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Structural and Phase Transformation Behaviour of Electroless Ni–W–Cr–P Alloy Coatings on Stainless Steel

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Abstract—Ni–W–Cr–P alloy coatings were prepared by electroless deposition on stainless steel. The effects of heat-treatment on the structure and phase transformation behavior, microhardness of the Ni–W–Cr–P alloy coatings were mainly investigated. XRD analysis shows that as-deposited Ni–W–Cr–P coatings were microcrystalline; the precipitation of Ni_3P was observed at the annealing temperature of 400°C; after heat-treatment at 500°C the crystallization of Ni_3P and Ni was near completion; at 600°C new phase $Cr_{1.12}Ni_{2.88}$ was observed and Ni_3P began to decompose. $Cr_{1.07}Fe_{18.93}$ and $Ni_{17}W_3$ were formed when heated at 700°C, and Ni_3P was not found. With increasing temperature to 800°C, $FeNi_2P$ and $Cr_4Ni_{15}W$ were the only two dominant phases. The experimental results reveal that with an increase in the annealing temperature, microhardness of the Ni–W–Cr–P alloy coatings increased, reached the maximum value at 700°C, and then decreased slightly. Annealing temperature dependence of the microhardness and corrosion resistance of the coatings was also observed. The related strengthening mechanism in the electroless deposited Ni–W–Cr–P alloy coatings is also discussed.

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INTRODUCTION

Stainless steel is widely used in various industries due to its excellent properties. While, with low hardness and poor wear resistance, corrosion process of stainless steel will accelerate when micro scratch occur on the surface followed by the formation of microcell. As a convenient surface treatment technique, electroless Ni–P plating is a very effective method to improve the properties of stainless steel due to its excellent hardness, wear resistance and corrosion resistance [1–3].

Many investigations have been reported on introduction of W or Cr into the binary electroless Ni–P deposit to form ternary Ni–W–P, Ni–Cr–P alloy coatings to further enhance the deposit properties because of their high melting temperature and unusual mechanical properties [4–14]. However, to date there are few reports 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. The effects of the annealing temperature on the crystal structure, microhardness, and corrosion resistance of Ni–W–Cr–P alloy coatings were mainly studied. The related mechanism for enhanced microhardness and corrosion resistance of the alloy coatings with proper annealing temperature was also discussed.

EXPERIMENTAL

Stainless steel (20 mm × 20 mm × 1 mm) was used as substrate. The surface of stainless steel is easily passivated, thus is harmful for electroless plating. There are two main factors contributed to this: elevated electrode potential and poor adhesion between the substrate and the plating. Then, prior to plating, the samples were subjected to shot blast treatment to obtain clean and fresh surface with proper roughness. Then the samples were degreased in hot alkaline solution for 10 min, rinsed in running water and deionized water. The degreased samples were deoxidized in dilute hydrochloric acid solution for 2 min, rinsed in running water and deionized water. Finally, the samples were immediately immersed in the electroless plating solution for deposition. Ni–W–Cr–P alloy coatings were prepared by altering the chemistry solution with proper ratio of A : B solution. The pH value of the plating bath was adjusted with ammonia and 30% acetic acid to 8.8–9.2, and the plating time was 2 h at a bath temperature of 85–90°C. The compositions of the bath and the operating conditions for Ni–W–Cr–P alloy coatings are shown in Table 1. After plating,

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Table 1. Composition and operating conditions of the electroless Ni–W–Cr–P bath

Chemical compounds A	Concentration	Chemical compounds B	Concentration
$NiSO_4 \cdot 6H_2O$	30–40 g/L	$CrCl_3 \cdot 6H_2O$	10–15 g/L
$Na_2WO_4 \cdot 2H_2O$	25–30 g/L	$NaH_2PO_4 \cdot H_2O$	10–20 g/L
$Na_3C_6H_5O_7 \cdot 2H_2O$	80–100 g/L	$K_2C_2O_4 \cdot H_2O$	4–6 g/L
NH_4Cl	40–60 g/L	$NaC_2H_3O_2$	10–20 g/L
$NaH_2PO_2 \cdot H_2O$	10–20 g/L		
$NH_3 \cdot H_2O$	10–20 ml/L		
Stability	10–30 mg/L	Stability	10–20 mg/L
pH	8.8–9.2		4–6

again the sample was rinsed in running water and deionized water, dried and preserved for characterization.

To investigate the effects of heat treatment at temperatures ranging from 300 to 800°C on the structure and hardness of the deposits, annealing was carried out in a tube resistance furnace with N_2 purged for 1 h and the sample was then furnace-cooled to room temperature.

Elemental compositions of the deposits were determined with an X-ray fluorescent spectrometer. Scanning electron microscope (**SEM**, JSE-5900LV) was employed to study the surface morphology as well as cross-section of the deposit in as-plated condition.

The structures of the Ni–W–Cr–P deposits both in as-plated and heat-treated conditions were evaluated with an X-ray diffractometer (DX-1000, Dandong, China) using CuK_α radiation. The chemical composition of the layers was measured by Rigaku X-ray Fluorescence ZSX100e.

Microhardness measurements were done using a HV2100 microhardness tester. Five readings were taken on each deposit and the values were then averaged.

Table 2. Compositions of as-deposited Ni–W–Cr–P alloy coatings with different ratios of A to B

A : B	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

The polarization curves of the alloy coatings were measured using Autolab PG302 Potentiostat Electrochemistry Workstation.

RESULTS AND DISCUSSION

Elemental composition and SEM analysis of electroless Ni–W–Cr–P alloy coatings. The compositions of as-plated electroless Ni–W–Cr–P coatings with different ratio of A solution to B analyzed by X-ray fluorescent spectrometer (Rigaku X-ray Fluorescence ZSX100e) are listed in Table 2.

Figure 1 shows SEM image of the surface of Ni–W–Cr–P deposit in as-plated condition prepared with the ratios of A solution to B as 1 : 1. The surface morphology of the deposit is homogeneous and compact. The quaternary Ni–W–Cr–P alloy deposit exhibited nodular structure. The particles are of different sizes, irregularly cellular. The deposit thickness was around 10 μm through SEM analysis of the cross-section of the deposit as shown in Fig. 2.

Phase transformation behavior of electroless Ni–W–Cr–P alloy coatings. Figures 3–10 shows the X-ray diffraction patterns of the Ni–W–Cr–P quaternary alloy coatings in as-plated condition and heated at various temperatures for 1 h.

Figure 3 show the XRD patterns of substrate (stainless steel) and as-deposited Ni–W–Cr–P alloy coatings without annealing temperature, respectively. As shown in Fig. 3 (curve *2*), there is a noncrystal peak at $2\theta = 45°$. So it was thought that the asdeposited alloy coatings belong to amorphous structure. There is no obvious change in the diffraction pattern of the deposit heated at 300°C, as shown in Fig. 4. In Ni–W–Cr–P system, the original amorphous structure was transformed into a mixture of amorphous, Ni and Ni_3P crystallites at 400°C as shown in Fig. 5. It could also be found that the deposit started to gave rise to precipita-

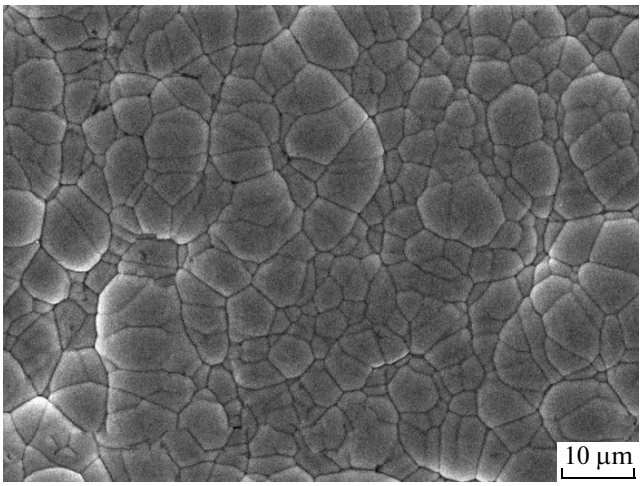

Fig. 1. SEM image of surface morphology of as-plated electroless Ni–W–Cr–P alloy coating (×2000).

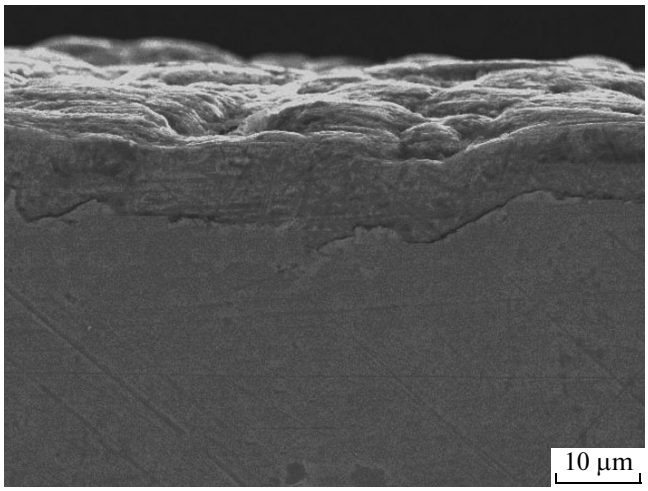

Fig. 2. SEM image of cross-section of as-plated electroless Ni–W–Cr–P alloy coating (×2000).

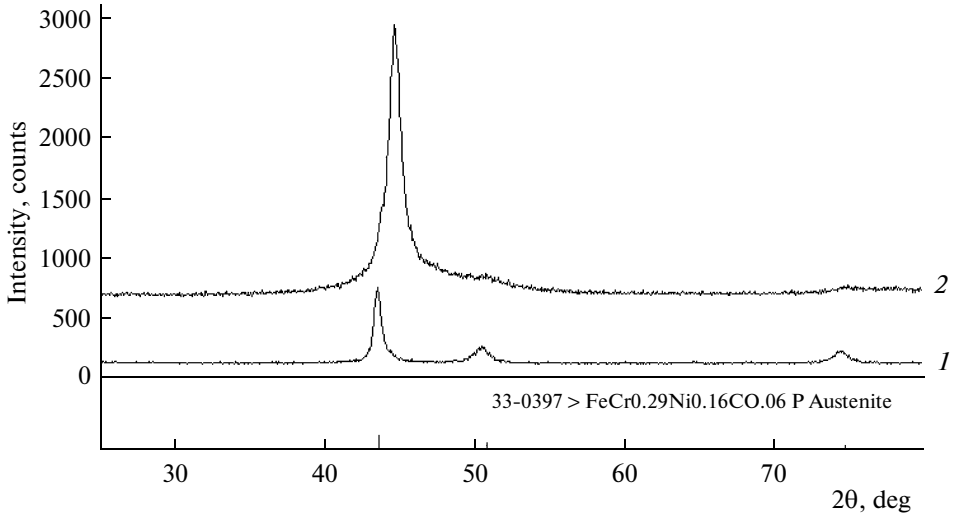

Fig. 3. XRD patterns of the stainless steel substrate.

tion of fine Ni_3P grains. From Fig. 6, it is evident that after annealed at 500°C, reflections of both Ni_3P and Ni phases were further sharpened into well-defined diffraction peaks, which indicates that crystallization process of N_3P and Ni was near completion. As is shown in Fig. 7, diffraction peaks of $Cr_{1.12}Ni_{2.88}$ was observed and the intensity of diffraction peaks of Ni_3P decreased which means it began to decompose after annealed at 600°C. With increasing temperature to 700°C, the diffraction refection indicates that N_3P completely disappeared, and new phases of $Cr_{1.07}Fe_{18.93}$ and $Ni_{17}W_3$ were the only two dominant phases, as shown in Fig. 8. The alloy coatings annealed at 800°C consisted of $FeNi_2P$ and $Cr_4Ni_{15}W$ phases (Fig. 9).

Microhardness of electroless Ni–W–Cr–P alloy coating. The effects of heat treatment on the hardness of electroless Ni–W–Cr–P alloy coatings was studied.

Figure 10 shows that with a microhardness of 574HV in as-deposited condition, hardness of the quaternary Ni–W–Cr–P alloy coatings increased with the increasing annealing temperature, until reached the maximum value of 964HV when heated at 700°C for 1 h. Then it slightly decreased after heated at 800°C. According to the analysis of phase transformation behaviors of the deposits above, it can be con-

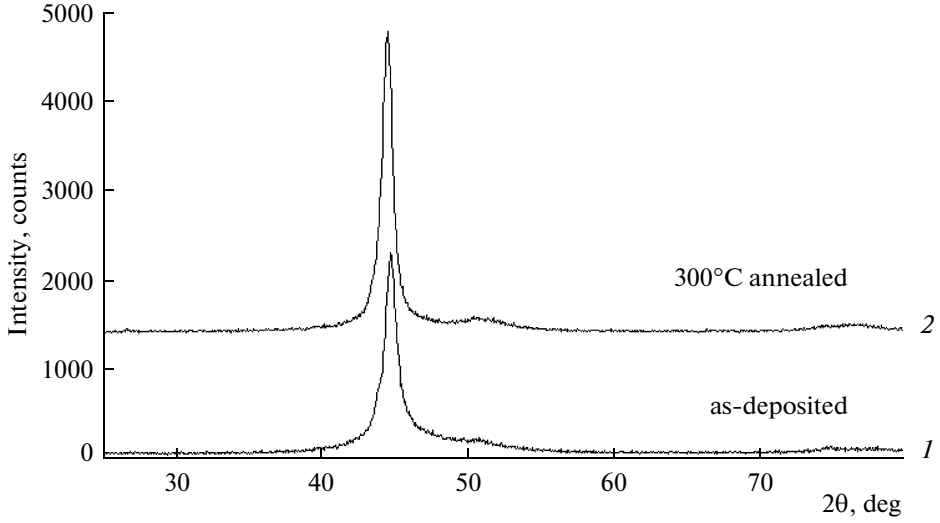

Fig. 4. XRD pattern of the Ni–W–Cr–P alloy coating annealed at 300°C for 1 h.

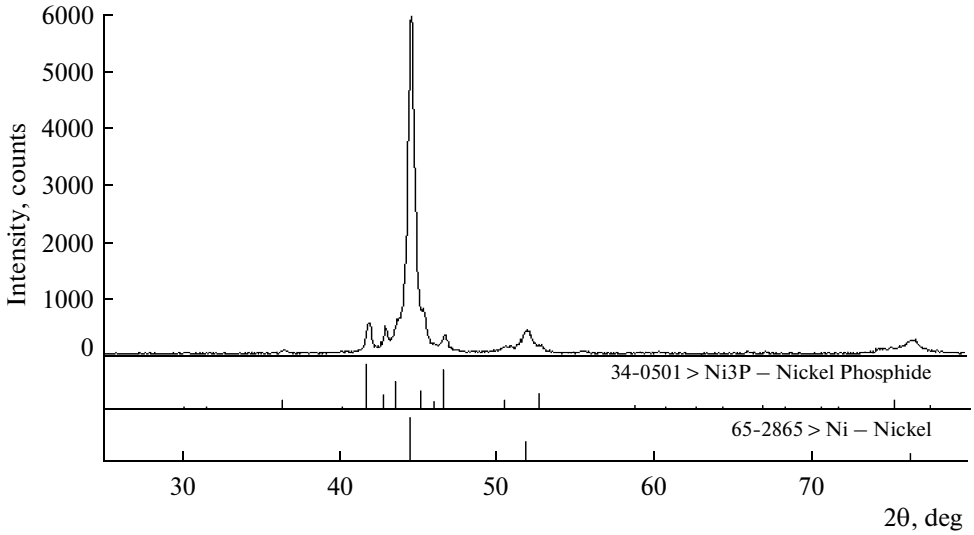

Fig. 5. XRD pattern of the Ni–W–Cr–P alloy coating annealed at 400°C for 1 h.

cluded that after annealing above 300°C, the enhanced hardness has been mainly attributed to the increase in the number of fine Ni microcrystallites. Precipitation hardening of fine Ni_3P crystallites is responsible for the considerable increase in hardness at 400°C. After the heat-treatment at 500°C, in spite of the growth of Ni and Ni_3P particles the hardness of the deposit continue to increase. After heated above 600°C, Ni_3P started to decompose, but the hardness of the deposit did not decrease until at 800°C. Slight increase in hardness at 600 and 700°C may be a result of the formation of new phases $Cr_{1.07}Fe_{18.93}$ and $Ni_{17}W_3$ the hardening mechanism of which need to be further investigated. With increasing temperature to 800°C, hardness decreased while still remained a relatively high value of 804HV.

The incorporation of Cr in Ni–W–P deposit make the phase transformation behavior more complex, and the formation of various kinds of intermetallic compounds impede the decrease in the hardness.

Corrosion resistance of electroless deposited Ni–W–Cr–P alloy coating. In order to evaluate the corrosion resistance of Ni–W–Cr–P alloy coatings, as-

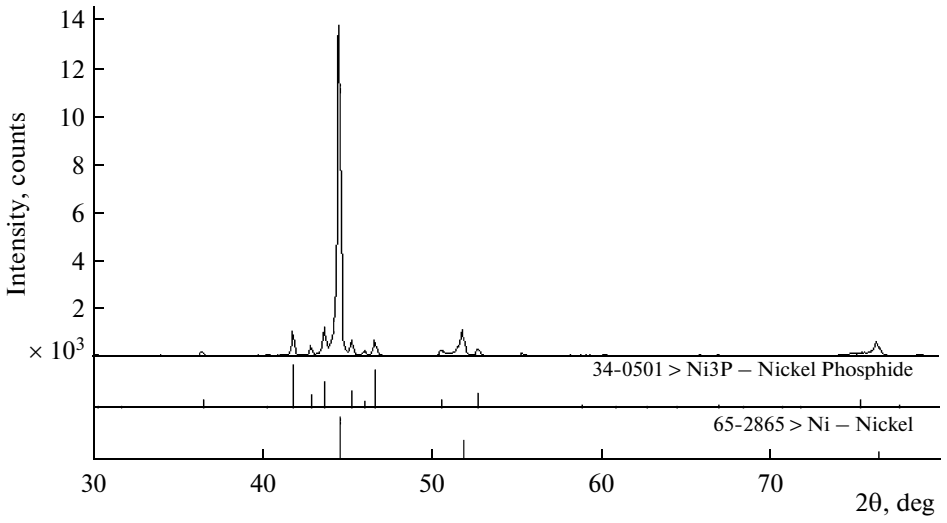

Fig. 6. XRD pattern of the Ni–W–Cr–P alloy coating annealed at 500°C for 1 h.

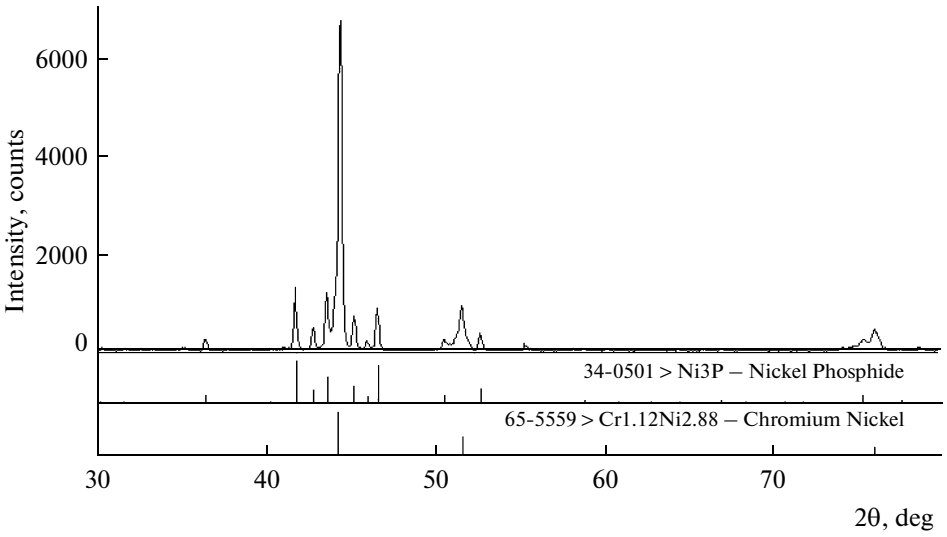

Fig. 7. XRD pattern of the Ni–W–Cr–P alloy coating annealed at 600°C for 1 h.

deposited (i.e., without annealing) Ni–P, Ni–W–P, and Ni–W–Cr–P alloy coatings with the same thicknesses were put into the solution of 10% NaOH, 5% NaCl, 10% HCl and 10% H_2SO_4 for 12 days, respectively. Corrosion rate of these alloy coatings is calculated by weight method. Detailed results were shown

Table 3. Microhardness of Ni–W–Cr–P alloy coatings heated at different temperatures

As-deposited coatings	10% NaOH	5% NaCl	10% HCl	10% H_2SO_4
Ni–P	1.33	1.14	330	70
Ni–W–P	1.22	0.11	300	42
Ni–W–Cr–P	1.10	0.07	260	26

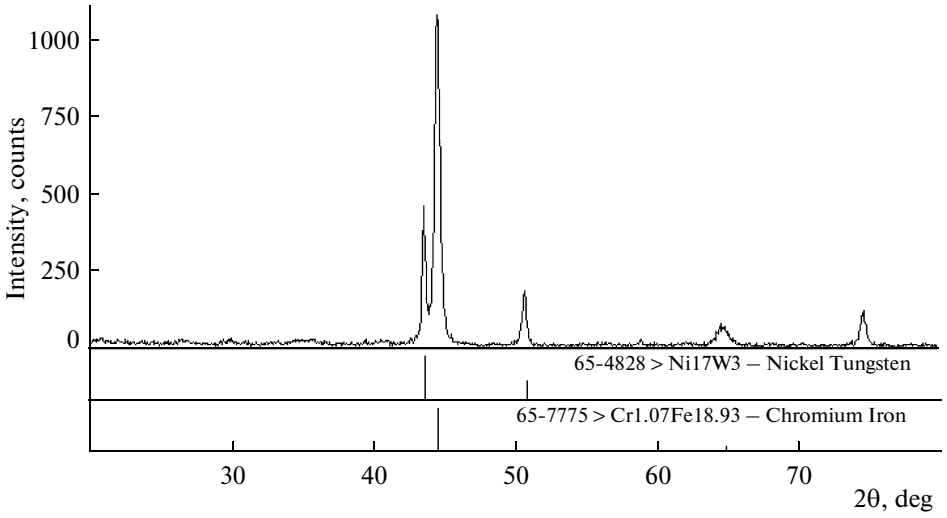

Fig. 8. XRD pattern of the Ni–W–Cr–P alloy coating annealed at 700°C for 1 h.

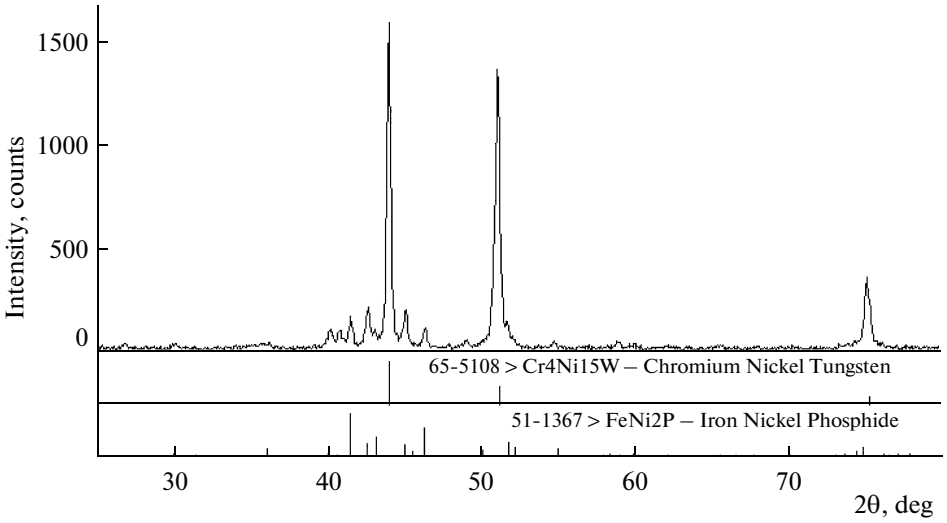

Fig. 9. XRD pattern of the Ni–W–Cr–P alloy coating annealed at 800°C for 1 h.

in Table 3. It was found from Table 3 that the corrosion resistance of as-deposited Ni–W–Cr–P alloy coatings shows better than those of Ni–P and Ni–W–P coatings in different mediums, especially for 10% H_2SO_4. The Ni–W–Cr–P alloy coatings is still bright except for 10% NaOH solution. As a result, the as-

Table 4. Corrosion rate of as-deposited coatings in different mediums (mg/(d cm^2))

Annealing temperature, °C	25	300	400	500	600	700	800
Microhardness (HV)	574	673	825	908	928	964	804

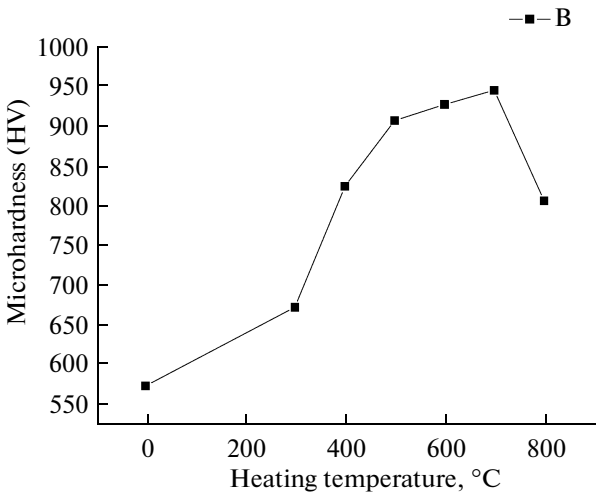

Fig. 10. Microhardness of the Ni–W–Cr–P alloy coatings at different annealing temperatures for 1 h.

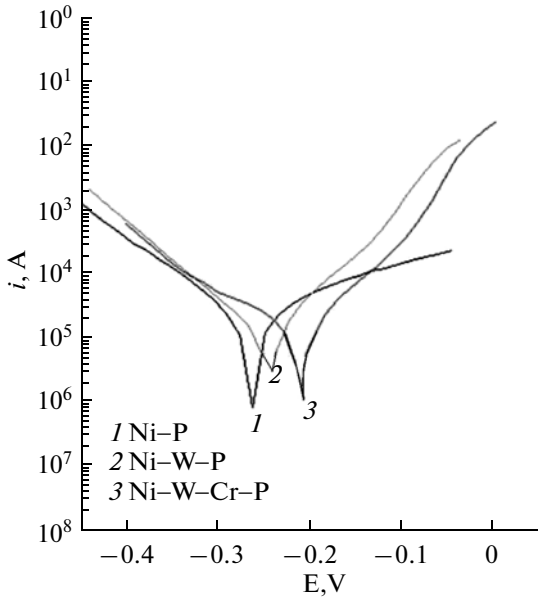

Fig. 11. Polarization curves of as-deposited electroless Ni–P, Ni–W–P, and Ni–W–Cr–P alloy coatings in 10% H_2SO_4 solution.

deposited Ni–W–Cr–P alloy coatings show good corrosion resistance.

Polarization curves of as-deposited Ni–P, Ni–W–P and Ni–W–Cr–P coatings with identical thickness in 10% H_2SO_4 solution were shown in Fig. 11, the electrochemical corrosion parameters obtained from which are listed in Table 4. It is clearly seen from Fig. 11 that the as-plated Ni–W–Cr–P deposit has the highest corrosion potential, E_{corr}, as well as the lowest corrosion current density, i_{corr}, and thus is more corrosion resistant than binary Ni–P and ternary Ni–W–P deposits.

CONCLUSIONS

In the present study, the Ni–W–Cr–P alloy coatings were prepared by electroless deposition.

After shot blast treatment, a clean and fresh surface with proper roughness of the stainless steel substrate was obtained.

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 microcrystalline; the precipitation of Ni_3P was observed at the annealing temperature of 400°C; after heat-treatment at 500°C the crystallization of Ni_3P and Ni was near completion. At 600°C new phase $Cr_{1.12}Ni_{2.88}$ was observed and Ni_3P began to decompose. $Cr_{1.07}Fe_{18.93}$ and $Ni_{17}W_3$ were formed when heated at 700°C, and Ni_3P was not found. With increasing temperature to 800°C, $FeNi_2P$ and $Cr_4Ni_{15}W$ were the only two dominant phases.

The hardness of electroless Ni–W–Cr–P alloy coatings increased with the increasing annealing temperature, reached the maximum value of 964HV when heated at 700°C for 1 h. Then it decreased after heated at 800°C, but still remained a relatively high value of 804HV.

The Ni–W–Cr–P alloy coatings were more corrosion resistant than Ni–P and Ni–W–P alloy coatings in as-deposited condition in 10% H_2SO_4 medium.

REFERENCES

1. Hu, Y.J., Xiong, L., and Meng, J.L., Electron Microscopic Study on Iterfacial Characterization of Electroless Ni–W–P Plating on Aluminium Alloy, *Appl., Surf. Sci.*, 2007, vol. 253, no. 11, pp. 5029–5034.
2. Takacs, D., Sziraki, L., Toeroek, T.I., et al., Effects of Pre-Treatments on the Corrosion Properties of Electroless Ni–P Layers Deposited on $AlMg_2$ Alloy, *Surf. Coatings Technol.*, 2007, vol. 201, no. 8, pp. 4526–4535.
3. Maura, C., Andrea, S., Bernhard, E., and Antonella, R., The Corrosion Resistance of Electroless Deposited Nano-Crystalline Ni–P Alloys, *Electrochim. Acta*, 2008, vol. 53, no. 8, pp. 3364–3370.
4. Hamdy, A.S., Shoeib, M.A., Hady, H., and Abdel Salam, O.F., Corrosion Behavior of Electroless Ni–P Alloy Coatings Containing Tungsten or Nano-Scattered Glumina Composite in 3.5% NaCl Solution, *Surf. Coatings Technol.*, 2007, vol. 202, no. 1, pp. 162–171.
5. Ievlev, V.M., Shvedov, E.V., Soldatenko, S.A., et al., Silicide Formation during Heat Treatment of thin Ni–Pd Solid-Solution Films and Pt/Ni Bilayers on (111)Si, *Inorg. Mater.*, 2006, vol. 42, no. 2, pp. 151–159.
6. Hu, Y.J., Wang, T.X., Meng, J.L., and Rao, Q.Y., Structure and Phase Transformation Behaviour of Electroless Ni–W–P on Aluminium Alloy, *Surf. Coatings Technol.*, 2006, vol. 201, nos. 3–4, pp. 988–992.

7. Zaitsev, A.I., Zaitseva, N.E., and Shakhpazov, E.K., Thermodynamic Properties of Intermediate Ni–P Phases (26–32.5 at % P) between 971 and 1440 K, *Inorg. Mater.*, 2003, vol. 39, no. 5, pp. 427–432.
8. Tien, S.K., Duh, J.G., and Chen, Y.I., Structure, Thermal Stability and Mechanical Properties of Electroless Ni–P–W Alloy Coatings during Cycle Test, *Surf. Coatings Technol.*, 2004, vol. 177–178, pp. 532–536.
9. Tsai, Y.Y., Wu, F.B., Chen, Y.I., et al., Thermal Stability and Mechanical Properties of Ni–W–P Electroless Deposits, *Surf. Coatings Technol.*, 2001, vol. 146–147, pp. 502–507.
10. Gao, Y., Zheng, Z.J., Zhu, M., and Luo, C.P., Corrosion Resistance of Electrolessly Deposited Ni–P and Ni–W–P Alloys with Various Structures, *Properties, Microstructure Proc., Ser. A*, 2004, vol. 381, nos. 1–2, pp. 98–103.
11. Balaraju, J.N., Jahan, S.M., and Rajam, K.S., Studies on Autocatalytic Deposition of Ternary Ni–W–P Alloys Using Nickel Sulphamate Bath, *Surf. Coatings Technol.*, 2006, vol. 201, nos. 3–4, pp. 507–512.
12. Szczygiel, B., Turkiewicz, A., and Serafinczuk, J., Surface Morphology and Structure of Ni–P, Ni–P–ZrO_2, Ni–W–P, Ni–W–P–ZrO_2 Coatings Deposited by Electroless Methos, *Surf. Coatings Technol.*, 2008, vol. 202, no. 9, pp. 1904–1910.
13. Palaniappa, M. and Seshadri, S.K., Stuructured and Phase Transformation Behaviour of Electroless Ni–P and Ni–W–P Deposits, *Properties, Microstructure Proc.*, 2007, vol. A460–A461, pp. 638–644.
14. Tien, S.K., Duh, J.G., Chen, Y.I. The Influence of Thermal Treatment on the Microstructure and Hardness in Electroless Ni–P–W Deposit, *Thin Solid Films*, 2004, vols. 469–470, pp. 333–338.