Article ID: 1003 - 6326(2003)01 - 0025 - 04

Influences of heat treatment on electrochemical characteristics of $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ hydrogen storage electrode alloy①

LIU Yong-feng(刘永锋), PAN Hong-ge(潘洪革), GAO Ming-xia(高明霞),
ZHU Yun-feng(朱云峰), LEI Yong-quan(雷永泉)
(Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China)

Abstract: The influences of annealing treatment on the electrochemical and structural properties of $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ hydrogen storage alloy were investigated by means of electrochemical studies and X-ray diffraction(XRD) analyses. The XRD results reveal that the peak width gets narrower with increasing annealing temperature, which can be ascribed to the structural change and more homogeneous composition after being annealed. Electrochemical studies show that the discharge capacity and the cycle stability of the alloy electrodes increase after being annealed. The maximum discharge capacity, exchange current density J_0 and limiting current density J_L of the as-cast alloy are 388 mA·h/g, 340.5 mA/g and 3 068 mA/g, respectively, and they are increased to 400 mA·h/g, 372.1 mA/g and 3 399 mA/g for the alloy annealed at 1 123 K for 8 h, respectively. Meanwhile, as the discharge current density is 1 250 mA/g, the high rate dischargeability(HRD) increases from 77.4% for the as-cast alloy to 83.3% for the alloy annealed at 1 123 K.

Key words: heat treatment; $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ hydrogen storage alloy; electrochemical properties
CLC number: TG 139 **Document code:** A

1 INTRODUCTION

During the last decade, the demand for the nickel/metal-hydride (Ni/MH) secondary batteries has been growing rapidly because of their high energy density, high HRD, long charge-discharge cycle life and friendly environmental properties[1-4]. Hydrogen storage alloys, as the negative electrode materials in the Ni/MH secondary batteries, have been extensively studied. Among all the hydrogen storage alloys studied previously, the rare earth based AB_5-type alloys are most systematically studied and most widely used as the active material of metal hydride electrodes in Ni/MH batteries. But, they are now not very satisfied due to their limited discharge capacity(280 - 320 mA·h/g)[5-7]. Meanwhile, the Ti- or Zr-based AB_2-type alloys(Laves type) have also been largely investigated for their inherent high hydrogen absorption, but they suffer from passivation, slow activation and/or bad corrosion-resistant[8]. At present, the research is focused on the alloys with higher energy density, rapid activation, long cycle life and low cost. Recent investigations on the R-Mg-Ni system hydrogen storage alloys result in a new series of ternary alloys with a general formula RMg_2Ni_9 (R= rare earth or Ca element)[9-12]. The electrochemical and structural properties of La-Mg-Ni_x (x = 3 - 3.5) system alloys have been reported by Kohno[13].

In this investigation, we apply the annealing treatment to the $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy, and investigate its resultant influences on the electrochemical properties and microstructure.

2 EXPERIMENTAL

$La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy sample was prepared by magnetic levitation melting under vacuum and remelted three times for homogeneity. All starting elemental metals have a purity higher than 99.9%. Some of the alloy was annealed for 8 h at 1 123 K or 1 223 K in vacuum. Then, all the alloy samples were ground mechanically into powders(< 50 μm) and used for both electrochemical measurements and X-ray diffraction(XRD) analysis.

All test electrodes were prepared by cold pressing to pellets under a pressure of 20 MPa after mixing 0.1 g alloy powder with 0.3 g carbonyl nickel powder. The electrochemical measurements were performed at 303 K in a half-cell consisting of a working electrode (MH electrode), a sintered $Ni(OH)_2$/NiOOH counter electrode and an Hg/HgO reference electrode. 6 mol/L KOH solution was used as the electrolyte. The discharge capacity of the electrode was determined by the galvanostatic method. Each electrode was charged at 100 mA/g for 5 h and discharged at 100 mA/g to the cut-off potential of - 0.5 V vs Hg/HgO reference electrode. In order to investigate

① **Foundation item:** Project(50131040) supported by the National Natural Science Foundation of China
Received date: 2002 - 01 - 29; **Accepted date:** 2002 - 04 - 15
Correspondence: PAN Hong-ge, Professor of Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China, Tel: + 86-571-87952576, Fax: + 86-571-87951152, E-mail: pan_hg@mail.hz.zj.cn, Homepage: http://www.Honggepan.com

high rate dischargeability, the discharge capacities at various discharge current densities were determined. The linear polarization curves and Tafel polarization curves of the test electrodes were determined by scanning the electrode potential (Solartron SI1287 polentiostat) at 0.1 mV/s from − 5 mV to 5 mV (vs. open circuit potential) and 5 mV/s from − 400 mV to 400 mV (vs. open circuit potential) at 50% depth of discharge (DOD), respectively.

The crystal structures were determined by X-ray powder diffraction (XRD) using CuK_α radiation.

3 RESULTS AND DISCUSSION

Fig. 1 shows the cycle life curves of $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy electrode. It is obvious that the cycle stability of the alloy electrodes increases markedly after annealing treatment, which indicates that the heat treatment is an effective way to improve the cycle life of metal hydride alloy electrodes due to the great suppression of the pulverization and corrosion of the annealed alloy[14]. The alloy annealed at 1 223 K shows the longest cycle life compared with the others. After heat treatment, a structural change and more homogeneous compositional distribution would be observed. Fig. 2 shows the XRD patterns of $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy. It can be seen that the width of the diffraction peaks becomes narrow after annealing treatment. The full width at half maximum (FWHM) of the most intense diffraction peak of $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ electrode alloys is summarized in Table 1. It has been reported that the diffraction peaks of rare earth based hydrogen storage alloys sharpen after annealing treatment due to the composition homogenization[15], which is beneficial to the improvement of the electrochemical properties. The maximum discharge capacities are shown in Fig. 3. It can be seen that the maximum discharge capacities of the annealing samples are higher than those of the as-cast sample. After being annealed at 1 123 K for 8 h, the maximum discharge capacity increases from 388 mA·h/g to 400 mA·h/g the alloy annealed. However, the maximum discharge capacity of at 1 223 K is lower than that of the alloy annealed at 1 123 K. Sakai et al[16] suggested that some crystal boundaries of the alloy were remelted and oxidized when the annealing temperature was close to the alloy melting point, which induced the decay of the discharge capacity and the slow hydride-dehydride reaction. Moreover, the kinetics of the electrochemical

Table 1 FWHM of $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ electrode alloys

Sample	FWHM
As-cast	0.290 1
Annealed at 1 123 K	0.277 1
Annealed at 1 223 K	0.198 8

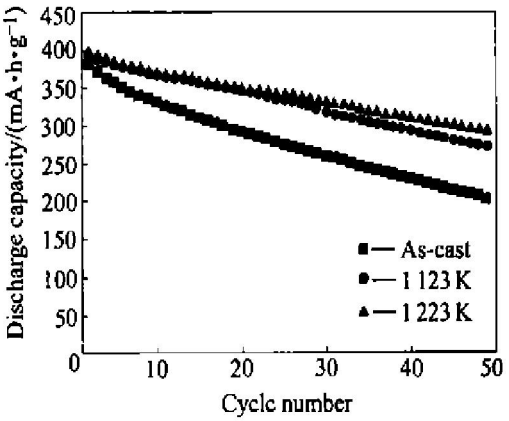

Fig. 1 Discharge capacity vs cycle number for $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy electrode at 303 K

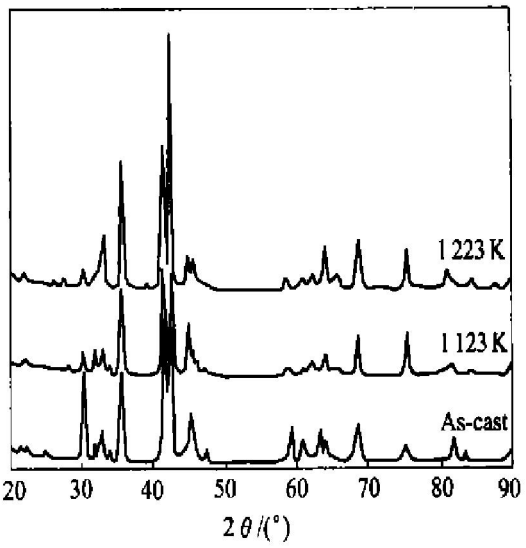

Fig. 2 XRD patterns of $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy

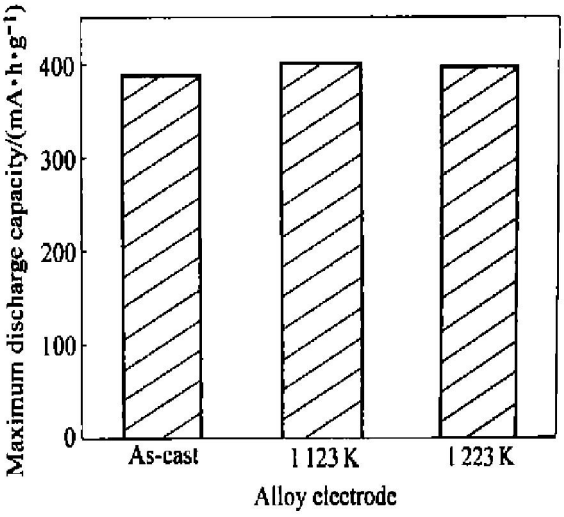

Fig. 3 Maximum discharge capacity of $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy electrode at 303 K

hydrogen reaction decreases.

Fig. 4 shows the relationship between discharge capacity and discharge current density of the $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy electrode. The high rate dischargeability (HRD) is calculated from the following formula:

$$H_{HRD}=\frac{C_d}{C_d+C_{100}}\times 100\% \quad (1)$$

where C_d is the discharge capacity with cut-off potential of − 0.5 V vs Hg/HgO reference electrode at the discharge current density J_d, C_{100} is the residual discharge capacity with cut-off potential of − 0.5 V vs Hg/HgO reference electrode at the discharge current density J = 100 mA/g after the alloy electrode has fully discharged at the large discharge current density(J_d). It is found that the H_{HRD} of the $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy electrode varies in the following sequence: annealed at 1 123 K> as-cast> annealed at 1 223 K. As the discharge current density is 1 250 mA/g, the H_{HRD} of the as-cast sample is 77.4%, and those of the samples after being annealed at 1 123 K and 1 223 K are 83.3% and 70.7%, respectively.

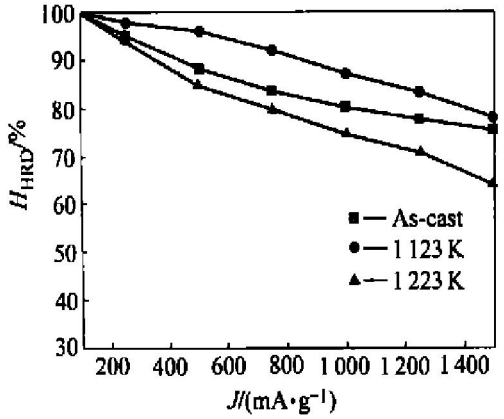

Fig. 4 High rate dischargeability of $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy electrode at 303 K

The exchange current density, J_0, is generally used to measure the kinetics of the electrochemical hydrogen reaction[17]. It is determined by measuring the current at different overpotentials. When the overpotential is changed within a small range, the exchange current density can be estimated from the slope of the obtained micropolarization curve since the curve is approximately linear. Fig. 5 shows the linear polarization curves of the $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy electrode. The reaction resistance decreases when the annealing temperature is 1 123 K, and then increases with increasing annealing temperature. The variation is consistent with that of the high rate dischargeability. The exchange current density J_0 can be calculated according to following expression[17]:

$$J_0=\frac{J_d RT}{F\eta} \quad (2)$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant and η is the total overpotential. The exchange current densities J_0 calculated by Eqn. (2) are listed in Table 2. The exchange current density J_0 increases after being annealed at 1 123 K and then decreases after being annealed at 1 223 K. The exchange current densities J_0 of the as-cast, the alloys annealed at 1 123 K and 1 223 K are 340.5 mA/g, 372.1 mA/g and 266.3 mA/g, respectively.

The Tafel polarization curves of the $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy electrodes are shown in Fig. 6. The limiting current density J_L that can be obtained from Fig. 6 is also listed in Table 2. The

Table 2 Exchange current density J_0 and limiting current density J_L of $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy electrode

Sample	J_0/(mA·g^{-1})	J_L/(mA·g^{-1})
As-cast	340.5	3 068
Annealed at 1 123 K	372.1	3 399
Annealed at 1 223 K	266.3	2 454

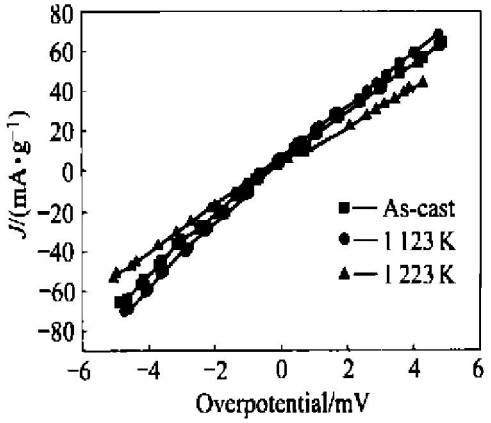

Fig. 5 Linear polarization curves for $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy electrode measured at 50% depth of discharge(DOD) and 298 K

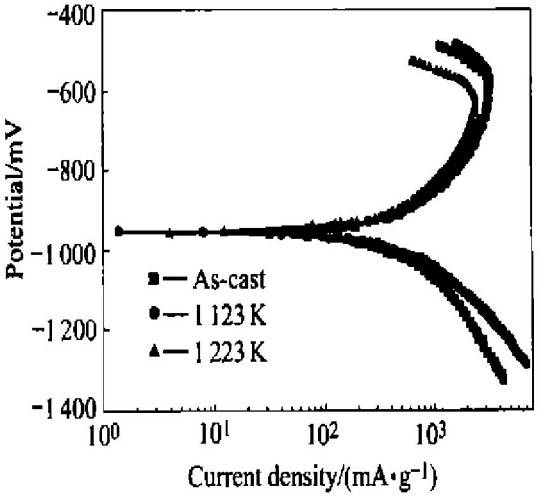

Fig. 6 Tafel polarization curves for $La_{0.75}Mg_{0.25}Ni_{2.8}Co_{0.5}$ alloy electrode measured at 50% depth of discharge (DOD) and 298 K

limiting current density J_L of the as-cast alloy is 3 068 mA/g, and those of the alloys after being annealed at 1 123 K and 1 223 K are 3 399 mA/g and 2 454 mA/g, respectively. So the limiting current density J_L first increases and then decreases with increasing annealing temperature. The influence of heat treatment on the limiting current density is consistent with that of the high rate dischargeability and the exchange current density.

4 CONCLUSIONS

The diffraction peak width of the alloys changes narrower with increasing annealing temperature, which is due to the structural change after being annealed. The maximum discharge capacity and the cycle stability of the alloy electrodes increase after being annealed, and the alloy annealed at 1 123 K shows the highest capacity and the cycle life of the alloy annealed at 1 223 K is the best. Moreover, the exchange current density J_0 and the limiting current density J_L of the alloy electrode increase when the annealing temperature is 1 123 K and decrease when the annealing temperature is 1 223 K. The influence of heat treatment on the high rate dischargeability is consistent with that of the limiting current density and the exchange current density.

REFERENCES

[1] Willems J J G. Metal hydride electrodes stability of $LaNi_5$-related compounds[J]. Philips J Res, 1984, 39(1): 1.

[2] Sakai T, Miyamura H, Kuriyama N, et al. Metal hydride anodes for nickel-hydrogen secondary battery[J]. J Electrochem Soc, 1990, 137: 795 - 799.

[3] Pan H G, Ma J X, Wang C S, et al. Effect of Co content on the kinetic properties of the $MlNi_{4.3-x}Co_xAl_{0.7}$ hydride electrodes[J]. Electrochim Acta, 1999, 44: 3977 - 3987.

[4] PAN Hong-ge. Calculation of electrochemical overpotential and concentration overpotential based on curve of anodic polarization in hydrogen storage alloy electrode[J]. Trans Nonferrous Met Soc China, 1999, 9(2): 260 - 264.

[5] CHEN Wei-xiang, QI Jian-qin, CHEN Chang-pin. Effects of Ca-substitution and surface treatment on electrochemical performances of $Ml_{1-x}Ca_xNi_{4.0}Co_{0.6}Al_{0.4}$ hydrogen storage alloy electrodes[J]. Trans Nonferrous Met Soc China, 1999, 9(3): 487 - 492.

[6] LI Quan-an, SANG Ge, LI Jian-wen, et al. Electrochemical properties of non-stoichiometric hydrogen storage alloy $Ml(Ni_{0.71}Co_{0.15}Al_{0.06}Mn_{0.08})_x$[J]. The Chinese Journal of Nonferrous Metals, 2000, 10(5): 659 - 662. (in Chinese)

[7] ZHANG Shu-kai, LEI Yong-quan, CHEN Li-xin, et al. Electrode characteristics of non-stoichiometric $Ml(NiMnAlFe)_x$ alloys[J]. Trans Nonferrous Met Soc China, 2001, 11(2): 183 - 187.

[8] Reilly J J. Metal hydride electrodes[A]. Besenhard J O. Handbook of Battery Materials[M]. New York: Wiley. 2000.

[9] Kadir K, Sakai T, Uehara I. Synthesis and structure determination of a new series of hydrogen storage alloys; RMg_2Ni_9 (R = La, Ce, Pr, Nd, Sm and Gd) built from $MgNi_2$ Laves-type alternating with AB_5 layers[J]. J Alloys Compd, 1997, 257: 115 - 121.

[10] Kadir K, Kuriyama N, Sakai T, et al. Structural investigation and hydrogen capacity of $CaMg_2Ni_9$: a new phase in the AB_2C_9 system isostructural with $LaMg_2Ni_9$[J]. J Alloys Compd, 1999, 284: 145 - 154.

[11] Kadir K, Sakai T, Uehara I. Structural investigation and hydrogen capacity of YMg_2Ni_9 and $(Y_{0.5}Ca_{0.5})(MgCa)Ni_9$: a new phase in the AB_2C_9 system isostructural with $LaMg_2Ni_9$[J]. J Alloys Compd, 1999, 287: 264 - 270.

[12] Kadir K, Sakai T, Uehara I. Structural investigation and hydrogen capacity of $LaMg_2Ni_9$ and $(La_{0.65}Ca_{0.35})(Mg_{1.32}Ca_{0.68})Ni_9$ of the AB_2C_9 type structure[J]. J Alloys Compd, 2000, 302: 112 - 117.

[13] Kohno T, Yoshida H, Kawashima F, et al. Hydrogen storage properties of new ternary system alloys: La_2MgNi_9, $La_5Mg_2Ni_{23}$, La_3MgNi_{14}[J]. J Alloys Compd, 2000, 311: 5 - 7.

[14] HU Wei-Kang, Dong-Myung Kim, Seok-Won Jeon, et al. Effect of annealing treatment on electrochemical properties of Mn-based hydrogen storage alloys for Ni/MH batteries[J]. J Alloys Compd, 1998, 270: 255 - 264.

[15] Nakamura Y, Nakamura H, Fujitani S, et al. Homogenizing behavior in a hydrogen-absorbing $LaNi_{4.55}Al_{0.45}$ alloy through annealing and rapid quenching[J]. J Alloys Compd, 1994, 210: 299 - 303.

[16] Sakai T, Hazama T, Miyamura H, et al. Rare-earth-based alloy electrodes for a nickel-metal hydride battery[J]. J Less-Common Met, 1991, 172 - 174: 1175 - 1184.

[17] Notten P H L, Hokkeling P. Double-phase hydride-forming compounds: a new class of highly electrocatalytic materials[J]. J Electrochem Soc, 1991, 138: 1877 - 1882.

(Edited by HUANG Jin-song)