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Effect of heat treatment on the structure and properties of electrolessly deposited Ni-W-Cr-P alloy coatings on aluminum alloy

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Abstract

Ni-W-Cr-P alloy coatings were prepared by electroless deposition on Al_9Si compound. The effect of heat treatment on the structure and property of prepared coatings was validly investigated. XRD analysis showed that the as-deposited coatings were Ni-W-Cr-P solid solution. Interestingly, the Ni_3P phase was observed in the samples annealed at 400 ℃, meanwhile, the heat treatment at 500 ℃ process resulted in the formation of Ni_3P, $Cr_{1.12}Ni_{2.88}$ and $Al_{0.983}Cr_{0.017}$ phases. Two brand new $(AlSi)_7Ni_3$ and Al_3Ni_2 phases were identified in the coatings annealed at 600 ℃. The experimental results reveal that the as-deposited Ni-W-Cr-P alloy coatings exhibit higher microhardness and better corrosion resistance comparing with those of as-deposited Ni-P and Ni-W-P coatings. At higher annealing temperature, the microhardness of the Ni-W-Cr-P alloy coatings increased, got to the maximum value at 500 ℃, and decreased slightly for the samples annealed at higher temperature. It is worth noting that the corrosion resistance was also remarkably improved by heat treatment.

Key words: electroless deposition, Ni-W-Cr-P alloy coatings, heat treatment, phase transformation behavior, microhardness, corrosion resistance

1. Introduction

Aluminum alloys have many applications in industry due to their low density, high mechanical strength, good ductility, electrical and thermal conductivity, etc. [1]. However, some shortcomings, such as low hardness and poor wear resistance, should be overcome to further extend their applications. So far, Ni-P chemical plating is a very effective method to improve the properties of aluminum alloys due to the excellent corrosion resistance of the coatings, as well as their wear resistance and hardness [2, 3].

Up till now, many investigations have been conducted on introduction of W or Cr into the binary electroless Ni-P deposits to form ternary Ni-W-P or Ni-Cr-P alloy coatings, and, at a great extent, improved the deposit properties owing to their high melting temperature and unusual mechanical properties [4-14]. However, as far as we know, there are few papers on the preparation of the quaternary Ni-W-Cr-P alloy coatings by electroless deposition.

In the present study, the quaternary Ni-W-Cr-P alloy coatings were prepared by introduction of Cr into electroless Ni-W-P deposits. Ni-P and Ni-W-P alloy coatings were also prepared for comparison. The effects of heat treatment on the structure and property of Ni-W-Cr-P deposits on aluminum alloy were investigated. The mechanisms of the improvement of microhardness and corrosion resistance of the alloy coatings were also discussed. The optimized annealing temperature was found to be 500 ℃.

2. Experimental details

The cuboidal samples of Al_9Si compound (30 mm × 12 mm × 2 mm) were used as the substrate. Prior to plating, the samples were subjected to a shot blast treatment to obtain clean and fresh surface with proper roughness. And then they were, firstly, degreased in a hot alkaline solution for 10 min, then rinsed in running water and deionized water. The de-

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Table 1. Composition and concentration of the electroless Ni-W-Cr-P bath

I		II	
Chemical compounds	Concentration	Chemical compounds	Concentration
$NiSO_4 \cdot 6H_2O$	30–40 g L^{-1}	$CrCl_3 \cdot 6H_2O$	10–15 g L^{-1}
$Na_2WO_4 \cdot 2H_2O$	25–30 g L^{-1}	$NaH_2PO_4 \cdot H_2O$	10–20 g L^{-1}
$Na_3C_6H_5O_7 \cdot 2H_2O$	80–100 g L^{-1}	$K_2C_2O_4 \cdot H_2O$	4–6 g L^{-1}
$NH_4 \cdot Cl$	40–60 g L^{-1}	$NaC_2H_3O_2$	10–20 g L^{-1}
$NaH_2PO_4 \cdot H_2O$	10–20 g L^{-1}		
$NH_3 \cdot H_2O$	10–20 ml L^{-1}		
Stability	10–30 mg L^{-1}	Stability	10–20 mg L^{-1}
PH	8.8–9.2	PH	4–6

greased substrates were further deoxidized in dilute hydrochloric acid solution for 2 min, then rinsed in running water and deionized water once again. Finally, the pretreated substrates were immediately immersed in the electroless plating solution for deposition. Several kinds of Ni-W-Cr-P alloy coatings were prepared by altering the chemical compositions of the plating solution. The pH value of the plating bath was adjusted with ammonia and 30 % of acetic acid to 8.8–9.2, and the plating time was fixed for 2 h at a bath temperature of 85–90 ℃. The detailed compositions of the bath and the operating conditions for preparing Ni-W--Cr-P alloy coatings are listed in Table 1. After plating, the as-deposited samples were rinsed in running water and deionized water, dried in the air, and then preserved for further characterizations.

To investigate the effect of heat treatment, the as--deposited samples were annealed with the protection of graphite powder in a muffle furnace for 1 h at 300 ℃, 400 ℃, 500 ℃ and 600 ℃. After annealing, the samples were furnace-cooled to room temperature.

Microstructural analyses of the Ni-W-Cr-P deposits were performed by means of X-ray diffractometer (DX-1000, Cu Kα radiation, Dandong, China) and scanning electron microscope (SEM, JSE-5900LV). The chemical composition of the layers was determined by Rigaku X-ray Fluorescence ZSX100e spectrometer.

Furthermore, the microhardness measurements were carried out with the HV2100 microhardness tester at five points on each sample and the mean values were calculated.

Potentiodynamic polarization was performed in 10 vol.% H_2SO_4 solution to study the corrosion behavior of the deposits. The measurements were carried out using an Autolab PGSTAT30 galvanostat/potentiostat system of ECO Chemie. The conventional three-compartment glass cell was employed, in which a platinum foil was served as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

Table 2. Chemical compositions of as-deposited Ni-W-Cr-P alloy coatings prepared by several plating solutions with different ratios of I and II

I : II (volume)	Ni (wt.%)	P (wt.%)	W (wt.%)	Cr (wt.%)
4 : 6	87.1	5.6	4.1	3.2
5 : 5	86.6	5.2	5.2	3.0
6 : 4	86.6	5.0	5.7	2.7
7 : 3	86.6	4.8	6.1	2.5
8 : 2	86.9	4.6	6.2	2.3

3. Results and discussion

3.1. Chemical composition and SEM analysis of electroless Ni-W-Cr-P alloy coatings

The chemical compositions of plating solutions for as-deposited Ni-W-Cr-P coatings, named as I and II, are listed in Table 2. When increasing the amount of I in the plating solutions, the contents of Ni are almost to be about 87 %, however, the contents of P, W and Cr change slightly from 5.6 % to 4.6 %, 4.1 % to 6.25 % and 3.2 % to 2.3 %, respectively. Thus, it is believed that the chemical compositions of all the as-deposited samples can be controlled within the proper range.

Figure 1a shows SEM image of the surface morphology of Ni-W-Cr-P coating prepared with the 1 : 1 volume ratio of solutions I and II. The surface morphology of the coating is homogeneous and compact, and it can be found that the coating consists of a series of nodular particles. These particles are of different size and are filled with some irregularly cellular ones. The coating thickness measured with the SEM cross--sectional image is about 12 μm (Fig. 1b).

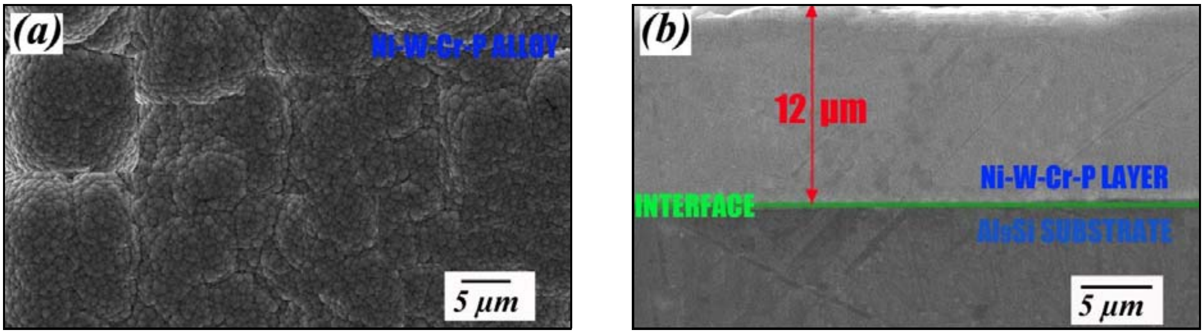

Fig. 1. SEM images of (a) surface morphology (×2000) and cross-section (×5000) of as-plated electroless Ni-W-Cr-P coating.

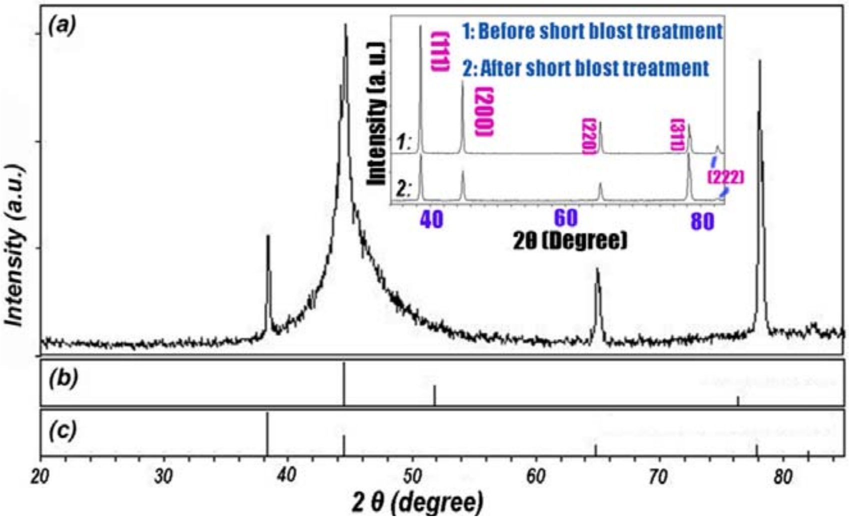

Fig. 2. (a) XRD spectra of the as-deposited Ni-W-Cr coating, the aluminum alloy substrate before and after shot blast treatment (inset). (b) and (c) Joint Committee for Powder Diffraction Standards (JCPDS) file numbers 65-2865: Ni and 65-8554: Al_9Si.

3.2. Phase transformation behavior of electroless Ni-W-Cr-P alloy coatings

Figures 2–6 show the X-ray diffraction patterns of the as-deposited Ni-W-Cr-P quaternary alloy coatings and the patterns of those heated at various temperatures for 1 h. The XRD results reveal that peaks of aluminum alloy substrate can be indexed in all the diffraction spectra with the exception of the sample annealed at 600 ℃ (Fig. 6). Here, a strong Al_9Si (311) preferential orientation is observed in the as-deposited condition, however, it is nearly eliminated after heat treatments. By comparing the diffraction spectra of the substrates before and after shot blast treatment (inset of Fig. 2a), similar results have also been achieved. Thus, it is believed that the preferential orientation was caused by shot blast treatment.

In Fig. 2a, a wide angular range of approximately 40–60 ℃ (2θ) is exhibited, which is actually a broadened peak of Ni (111). No other phases have been found, thus it is believed that the Ni-W-Cr-P solid solution is the only phase in the as-deposited samples. After heating at 300 ℃ for 1 h, as shown in Fig. 4a, the broadened Ni (111) becomes a narrow peak together with the Ni (200) shoulder. And in this case, it can be deduced that the Ni-W-Cr-P solid solution has been reorganized during annealing. After annealing at temperature of 400 ℃, it can be found that there is the Ni_3P phase in the coating. Here, Ni and Ni_3P are the only two dominant phases in spite of some Al_3SiCr. And, yet, the formation of Al_3SiCr indicates the interdiffusion between the coating and the substrate. Figure 5 shows that the broadened peaks of both Ni_3P and Ni phases have been further sharpened into well-defined diffraction peaks, indicating that crystallization process of Ni_3P and Ni was nearly saturated. Hereby, intermetallic compounds between Cr, Ni, or Al such as $Cr_{1.12}Ni_{2.88}$ and $Al_{0.983}Cr_{0.017}$ phases have been observed. Meanwhile, tungsten has been also, though just a little, dissolved in Ni matrix, and no evidence of diffraction peaks of W or its compounds has been detected. As is shown in Fig. 6, diffraction peaks of NiO have still been found even under the protection of graphite powder, in the as-deposited

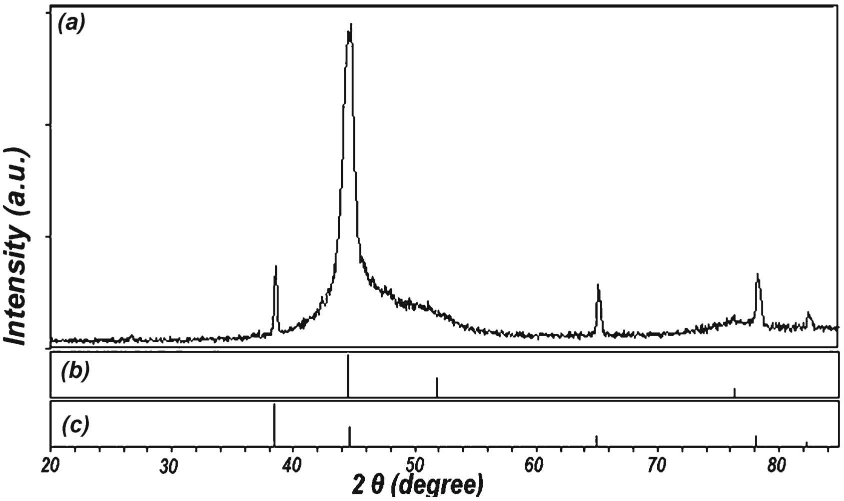

Fig. 3. (a) XRD spectrum of the Ni-W-Cr-P alloy coating annealed at 300 ℃ for 1 h. (b) and (c) Joint Committee for Powder Diffraction Standards (JCPDS) file numbers 65-2865: Ni and 65-8554: Al_9Si.

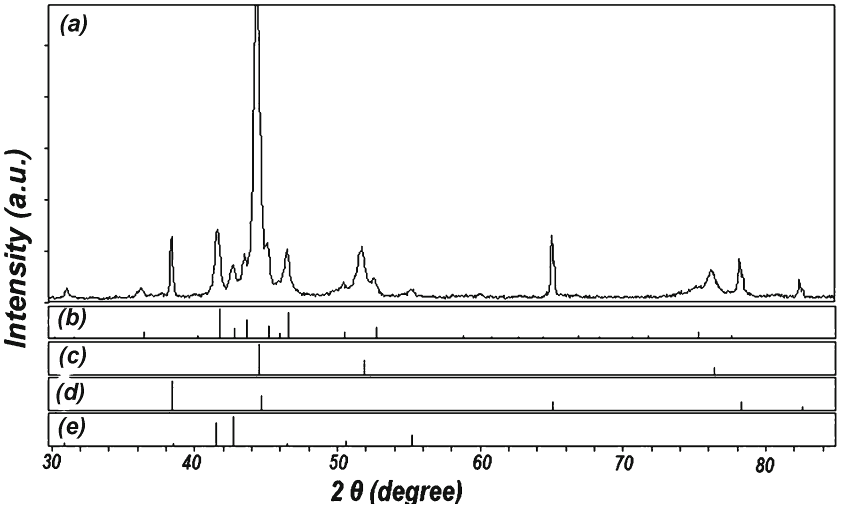

Fig. 4. (a) XRD spectrum of the Ni-W-Cr-P alloy coating annealed at 400 ℃ for 1 h. (b)–(e) Joint Committee for Powder Diffraction Standards (JCPDS) file numbers 34-0501: Ni_3P, 65-2865: Ni, 65-8554: Al_9Si and 43-1443: Al_3SiCr.

sample annealed at 600 ℃, and the diffraction peaks of Ni_3P become extremely sharp. The coating and substrate have been subjected to further interdiffuse at the annealing temperature of 600 ℃, which result in the formation of $(AlSi)_7Ni_3$ and Al_3Ni_2 phases, associated with the disappearance of diffraction peaks of aluminum alloy substrate.

3.3. Microhardness of electroless Ni-W-Cr-P alloy coatings

Figure 7 illustrates the effect of heat treatment on the hardness of electroless Ni-W-Cr-P alloy coatings. For comparison, the effects of heat treatment on the hardness of Ni-P and Ni-W-P alloys were also investigated.

Curve (3) of Fig. 7 represents the hardness of the quaternary Ni-W-Cr-P alloy coating as a function of annealing temperature. Starting with a microhardness of 580 HV in as-deposited condition, the hardness of the quaternary Ni-W-Cr-P alloy coating increases with the increasing of annealing temperature, until reaching the maximum value of 927 HV for the samples annealed at 500 ℃ for 1 h. Then, the subsequent increasing of annealing temperature to 600 ℃ results in the slight decrease of microhardness. According to the results of X-ray analysis, it can be concluded that after annealing at or above 300 ℃, the enhanced hardness has been mainly attributed to the appearance of Ni and Ni_3P phases. Maximum hardness is achieved after annealing at 500 ℃ due to the increased amounts of Ni and Ni_3P phases. Annealing at temperatures above 500 ℃, because of the oxidation of coating, resulted in pronounced decrease of the

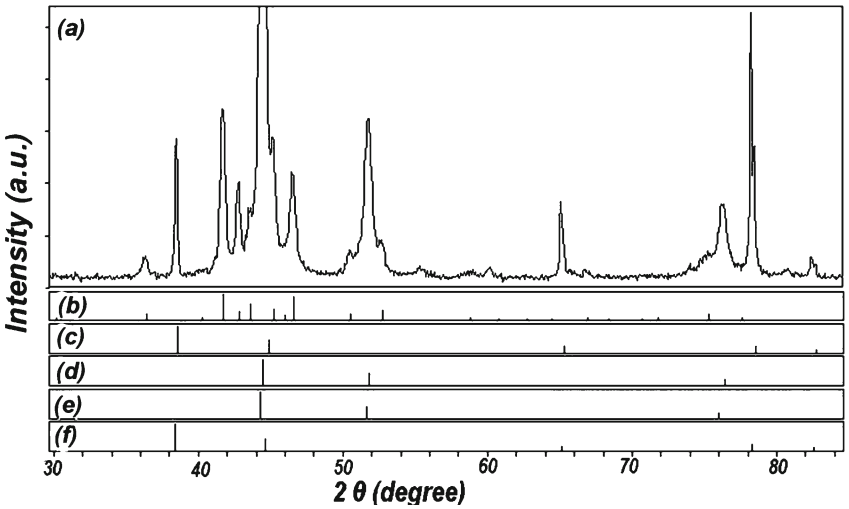

Fig. 5. (a) XRD spectrum of the Ni-W-Cr-P alloy coating annealed at 500 ℃ for 1 h. (b)–(f) Joint Committee for Powder Diffraction Standards (JCPDS) file numbers 34-0501: Ni_3P, 65-8554: Al_9Si, 65-2865: Ni, 65-5559: $Cr_{1.12}Ni_{2.88}$ and 65-7336: $Al_{0.983}Cr_{0.017}$.

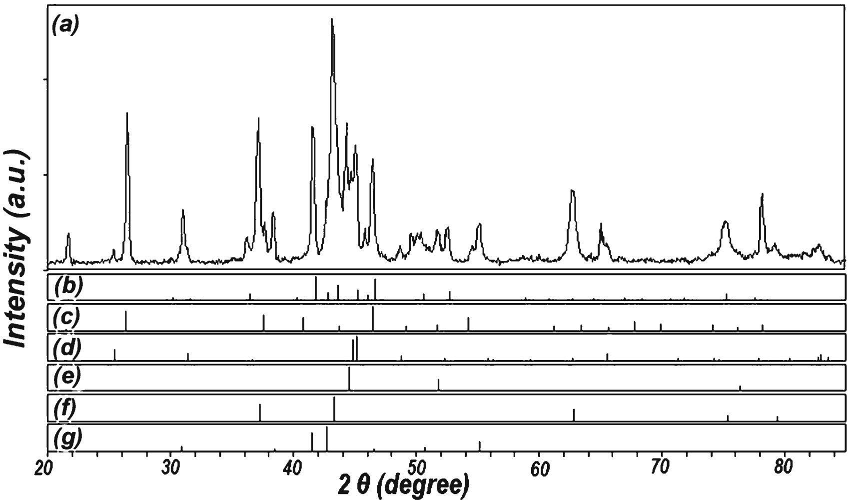

Fig. 6. (a) XRD spectrum of the Ni-W-Cr-P alloy coating annealed at 600 ℃ for 1 h. (b)-(g) Joint Committee for Powder Diffraction Standards (JCPDS) file numbers 34-0501: Ni_3P, 18-0044: $(AlSi)_7Ni_3$, 65-3454: Al_3Ni_2, 65-2865: Ni, 71-1178: NiO and 43-1443: Al_3SiCr.

hardness comparing to that of 500 ℃ annealed sample.

Furthermore, it is very clear, that microhardness of quaternary Ni-W-Cr-P coating is higher than that of Ni-P and Ni-W-P deposits, see Fig. 7. Thus, it is believed that the incorporation of Cr in Ni-W-P deposit can further enhance the microhardness of the electroless coating. It should be also pointed out that binary and ternary deposits reached a maximum hardness after annealing at 400 ℃, what agreed with many reports very well [6–9], while the quaternary deposits required annealing at 500 ℃.

3.4. *Corrosion resistance of chemical electroless Ni-W-Cr-P alloy coating*

To investigate the corrosion resistance effect of Ni-W-Cr-P coating, the measurements of potentiodynamic polarization properties were carried out.

Figure 8a shows the polarization curves of as-deposited Ni-P, Ni-W-P and Ni-W-Cr-P coatings with identical thickness in 10 vol.% H_2SO_4 solution. The corresponding electrochemical corrosion parameters are listed in Table 3. It is clearly pointed out that the as-deposited Ni-W-Cr-P coating has the highest corrosion potential, $E_{\mathrm{corr}} = -206\,\mathrm{mV}$, as well as the lowest corrosion current density, $i_{\mathrm{corr}} = 7.709\,\mu\mathrm{A\,cm}^{-2}$. Thus, it is believed that the Ni-W-Cr-P coating is more corrosion resistant than binary Ni-P and ternary Ni-W-P deposits.

Figure 8b shows polarization curves of Ni-W-Cr-P alloy coatings as a function of annealing temperature. The corresponding electrochemical corrosion paramet-

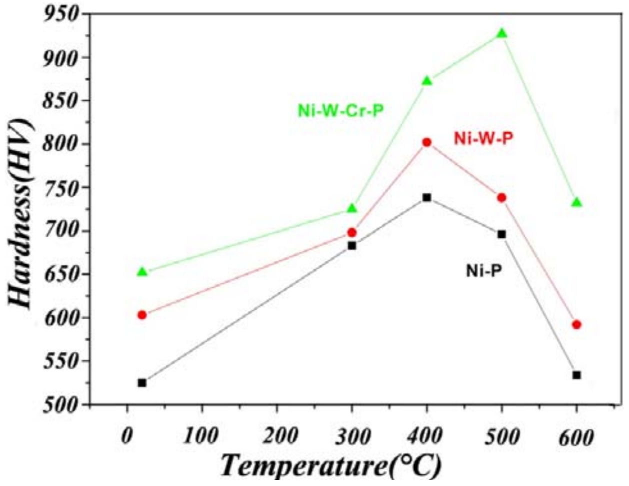

Fig. 7. Microhardness of the deposits at different annealing temperatures for 1 h: (1) Ni-P, (2) Ni-W-P, (3) Ni-W-Cr-P.

Table 3. Corrosion parameters of as-deposited electroless Ni-P, Ni-W-P and Ni-W-Cr-P alloy coatings in 10 vol.% H_2SO_4 solution

As-deposited coatings	E_{corr} (mV)	i_{corr} (μA cm^{-2})	R_{p} (Ω cm^{-2})
Ni-P	−263	18.58	1219
Ni-W-P	−243	8.931	1332
Ni-W-Cr-P	−206	7.709	1266

Table 4. Corrosion parameters of electroless Ni-W-Cr-P alloy coatings at different annealing temperatures for 1 h in 10 vol.% H_2SO_4 solution

Ni-W-Cr-P alloy coatings	E_{corr} (mV)	i_{corr} (μA cm^{-2})	R_{p} (Ω cm^{-2})
As-deposited	−206	7.709	1266
Annealed at 300 °C for 1 h	−197	7.349	1051
Annealed at 400 °C for 1 h	−319	37.03	458.2
Annealed at 500 °C for 1 h	−296	36.6	413.3
Annealed at 600 °C for 1 h	−402	776.8	16.51

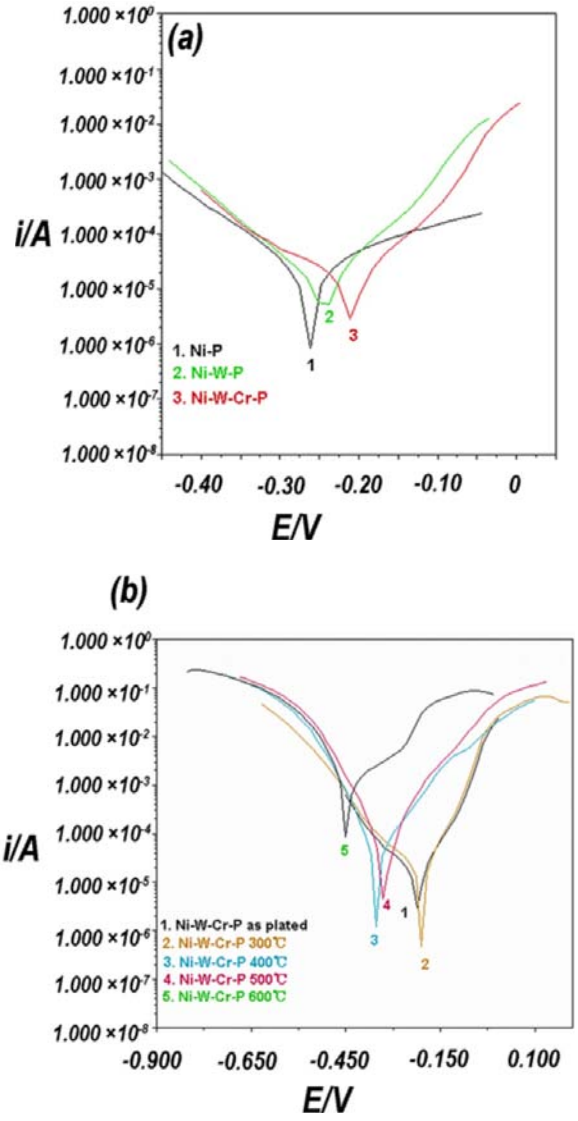

Fig. 8. Polarization curves of (a) as-deposited electroless (1) Ni-P, (2) Ni-W-P, and (3) Ni-W-Cr-P alloy coatings in 10 vol.% H_2SO_4 solution, and (b) Ni-W-Cr-P alloy coatings heated at different temperatures for 1 h: (1) as-deposited, (2) 300 °C, (3) 400 °C, (4) 500 °C, (5) 600 °C.

ers are listed in Table 4. As discussed above, the as-deposited Ni-W-Cr-P alloy coating exhibits a better corrosion resistance, while after heating at 300 °C for 1 h, the corrosion resistance is further improved. As it is concluded from the results of XRD analyses, the Al_9Si (311) preferential orientation, which was firstly occurred on the surface of aluminum alloy substrate after shot blast treatment, remained in the as-deposited coating. However, it was nearly eliminated after annealing at 300 °C. Thus, it can be deduced that the improved corrosion resistance must be related to the disappearance of Al_9Si (311) preferential orientation. After heat treatment at 400 °C, the appearance of phases Ni_3P and Ni resulted in a slight decrease in corrosion resistance. It is interesting to point out that the corrosion resistance increases again at 500 °C, and this phenomenon is probably attributed to the formation of $Cr_{1.12}Ni_{2.88}$ and $Al_{0.983}Cr_{0.017}$ phases. When the as-deposited Ni-W-Cr-P alloy coating was annealed at 600 °C, the NiO phase had been obtained, and finally, the corrosion resistance decreased.

4. Conclusions

In the present study, the Ni-W-Cr-P alloy coatings were prepared by electroless deposition. The experimental results can be concluded as follows:

(1) After shot blast treatment, the aluminum alloy substrate with a clean and fresh surface of proper roughness was obtained. The occurrence of preferential orientation of $AlSi_9$ (311) peak was also observed.

(2) Heat treatment has a significant effect on the structure of the Ni-W-Cr-P alloy coatings. As-deposited Ni-W-Cr-P alloy coatings were Ni solid solutions. The $AlSi_9$ (311) preferential orientation was eliminated and Ni started to precipitate after heating at 300 ℃. The precipitation of Ni_3P was observed in the samples annealed at 400 ℃. Interdiffusion between the deposited coatings and the substrate took place. Heat treatment at 500 ℃ resulted in the completion of crystallization of Ni_3P as well as the formation of $Cr_{1.12}Ni_{2.88}$ and $Al_{0.983}Cr_{0.017}$ phases. After annealing at 600 ℃, the coatings were oxidized and $(AlSi)_7Ni_3$ and Al_3Ni_2 phases were observed.

(3) Microhardness of Ni-W-Cr-P alloy coatings is higher than that of Ni-P and Ni-W-P alloy coatings in both as-deposited and heat-treated conditions. Microhardness increases with the increasing annealing temperature, reaches the maximum value of 927 HV after heat treatment at 500 ℃, and then slightly decreases after annealing at 600 ℃.

(4) The Ni-W-Cr-P alloy coatings are more corrosion resistant than Ni-P and Ni-W-P alloy coatings in as-deposited condition in 10 % H_2SO_4 medium. Moreover, the corrosion resistance of Ni-W-Cr-P alloy coatings is remarkably affected by the annealing temperature and the best corrosion resistance is obtained after annealing at 300 ℃.

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