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Surface analysis, hydrogen adsorption and electrochemical performance of alkali-reduce treated hydrogen storage alloy^①

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[Abstract] The hydrogen storage alloy powders ($\text{M}\text{Ni}_{4.0}\text{Co}_{0.6}\text{Al}_{0.4}$, $\text{M}=\text{rich La mischmetal}$) were treated in a hot 6 mol/L $\text{KOH} + 0.02 \text{ mol/L KBH}_4$ solution, the surface compositions and chemical states of the treated and untreated alloys were analyzed by XPS and EDX, the hydrogen adsorption on the surface of these alloys was evaluated by thermal desorption spectroscopy (TDS), the effects of the surface treatment on the electrochemical performances of the alloy electrodes were investigated. The results show that the hydrogen adsorption is greatly strengthened by the surface modification, and hence leads to marked improvement in the electrocatalytic activity, the treated alloy exhibits higher exchange current density and lower apparent activation energy for the hydrogen electrode reaction than the untreated alloy.

[Key words] hydrogen storage alloy; surface treatment; thermal desorption spectroscopy (TDS); electrocatalytic activity; apparent activation energy

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1 INTRODUCTION

The hydrogen storage alloys based on mischmetal have been more extensively investigated and most widely applied in the Ni/MH batteries. Some properties of the alloys such as the equilibrium dissociation pressure, hydrogen storage capacity and formation enthalpy of hydride are greatly affected on the alloy bulk composition. On the other hand, the composition and chemical states of the alloy surface can strongly influence the electrochemical characteristics of the alloy electrode such as activation behavior, electrocatalytic activity and corrosion resistance against alkaline electrolyte, and the internal pressure and cycle life of Ni/MH battery. Therefore, the surface characteristics of the alloys play an important role on their electrochemical application. The surface treatment in a hot alkaline solution has been confirmed to be an effective method to improve the electrochemical performances of the alloy electrodes^[1~8]. Iwakura et al^[1,2] found that adding reducing agent in the alkaline solution would further improve the effects of the alkali treatment on the electrochemical performances.

High electrocatalytic activity is essential for the hydrogen storage alloy to be applied in Ni/MH batteries. According to the well-known electrocatalytic

“volcano plots” for the hydrogen electrode reaction on the metal electrode, the electrocatalytic activity should have a close relation to the hydrogen adsorption strength on the alloy surface. In present work, we analyze the surface compositions and chemical state of the alkali-reduce treated alloy by XPS and EDX, and evaluate the effects of the surface treatment on the hydrogen adsorption on the alloy surface by TDS. The effects of the surface treatment on the electrochemical performances of the alloy electrode are also discussed.

2 EXPERIMENTAL

The hydrogen storage alloy powders ($\text{M}\text{Ni}_{4.0}\text{Co}_{0.6}\text{Al}_{0.4}$, $\text{M}=\text{La rich mischmetal}$, with size of less than 74 μm) were treated in 6 mol/L $\text{KOH} + 0.02 \text{ mol/L KBH}_4$ solution at 80 °C for 6 h, then filtrated and washed thoroughly with distilled water, finally dried in vacuum. The alloy surface was characterized by XPS and EDX before and after treating.

TDS measurement was programmed on a temperature controller at a heating rate of 3 K/s and at different hydrogen exposures employing an ultra-high-vacuum chamber (ADES400, the background of the vacuum degree is superior to $2 \times 10^{-8} \text{ Pa}$) equipped with a mass spectrometer (QWS200, Ger-

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many). The tested sample was placed in the specimen cell with double layer quartz. A thermocouple of NiCr/NiAl was placed in the inner of the sample for testing temperature. Before TDS measurement, the sample was preheated to 500 °C for 30 min in order to remove the gas adsorption on the alloy surface. High pure hydrogen (99.99%) was introduced through an ultra vacuum valve at room temperature, and hydrogen exposure was tested by a vacuum meter (1 L = 10⁻⁶ torr•s).

The electrode was prepared by pressing the mixtures of 0.100 g of the alloy powders with 0.200 g fine copper particles at 20 MPa to form a 10 mm diameter pellet. The electrochemical measurements were carried out in a two-compartment gas cell separated with sintered glass. A sintered nickel hydroxide electrode with sufficient capacity was used as a counter electrode, 6 mol/L KOH solution as electrolyte, and Hg/HgO (6 mol/L KOH) electrode as a reference electrode. The charging/discharging cycles were carried out at a constant current density of 100 mA/g at room temperature. The alloy electrode was charged for 3.5 h and then discharged to cut-off voltage of -0.600 V vs Hg/HgO. The polarization curves were measured at a scan rate 1 mV/s and 50% depth of discharge (DOD). The exchange current density J_0 was calculated from the slope of polarization curves according to the equation^[9] as

$$J_0 = \left(\frac{L}{\eta} \right) \eta^{-0.5} \cdot \frac{RT}{F} \quad (1)$$

where J , η , R , T and F are polarization current density, overpotential, gas constant, absolute temperature and Faraday constant, respectively. The apparent activation energy E_a of hydrogen electrode reaction on the alloy electrode can be calculated from the temperature dependence of the exchange current densities according to the equation as^[10]

$$E_a = -R \cdot \frac{\partial \ln J_0}{\partial (1/T)} \quad (2)$$

3 RESULTS AND DISCUSSION

3.1 Surface analyses of hydrogen storage alloys by XPS and EDX

XPS spectra of Ni2p and La3d are shown in Fig. 1, in which the highest peaks at about 82.0 eV are the overlap peaks of Ni2p_{1/2} and La3d_{3/2}. All the La on the untreated and treated alloys exist as oxide and hydroxide on the top surface of the untreated and treated alloy surface because the core level spectra of Ni2p_{1/2} attributed to the metallic Ni is not found before Ar⁺ sputtering. However, after Ar⁺ sputtering only 2 min for the treated alloy, the peak of the metallic Ni2p_{1/2} at 869.5 eV is apparently observed as shown in Fig. 1(b), which means that Ni element

exists mainly in the metallic state. This fact means that the nickel oxide and hydroxide on the alloy surface could be reduced by chemical reduction treatment in a hot 6 mol/L KOH + 0.02 mol/L KBH₄ solution. However, when the treated alloy is exposed to the air, the metallic Ni on the top surface should be oxidized again, and so the metallic states Ni is not found on the top surface before Ar⁺ sputtering. For the untreated alloy, when it takes the Ar⁺ sputtering of about 10 min, the peak of metallic state Ni2p_{1/2} at 869.6 eV can be obviously found as shown in Fig. 1(a).

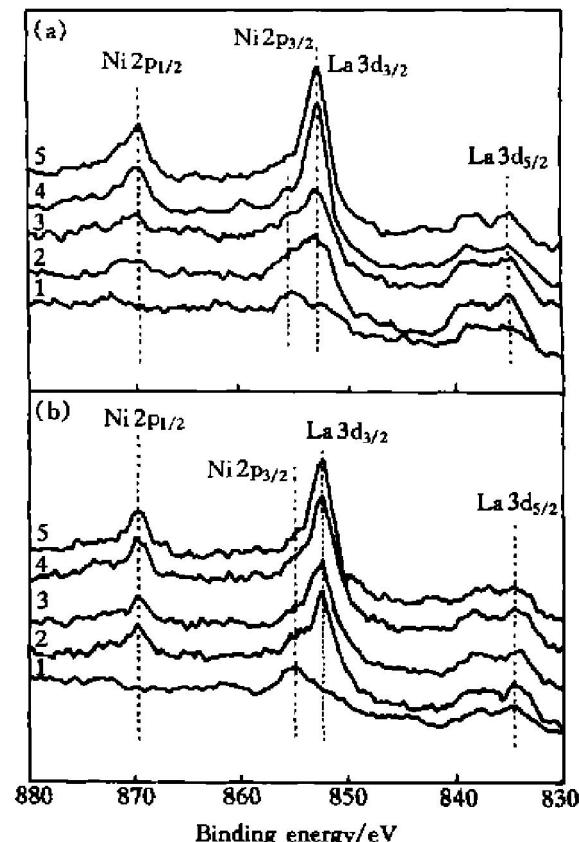


Fig. 1 XPS spectra for Ni2p and La3d of untreated alloy (a) and treated alloy (b)

(1) —Ar⁺ sputtering 0 min; (2) —Ar⁺ sputtering 2 min;
(3) —Ar⁺ sputtering 5 min; (4) —Ar⁺ sputtering 10 min;
(5) —Ar⁺ sputtering 20 min

The surface composition of the treated and untreated alloys were analyzed by EDX, the results are summarized in Table 1, the results show that after treatment Al content on the alloy surface greatly de-

Table 1 Surface components of alloy before and after treatment analyzed by EDX (%, %)

Sample	La	Ce	Pr	Nd	Ni	Co	Al
Untreated alloy	11.69	0.80	1.78	0.71	54.77	7.69	22.55
Treated alloy	15.67	1.35	2.11	1.27	65.23	9.41	4.96

creases, whereas nickel component increases. The Ni-rich and Al-poor surface layer were believed to facilitate the improvement in activation behavior and electrocatalytic activity of the alloy electrodes as well as the cycles number of Ni/MH battery^[1, 2, 5~8].

3.2 TDS of hydrogen from alloys surface

Fig. 2 shows the TDS of hydrogen from the surface of the untreated and treated hydrogen storage alloys. For the untreated alloy, there is only one thermal desorption peak at about 400 K, which is called as α -peak. For the treated alloy, three peaks of the hydrogen thermal desorption are found, and called as α -peak at 400 K, β -peak at 530 K and γ -peak at 640 K, respectively. The facts indicate that the TDS structures of hydrogen from the alloy surface are apparently changed by this surface treatment. The thermal desorption peaks of hydrogen at different temperatures are attributed to the different adsorption states of the hydrogen on the alloy surface. Since that the surface of the rare-earth-nickel system hydrogen storage alloy is easily oxidized, the metal oxide film on the alloy surface interfaces with the hydrogen adsorption and hydrogen electrode reaction^[1, 2]. The temperature of hydrogen thermal desorption peak from the untreated alloy surface is lower than that of the treated alloy. After the surface treating, the hydro-

gen adsorption on the alloy surface was strengthened because a Ni-rich surface layer was produced and the surface oxide film was eliminated^[1, 2, 5~8]. The different thermal desorption peaks of hydrogen from the treated alloy surface were likely to attributed to the different micro-surface compositions and chemical states. Further researches are required to understand it. In a word, it can be concluded that the surface modification not only changes the TDS structure of hydrogen from the alloy surface but also enhances the hydrogen adsorption on the alloy surface.

3.3 Electrochemical performances of treated and untreated alloys

Fig. 3 shows the discharge capacity and activation behavior of the hydrogen storage alloy electrode before and after surface treatment. It was found that after surface treatment, the alloy electrode has more initial capacity and better activation behavior in comparison with the untreated alloy. This agrees with the results reported in our previous work^[5~8] and by other researchers^[1~3]. The polarization curves of the untreated and treated alloy electrodes at the first cycle are shown in Fig. 4, in which one can see that the overpotential for the treated alloy electrode is less than that of the untreated one. The fact means that the surface treatments improve the initial electrocatalytic activity of the alloy electrodes.

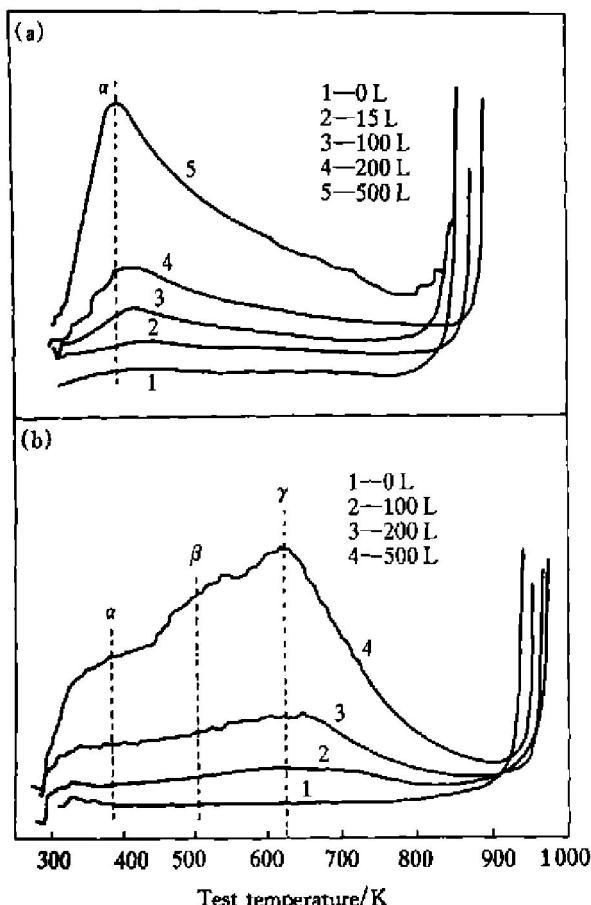


Fig. 2 TDS of hydrogen from untreated alloy surface at different hydrogen exposures

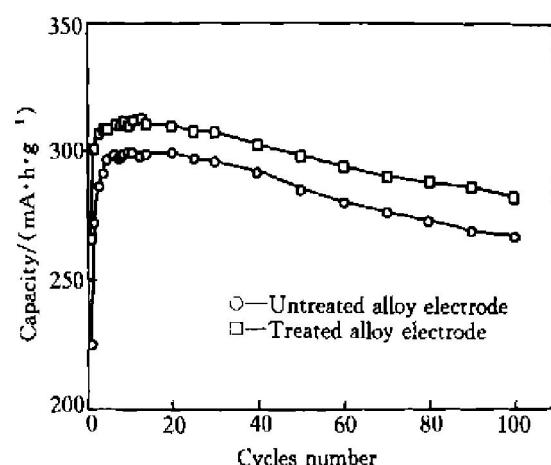


Fig. 3 Discharge capacity of alloy electrode as function of cycles number

The exchange current density is believed to be a measure of the electrocatalytic activity for electrode reaction. Fig. 5 shows the exchange current density varies with the cycle number. At the first cycle, the exchange current density of the alloy electrode increases from 49 mA/g for the untreated alloy electrode to 95 mA/g for the treated alloy electrode. As shown in Fig. 5, the exchange current density increases with increasing cycles number. It is well known that with the charge/discharge cycle proceeding, the fresh surface is produced and the specific surface area is

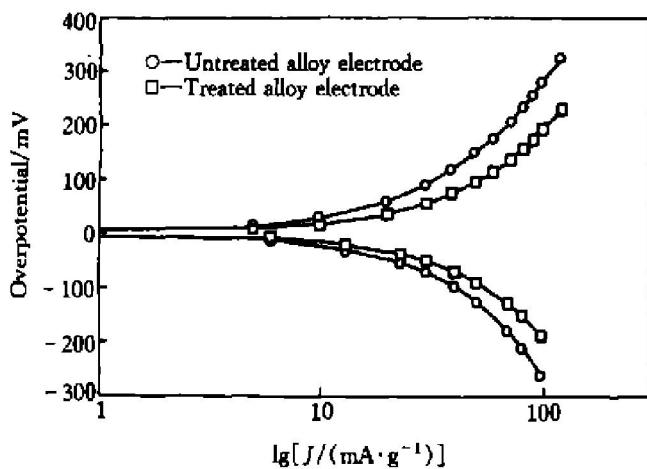


Fig. 4 Polarization curves of hydrogen storage alloy electrode at first cycle at depth of discharge of 50%

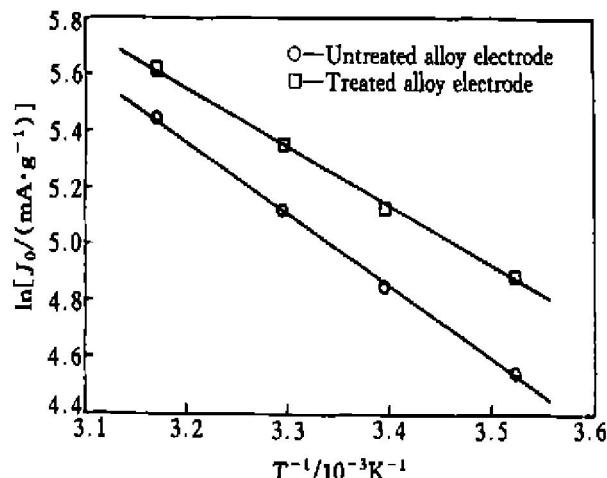


Fig. 6 Arrhenius plots for hydrogen electrode reaction on untreated and treated alloy surface at 10th cycle (depth of discharge is 50%)

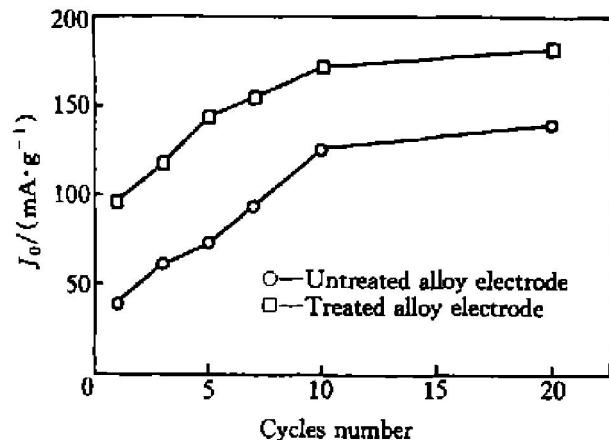


Fig. 5 Exchange current density of untreated and treated alloy electrode varies with cycles number at room temperature (depth of discharge is 50%)

augmented because of the crack and pulverization of the alloy particles, which lead to the activation of the alloy electrode^[2]. It is noticed that at the same cycle, the exchange current density of the treated alloy electrode is larger than that of the untreated one at any time. This fact indicates that the treated alloy electrode exhibits higher electrocatalytic activity than the untreated one. Fig. 6 is the Arrhenius plots of the hydrogen electrode reaction on the alloy electrodes. The apparent activation energy can be calculated from the slopes of the Arrhenius plots of the exchange current densities using Eqn. (2). It is found that the apparent activation energy is reduced by the surface modification from 21.3 kJ/mol for the untreated alloy electrode to 18.1 kJ/mol for the treated alloy electrode. It is hence concluded that the surface treatment not only improves the exchange current density of hydrogen electrode reaction on the hydrogen storage alloy electrode, but also reduces the apparent activation energy.

It is acceptable that the electrocatalytic activity of the metal electrodes has a close relation to the hydrogen adsorption heat on the metal surface. The well-known electrocatalytic "valcano plots" for hydrogen electrode reaction on the metal electrode shows that the electrode exhibiting high electrocatalytic activity is attributed to the intermediate hydrogen adsorption strength on the metal surface^[11]. For example, Pt and Pd have the maximum electrocatalytic activity for hydrogen electrode reaction because the hydrogen adsorption strength on Pt or Pd surface is intermediate. For the hydrogen storage alloy electrodes, the electrode reaction consists of the following three steps: the dissociation of a water molecule on the alloy surface, hydrogen atom adsorption on the alloy surface and the diffusion of hydrogen atom from the alloy surface onto the bulk. Thereby, the adsorbed hydrogen atom on the alloy surface can be considered as an intermediate for the hydrogen electrode reaction on metal hydride electrode. According to the well-known principle in catalysis, a rather strong M-H bonding would yield a surface species essentially immobile and need high activation energy for further transformation. Conversely, a very weak M-H bonding would lead to desorption the alloy surface before the subsequent transformation^[11]. Because of the oxide film and segregation of La on the $\text{M} \text{Ni}_{0.4} \text{Co}_{0.6} \text{Al}_{0.3}$ alloy surface, the hydrogen adsorption on the untreated alloy surface should be very weak as proved by TDS in Fig. 2. It has confirmed that the surface alkaline reducing treatment not only produces the nickel-rich surface layer because of prefrontal dissolution of Al or Mn, but also augments the specific surface area and eliminates the surface oxide film^[1, 2, 5~8]. The Ni-rich surface layer, which exists in Raney Ni or cluster, and larger specific surface area can markedly enhance the hydrogen adsorption on the

alloy surface. Therefore, the electrocatalytic activity for hydrogen electrode reaction on the alloy surface was greatly improved by the alkaline reducing surface treatment. The treated alloy electrode exhibits higher exchange current density and lower apparent activation energy for the hydrogen electrode reaction than the untreated alloy electrode.

4 CONCLUSION

The hydrogen storage alloy ($MnNi_{4.0}Co_{0.6}Al_{0.4}$) was treated in a hot alkaline solution containing KBH_4 as reducing agent. The results of XPS and EDX analysis show that the nickel oxide on the alloy surface was reduced and the Ni-rich and Al-poor surface layer was produced after this surface treatment. It was found that the surface treatment improved the hydrogen adsorption on the alloy surface by TDS. There were three TDS peaks of the hydrogen from the treated alloy surface, while there was a TDS peak of the hydrogen from the untreated alloy surface. Furthermore, the temperature of dominant peak for treated alloy was higher than that for the untreated alloy, which indicated the hydrogen adsorption on the alloy surface was enhanced by the surface treatment. The effects of the surface treatment on the electrochemical performances of the alloy electrode were also investigated. It was found that its discharge capacity, activation behavior and electrocatalytic activity were improved by the surface treatment. The treated alloy exhibited higher exchange current density and lower apparent activation energy for the hydrogen electrode reaction than the untreated one. According to the well-known electrocatalytic “volcano plots” for hydrogen electrode reaction on the metal electrode^[1], the electrocatalytic activity of the alloy electrode was greatly improved because of the surface treatment enhancing the hydrogen adsorption on the alloy surface.

[REFERENCES]

[1] Iwakura C, Matsuoka M, Asai K, et al. Surface modifi-

cation of metal hydride negative electrodes and their charge/discharge performance [J]. J Powder Sources, 1992, 38: 335– 343.

- [2] Matsuoka M, Asai K, Fukumoto Y, et al. Surface modification of hydrogen storage alloy electrode with an alkaline solution containing KBH_4 as a reducing agent [J]. Electrochim Acta, 1993, 38(5): 659– 662.
- [3] Ikawa K, Horiba T, Ogura T, et al. Methods of surface treatments on $MnNi_5$ -based hydrogen storage alloys and their electrochemical characteristics [J]. Denki Kagaku, (in Japanese), 1994, 62: 822– 829.
- [4] Ikoma M, Komari K, Kaida S, et al. Effect of alkali treatment of hydrogen storage alloy on the degradation of Ni/MH batteries [J]. J Alloys and Comp, 1999, 284: 92– 98.
- [5] CHEN W X, TANG Z Y, GUO T H, et al. Effects of surface treatment on performances of metal hydride electrodes and Ni/MH batteries [J]. J Powder Sources, 1998, 74: 34– 39.
- [6] CHEN W X. Improvement in electrochemical performances of $Mn(NiCoMnAl)_5$ electrodes by surface modification [J]. Trans Nonferrous Met Soc China, 1998, 8 (2): 250– 255.
- [7] CHEN W X. Cyclic voltammetry and electrochemical impedance of $MnNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3}$ alloy electrode before and after treatment with a hot alkaline solution containing reducing agent [J]. J Power Sources, 2000, 90: 201– 205.
- [8] CHEN W X. Effects of surface treatments of $MnNi_{4.0}Co_{0.6}Al_{0.4}$ hydrogen storage alloy on the activation, charge/discharge cycle and degradation of Ni/MH batteries [J]. J Powers Sources, 2001, 92: 102– 107.
- [9] Fukumoto Y, Miyamoto M, Matsuoka M, et al. Effect of the stoichiometric ratio on electrochemical properties of hydrogen storage alloys for nickel–metal hydride batteries [J]. Electrochim Acta, 1995, 40: 845– 848.
- [10] Miao H J, Piron D J. Composite coating electrodes for hydrogen evolution reaction [J]. Electrochim Acta, 1993, 38: 1079– 1085.
- [11] Ezaki H, Morinaga M, Watanabe S. Hydrogen overpotential for transition metals and alloy, and its interpretation using an electronic mode [J]. Electrochim Acta, 1993, 38: 557– 564.

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