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Review

Effect of Mg on the hydrogen storage characteristics of $Ml_{1-x}Mg_xNi_{2.4}Co_{0.6}$ ($x = 0$–0.6) alloys

Rui Tang [a,b,*], Yongning Liu [a], Changchun Zhu [b], Jiewu Zhu [a], Guang Yu [a]

[a] *State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China*
[b] *School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, China*

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Abstract

$Ml_{1-x}Mg_xNi_{2.4}Co_{0.6}$ ($x = 0$–0.6) hydrogen storage alloys were prepared by inductive melting and the effect of Mg on the crystal structure and hydrogen storage characteristics was investigated. These alloys are confirmed to be $LaNi_3$ phase with the $PuNi_3$ type structure. The Mg substitution for Ml in the alloys leads to a shrinkage of the unit cell volume and a reduction of the stability of alloy hydrides. With increasing the Mg substitution for Ml, the atom ratio of hydrogen to alloy (H/M) decreases, but the weight ratio of H/M and the discharge capacity of electrodes increase in a certain range of Mg content ($x \leq 0.4$). The $Ml_{0.6}Mg_{0.4}Ni_{2.4}Co_{0.6}$ alloy has the highest weight ratio of H/M (1.75 wt.%) at 1 MPa H_2 and 298 K and the largest discharge capacity of electrodes (326 mAh g^{-1}). In addition, the increase of Mg substitution for Ml results in better high-rate dischargeability and cycling stability of electrodes.

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Keywords: Hydrogen storage alloys; Crystal structure; Hydrogen storage capacity; Ni-MH battery

Contents

1. Introduction

Hydrogen storage alloys have been widely used as the negative electrode materials in nickel-metal hydride (Ni-MH) batteries. At present, the main commercial electrode alloys are the rare earth-based AB_5 type alloys with limit capacity (∼320 mAh g^{-1}). To enhance the energy density of Ni-MH batteries, it is necessary to increase the capacity of electrode alloys. Recently, a series of R–Mg–Ni-based (where R denotes rare earth metals) alloys with a higher capacity than that of the AB_5 type alloys has attracted much attention [1–14]. For example, the $LaMg(NiCo)_x$ ($x = 3.0$–3.5) alloys were found to have much higher discharge capacity, 387–410 mAh g^{-1}, than that of the commercial AB_5 type alloys [1]. It was reported that the Mg-contained $LaNi_3$ phase, as the matrix or the secondary phase in these alloys, was the key factor for the capacity [2–4]. However, the systematic investigation on the hydrogen storage characteristics of the Mg-contained $LaNi_3$ phase has not yet been reported. In this work, a series of $Ml_{1-x}Mg_xNi_{2.4}Co_{0.6}$ ($x = 0$–0.6) alloys were prepared to investigate the effect of

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[*] Corresponding author. Tel.: +86 298 2669071; fax: +86 298 3237910.
E-mail address: xajttr@163.com (R. Tang).

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Mg on the crystal structure and hydrogen storage characteristics.

2. Experimental details

The $Ml_{1-x}Mg_xNi_{2.4}Co_{0.6}$ ($x = 0$–0.6) alloy (where Ml denotes La-rich mixed rare earth composed of 87 wt.% La, 6 wt.% Ce, 4 wt.% Pr, 2.5 wt.% Nd and 0.5 wt.% impurity; other elements have a purity more than 99.9 wt.%.) was prepared by inductive melting under argon atmosphere and then annealed at 1273 K for 10 h under vacuum. To obtain an accurate composition, a little excess of Mg was considered during preparation because Mg has a high vapor pressure and is easy to be evaporated. The composition of the prepared alloy ingot was examined by means of atomic absorption spectrometry. The results showed that the difference between the obtained composition and the calculated value according to the chemical formula was less than 0.01 wt.% for each element. The prepared alloy ingot was mechanically pulverized to powder and then passed through a 200 mesh sieve.

Crystallographic characteristics of the alloys were carried out using a D/max-3A X-ray diffractometer (XRD) with Cu Kα radiation.

The hydrogen storage capacity and pressure–concentration–temperature (PCT) curves of the alloys were measured using a Sievert's type apparatus. At first, the reaction container (which contained 10 g of alloy powder) was heated to 353 K and the air was evacuated. After the samples were full activated though three absorbing/desorbing hydrogen cycles, the measurements started.

0.5 g of alloy powder mixed well with additive and blinding polymer solution was pasted into a porous nickel foam (size 4 cm × 3 cm) and then dried under vacuum at 363 K and finally pressed into the MH working electrode. A $Ni(OH)_2$ electrode (whose preparation process was the same as the working electrode) with a capacity of four times higher than that of the working electrode and a Hg/HgO (6N KOH) electrode were used as the counter electrode and reference electrode, respectively. The electrochemical properties of the alloy electrodes were measured in a half-cell with 6N KOH solution at 298 K. The electrode activation and measurement of electrochemical capacity were carried out at the charge/discharge current of 100 mA g^{-1} with 4 h for charge and the cut-off potential of −0.7 V (versus Hg/HgO) for discharge. To evaluate the rate discharge ability, the discharge current was changed from 100 to 1200 mA g^{-1}. The measurement for cycling stability was carried out at the charge/discharge current of 300 mA g^{-1}.

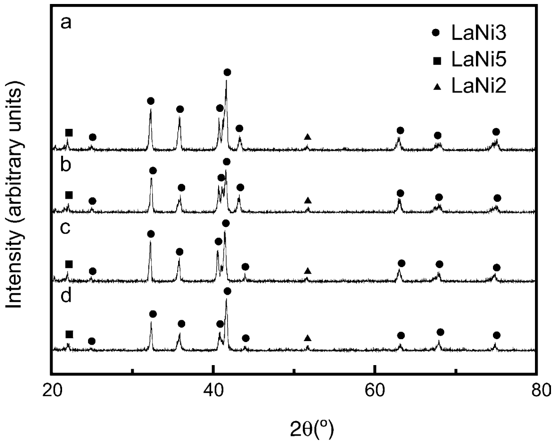

Fig. 1. XRD patterns of $Ml_{1-x}Mg_xNi_{2.4}Co_{0.6}$ ($x = 0$–0.6) alloys: (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.4$ and (d) $x = 0.6$.

3. Results and discussion

Fig. 1 shows the XRD patterns of $Ml_{1-x}Mg_xNi_{2.4}Co_{0.6}$ ($x = 0$–0.6) alloys. It can be seen that except for several small peaks due to the impurity phases ($LaNi_5$ and $LaNi_2$), all the other peaks correspond to $LaNi_3$ phase with the rhombohedral $PuNi_3$ type structure. The crystallographic parameters are shown in Table 1. The Mg substitution for Ml in the alloys leads to a decrease of both lattice constants and a shrinkage of the unit cell volume due to the atomic radius of Mg (1.72 Å) being smaller than those of rare earth elements (1.82–1.88 Å). When the Mg substitution for Ml was not more than 40% ($x \leq 0.4$), the shrinkage of unit cell volume ($\Delta V/V$) was not great. However, when the Mg substitution for Ml amounted to 60% ($x = 0.6$), the unit cell shrank greatly and its shrinkage percentage amounted to 5.36%.

Fig. 2 shows the hydrogen storage capacity of $Ml_{1-x}Mg_xNi_{2.4}Co_{0.6}$ alloys at 1 MPa H_2 and room temperature (298 K). With increasing the Mg substitution for Ml in the alloys, the atom ratio of hydrogen to alloy (H/M) decreased from 1.25 ($x = 0$) to 0.5 ($x = 0.6$). This means that the increase of Mg substitution for Ml results the decrease of available sites for hydrogen storage due to the shrinkage of unit cell volume. However, when the Mg substitution for Ml was not more than 40%, the weight ratio of H/M is not in accord

Table 1
Crystallographic parameters of $Ml_{1-x}Mg_xNi_{2.4}Co_{0.6}$ ($x = 0$–0.6) alloys

Sample x	Lattice constants		Unit cell volume ($Å^3$)	Shrinkage of unit cell volume (%)
	a (Å)	c (Å)		
0	5.051	24.413	539.4	–
0.2	5.035	24.299	533.5	1.09
0.4	5.018	24.187	527.4	2.22
0.6	4.963	23.932	510.5	5.36

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