gauze by spot-welding to prepare the hydrogen storage alloy electrode (MH electrode). Electrochemical measurements were performed at 298 K in a half-cell consisting of a prepared MH electrode and a sintered $Ni(OH)_2$/NiOOH counter electrode with an excess capacity immersed in 6 mol L^{-1} KOH electrolyte. The discharge capacity and cycle stability were measured by galvanostatic method as follows: each electrode was charged at 70 mA g^{-1} for 6 h, which was followed by a 5-min break, and then was subsequently discharged at 70 mA g^{-1} to the cut-off potential of 1.0 V versus the counter electrode. All tests were measured at room temperature (298 K).

Results and discussion

Phase structure

Fig. 1 shows the refined analysis of XRD patterns for the $LaY_2Ni_{8.2}Mn_{0.5}Al_{0.3}$ (AB_3-type), $LaY_2Ni_{9.7}Mn_{0.5}Al_{0.3}$ (A_2B_7-type) and $LaY_2Ni_{10.6}Mn_{0.5}Al_{0.3}$ (A_5B_{19}-type) alloys, and the results are listed in Table 1. The alloys have a multiphase microstructure. The AB_3-type alloy consists of LaY_2Ni_9-type phase, Ce_2Ni_7-type phase and a notably small quantity of $LaNi_5$-type phase. The A_2B_7-type alloy consists of Ce_2Ni_7-type phase and Gd_2Co_7-

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