

Process optimization of electroless copper plating and its influence on electrochemical properties of AB₅-type hydrogen storage alloy

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Abstract: The amount of Cu coating by chemical plating was investigated based on quadratic regression orthogonal experimental design being adapted to the variation law of temperature, pH value and Ni²⁺ concentration, and the relevant regression equation was expressed as $y=2.1609+0.5295\times 10^{-3}T^2-0.0342P^2-0.0265N^2+0.0023TP+0.0020TH+0.0199PN-0.0959T+0.3814P-0.2073N$. The results showed that the deposition rate augmented with the increasing in temperature, pH value and Ni²⁺ concentration. The experimental parameters of the optimal coating were temperature 75 °C, pH value 8.5 and Ni²⁺ concentration 1.2 g/L. The electrochemical tests indicated that the cycle stability increased from 60.66% to 75.58%, indicating that the treated alloy exhibited better corrosion resistance.

Keywords: hydrogen storage alloy; electroless copper plating; electrochemical performance; rare earths

Nickel-metal hydride (Ni-MH) secondary batteries using hydrogen storage alloy as the negative electrode have been recognized to be an important power source for various appliances due to high energy density, high charge-discharge ability, long cycle life, safety and non-pollution characteristics^[1-3]. Surface structures of alloys are dominant factors that affect battery performance. Different approaches such as acid-alkaline treatments^[4,5], mechanical milling^[6,7], electroless plating and depositional technology^[8] have been carried out for modifying the surface structures, and electroless Cu plating has been proved to be an effective method to improve the electrochemical properties.

Deng et al.^[9] have noticed an improvement in electrochemical performance by coating Cu over the uncoated alloy. Sakai et al.^[10] discovered that electroless 20% Cu coating could eliminate oxygen, reduce the internal pressure of the batteries, and prolong the cell life. Wei et al.^[11] reported that the electroless Cu coating for AB₅ type metal hydride alloy improved its activation capacity. They also observed a decrease in charge transfer resistance and an increase in electrochemical activity.

But there is no systemic research on the variation law of alloy coating being adapted to the various factors in the process of electroless Cu plating. This paper researched the parameters of electroless Cu coating based on the quadratic regression orthogonal design, and the purpose is to investigate the effect of different Cu coating mass on electrochemical performance.

1 Experimental

1.1 Electroless Cu plating

Lanthanum-rich $MmNi_{3.55}Co_{0.7}Mn_{0.4}Al_{0.3}Cu_{0.05}$ hydrogen storage alloy was used in this study. The alloy powder with particle sizes from 46 μm to 75 μm was used for electroless Cu plating. Prior to coating, the alloy was sensitized by being immersed in acidified HCL (1 mol/L) for 1 min to remove the surface oxide, then we rinsed the alloy powder with deionized water, filtered and dried it in vacuum oven at 60 °C.

pH value (7–10), temperature (60–90 °C), Ni²⁺ concentration (1–3 g/L) were selected as the investigation factors, and sodium hypophosphite (30 g/L) as reductant, sodium citrate (23.5 g/L) as complexing agent, and nickel sulfate as re-activation agent. Electroless deposition of Cu was carried out with moderate stirring in an alkaline hypophosphite bath at 65–85 °C for 30 min. The pH was monitored between 7 to 9 by NH₄OH. After deposition, the alloy powder was rinsed with deionized water, filtered and dried in vacuum oven at 60 °C.

1.2 Cu coating mass

The Cu coating mass was identified by spectrophotometer method. In pH=9 alkaline solution, copper ion and DDTC-Na generated yellowish-brown colloid compound, molar ratio of which was 1:2, and its maximum absorption wavelength was 452 nm.

Coated alloy of 0.2 g was dissolved in 3 mol/L hydrochloro-

ric acid we diluted the solution in copper standard solution range, then added superfluous DDTC-Na solution, adjusted pH value to 9, determined absorbance in spectrophotometer, and calculated the copper coating amount.

1.3 Physical characterization

SEM analysis was performed to examine the surface morphology of the bare as well as coated alloy powders using SSX-550 microscope. Powder X-ray diffraction data of the bare and microencapsulated alloys were collected using a PANalytical X'per PRO model diffractometer with Cu K α radiation.

1.4 Charge-discharge experiments

Metal hydride electrodes for bare and coated alloys were prepared with 0.2 g alloy powder. Slurry of the alloy powder with appropriate amounts of conducting material (Ni powder T255) and binder (polytetrafluoroethylene) were applied on both sides of nickel mesh substrate. The electrode was pressed under 20 MPa at 120 °C. The excess nickel hydroxide (Ni(OH)₂/NiOOH) electrode was used as the positive electrode. A polyamide nonwoven cloth was used as the separator. The negative electrode was sandwiched between two positive electrodes. Solution of 6 mol KOH was used as electrolyte. Charge-discharge cycling was performed at a current density of 100 mA/g in a DC-5 battery tester for activation experiments. Charging was done for 5 h and discharge was done till the potential of the metal hydride alloy electrode reached -0.6 V with respect to the Hg/HgO reference electrode. Activation experiments were done with an overcharge factor of 60% after a pause of 10 min after full charge. Charge and discharge cycles at the current density of 300 mA/g were conducted to test the cycle life of the metal-hydride electrodes. Charging was done for 1.2 h and discharge was done till the potential of the metal hydride alloy electrode reached -0.6 V with respect to the Hg/HgO reference electrode.

Table 2 Three factors quadratic orthogonal regression test*

Number	X ₀	X ₁	X ₂	X ₃	X ₄	X ₅	X ₆	X ₇	X ₈	X ₉	y/%
1	1	-1	-1	-1	1	1	1	0.27	0.27	0.27	0.424977
2	1	-1	-1	1	1	-1	-1	0.27	0.27	0.27	0.315097
3	1	-1	1	-1	-1	1	-1	0.27	0.27	0.27	0.302814
4	1	-1	1	1	-1	-1	1	0.27	0.27	0.27	0.311701
5	1	1	-1	-1	-1	-1	1	0.27	0.27	0.27	0.189247
6	1	1	-1	1	-1	1	-1	0.27	0.27	0.27	0.197991
7	1	1	1	-1	1	-1	-1	0.27	0.27	0.27	0.212724
8	1	1	1	1	1	1	1	0.27	0.27	0.27	0.230432
9	1	-1.215	0	0	0	0	0	0.746	-0.73	-0.73	0.45055
10	1	1.215	0	0	0	0	0	0.746	-0.73	-0.73	0.274182
11	1	0	-1.215	0	0	0	0	-0.73	0.746	-0.73	0.24701
12	1	0	1.215	0	0	0	0	-0.73	0.746	-0.73	0.220115
13	1	0	0	-1.215	0	0	0	-0.73	-0.73	0.746	0.249371
14	1	0	0	1.215	0	0	0	-0.73	-0.73	0.746	0.268852
15	1	0	0	0	0	0	0	-0.73	-0.73	-0.73	0.247283

* X represents influencing factors; y represents Cu coating mass

2 Results and discussion

2.1 Quadratic regression orthogonal design

The experiments were based on quadratic regression orthogonal design ($\gamma=1.215$) to investigate the mass changes of Cu coating corresponding with temperature, pH value and Ni²⁺ concentration. The codes of factors are shown in Table 1. Table 2 shows the experimental scheme of the quadratic regression orthogonal design and the corresponding Cu coating quality.

Based on the experiments, the relevant regression equation was expressed as follows:

$$y=2.1609+0.5295 \times 10^{-3}T^2-0.0342P^2-0.0265N^2+0.0023TP+0.0020TN+0.0199PN-0.0959T+0.3814P-0.2073N$$

where y represents Cu coating mass, T temperature (°C), P pH value, and N the concentration of nickel sulfate (g/L).

The F tests (regression significance tests) of the regression equation are as follows:

$$S_{total}=0.081427$$

$$S_{regression}=0.071767$$

$$S_{remain}=S_{total}-S_{regression}=0.00366$$

$$F_{total}=14$$

$$F_{regression}=9$$

$$F_{remain}=5$$

$$F=(S_{regression}/f_{regression})/(S_{remain}/f_{remain})=(0.071767/9)/(0.00366/5)=11.8043$$

$$F=11.8043>F_{(0.01)}^{(9,5)}=10.15$$

Table 1 Codes of the factors

Factors	Temperature/°C	pH	Nickel sulfate/(g/L)
Number	X ₁	X ₂	X ₃
Datum level (0)	75	8.5	2
Constant intervals (Δ_j)	10	1	0.8
+1	85	9.5	2.8
-1	65	7.5	1.2
+ γ	87.15	9.715	2.972
- γ	62.85	7.285	1.028

The *F* tests indicated that the experiments were significant in 0.01 level, so the equation could be used on the variation law of Cu coating quality.

2.2 Effect of process conditions on Cu coating mass

2.2.1 The effect of pH value on Cu coating mass Fig. 1 shows the effect of pH value on Cu coating mass at 80 °C. The results showed that the quality changes divided into three steps with the increasing in pH value.

The coating amount increased rapidly when pH value augmented from 7.5 to 8. The line is steeper with increasing in the Ni²⁺ concentration. This is because that OH⁻ is the reactant of the anodic reaction which is the controlling step of electroless plating^[12]. The reaction rate increased as pH value raised. In the second stage, the increasing tendency became slow, when pH value increased from 8 to 8.5. And this tendency decreased while pH value exceeded 8.5. The augmentation of pH value could promote the process of side reaction, $H_2PO_2^- + 2Cu^{2+} + 4OH^- \rightarrow Cu_2O \downarrow + H_2PO_3^- + 2H_2O$, the Cu₂O content increased in the coating, and this phenomenon caused the coating to exhibit chocolate brown and the conductivity to declined. Therefore, pH value should be kept in the range of 8–9.

2.2.2 The effect of Ni²⁺ concentration on Cu coating mass

Fig. 2 shows the effect of Ni²⁺ concentration on Cu coating mass at 80 °C. The results showed that the quality changes divided into three steps with the increasing in Ni²⁺ concentration.

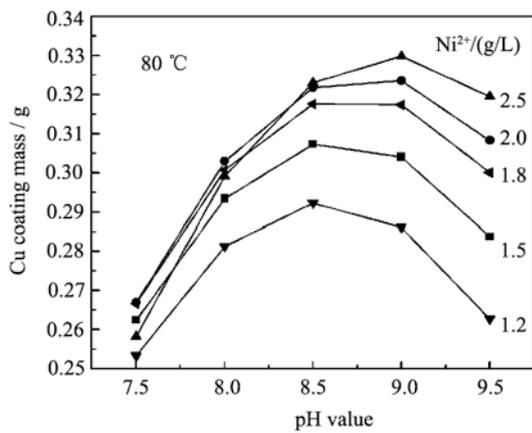


Fig. 1 Effect of pH value on Cu coating mass

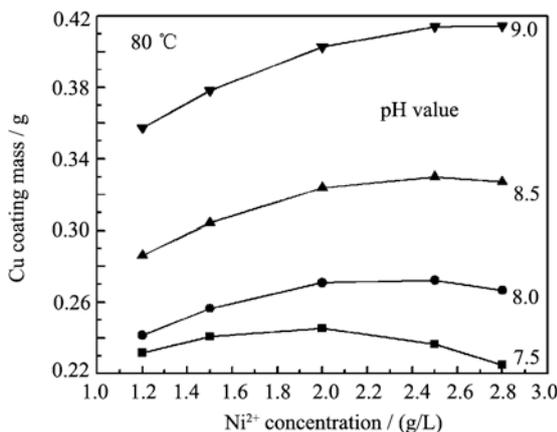


Fig. 2 Effect of Ni²⁺ concentration on Cu coating mass

The coating amount increased rapidly when Ni²⁺ concentration raised from 1.2 g/L to 1.5 g/L, this is due to the augmentation of deposition rate. The increasing tendency became slow when Ni²⁺ concentration increased from 1.5 g/L to 2 g/L, as the pH value was higher, the line was steeper, and this tendency decreased while Ni²⁺ concentration exceeded 2 g/L. Cu has lower self catalytic action in the hypophosphite system, so re-activation agent Ni²⁺ must be added, however, when the proportion of Ni²⁺/Cu²⁺ is too large, the stability of bath declines, conductivity decreases, the reaction of electroless plating can not continue. So Ni²⁺ concentration should be controlled in the range of 1–2 g/L.

2.2.3 The effect of temperature on Cu coating mass Fig. 3 shows the effect of temperature on Cu coating mass, when Ni²⁺ concentration is 2.0 g/L. The results showed that the quality changes divided into three steps with the increasing in temperature.

The coating amount had no significant changes when temperature increased from 65 °C to 70 °C. The increasing tendency became slow when temperature augmented from 70 °C to 75 °C, but the amount increased rapidly after 75 °C. Based on the collision theory, when temperature rose, the reaction rate augmented, but this augmentation caused the coating state to be significantly rough micropores on alloys surface, which presented chocolate brown color. So temperature should be controlled in 75–85 °C range; in this range, faster deposition rate and better stability could be obtained.

2.3 Micro-morphology analysis

According to the regression equation: $y = 2.1609 + 0.5295 \times 10^{-3}T^2 - 0.0342P^2 - 0.0265N^2 + 0.0023TP + 0.0020TN + 0.0199PN - 0.0959T + 0.3814P - 0.2073N$, pH value was the most important factor of electroless copper plating process, and the interaction of different factors was not obvious. Therefore, we chose the representative samples, to investigate the changes of phase composition and surface morphology by XRD and

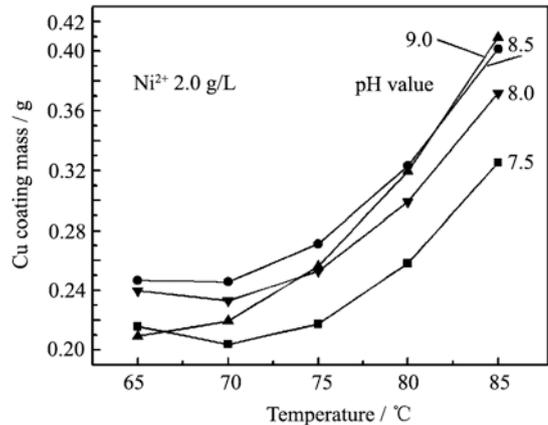


Fig. 3 Effect of temperature on Cu coating mass

Table 3 Process conditions of samples

Samples	Temperature/°C	pH value	Ni ²⁺ concentration/(g/L)
1	85	9.5	1.2
2	75	8.5	1.2
3	65	7.5	1.2

SEM analyses. The process conditions as are follows.

2.3.1 The SEM analyses of uncoated and coated alloys Fig. 4 shows the XRD analyses of uncoated and coated alloys: the bare hydrogen alloy is single-phase structure, and the treated alloy surface showed Cu diffraction peak, mainly replaced Ni element, forming compounds with the rare earth elements such as CeCo_{3.5}Cu_{1.5} and Cu₃Nd. So the surface modification could form deposition layer on the alloy surface.

2.3.2 The surface morphology of bare and coated alloys

Fig. 5 shows the alloy surface morphology of uncoated and coated alloys. Fig. 5(a) shows that the bare alloy surface was smooth and temper. Fig. 5(b) shows different size spherical particles dispersed on the treated alloy surface, some small particle peripheral dispersed abnormally in the large particles, and the thickness of the coating was deep. Fig. 5(c) shows that flat detailed spherical particles dispersed on the treated alloy surface, basically had no void. Fig. 5(d) shows that the particles are obviously small when the coating,

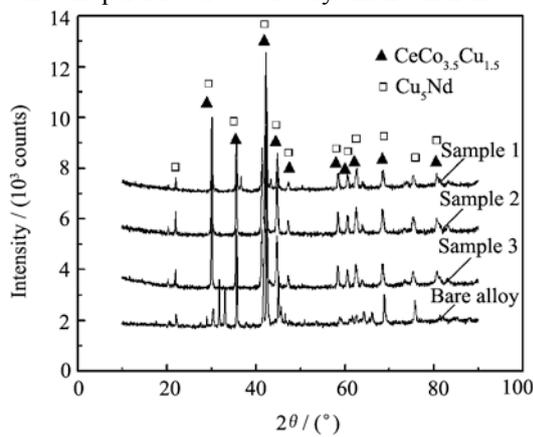


Fig. 4 X-ray diffraction of uncoated and Cu coated alloys

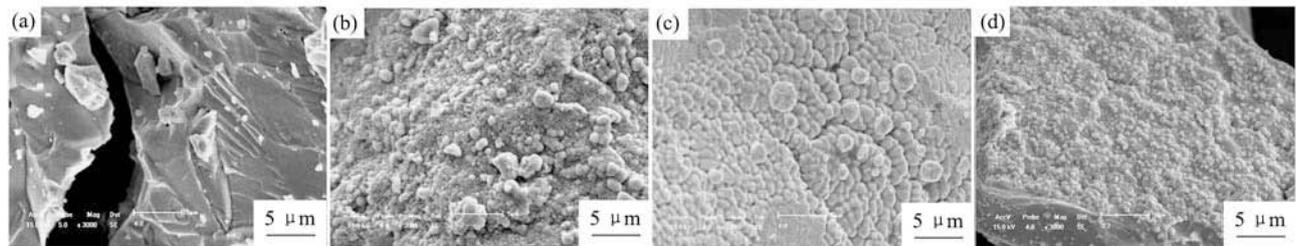


Fig. 5 SEM analyses of the uncoated and Cu coated alloy
(a) Bare alloy; (b) Sample 1; (c) Sample 2; (d) Sample 3

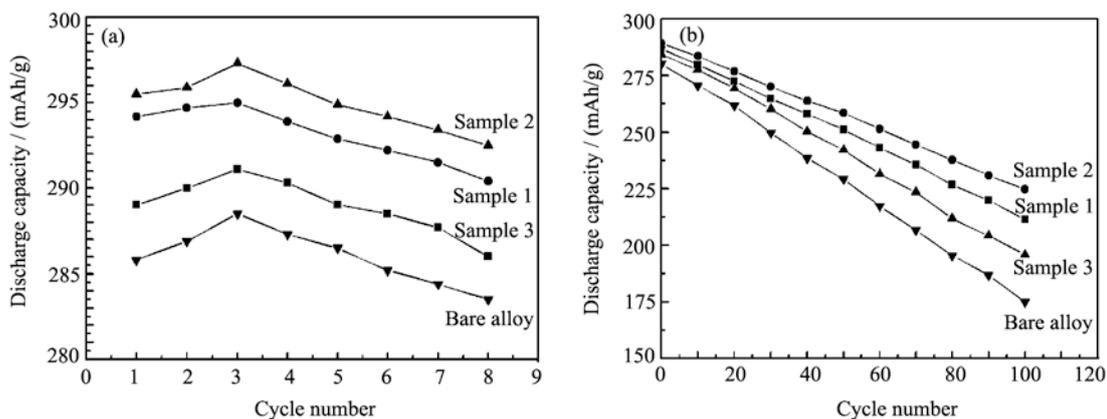


Fig. 6 Electrochemical performance of uncoated (a) and Cu coated (b) hydrogen storage alloy

quality is light and distinct void between particles existed.

2.4 Effect of Cu coating on electrochemical performance

Essentially there is an activation process for a transition of metals and alloys to metal-hydrides. Fig. 6(a) shows the activation performance of uncoated and coated MmNi_{3.55}Co_{0.7}Mn_{0.4}Al_{0.3}Cu_{0.05} alloys. All the alloys got their maximum discharge capacity in the third cycle. The maximum capacity of uncoated alloys was 288.5 mAh/g that of three coated alloys were 293.9, 297.3 and 290.3 mAh/g, respectively. Fig. 6(b) shows the cycle stability of uncoated and coated MmNi_{3.55}Co_{0.7}Mn_{0.4}Al_{0.3}Cu_{0.05} alloys. The cycling capacity retention rate is expressed as $S_{100} = (C_{100}/C_{max}) \times 100\%$ (where C_{max} is the maximum discharge capacity, C_{100} is the discharge capacity at the 100th cycle) of alloy increased from 60.66% to 75.58%, indicating that the treated alloy exhibited a better corrosion resistance. The main reason for the increase in anti-corrosion is ascribed to the formation of Cu-coating with good corrosion resistance in the alkaline solution after surface treatment. And the optimum electroless plating conditions were temperature 75 °C, pH value 8.5 and Ni²⁺ concentration 1.2 g/L.

Table 4 Electrochemical performance of uncoated and Cu coated hydrogen storage alloy

Samples	$C_{max}/(\text{mAh/g})$	Cycle	S_{100}
Sample 1	293.9	3	75.58%
Sample 2	297.3	3	71.93%
Sample 3	290.3	3	67.45%
Bare alloy	288.5	3	60.66%

3 Conclusions

1. The regression equation was obtained based on the quadratic regression orthogonal design: $y=2.1609+0.5295\times 10^{-3}T^2-0.0342P^2-0.0265N^2+0.0023TP+0.0020TH+0.0199PN-0.0959T+0.3814P-0.2073N$. The pH value was the main factor of electroless copper plating; the interaction of different factors was not significant. The results showed that the deposition rate augmented with the increasing in temperature, pH value and Ni^{2+} concentration.

2. All the alloys reached their maximum capacity in the third cycle. Activation capacity was slightly changed by electroless copper plating, but the cycle stability improved from 60.66% to 75.58%, indicating that the treated alloy exhibited better corrosion resistance. The experimental parameters of the optimum conditions were temperature 75 °C, pH value 8.5 and Ni^{2+} concentration 1.2 g/L.

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