Powder Technology 221 (2012) 365–370

Contents lists available at SciVerse ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Effect of AB_5 alloy on electrochemical properties of $Mm_{0.80}Mg_{0.20}Ni_{2.56}Co_{0.50}Mn_{0.14}Al_{0.12}$ hydrogen storage alloy

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ARTICLE INFO

Article history:
Received 15 September 2011
Received in revised form 6 January 2012
Accepted 16 January 2012
Available online 25 January 2012

Keywords:
Hydrogen storage alloy
AB_3-type alloy
AB_5-type alloy
Electrochemical properties

ABSTRACT

The La–Mg–Ni based composites $Mm_{0.80}Mg_{0.20}Ni_{2.56}Co_{0.50}Mn_{0.14}Al_{0.12}$– x wt.% AB_5 ($x=0$, 10, 20, 30) alloys were successfully synthesized by ball milling method. The structure and electrochemical characteristics of composites have been investigated systematically. The XRD spectroscopy shows that all these composites are mainly composed of La_2Ni_7 phase and $LaNi_5$ phase. The electrochemical studies suggest that the maximum discharge capacity (C_{max}) of alloy electrodes decreases slightly from 361.8 mAh/g ($x=0$) to 337.9 mAh/g ($x=10$), 353.9 mAh/g ($x=20$) and 352.8 mAh/g ($x=30$), while the cycle durability of the composite electrodes is significantly improved. Moreover, the electrochemical kinetic measurements indicate that the $x=20$ composite alloy electrode presents the best overall electrochemical properties.

1. Introduction

The new series of AB_3-type La–Mg–Ni system hydrogen storage alloys are expected as a highly promising hydrogen storage material due to their relatively high hydrogen storage capacity (360–410 mAh/g) under ambient conditions [1]. However, their practical application was hindered due to the high degradation of discharge capacity in KOH solution during consecutive cyclic process. Recently, Liu et al. [2] reviewed the development of the new R–Mg–Ni-based hydrogen storage alloys that have been developed over the last decade as the most promising next generation negative electrode materials of Ni/MH batteries. In order to improve the cyclic stability of La–Mg–Ni electrode alloys, researchers [3–11] mainly adopted the partial substitutions of nickel and/or lanthanum with other metals. Further, Chu et al. [12] indicated that after formation composites with $Ti_{0.17}Zr_{0.08}V_{0.35}Cr_{0.1}Ni_{0.3}$, the maximum discharge capacity of nonstoichiometric AB_3-type $La_{0.7}Mg_{0.3}Ni_{3.5}$ electrode decreased slightly; while the cyclic capacity retention rate of composite electrodes was significantly improved. Though some important progresses on the La–Mg–Ni system electrode alloys have been obtained, it is a long distance to take La–Mg–Ni electrode alloy from laboratory to market due to the poor cyclic stability of the alloy.

In the last decades, the AB_5-type hydrogen storage alloys had been intensively investigated. Some alloys of this type exhibited an excellent cyclic stability during the charge/discharge cycles. But this type of alloys has its inherent disadvantage that the discharge capacity was not satisfactory.

Therefore, it can be expected that the cycle durability of La–Mg–Ni-based alloy electrode could be improved through incorporating with additional AB_5-type alloy powders.

In the present work, the composite alloys were prepared by ball milling $Mm_{0.80}Mg_{0.20}Ni_{2.56}Co_{0.50}Mn_{0.14}Al_{0.12}$ alloy with different amounts of AB_5-type alloy, which resulted in the appreciable increase of the cycle performance of the composite electrodes. The structural and overall electrochemical properties of the composites were hereby investigated in detail.

2. Experimental

The AB_3-type $Mm_{0.80}Mg_{0.20}Ni_{2.56}Co_{0.50}Mn_{0.14}Al_{0.12}$ alloy (the La-rich mischmetal Mm consists of 97.15% La, 1.58% Ce, 0.25% Pr and 1.02% Nd) and AB_5-type alloy $MlNi_{3.5}Co_{0.6}Mn_{0.4}Al_{0.5}$ alloy (Ml consists of 37.7% La, 38.9% Ce, 6.3% Pr and 17.1% Nd) were prepared by induction melting under argon atmosphere and remelted four times for homogeneity. The purity of all the constituent metal elements was over 99.0%. The prepared ingots was mechanically crushed and ground into the powder of 200 mesh size for ball milling.

The $Mm_{0.80}Mg_{0.20}Ni_{2.56}Co_{0.50}Mn_{0.14}Al_{0.12}$– x wt.% AB_5 ($x=0$, 10, 20, 30) composites were prepared by ball milling. x wt% ($x=0$, 10, 20, 30) AB_5-type alloy as an additive was mixed homogenously into the AB_3 alloy, and ground by QM-1SP planetary ball miller under argon atmosphere for 1 h. In each stainless milling pot, the ball-to-powder weight ratio was 15:1. The structure and surface morphologies of the $Mm_{0.80}Mg_{0.20}Ni_{2.56}Co_{0.50}Mn_{0.14}Al_{0.12}$–$x$ wt.% AB_5 ($x=0$, 10, 20, 30) alloys were collected by powder X-ray diffraction (D/max-2550,

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doi:10.1016/j.powtec.2012.01.026

Cu K radiation, λ = 0.154178 nm) and scanning electron microscopy (SEM, JSM-6360 LV).

The test electrodes were prepared by cold pressing a mixture of 0.10 g alloy powders with 0.20 g carbonyl nickel powders into a pellet of 10 mm in diameter under a pressure of 10 MPa. The pellet was sandwiched between two nickel foam plates and subsequently spot-welded with a copper wire.

The alloys electrodes were soaked in 6 mol/L KOH aqueous solution for 4 h before electrochemical measurements. The charge/discharge tests were performed by a Land 5.3 B Battery Test instrument in half-cell consisting of working electrode, counter electrode ($Ni(OH)_2$/NiOOH) and 6.0 mol/L KOH as electrolyte. The electrodes were charged for 6 h at a current density of 100 mA/g, rested for 5 min and then discharged to the cut-off potential of 1.0 V at a current density of 50 mA/g.

PARSTAT 2273 advanced electrochemical system was used for CV (scanning rate: 0.5 mV/s, potential range: −1.2–−0.2 V vs. Hg/HgO), linear polarization (scanning rate: 0.1 mV/s, −5–5 mV vs. open circuit potential, 50%DOD), anodic polarization (scanning rate: 0.5 mV/s, 0–500 mV vs. open circuit potential, 50%DOD), EIS (amplitude: 5 mV, frequency range: 1×10^3 Hz ~ 1×10^{-4} Hz, 50%DOD) and potentiodynamic polarization measurement (scanning rate: 0.1 mV/s, potential range: −1.0–−0.2 V vs. Hg/HgO).

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the X-ray diffraction patterns of the AB_5 alloy, $Mm_{0.80}Mg_{0.20}Ni_{2.56}$–$Co_{0.50}Mn_{0.14}Al_{0.12}$, and $x = 10$ composite alloy. The lattice parameters of alloy phases, which are obtained from XRD data by the software Jade 5.0, are listed in Table 1. It shows that the AB_5-type alloy exhibits the diffraction peaks corresponding to the $LaNi_5$ phase with the $CaCu_5$-type hexagonal structures, and the $Mm_{0.80}Mg_{0.20}Ni_{2.56}$–$Co_{0.50}Mn_{0.14}Al_{0.12}$ and $x = 10$ composite alloy consist of $LaNi_5$ phase (PDF card no. 65–0093) and La_2Ni_7 phase (PDF card no. 22–0640). The results in Table 1 indicate that the introduction of AB_5 alloy leads to an increase of the *c* parameter and cell volume of the La_2Ni_7 phase, and a decrease of the lattice parameter *c* and cell volume of the $LaNi_5$ phase, suggesting that the AB_5 alloy may enter the La_2Ni_7 phase.

3.2. The surface morphology of the composite particles

Fig. 2 presents the SEM morphologies of the $Mm_{0.80}Mg_{0.20}Ni_{2.56}$-$Co_{0.50}Mn_{0.14}Al_{0.12}$ alloy and $x = 10$, 20 composite alloys. It clearly shows that all of the alloy particles exhibit irregular shape and the surface are rough. The particle sizes of the alloys and the interspaces become smaller after ball milling, indicating that some fresh surface has been exposed during the process of milling, which is responsible for the improvement of the electrode performance [13].

Table 1
The lattice parameters of the AB_5 and $Mm_{0.80}Mg_{0.20}Ni_{2.56}Co_{0.50}Mn_{0.14}Al_{0.12}$–*x* wt.% AB_5 ($x = 0$, 10) alloy electrodes.

Samples	Phase	Lattice parameter (Å)		Cell volume (Å3)
		a	c	
AB_5	$LaNi_5$	5.063	4.063	90.20
$x = 0$	$LaNi_5$	5.015	3.997	87.04
	La_2Ni_7	5.074	24.358	543.05
$x = 10$	$LaNi_5$	5.023	3.983	87.01
	La_2Ni_7	5.072	24.605	548.34

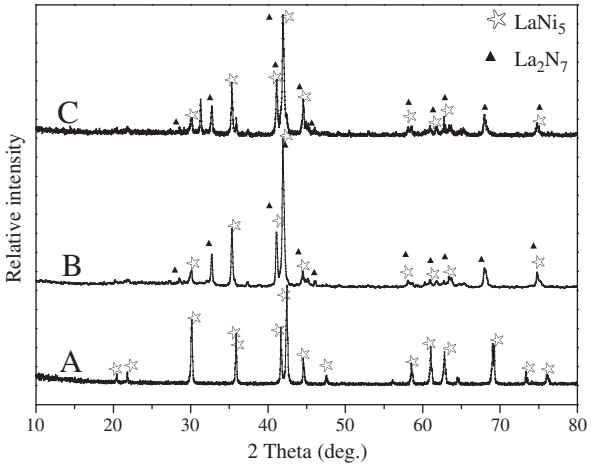

Fig. 1. X-ray diffraction patterns of the AB_5, $Mm_{0.80}Mg_{0.20}Ni_{2.56}Co_{0.50}Mn_{0.14}Al_{0.12}$, and $x = 10$ alloys. (A) AB_5 alloy; (B) $Mm_{0.80}Mg_{0.20}Ni_{2.56}Co_{0.50}Mn_{0.14}Al_{0.12}$ alloy; and (C) $x = 10$ alloy.

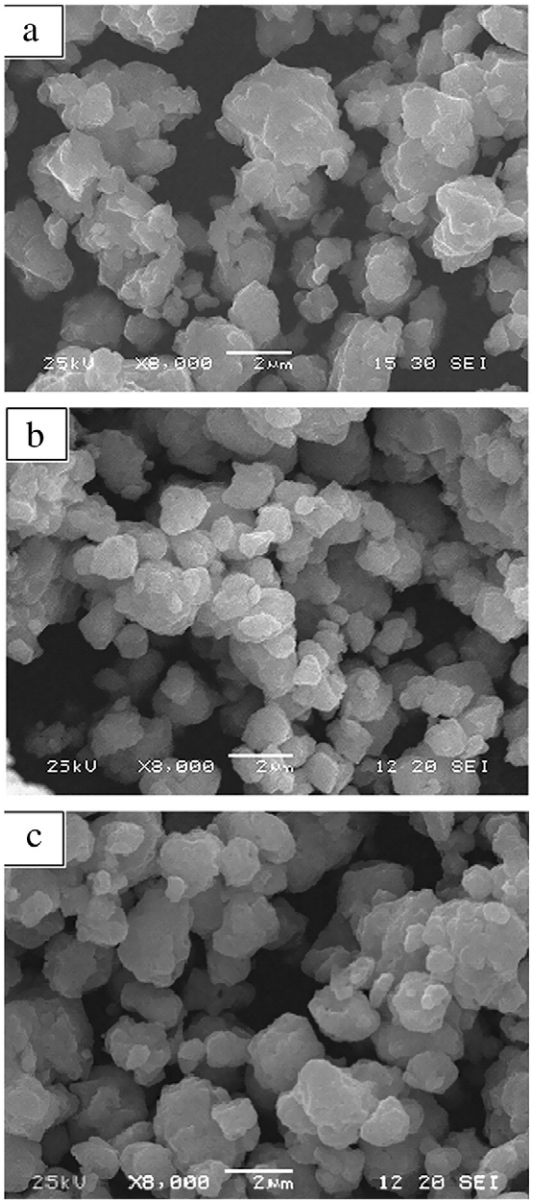

Fig. 2. SEM images of $Mm_{0.80}Mg_{0.20}Ni_{2.56}Co_{0.50}Mn_{0.14}Al_{0.12}$–*x* wt% AB_5 ($x = 0$, 10, 20, 30) composites: (a) $x = 0$; (b) $x = 10$; (c) $x = 20$.