MORPHOLOGICAL, STRUCTURAL, MICROHARDNESS AND ELECTROCHEMICAL CHARACTERIZATIONS OF ELECTRODEPOSITED Cr AND Ni–W COATINGS

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Abstract

Currently, Ni-Cr coatings are widely used in a number of important applications due to their excellent properties. In this study, Ni-Cr alloys were electrodeposited from citrate bath onto Cu substrates by using different values of applied current densities. The effects of plating deposition current density on morphological and structural characterization of Ni-Cr electrodeposited coatings were investigated by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD). Microhardness of the coatings is also evaluated using Vickers's microhardness. Potentio-dynamic polarization and electrochemical impedance spectroscopy (EIS) tests in 3.5 wt % NaCl solution were used to evaluate corrosion résistance of Ni-Cr coatings. The results showed that the surface morphology of the all coatings contained micro cracks and pores. XRD patterns indicate the formation of Ni-Cr and Cr_3Ni_2 phases. Microhardness measurements show that all Ni-Cr samples are harder than copper substrate. Electrochemical tests show that 3 $A.dm^{-2}$ is an optimal value of applied current density in the sense of the least value of E_{corr} = -12.3 mV and the best charge transfer resistance R_p = 303.03 $\Omega.cm^2$.

Keywords: electrodeposition, Ni-Cr alloy coatings, EIS, microhardness,

1 Introduction

Surface failures, one of the more important problems encountered in the industry, are due to wear, corrosion, fatigue, etc. [1]. In order to improve the properties of the surface against corrosion and increase the service life of metallic components, various modifications could be applied such as alloying a nickel based layer with other element like Mo, W, Al, SiC, Co [2-7]. Despite these coatings, Ni-Cr alloys exhibit better corrosion resistance and superior hot corrosion resistance due to the formation of a continuous chromia scale [8, 9] which permits the use of these alloys in many industrial applications. But a significant disadvantage of the addition of hexavalent chromium (IV) in Ni-Cr alloys is extremely restricted due to its hazardous action for environment [1, 11]. Therefore the development of new coatings Ni-Cr from eco-friendly bath containing divalent nickel and trivalent Cr which are less hazardous ions to replace hexavalent Cr deposits under the name ‹clean technology› in electroplating industry. Recently, a number of experimental studies were carried out on the electrodeposition of Ni-Cr alloys. Zhou

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Yue et al. [9] found that the microhardness and wear corrosion increase with the increase of Cr nanoparticles content in the Ni matrix. Whereas, Ching et al.[11] have reported that the hardness of Ni-rich deposits diminishes and corrosion resistance of Cr-rich deposits decreases by increasing annealing temperature due to through deposit cracking after annealing. Hui Zhang et al. [12] have reported that the corrosion resistance of the Ni-Cr coatings obtained from DMF mixed bath is much better than that obtained from aqueous bath. Etminanfar et al. [13, 14] have fabricated Ni-Cr multilayer electrodeposits with high corrosion resistance by using pulse current and modulated agitation. The improvement of the surface quality likely relates to the early release of hydrogen during the 'off' period of the pulse electroplating. Although there are several researches on electrodeposition of Ni-Cr alloys, there exist limited studies about the effect of current density on the characteristics of Ni-Cr coatings, electrodeposited from divalent nickel and trivalent chromium sulfate bath with alkaline tri sodium citrate as complexing agent. In the present study, direct current (DC) electrodeposition method was used to fabricate Ni-Cr alloy coatings. The aim of this work is to investigate the effect of plating deposition current density on the Ni-Cr electrodeposited coatings.

2 Experimental procedure

The Ni-Cr coatings were obtained by direct current density (DC) electrodeposition from an aqueous electrolyte containing nickel sulfate ($NiSO_4$, $6H_2O$), chromium trivalent sulfate ($Cr_2(SO_4)_3$, $6H_2O$), sodium sulfate (Na_2SO_4), tri-sodium citrate ($Na_3C_6H_5O_7$, $2H_2O$), and boric acid (H_3BO_3) which was used to keep the pH constant **(Table 1)**. Bi-distilled water was used for electrolyte preparation. Copper substrates (99.9 %) with of 20 ×10 ×0.19 mm^3 were used as cathode. However, the anode was a nickel sheet (20×10×2 mm^3) of commercial purity (99.99 %). Prior to deposition, the substrates were degreased in alkaline solution to remove oil and greases then pickled in a dilute acid (10 %) HCl to remove the oxide traces and finally washed with bi-distilled water, then with acetone. The electrolyte temperature was kept at 30 °C during the process; however pH value of the bath was adjusted by addition of the aqueous HCl or NaOH solution. Electrodeposition process was performed at different current densities 1, 3, 5 and 8 $A.dm^{-2}$ for 60 minutes.

To evaluate the adherence of Ni-Cr alloy coatings, the coated samples were heated at 250 °C for 30 min, which were subsequently quenched in water at ambient temperature [15]. The morphology of Ni-Cr alloy coatings was examined by FEI QUANTA 200 scanning electron microscopy (SEM). Structural investigation was conducted by X-ray diffraction (XRD) using a Bruker diffractometer (D8Advance model) with Cu Kα-radiation (1.5406 Å). Microhardness were carried out using Vickers machine with an applied load of 10 N for 10 s, the mean values of at least five measurements conducted at various locations on each sample were considered.

Corrosion experiments were performed in two ways: potentio-dynamic polarization and electrochemical impedance spectroscopy (EIS). The measurements were made using a voltalab (PGZ402), which was connected to a three electrode electrochemical cell. The electrolyte used was a 3,5 wt% NaCl solution at room temperature. A saturated calomel electrode (SCE) was used as the reference electrode, and platinum electrode was used as the auxiliary electrode. The Ni-Cr alloy coatings were used as the working electrodes. Prior to the corrosion tests, the samples were immersed into the electrolyte for about 30 min to stabilize the open circuit potential. EIS tests were done in open circuit potential with an AC signal application in a frequency range from 10 KHz to 50 mHz and amplitude of 10 mV. The potentio-dynamic polarization tests were conducted with a scan rate of 10 mV/s.

Table 1 Bath composition and deposition conditions for Ni-Cr alloy coatings

Bath composition	Concentration (g/l)	Experimental conditions
$NiSO_4$. $6H_2O$ $Cr_2S_3O_{12}$. xH_2O H_3BO_3 $Na_3C_6H_5O_7$. $2H_2O$ Na_2SO_4	26 45 18 80 14	Current density ($A.dm^{-2}$) ~ 1-8 pH = 5 Time (60 min) Temperature (30 °C)

3 Results and discussion

3.1 Morphological characteristics

Fig. 1 illustrates the surface morphologies of Ni-Cr coatings electrodeposited on Cu substrates under different current densities. Before SEM characterization, it was remarkable that the electroplating alloys become darker with increase of current density, which can be caused by the formation of hydroxide compounds and thus changes within the morphology. All the deposits show nodular surface morphology with microcracks, which increase by increasing the current density. The formation of microcracks is encouraged by hydrogen intensification under the effect of increasing current density [15]. These cracks become wider as the applied current density increase to more than $3A.dm^{-2}$, which can be attributed to the high levels of internal stresses and hydrogen evolution rise. Furthermore, the adsorption of chromium hydroxide compounds on the coating surface can also increase cracking. Numerous researches have emphasized this result and found that the formation of cracks is the characteristic of Cr electrodeposits [16].

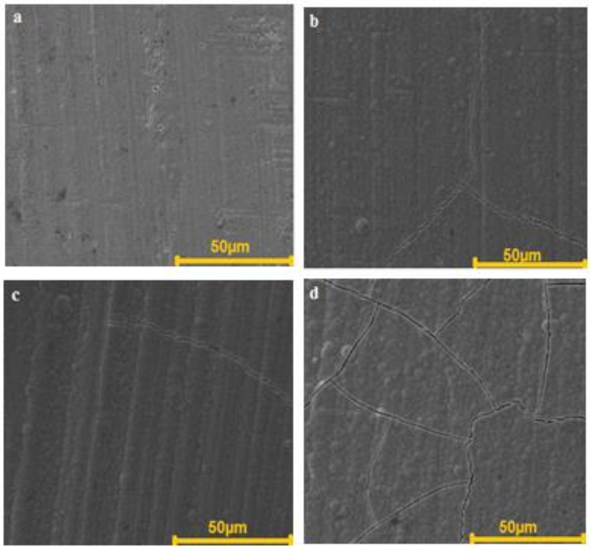

Fig. 1 SEM images of Ni-Cr coatings electrodeposited at: (a) 1 $A.dm^{-2}$, (b) 3 $A.dm^{-2}$, (c) 5 $A.dm^{-2}$ and (d) 8 $A.dm^{-2}$

3.2 Chemical composition

The effect of current density on Ni and Cr content of the alloys is presented in Table 2. As general analysis of this result, we can consider the content of chromium of the alloy as traces, where its percentage is very small compared to the nickel content of the alloy. Taking into consideration the diffusion theory, it is reported that enhancing of current density makes more chromium precipitate on the cathode surface, as chromium is more active than nickel [16, 17]. Despite everything, as sodium tri-citrate was used as complexing agent to facilitate production of chromium complex with nickel, the traces content of Cr of Ni-Cr alloy may be caused by the formation of inert chromium hydroxide around the surface of the cathode.

Table 2 Hardness and chemical composition of different samples.

Plating current density (A.dm^{-2})	**Hardness (Hv)**	**Ni content (wt%)**	**Cr content (wt%)**
1	254,26	94.29	0.08
3	435,73	97.35	0.41
5	483,83	96.82	0.25
8	499,76	98.12	0.16
Cu substrate	144.53	-	-

3.3 Microhardness and XRD measurements

The hardness values of Ni-Cr alloy deposits electroplated with different current densities are shown in **Table 2**. It can be seen that the hardness values increase with increasing electrodeposition current density. The hardness of Ni-Cr alloy deposit is approximately 500 Hv after depositing at 8 A.dm^{-2}, almost twice that of deposited at 1 A.dm^{-2} (254 Hv), indicating that Ni-Cr alloy deposits can be hardened through increasing current density. Chromium is harder than copper substrate and increasing of electrodeposition current density can increase microhardness of the deposits [8].

XRD measurements were used to determine the phases present in the electrodeposited coatings with different applied current densities. From **Fig. 2**, no diffraction peaks of Cu are found in all patterns indicating that copper substrates are completely covered by the coatings, which evidence that the above mentioned cracks were superficial and did not reach to the substrate. The diffraction peaks corresponding to NiCr and Ni_2Cr_3 alloys are found on all the curves, indicating the microcrystalline structure of the coatings.

Fig. 2 shows the peaks located at 2θ = 39° and 48° represent NiCr crystalline phase and correspond to the following planes: (200) and (211) respectively. The peaks recorded at 2θ = 43° and 47° represent Ni_2Cr_3 crystalline phase and correspond to the following planes: (330) and (331) respectively. In contrast, increasing the current density to 8 A.dm^{-2} leads to the appearance of new peaks corresponding to NiCr and Ni_2Cr_3 phases preferred growth at 2θ = 40° and 48° respectively.

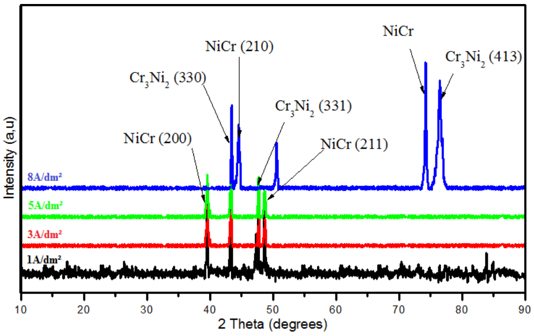

Fig. 1 XRD patterns of different Ni-Cr alloy coatings

3.4 Electrochemical corrosion tests

The potentiodynamic polarization curves of the different coatings are presented in **Fig. 3**. The Tafel extrapolation method is used to evaluate the electrochemical specifications, which are presented in **Table 3**. It is clearly seen that a nobler Ni-Cr alloy coating electroplated at 3 A.dm^{-2} has the highest value of corrosion resistance Rp = 303.03 Ω.cm² and the least negative corrosion potential E_{corr} = -12.3 mV, which presents an important result to improve electrochemical behavior of copper substrate. Lower corrosion resistance of Ni-Cr coating electroplated at 1 A.dm^{-2} is as a result of micro cracks density of these coatings.

Table 3 Fitting results of polarization curves

Current density (A.dm^{-2})	**R_p (Ω.cm²)**	**I_{corr} (μA/cm²)**	**E_{corr} (mV)**
1	39.56	3.2068	-69.9
3	303.03	0.0921	-12.3
5	113.11	0.0958	-94.2
8	189.56	0.0597	-112.0
substrate	17.38	1.2055	-74.1

Corrosion behavior of the coatings was also studied through EIS test. **Fig. 5** shows the Nyquist plots of different coatings. It is obvious that there is just one loop in each diagram. As illustrated in **Fig. 6**, an equivalent circuit is presented to analyze and compare the results. The represented elements shown in the circuit is R_s (solution resistance), R_p (charge transfer resistance of the electrode reactions) and C (the double layer capacitance between the electrolyte and the coating).

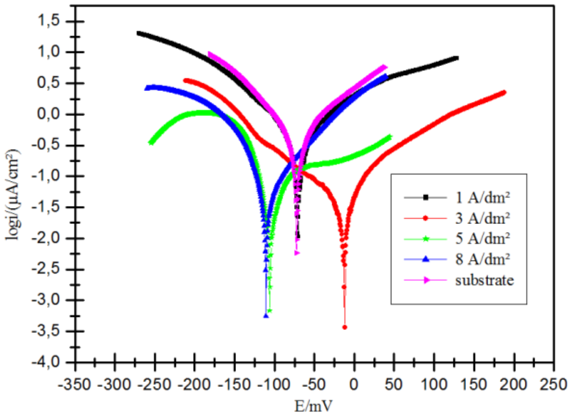

Fig. 2 Polarization curves of Ni-Cr alloy coatings electrodeposited with different current densities

Table 4 Equivalent circuit parameters for different samples

Current density (A.dm^{-2})	**R_p (KΩ.cm²)**	**R_s (Ω.cm²)**	**C_p (μF/cm²)**
1	138.0	164.4	14.52
3	172.4	-100	11.62
5	57.06	-34.0	22.31
8	36.19	-13.1	69.47
substrate	2.622	9.271	1.213

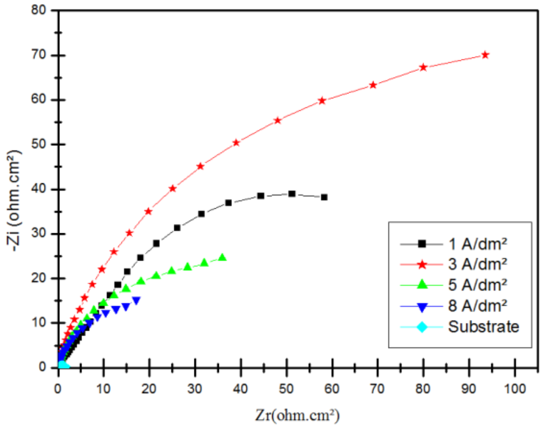

Fig. 3 Nyquist plots of the different Ni-Cr coatings electrodeposited with different current densities

As reported, increasing R_p signifies improvement of corrosion resistance [16, 18]. Among the samples, the Ni-Cr coating depositing at 3 $A.dm^{-2}$ shows the maximum Rp value due to high value of Cr content of alloy. Moreover, Table.4 shows that all Ni-Cr coatings have better charge transfer resistance than copper substrate, which is in agreement with the polarization results.

Increasing of the Cp value indicate large surface area in contact with corrosive solution increasing of crack density [19].

As a result of increasing electroplating current density to more than 3 $A.dm^{-2}$, Cp value is increased due to larger contact area of coatings with solution which in turn enhanced of microcraks density in the deposits.

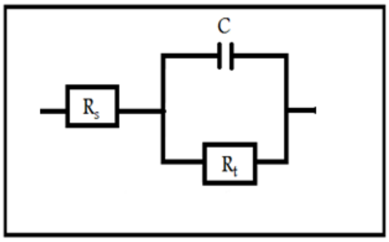

Fig. 4 Equivalent circuit used for fitting the electrochemical impedance data

Conclusions

In this work, the effects of electrodeposition current density on surface morphology, microhardness of Ni-Cr, as well as their structural and electrochemical characteristic was investigated. Thermal shock test reveals that Ni-Cr coating deposited presents a good adherence to copper substrate and presented nodular surface morphology with microcraks, which its density is dependent on electrodeposition current density. The chemical composition of Ni-Cr alloy varies nonlinearly and showing that Cr content of alloy presented as traces. X-ray diffraction patterns of all Ni-Cr coatings exhibit mainly the NiCr and Ni_2Cr_3 phases' structure of then Ni–W solid solution. Microhardness test show that Ni-Cr alloy coating is harder than copper substrate and their values is proportional with electrodeposition current density. Basing on potentiodynamic polarization and EIS measurements, the Ni-Cr alloy coating, electrodepositing at 3 A.dm^{-2}, has the lowest corrosion current density and the best charge transfer resistance among all the deposits.

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