

CHARACTERIZATION OF NI-CO COATINGS ELECTRODEPOSITED FROM ELECTROLYTES WITH DIFFERENT CO CONCENTRATIONS

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ABSTRACT

In this work, Ni-Co composite coatings with different Co contents were prepared by electrodeposition from modified Watts bath containing different Co^{+2} amounts. The effects of Co contents on the composition, crystal structure, surface morphology, and corrosion resistance of the Ni-Co composite coatings were investigated. Morphology and microstructure were studied by scanning electron microscope and XRD analysis. Pebbly, spherical granular and acicular morphology were illustrated with SEM micrographs and combination of fcc and hcp structure were characterized by XRD patterns which depended strongly on cobalt content in the deposit. The electrochemical properties of Ni-Co alloy coatings were evaluated in 3.5 % NaCl solution by means of potentiodynamic polarization technique. A better corrosion resistance was obtained for pure nickel deposit.

KEYWORDS: Ni-Co composite coating; Electrodeposition; Morphology; Electrochemical properties; Corrosion resistance.

1 INTRODUCTION

Many attempts have been made to find methods for enhancing the surface properties of metal components to protect against corrosion and wear and reducing their costs since all of them are the effective factors in the degradation of industrial parts. Electro-deposition is considered as one of the most important and cost effective industrial techniques for producing protective coatings. It is conducted at normal pressure and ambient temperatures and provides high deposition rate and high throwing power. Electro-deposition of Ni and Ni-alloy coatings has found widespread use in many industrial fields [1]. Therefore, the interests focused on the electro-deposited NiCo and NiCo based metal matrix composite (MMCs) coatings due to their superior properties, such as higher hardness, improved anti-wear. This phenomenon means that the less noble metal Co is preferentially deposited [2]. The properties of Ni-Co alloys depend strongly on cobalt content. The content of cobalt in the Ni-Co deposit can be controlled by experimental parameters, such as electrolyte composition, pH, stirring, temperature, deposition potential or current, etc [3, 4]. The effects of Co on the microstructure and properties, especially the texture, corrosion resistance and hardness of the composite coatings need further investigation.

The purpose of this work is to investigate the influence of electrolyte composition on the surface morphology, the chemical content of binary alloys and the corrosion resistance as well as some other properties.

2 EXPERIMENTAL

Ni-Co alloys were electrodeposited from a typical Watts-type electrolyte. The bath composition and deposition conditions were listed in table 1 and the total concentration of NiCl_2 and CoCl_2 was kept at 0.10 M. In addition, pure Ni deposit coating was also produced for comparison purpose.

The Ni-Co composite coatings were deposited on pretreated P265N.B steel substrate used as a cathode; a pure Ni sheets were used as the anode. Substrates were mechanically polished up to 1200 grade abrasive paper, then degreased and activated in the 10% HCl solution, finally rinsed with distilled water. The PH of the bath was controlled and adjusted at 4.0 using diluted ammonia or diluted sulfuric acid. The above mentioned parameters as well as bath composition were selected based on the previous study.

The composition of basic electroplating bath of Ni-Co alloys deposition and condition deposition were shown in table 1.

The morphology and the microstructure of the coatings were investigated using a JSM-6390 Lv scanning electron microscopy (SEM). The compositions of Ni-Co coatings were determined with energy dispersive x-ray spectroscopy (EDS) analysis tool attached to SEM. Structural investigations and phase composition of the coatings were conducted by XRD method using a Bruker diffractometer (D8 Advance model) with $\text{Cu K}\alpha$ -radiation (1.5406 Å).

Table01: Bath compositions and deposition conditions for Ni-Co coatings. The total concentration of NiCl₂ and CoCl₂ is 0.10 M

Bath composition	Concentration (mol.l ⁻¹)
NiCl ₂ .6H ₂ O	0.75, 0.50, 0.25,0.00
CoCl ₂ .6H ₂ O	0.25, 0.50, 0.75, 0.10
H ₃ BO ₃	0.3
NH ₄ Cl	0.4
NaCl	0.1
Electrodeposition parameter	
Current density (A.dm ⁻²)	3
Temperature (C°)	48
PH	4
Deposition time (min)	60

The corrosion tests were carried out using potentiodynamic polarization method. Polarization measurements were conducted using a standard three-electrode cell with the coated samples as a working electrode, Pt as auxiliary electrode and saturated calomel electrode as a reference electrode, all immersed in 0.6M NaCl electrolyte. This cell was connected to VoltaLab 20 (PGP201) device working at a scanning rate of 0.5 mV/s. Corrosion rate (mm/y), corrosion potential E_{corr} (mV), and Tafel slopes (mV/s) were calculated using Tafel extrapolation technique provided by Volta Master 4 software.

3 RESULTS & DISCUSSION

3.1 Morphology

Surface morphology with different Co content was illustrated in Fig.1. It is clearly found that the morphology of the coatings is significantly influenced by Co²⁺ concentration in the plating bath Fig.1b-e. This effect is attributed not only to the composition difference but also to the phase transition of the deposited metallic atoms [5]. Fig.1a shows a typical morphology of a Watt Ni deposit, which has relatively large grain size and showed pebbly crystallites. At 25wt.% of Co content in the deposit leads to gradual decrease in the grain size as seen in Fig.1b. However, when Co content increases to 50wt.% and 100 wt.% Fig.1c-e, the morphology of Ni-Co alloy change dramatically to a rather regularly branched structure with extended acicular crystallites Fig.1d,e, [6].

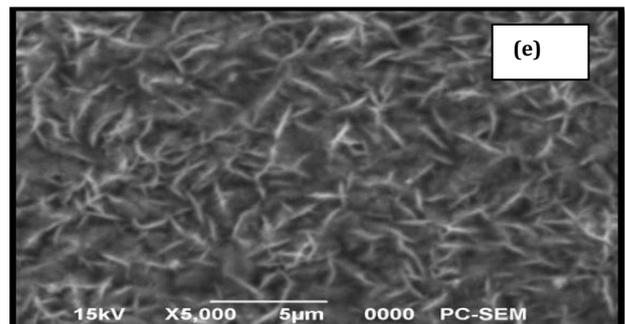
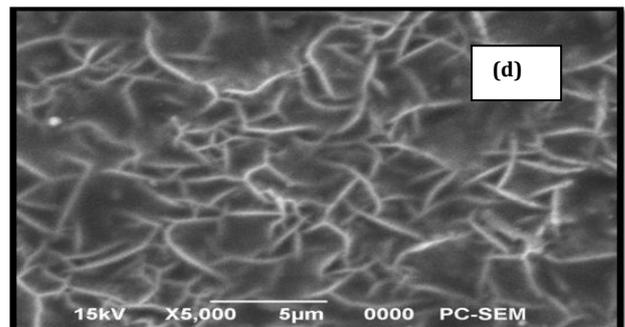
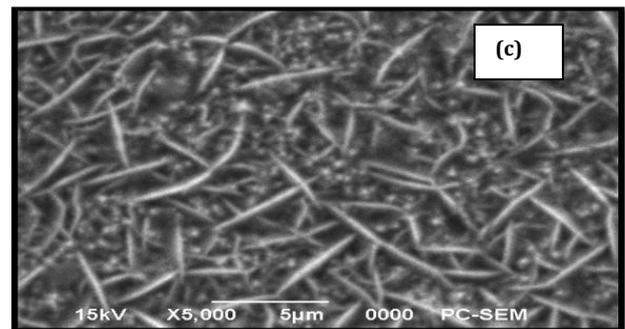
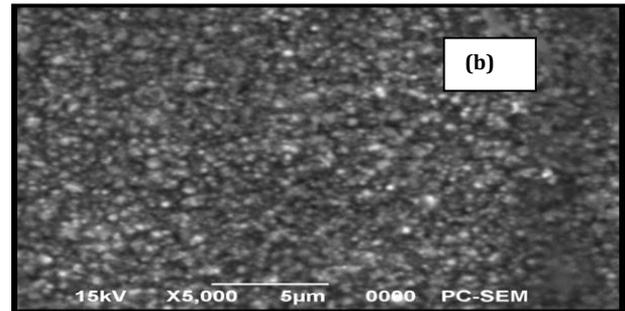
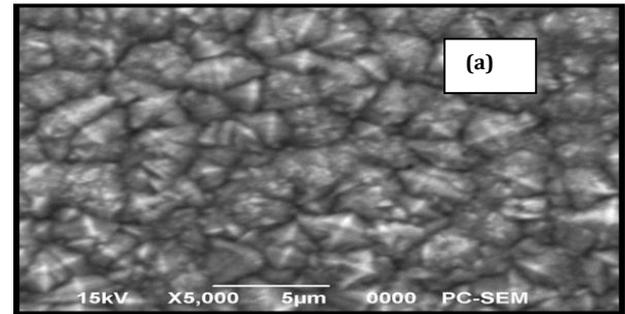
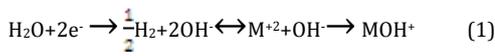


Figure 01: SEM morphologies of Ni-Co alloy deposits with their Co contents of (a) 0 wt.%, (b) 25 wt.%, (c) 50 wt.%, (d) 75 wt.%, (e) 100wt.%.

3.2 Chemical composition

By using EDS analysis, the cobalt content in the deposits is shown in Fig.2. As can be seen, the nickel and cobalt ions can be deposited onto the substrate. It is clear that the count of Co always much higher than of Ni even at low Co⁺² concentrations (Fig. 2b-2d) demonstrating the existence of anomalous codeposition in the Ni-Co system. Namely, the less noble metal Co is preferentially deposited. Several studies have been put in literature to understand these phenomena. This refers to the anomalous behavior of nickel and cobalt ions which was studied by Liang Liang and Kharmachi [3, 5, and 7]. They have proposed an electrodeposition mechanism characterized by the rise of pH at the cathode. This locale increase in pH caused by the precipitation of metal hydroxides on the cathode, the deposition process occurs in several steps based on adsorption of metal hydroxyl ions on the deposits Eq. (1, 2):



Where M represents Ni or Co atoms. The OH⁻ ion formed at the end of the reaction favors the formation of MOH⁺ and enhances the adsorption of MOH⁺. The adsorption ability of Co(OH)⁺ was considered to be higher than Ni(OH)⁺ this can cause enriching of binary alloy with less noble metal Co.

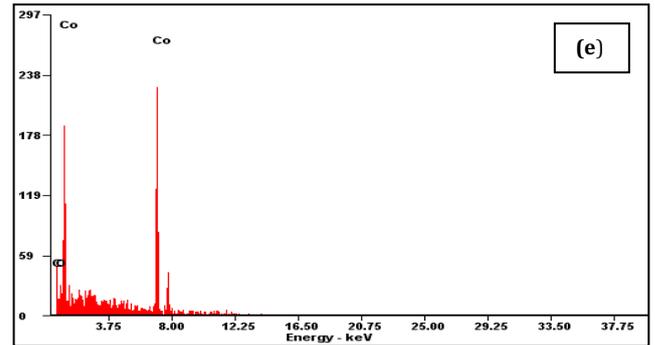
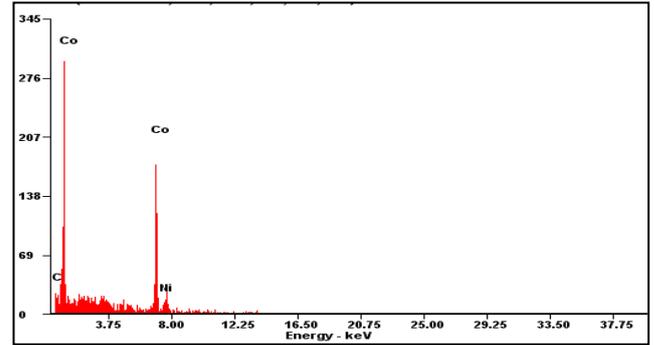
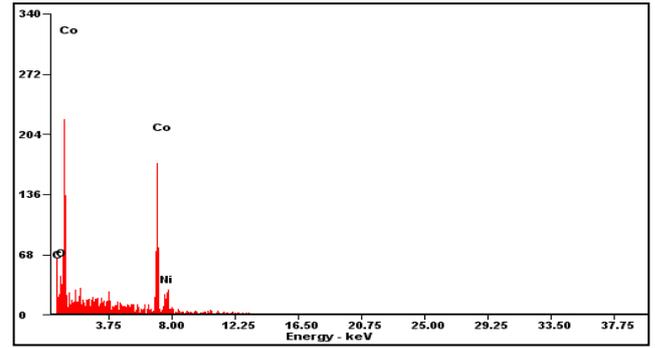
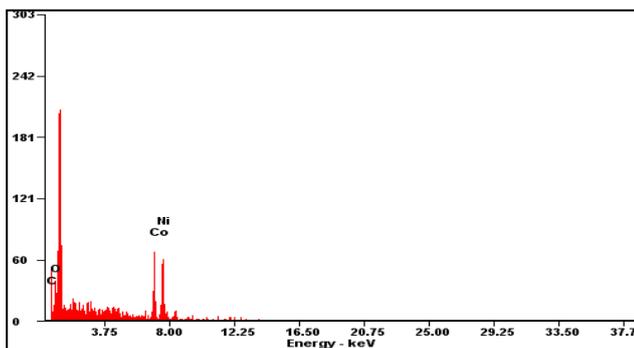
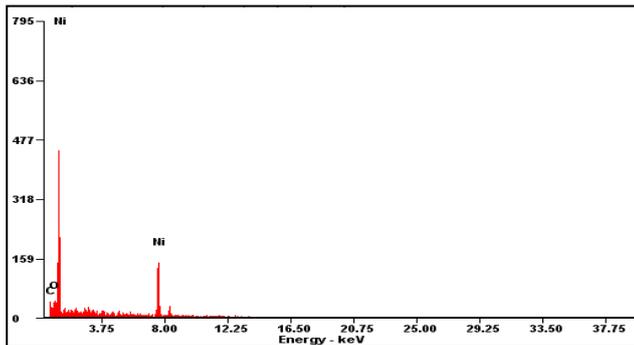


Figure 02: EDS of electrodeposited of Ni-Co composite coatings with different contents, (a) 0wt.% Co, (b) 25wt.% Co, (c) 50wt.% Co, (d) 75wt.% Co, (e) 100wt.% Co



3.3 Structure of the deposits

The phase composition and structure of pure Ni and Ni–Co alloys with different Co contents were investigated using XRD. The XRD patterns are shown in Fig.4. As can be seen, from Fig. 4a, the deposit has a single phase of face centered cubic (fcc) α -phase [8]. As can be seen in Fig. 3b–e, both the crystal structure and phase composition are mainly dependent on the Co contents in Ni–Co alloys. For the Ni-rich alloys with Co content less than or equal to 50 wt.% , showed the presence of (101) peak demonstrated the initial formation of hexagonal close packed (hcp) ϵ -phase, indicating that the crystal structure of the Ni-Co alloy changed from complete fcc into a mixed (majority of α -phase)+(minority of ϵ -phase) as shown in Fig.4b,c [9]. At above 50 wt.% , as shown in Fig 4d,e we can see that a very strong hcp (100) and (101) peak were observed. Therefore, it can be concluded that the phase structure of Ni-Co alloys

gradually changed from fcc α -phase into hcp ϵ -phase with the increase of Co content as shown in Fig.4 [10].

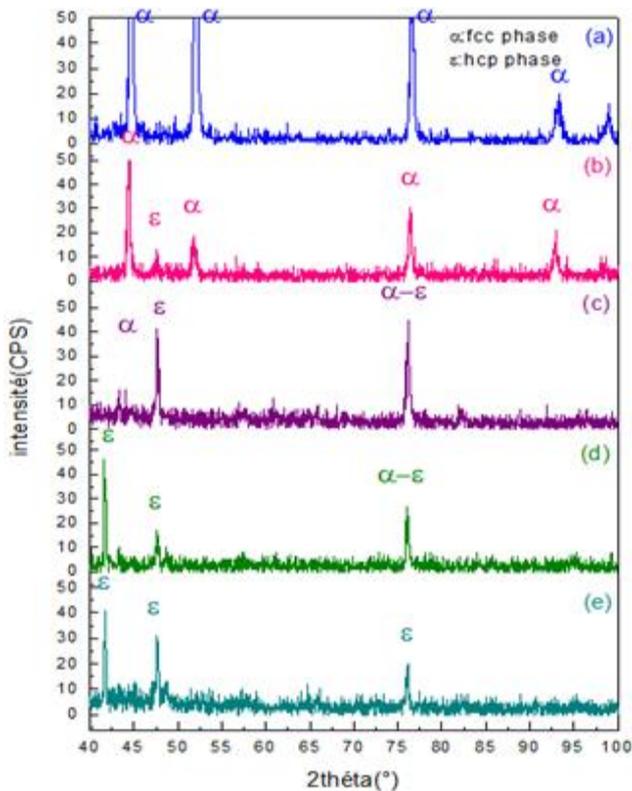


Figure 03: XRD patterns of Ni-Co alloy deposits with their Co contents of (a) 0 wt.%, (b) 25 wt.%, (c) 50 wt.%, (d) 75 wt.%, (e) 100 wt.%

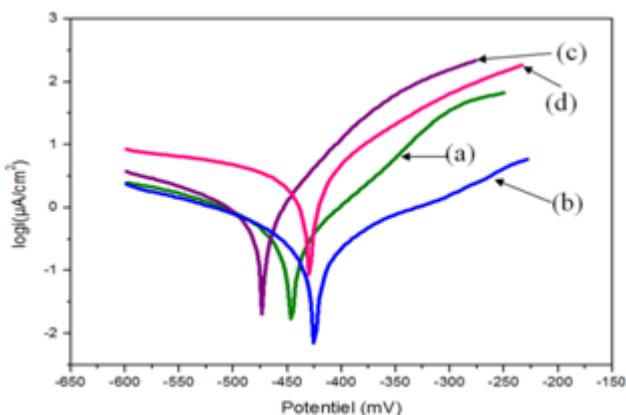


Figure 04: Potentiodynamic polarization curves of Ni-Co alloy deposits as a function of their Co contents of (a) 25 wt.%, (b) 50 wt.%, (c) 75 wt.%, (d) 100 wt.%

Table 02: Potentiodynamic polarization data of Ni-Co alloys in 3.5% NaCl electrolyte

Co Concentration	E_{corr} (mv)	I_{corr} ($\mu A.cm^{-2}$)	R_p ($\Omega.cm^2$)
25wt.%	-446.0	0.2298	57.34
50wt.%	-424.5	0.8149	49.36
75wt.%	-473.1	1.3936	26.05
100wt.%	-429.3	6.2497	5.34

3.4 Potentiodynamic polarization

The potentiodynamic polarization curves of the Ni-Co composite coatings are presented in Fig.3 and the corrosion parameters, such as corrosion potential (E_{corr}) and corrosion current (I_{corr}) obtained by using Tafel extrapolation plot of polarization curves, are summarized in table 2.

It could be found from table 2. That the corrosion current (I_{corr}) of the Ni-Co composite coatings increased with increasing Co contents. Comparing to the smaller corrosion current (I_{corr}) of 0.2298 $\mu A.cm^2$ for Ni-Co coating, it could be speculated that addition of Co deteriorated the corrosion resistance of the Ni-Co composite coatings and the corrosion resistance decrease with increasing Co contents. The decrease of the corrosion resistance of the Ni-Co composite coatings could be due to several factors. Firstly, alloying with Co decreases the corrosion resistance of the Ni by changing the nobility of materials [2], because Co is more active than Ni. Secondly, the formation of hcp Co also deteriorated the corrosion resistance of the coatings. In general two-phase structures are less corrosion resistant than single phase structures because galvanic cell can be easily formed between phases with different nobilities [1, 11-13].

So, a better corrosion resistance was obtained with rich nickel deposit. This result was confirmed with polarization resistance value (R_p) that was found to be the highest for (Ni-25wt.% Co) coating.

4 CONCLUSION

1. The Co content in Ni-Co alloys increased gradually with the increase of Co^{+2} concentration in the electrolyte, which is confirmed by the anomalous codeposition of iron group metal.
2. Surface morphology of Ni-Co alloys changed from pebbly structure into acicular structure when increasing Co content from 50 to 100wt.%. Both the crystal structure and phase composition are mainly dependent on the Co content in alloys. The phase structure of Ni-Co alloys gradually changed fcc into hcp with the increase of Co content.

3. The corrosion behavior of Ni-Co alloy coatings was evaluated by mean of potentiodynamic polarization study and a better corrosion resistance was obtained with rich nickel deposit (Ni-25wt.% Co). This result can be deduced from corrosion parameters obtained from Tafel plot.

As conclusion a coating with important amount of cobalt is less protective to steel carbon substrate than another with more nickel content.

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