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Effect of electroless plating nickel treatment on electrode properties of Zr-based AB_2 type alloy①

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[Abstract] An electroless plating nickel treatment was processed to improve the active behaviors and discharge capacities of Zr-based AB_2 alloys. The effects of the nickel coating on the surface appearance, the structure of the alloy powders and the electrode characteristics were investigated. It is found that the Ni-rich layer formed through electroless plating nickel treatment plays an important role on the initial activation property and the discharge capacity of Zr-based alloy. The optimal content of electroless plating nickel is about 15%, and the discharge capacity of the electrode can be increased to 400 $mA\cdot h\cdot g^{-1}$ after 6 cycles. Although coated nickel is beneficial for quick activation and discharge capacity, excessive electroless plating nickel can result in a decreased discharge capacity.

[Key words] Zr-based AB_2 alloy; electroless plating nickel; activation behavior; discharge capacity

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1 INTRODUCTION

In recent years, the Ni-metal hydride (Ni-MH) battery has gradually and steadily replaced the Ni-Cd battery and holds a large share in the secondary battery market[1~3]. However, its rivals such as the Li-ion secondary battery are challenging the status of the Ni-MH battery[4]. Future prospects of the Ni-MH battery depend on the development of advanced storage alloys with higher capacity and better performance.

Zr-based AB_2 type alloys, with a larger hydrogen storage capacity and longer cycle life than that of the conventional AB_5 alloys and reasonable durability in the electrolyte, are promising candidates as the negative electrode material in the Ni-MH battery[5,6]. However, their practical application may take some time as they have some inherent shortcomings such as slow activation process, poor rate capability compared with AB_5 alloys[7].

Many research efforts have been made to improve their activation and kinetic properties such as the addition of rare earth metals[8] and some pre-treatments like hot alkaline[9,10], addition of reducing agent in alkaline solution[11], hot charging treatment[12,13] and a fluorination treatment[14]. In this paper, an electroless plating nickel treatment is investigated by which Zr-based AB_2 alloys are treated and forms a functional Ni-rich surface layer. The effects of the amount of nickel on the electrochemical properties of the alloy are studied to optimize the treating condition and understand the improvement mechanisms.

2 EXPERIMENTAL

Zr-based AB_2 alloy $Zr_{0.9}Ti_{0.1}(Ni, Co, Mn, V)_{2.1}$ was prepared by vacuum induction melting under the purified argon atmosphere. Then the as-cast alloy specimens were mechanically ground to less than 75 μm for electroless plating nickel treatment.

The powders were chemically coated with 5%, 10%, 15%, 20%, and 25% Ni (mass fraction) respectively using the solution listed in Table 1. The electroless plating time was controlled corresponding to the content of Ni on the coating. The surface morphology was examined on the S360 type SEM from Cambridge Instrument Ltd., and the crystal structures of the alloys were confirmed by X-ray diffraction (XRD) using the Rigaku D/ max-γ_A device, Cu K_α radiation and optical filtering with the graphite monochromator.

The electrochemical properties were determined using a BT-2043 battery testing system made by Arbin Company, USA. The process of sample preparation was as follows. 1) Prepare 3.000 g mixture powder of Ni-coated hydrogen alloy and Ni with the ratio of 1∶3; 2) The powder was cold-pressed into electrode pellet (d = 25 mm) by a pressure of 624 MPa; 3) The pellet was sandwiched between two NiOOH/ Ni(OH)$_2$ electrodes with excessive capacity, and then put into a beaker with 6 mol/L KOH solution.

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Table 1 Basic composition of solution and operating condition for electroless plating nickel treatment

Item	Content	Value
Component of solution	$c(NiSO_4 \cdot 6H_2O)/(mol \cdot dm^{-3})$	0.25~ 0.35
	$c[(NH_4)_3C_6H_5O_7 \cdot 2H_2O]/(mol \cdot dm^{-3})$	0.45~ 0.52
	$\rho(NH_3 \cdot H_2O)/(g \cdot dm^{-3})$	0.04~ 0.06
	$c(NaH_2PO_2 \cdot H_2O)/(mol \cdot dm^{-3})$	0.2~ 0.6
	ρ(Thiourea)/$(g \cdot dm^{-3})$	0.004
	ρ(Active agent)/$(g \cdot dm^{-3})$	0.003~ 0.01
Operating condition	Rotation speed/$(r \cdot min^{-1})$	200
	pH	12~ 13.5
	Temperature/K	323 ±1

The discharge capacity measurement was controlled at (298 ±1) K. The sample was charged at a current density of $60\,mA \cdot g^{-1}$ for 8 h, rested for 5 min, and then discharged at the same current density with a cut-off voltage of 1.0 V.

The self-discharge capability measurement was controlled at (300 ±1) K. The samples were charged at a current density of $60\,mA \cdot g^{-1}$ for 8 h, rested for 30 d, and then discharged at the same current density with a cut-off voltage of 1.0 V.

When the discharge capacity was calculated, the mass of hydrogen storage alloy was only considered.

3 RESULTS

The XRD analysis results of the bare and Ni-coated (25%) alloy powders are shown in Fig. 1. It can be seen that the XRD pattern of the bare alloy powder shows the presence of the Laves C15 phase, which belongs to fcc structure. For the Ni-coated (25%) alloy powder, the characteristic peaks of Laves C15 phase are broadened and there exist nickel peaks. These might indicate that an absorption of hydrogen and deposition of a great deal of nickel into alloy occurred due to the hydrogen produced in the electroless plating process.

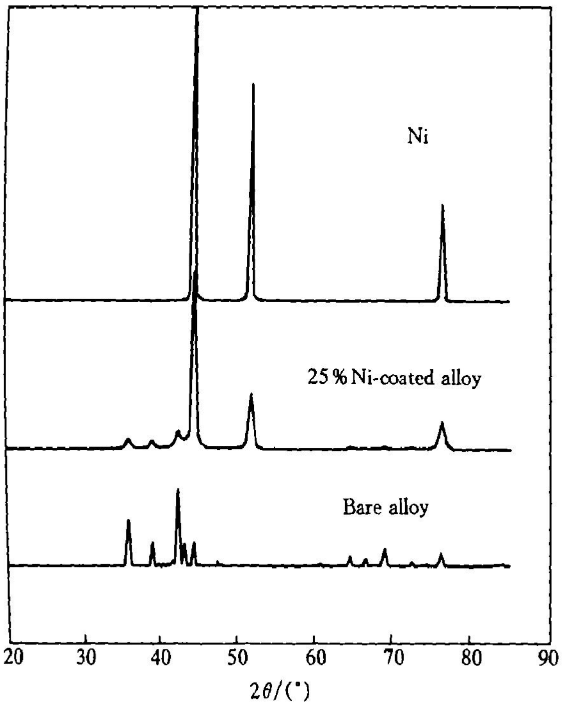

Fig. 1 XRD patterns for different samples

The surface morphologies of the nickel-coated alloy powders with 15%, 25% Ni respectively are shown in Fig. 2. There are some deposited nickel powders. It is obvious that the higher the content of nickel, the longer the electroless plating time is and the larger of the specific surface area is. Otherwise, a lot of nickel deposited form the alloy and the original particles are pulverized due to the hydrogen penetration during the coating process because of the high concentration of the reducing agent.

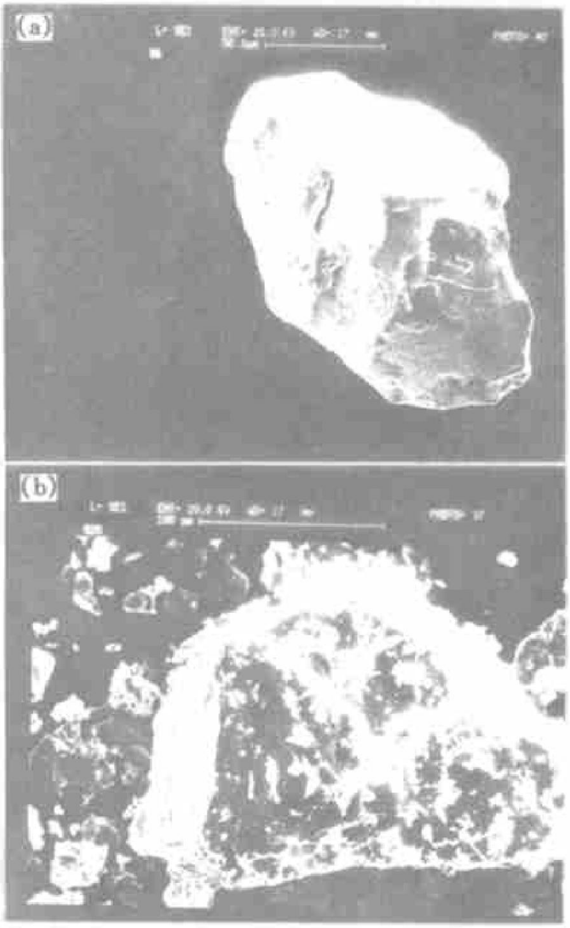

Fig. 2 SEM images for the bare (a) and 25% Ni-coated (b) Zr-based AB_2 alloy powders

Discharge capacities of the Ni-coated alloy electrodes as a function of cycle number are shown in Fig. 3. The initial discharge capacity of the electrode is increased from $16\,mA \cdot h \cdot g^{-1}$ for the bare alloy electrode to $170\,mA \cdot h \cdot g^{-1}$ for the Ni-coated (25%) alloy electrode, and the higher the content of the nickel, the larger the initial discharge capacity of the electrode is. The Ni-coated alloy electrodes have better activation behavior than that of the bare alloy electrode. For example, the Ni-coated (15%) alloy electrode only needs 6 cycles to gain the maximum capacity ($400 mA·h·g^{-1}$); while the maximum discharge capacity of $370.5 mA·h·g^{-1}$ for bare electrode is gained after 22 cycles. The maximum discharge capacity of each Ni-coated electrode is larger than that of the bare alloy. When the content of nickel increases from 5% to 15%, the maximum discharge capacity increases with increasing the content of coating nickel; but excessive coated nickel may result in a decreased discharge capacity.

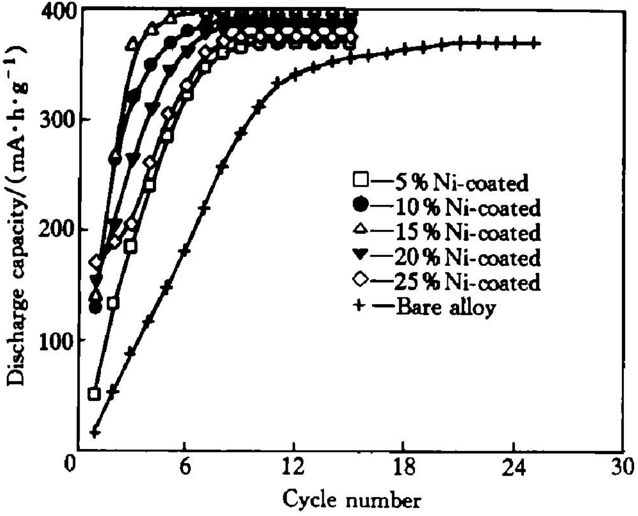

Fig. 3 Discharge capacity of alloy electrode as function of cycle number

The self-discharge capabilities of the electrodes are shown in Fig. 4, which can be expressed by the capacity keeping rate $K_{r,c}$:

$$K_{r,c} = \frac{C}{C_{max}} \times 100\%$$

where C is the discharge capacity of electrode after being rested for 30d, and C_{max} the maximum capacity after being activated fully. It can be found that the alloy electrodes with chemical coating nickel treatment have better $K_{r,c}$ than that of the bare alloy electrode. The $K_{r,c}$ of the electrode (25% Ni-coated) is up to 83%.

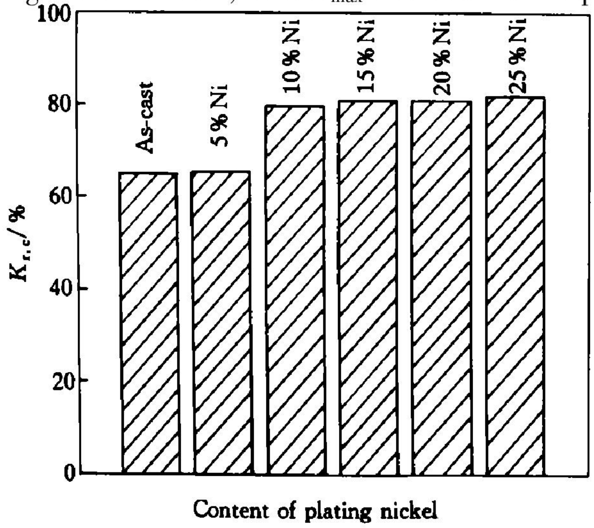

Fig. 4 Self-discharge capabilities of different alloy electrodes

4 DISCUSSION

For a metal hydride alloy electrode, the discharge process involves the following steps:

1) H desorption from the hydride;

2) H diffusion through the bulk of the alloy particle;

3) charge-transfer reaction on the alloy surface.

For a Zr-based AB_2 type alloy, the electrochemical kinetic property is usually considered to be limited by the charge-transfer reaction due to its poor surface activity. To improve the reaction capability of the alloy, it is necessary to increase the surface catalytic activity.

After the electroless plating nickel treatment, the surface catalytic activity is significantly enhanced by forming a nickel-rich surface layer and eliminating barrier films existing on the surface of the alloy, such as ZrO_2 and MnO_2. The specific surface area is also enlarged to a large extent by the pulverization caused by hydrogen penetration during coating process because of the high concentration of the reducing agent. But the discharge capacity can not always be increased with the content of the chemically coated nickel layer because: 1) some effective elements of the alloy are dissolved during electroless plating nickel treatment for a long time; 2) the alloy is disintegrated during plating process which brings about the gradual pulverization of the alloy, continuously enlargement of surface area, and production of fresh surface, resulting in continuous degradation of the alloy.

5 CONCLUSION

The active behavior of the Zr-based AB_2 alloy is successfully improved by electroless plating nickel treatment. It is found that the suitable content of coating nickel is beneficial for discharge and self-discharge capabilities; but an excessive coating nickel content should be avoided because it can reduce the discharge capacity.

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