

Electrodeposition, Structure and Corrosion Resistance of Nanocrystalline Ni—W Alloy

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Ni—W alloy was electrodeposited from the electrolyte solution containing sodium tungstate, nickel sulfate and ammonium citrate. The electrodeposition, heat treatment, structure, surface morphology and corrosion resistance in $w=0.03$ NaCl solution, of Ni—W alloys were studied by means of DSC, XRD, SEM and electrochemical techniques. The results showed that the obtained Ni—W alloy electrodeposit with W weight content ($w_W=0.471$) was presented in more typical nanocrystalline. After heat treatment at 400 °C for 1 h, the phase structure of the deposits was not obviously changed whereas the agglomerate for the reunion of tiny grains on deposit surface caused the granule in a more smooth morphology, the microhardness was slightly increased and the corrosion resistance was enhanced.

Keywords Ni—W alloy, nanocrystalline, electrodeposition

Introduction

Tungsten oxide rather than tungsten will be electrodeposited from aqueous solution containing tungstate itself. In conjunction with iron group metals such as nickel W can be induce-codeposited¹⁻⁴ in the form of Ni—W alloy. The characteristics of the codeposition is that the deposition potential of the alloy is more positive than that of WO_4^{2-} and Ni^{2+} existing alone.^{1,3,4} By the increase of W content in deposit the structures of Ni—W alloy electrodeposits will be turned from an intermetallic compound,⁵ a solid solution^{2,6,7} to a nanocrystalline or amorphous alloy⁸⁻¹¹ with W content at $w=0.43-0.44$.

The introduction of tungsten to the alloys improves their corrosion resistance, microhardness and thermal stability.¹⁰⁻¹⁸ The alloy can be used as electrocatalysis for hydrogen evolution^{19,20} and substrate of superconducting materials.⁶ Since Cr(VI) is harmful to environment and human body Ni—W alloy has been to a certain extent replaced for chromium.^{14,21-23}

In this paper Ni—W alloy was electrodeposited from the aqueous solution with sodium tungstate, nickel sulfate and ammonium citrate. The electrodeposition, structure, surface morphology and corrosion resistance in $w=0.03$ NaCl solution, of Ni—W alloys before and after heat treatment were studied by means of DSC, XRD, SEM and electrochemical techniques.

Experimental

The electrolyte contained $NiSO_4 \cdot 6H_2O$ (30 g/L), $Na_2WO_4 \cdot 2H_2O$ (65 g/L), $(NH_4)_3C_6H_5O_7$ (100 g/L). The solution was prepared with chemical pure reagents and distilled water, and was adjusted to pH=7.0—7.5 with $NH_3 \cdot H_2O$. Graphite panel was used as anode and stainless steel sheet as cathode with working area (3.0 cm×2.5 cm). The plating solution was magnetically stirred. Current density was 8.0 A·dm⁻², temperature 60 °C and deposition time 80 min. The obtained Ni—W alloy deposits were separated mechanically from stainless steel.

Deposition current efficiency of the alloy is as follows:

$$\eta = \eta_W + \eta_{Ni} = \frac{w_W \cdot \Delta G / E_W}{I \cdot t} + \frac{w_{Ni} \cdot \Delta G / E_{Ni}}{I \cdot t} \quad (1)$$

where η_W and η_{Ni} are W and Ni partial current efficiency, E_W and E_{Ni} are W and Ni electrochemical equivalent values, $0.318 \times 10^{-3} \text{ g} \cdot \text{C}^{-1}$ and $0.304 \times 10^{-3} \text{ g} \cdot \text{C}^{-1}$ respectively, ΔG is the deposit weight (g), w_W and w_{Ni} are W and Ni weight portion values, I is current (A) and t deposition time (s).

In order to evaluate the coating structure development, the Ni—W alloy samples were heated at 400 °C for 1 h in a tube furnace with a nitrogen purge and heat rate 3 °C/min. Differential scanning calorimeter (DSC) experiments were carried out in a DSC204 (NETZSCH,

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Germany) thermal-analysis instrument under nitrogen atmosphere with the temperature increase at 20 °C/min.

Microhardness of as-plated and heat-treated specimens was determined using Model 71 Vickers microhardness tester made by the second optical instrument factory, Shanghai, China with a 100 g of load and contacting time 15 s.

The X-ray diffraction (XRD) experiments were carried out on the X-ray rotating powder diffractometer of D/MAX-RC (Rigaku, Japan) with Cu K α radiation, tube potential 40 kV, tube current 30 mA and scan rate 6 (°)/min. Grain size is as follows:

$$D_{hkl} = k\lambda / (\beta \cos \theta) \quad (2)$$

where k is Scherrer constant with the value of 1, λ X-ray wavelength ($\lambda = 0.15406$ nm for Cu target), θ Bragg angle, β peak half-width in radian unit.

Surface morphology of the deposit was tested with XL30 ESEM (Philips) scanning electron microscopy (SEM), 20 kV. The composition of the deposits on top surface was measured by energy dispersive spectroscopy (EDS) equipped in the SEM instrument.

Electrochemical experiments were carried out on a CHI 660 Electrochemical Station (CH Instruments, Inc., USA). A conventional three-electrode cell was used. The working electrode was the alloy before and after heat treatment. The reference electrode was saturated calomel electrode (SCE) and all potentials were referred to this, and platinum was used as counter electrode. The electrolyte was $w = 0.03$ NaCl solution. Before experiment the working electrode was first degreased with petroleum benzene and acetone, etched in 1 : 3 (V : V) nitric acid and hydrochloric acid, then washed with distilled water. The Tafel experiments were carried out at ± 250 mV in the range of open circuit potential, scan rate 1 mV·s⁻¹.

Results and discussion

Electrodeposition of Ni—W alloy

Ni—W alloy electrodeposits are shown in different adhesion abilities to stainless steel and to copper substrates. There is no interface between Ni—W alloy and steel, which causes the deposit in poor adhesion and internal stress.¹⁴ At the stated electrolyte solution and under plating conditions the obtained Ni—W electrodeposits are in poor adherence, tensile stress, metallic luster in appearance, $w_W = 0.471$ and $w_{Ni} = 0.529$. It can also be found that an interface leading to good adhesion of the alloy to the copper substrate will be formed, simply because of nickel and copper in similar crystallographic structure and the preferential deposition of Ni on copper.¹⁴

Though the deposition potential of Ni—W alloy is more positive than that of nickel or tungsten⁴ the alloy deposition is still accompanied with vigorous hydrogen evolution. In this experiment the deposition current efficiency η of the alloy is 44.0% with $\eta_W = 20.2\%$ and η_{Ni}

23.8%, much higher than 15%,¹⁴ lower than 70%—80%³ and similar to our former work.²⁴⁻²⁶ Cesuiles *et al.*²⁷ has reported that current efficiency would increase in the highest 3.2 times during deposition in the electrolyte with higher concentrations of citrate and nickel salt. Nevertheless the increasing content of nickel salt in solution will undoubtedly decrease W content of the alloy²⁵ since the reduction of nickel ions is in diffusion control^{10,28,29} and that of WO₄²⁻ in kinetic control.¹⁰ Only in the solution with the contents of nickel sulfate unchanged and sodium tungstate increased then the W content and structure of the obtained Ni—W alloy electrodeposits are almost kept in uniformity.²⁴

Heat treatment, structure and microhardness of Ni—W alloy

DSC plot for heat treatment of the alloy is shown in Figure 1. The result reveals that at the temperature range a gradual exothermic course instead of thermal peak above 100 °C is found during the alloy heat treatment. Combined with the XRD results it is suggested that there has only happened the coarsening of tiny crystals of the alloy and no new phase emerged. According to the phase diagram³⁰ Ni—W alloy would be formed in a supersaturated solid solution with W content above $w_W = 0.26$. Therefore the metastable structure of the obtained Ni—W ($w_W = 0.471$) in this experiment will inevitably transfer the alloy to a stable state, resulting in the coarsening of tiny crystals. At the same time during treatment with heat W is segregated to the top surface of the deposit.⁷

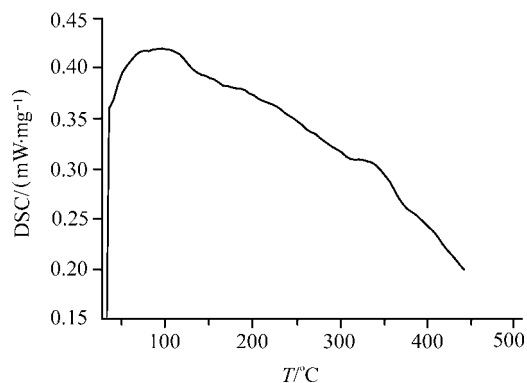


Figure 1 DSC plot of Ni—W alloy.

XRD patterns of the Ni—W alloy before and after heat treatment are presented in Figure 2. Their structural parameters and microhardness are shown in Table 1. From Figure 2, before and after heat treatment respectively the broad peaks can be found mainly at 2θ 43.58° and 43.47° corresponding to face-centered cubic (FCC) Ni(111) structure for Ni—W alloy. The grain sizes of the deposit have been changed from 4.8 nm as plate to 5.9 nm after treatment with heat. Therefore the structure combined with the result of Figure 1 is still presented in more obvious nanocrystalline characteristics. After treatment at 400 °C for 1 h the deposit will not be cry-

stallized. Yamasaki *et al.*¹¹ indicated that by the augment of W content in Ni—W alloy deposit the diffraction peaks in XRD plots were broadened. SchloBmacher *et al.*¹² pointed out the value of 2θ for (111) face diffraction peak was slightly shifted to a lower degree and the Ni—W alloy was still in a solid solution after treatments at temperature lower than 500 °C for 24 h. Only at temperature higher than 600 °C for 24 h Ni—W alloy could be crystallized with the evolution of Ni₄W. Obviously the results of this paper are accordant with the reports.

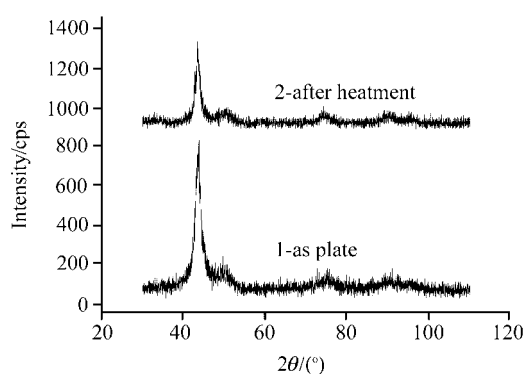


Figure 2 XRD patterns of Ni—W alloy before and after heat treatment.

Table 1 XRD results and microhardness of the deposits before and after heat treatment

	$2\theta/^\circ$	d/nm	D_{hkl}/nm	$H_v/(\text{kg}\cdot\text{mm}^{-2})$
As plate	43.58	0.2075	4.8	579
After heat treatment	43.47	0.2080	5.9	594

Comparison with the value 0.2034 nm of interplanar spacing (d) of pure nickel the d values of both the as-plated and heat-treated alloys are larger. It then can be deduced that in the solid solution of Ni—W alloy the spaces around the W atoms (0.137 nm in atomic semidiameter) are compressed and those around Ni (0.122 nm in atomic radius) are stretched, resulting in lattice distortion and imperfections.

Microhardness of Ni—W alloy electrodeposit would be enhanced by the increase of its W content,³¹ and affected by domain of size, coherency strains, dislocations and grain boundaries.³² XRD and DSC results illuminate the slight structural changes of Ni—W alloy after heat treatment at 400 °C for 1 h, and its microhardness is slightly enhanced from 579 $\text{kg}\cdot\text{mm}^{-2}$ as plate to 594 $\text{kg}\cdot\text{mm}^{-2}$ after heat treatment.

Surface morphology of Ni—W alloy

Most of Ni—W alloy electrodeposits appear in granular structure.^{3,10,13,14,20,24,31} Bratoeva³ reported that the surface morphology of Ni—W ($w_w=0.41$) alloy deposit was in agglomerates consisting of many crystallites with small dimensions (*ca.* 0.5 μm). Ni—W alloy

deposits were cracked because of their internal stress.^{14,20} In this experiment the surface morphologies of the obtained Ni—W alloy electrodeposits are shown in Figure 3. The as plated deposit (Figure 3a) is in a granular structure with 3—8 μm dimension. It is crack-free but grain boundaries can be seen among the agglomerates. After heat treatment (Figure 3b) the agglomerates of the deposit keep almost no changes but in smooth, and blue film on deposit surface can also be seen. This is undoubtedly attributed to the reunion of tiny grains and oxidation of W on deposit surface. According to these results and that W was segregated to the top surface of the deposit⁷ during treatment with heat the heated deposit with a stable state will be expected to show more excellent corrosion resistance.

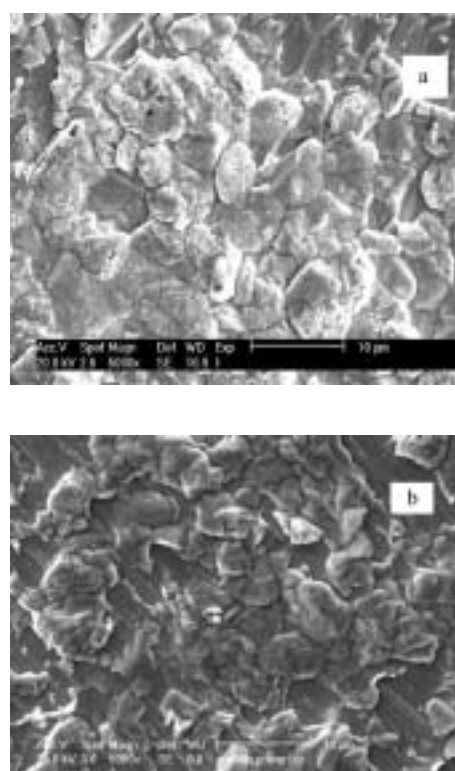


Figure 3 SEM plots of Ni—W alloy deposits before (a) and after (b) heat treatment.

Corrosion behavior of Ni—W alloy

Ni—W alloy was shown in good corrosion resistance in the boiling solution of condensed hydrochloric acid.¹⁷ Compared with Model 304 stainless steel Ni—W alloy was presented in much better corrosion resistance in H₂SO₄, HCl or NaCl solution.³³ The Tafel plots for the corrosion experiment of the obtained alloy in $w=0.03$ NaCl solution are shown in Figure 4. It can be calculated from the plots for the corrosion potential $E_{\text{Corr}}=-0.415$ V and corrosion current density $i_{\text{Corr}}=1.06\times 10^{-5}$ $\text{A}\cdot\text{cm}^{-2}$ for the plated Ni—W alloy deposit, and $E_{\text{Corr}}=-0.245$ V, $i_{\text{Corr}}=1.74\times 10^{-5}$ $\text{A}\cdot\text{cm}^{-2}$ for the heat treatment at 400 °C for 1 h. After treatment with heat the corrosion potential of the deposit has been shifted to a more positive value, indicating that the deposit will be

at a lower electrochemical activity. The corrosion current density is also much lower than $3.3 \text{ mA} \cdot \text{cm}^{-2}$ for Ni—W ($w_{\text{W}}=0.287$) and $0.8 \text{ mA} \cdot \text{cm}^{-2}$ for Ni—W ($w_{\text{W}}=0.324$) alloys¹⁰ in 3% NaCl solution.

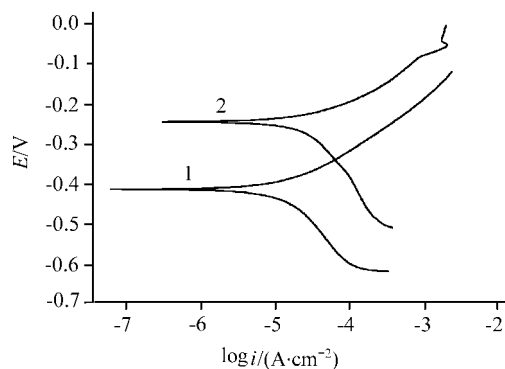


Figure 4 Tafel curves of Ni—W alloy deposits, before (curve 1) and after (curve 2) heat treatment.

Conclusion

A solid solution of Ni—W alloy with W content $w_{\text{W}}=0.471$ and current efficiency 44.0% could be electro-deposited from the electrolyte solution consisting of sodium tungstate, nickel sulfate and ammonium citrate. The alloy, presented in a nanocrystalline structure, was not crystallized and no new phase evolution after treatment at $400 \text{ }^{\circ}\text{C}$ for 1 h. After treatment with heat, first the agglomerates in 3—8 μm dimension of the deposit kept almost no changes but in smooth for the reunion and coarsening of tiny crystals, and grain size increased from 4.8 nm as plate to 5.9 nm and microhardness enhanced from $579 \text{ kg} \cdot \text{mm}^{-2}$ to $594 \text{ kg} \cdot \text{mm}^{-2}$, then the alloy was in a lower electrochemical activity with good corrosion resistance in $w=0.03$ NaCl solution. It was beneficial to enhance microhardness and corrosion resistance of the alloy after a proper heat treatment.

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