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Mechanical Characterization of Electrodeposition of Ni-P Alloy Coating

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The electrodeposition process plays a crucial role in the formation of thin films on materials, in particular, the electrodeposition of nickel-phosphorus because of its important properties. In this study, Ni-P coatings were deposited on X52 steel substrates by electrodeposition technique from a solution containing nickel sulfate, sodium hypophosphite (NaH_2PO_2). Composition, surface morphology, and mechanical properties of the Ni-P deposits were studied using SEM, EDAX, the Vickers method, weight loss and potentiodynamic polarization techniques. The effects of the current density were investigated on the surface morphology, phosphorus content, microhardness and corrosion of the coatings. It was observed that both the phosphorus content and microhardness are dependent on the current density. Results demonstrate that the morphology of the electrodeposited Ni-P alloys shows that the grains are spherical in nature for all the samples. It has been observed that the influence of current density on the P content of the deposit is an inverse relation with phosphorous content and also the as-plated coatings at current density of 5 $A{\cdot}m^{-4}$ exhibit the superior microhardness. Corrosion tests show that 5 $A{\cdot}m^{-4}$ is the best current density value which gives the best protection coating against corrosion.

Keywords: Ni-P alloy coatings, Microhardness, Corrosion, Current density, Potentiodynamic polarization, Electrodeposition.

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1. INTRODUCTION

Ni-P coatings are widely used in the aerospace, automotive and chemical industries, and also in oil production, they are also preferred for use in the electronic industry. The need for improving the corrosion protection of the metals has motivated the researchers to find superb new coatings or modify the existing ones. The preparation of thin film coatings using electrochemical methods is attractive due to their simplicity, and also controlling bath parameters (bath composition, pH, temperature). The physical and mechanical properties of the coatings can be modified within a certain range [1]. Thin film coating using electrochemical method is attractive because of its simplicity, the uniform and controllable deposition rate, operation at ambient temperature, the possibility to get multilayer and coat large surfaces in different shapes at low cost [2, 3]. Ni-P coatings can be deposited effectively on steel [4, 5], aluminum alloys [6], copper [7-10]. The electrodeposition process plays a crucial role in the formation of thin films on materials, occurring through the electrochemical reduction of metal ions in the electrolytic solutions. At this point, several investigators are interested in Ni-P coatings because of their important properties such as the corrosion resistance, good solder ability, high electrical conductivity, smooth surface formation and symmetry, low coefficient of friction, electrical activity and paramagnetic properties obtained by the simple electrochemical processes, and also for their shiny and smooth appearance, unlike the deposit of Ni [6-9, 11]. Despite the complexity of this deposit, its phase diagram shows the existence of several stable states depending on the percentage of phosphorus [12]. Ni-P coatings are divided into three categories: low, medium, and high P. Given that the P content largely determines the properties of Ni-P coatings, this shows the importance of the chemical composition of the electrodeposition bath [10]. The metallurgical properties of alloys are also dependent on percentages of phosphorus. The Ni-P alloy with P content greater than 8 wt. % (high phosphorus content) possesses excellent mechanical properties, such as hardness, wear resistance, and corrosion resistance [8, 10, 13]. More studies have been conducted on electroless Ni-P nanocomposites in recent decades. Ni-P-SiC, Ni-P-TiO_2, Ni-P-Al_2O_3, and Ni-P-CNT are successful examples that have attracted attention owing to the improved properties relative to the original Ni-P coatings [14]. Although there are several researches on electrodeposition of Ni-P alloys, there exist limited studies on the effect of current density on the characteristics of Ni-P coatings. In the present study, the direct current (DC) electrodeposition method was used to make Ni-P alloy coatings. The aim of this work is to investigate the effect of plating deposition current density on the Ni-P electrodeposited coatings.

2. EXPERIMENTAL PROCEDURES

2.1 Electrodeposition of Ni-P Coatings

The Ni-P coating was deposited on X52 steel substrates. The composition and operating parameters for electroplating are shown in Table 1. Bi-distilled water was used for electrolyte preparation. The coating was obtained by varying the current densities from 1 to 9 $A{\cdot}m^{-4}$. The electrodeposition cell contains a nickel sheet (30×10×2 mm^3) of commercial purity (99.99 %) as anode and X52 steel substrate (30×10×5 mm^3) was used as cathode. The substrates were mechanically polished

with SiC abrasive paper (120-1200). They were rinsed with distilled water, degreased in 50 g/l Na_2CO_3 and 15 g/l NaOH solution, then pickled in 10 % HCl solution to remove oxide traces, and finally washed with bi-distilled water. The pH value of the bath was adjusted by adding hydrochloric acid or sodium hydroxide solution.

Table 1 – Chemical composition and deposition parameters of Ni-P coatings

Deposition parameters	Values
$NiSO_4 \cdot 7H_2O$	52 g/l
$NaH_2PO_2.2H_2O$	26 g/l
H_3BO_3	24 g/l
NaCl	40 g/l
Temperature	75-80 °C
Current density	1-9 $A \cdot m^{-4}$
Deposition time	30 min
pH	3

2.2 Deposits Characterization

The Ni-P coating morphology was examined by FEI QUANTA 200 scanning electron microscopy (SEM). The Ni-P coating compositions were determined with energy dispersive X-ray spectroscopy (EDX) analysis tool attached to SEM. In order to test the Ni-P coating adhesion, the samples were heated for 30 min at 250 °C and then immersed in water at room temperature [15]. Hardness measurements were performed on the Wilson 402UD Wolpert instrument, according to the Vickers method, with an applied load of 100 N for 10 s. Mean values were taken for five measurements performed at different locations in each sample.

2.3 Corrosion Tests of the Deposits

The corrosion phenomenon has been investigated using two methods: weight loss and potentiodynamic polarization. Potentiodynamic polarization measurements were conducted at ambient temperature using an electrochemical measurement system controlled with a voltalab PGP 201 corrosion analysis. The tests were carried out in a three-electrode cell filled with 500 ml of 1 M HCl solution, with the NiP as the working electrode (1 cm^2), a Pt auxiliary electrode and a statured calomel reference electrode. All potentials are reported vs. SCE. For potentiodynamic polarization, the working electrode was in the form of a disc cut from X52 steel and coated specimens with an exposed area of 1 cm^2. A calomel electrode was placed close to the working electrode to minimize ohmic resistance. The potentiodynamic polarization tests were conducted with a scan rate of 20 mV/min and in a potential range from – 600 to – 200 mV. Corrosion rate (mm/y), corrosion potential E_{corr} (mV) and corrosion current density I_{corr} ($A \cdot m^{-4}$) have been calculated by using Tafel extrapolation technique provided by Volta Master 4 software.

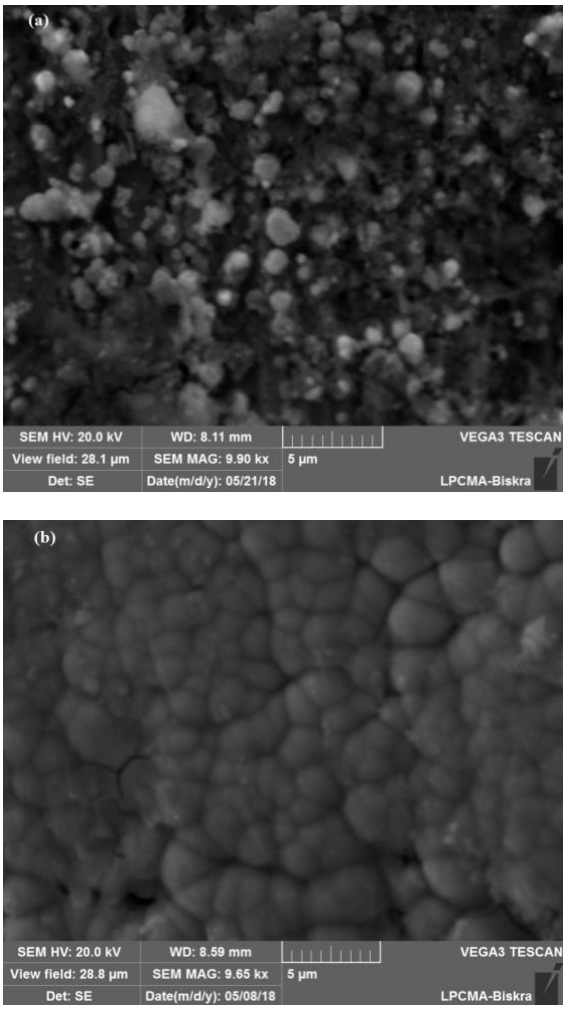
3. RESULTS AND DISCUSSION

3.1 Effect of Current Density on the Morphology

The surface morphology of the Ni-P coatings at different plating current densities (various concentrations of phosphorous) were studied using scanning electron microscopy (SEM). The morphological image shows that the grains are spherical in nature for all the samples. It can be observed that there is a detachment of grains as the applied current is increased. It also can be seen a slight difference that the boundary between nodes increases gradually with increasing amount of current density. Fig. 1b, d, e each shows a fissured area of Ni-P deposited coatings. This fissure area may be attributed to the internal stresses caused by the hydrogen reaction intensification [16]. It is noted that the morphology of these coatings is similar to those obtained by T. Mahalingam and K. Dhanapal [17, 18].

3.2 Effect of Current Density on the Coating P Content

In order to assess the effect of current density on the P content of the coating, samples were prepared with



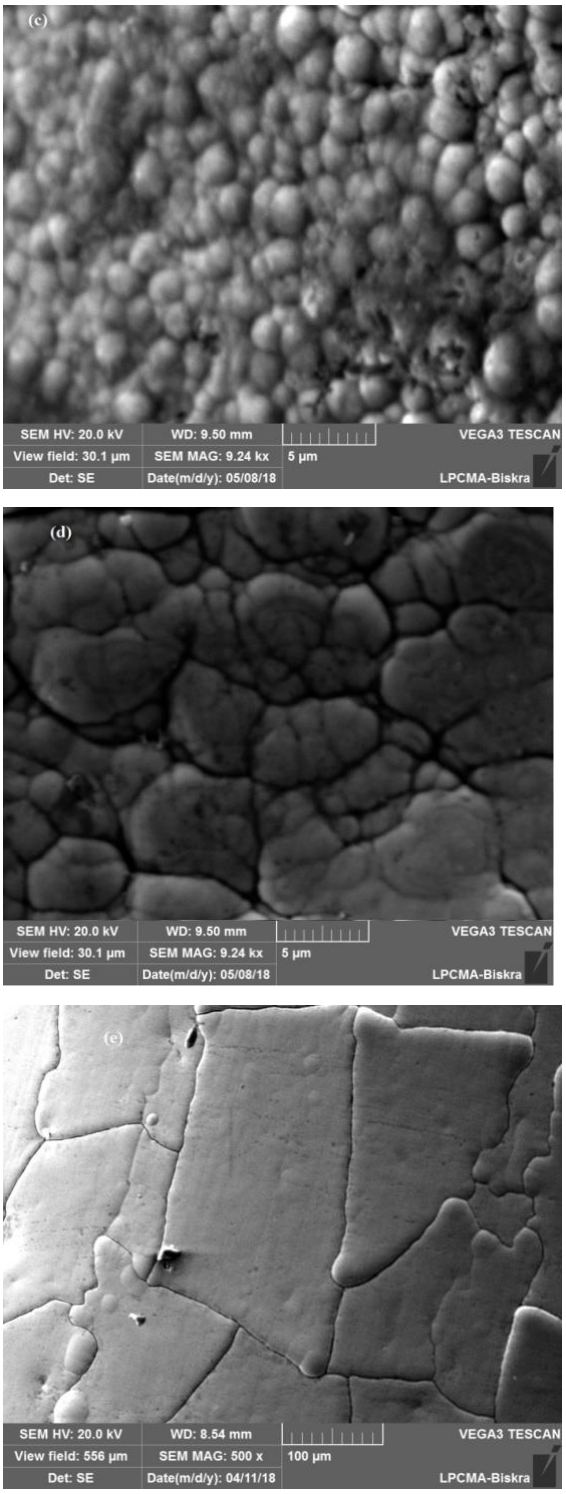


Fig. 1 – SEM images of Ni-P coatings electrodeposited at: (a) 1 A·m^{-4}; (b) 3 A·m^{-4}; (c) 5 A·m^{-4}, (d) 7 A·m^{-4}, (e) 9 A·m^{-4}

different current densities of 1-9 A·m^{-4} at 75-80 °C bath temperature. Fig. 2 illustrates the effect of current density on P (wt. %) content in alloys. The results showed that the P content in Ni-P coatings decreases with increasing current density. A general trend of a decreasing phosphorous content with increasing current density is reported in literature by many authors, although a large scatter between the data points of the different authors is noticed [6]. This behavior is due to the rise in the movement of the Ni ions towards the cathode as a result of variation of current density. The current density increase causes a drop of the phosphorus content in the deposit, which may be attributed to a partial restraint of P particles by nickel ions.

3.3 Effect of Current Density on the Hardness

Fig. 2 shows the hardness of the Ni-P coated samples. The values are the average of five measurements. It can be clearly seen that the coatings reached a higher hardness at current density of 5 A·m^{-4}. As shown, the hardness of the as-received coatings increases with decreasing P content. The coating (5 A·m^{-4} sample) with the P content of 13.97 wt. % has the highest degree of hardness 350.47 HVN_{100}, while 312.65 HVN_{100} is for the coating (1 A·m^{-4} sample) with the highest P content of 18.37 wt. %. The decrease in hardness at 7 A·m^{-4} and 9 A·m^{-4} is due to the heterogeneity of the coating (cracks). This increase is due to the change of microstructural phases and existence of Ni_3P compound in the coating [14, 19].

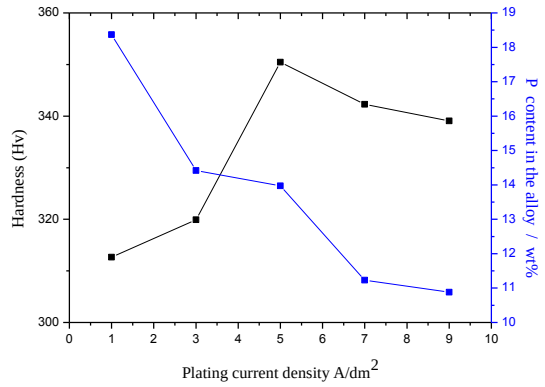


Fig. 2 – Effect of the current density on the hardness and concentration of P in the alloys

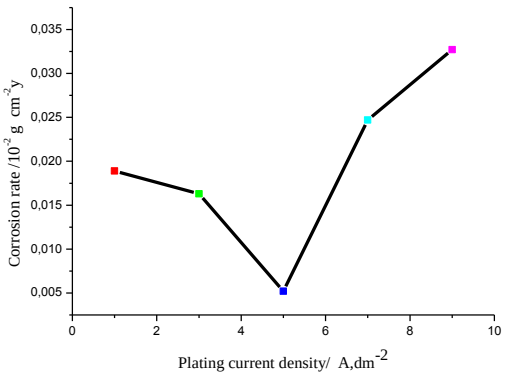


Fig. 3 – Corrosion rate variation for different current densities

3.4 Current Density Effect on Corrosion

3.4.1. Weight Loss

Corrosion tests are performed with weight loss method. Fig. 3 shows variation of the corrosion rate with the current density in 1 M HCl for 15 days immersion at room

temperature. Based on the results obtained, we note that the corrosion rate decreases with the increase of current density up to 5 A·m^{-4} (13.97 wt. % P) (high phosphorus is known for its excellent mechanical properties, such as hardness and corrosion resistance) and increases with increasing current density which is due to the heterogeneity and fissured surface of coatings. The reduction of the current density improves the corrosion resistance.

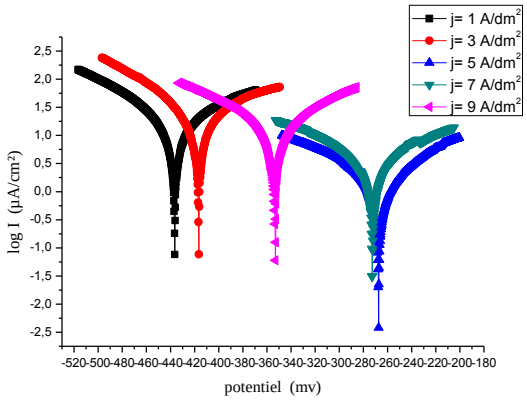


Fig. 4 – Polarization curves of Ni-P alloy coatings electrodeposited with different current densities

3.4.2. Polarization Curves

Fig. 4 shows the polarization curves of Ni-P coatings electrodeposited at different current densities in 1 M HCl solution. The polarization curve of the Ni-P (5 A·m^{-4}) coated sample is significantly shifted to more electropositive values, which means better corrosion properties of this sample. Based on the Tafel extrapolation analysis, the values of the corrosion potential, E_{corr}, and the corrosion current density, I_{corr}, for samples with the optimal Ni-P coating were determined. The values of the E_{corr} for the optimal Ni-P coating were – 267.4 mV, and the values of the I_{corr} for the optimal Ni-P coating were 2.6 µm/cm^2 (Table 2). In general, an amorphous Ni-P alloy coating has a better corrosion resistance than other coatings. The increased corrosion resistance of the Ni-P coating is due to the interaction of phosphorus with the acidic medium to form the hypophosphite anions (H_2PO^{-2}). The latter acts to form a barrier between the alloys and electrolyte to wetting the cooling of nickel atoms on the surface of the coating by inhibiting the mass transport of water [20]. The corrosion rate variations have the same appearance as those obtained by the weight loss technique.

Table 2 – Results of polarization measurements for Ni-P alloy coatings deposited at different current density values in 1 M HCl

J (A·m^{-4})	E (i = 0) (mV)	R_p Ohm·cm^2	I_{corr} (µA/cm^2)	Corrosion rate (µm/y)
1	– 436.5	934.98	20.1053	235.1
3	– 416.5	668.83	26.2974	307.5
5	– 267.4	9.71×10^3	2.0636	24.13
7	– 272.5	4.06×10^3	3.8793	45.37
9	– 353	1.03×10^3	14.0098	163.8

4. CONCLUSIONS

The Ni-P coatings were prepared by electrodeposition for different values of current density, weight loss and electrochemical polarization techniques. These methods were powerful techniques to investigate the corrosion protection performance of the Ni-P coatings. According to the results, the most important ones can be drawn as.

1. The thermal shock test reveals that the deposition of Ni-P has a good adhesion to the X52 steel substrate.
2. The coating morphology reveals that the alloys show that the grains are spherical in nature for all the samples. It also can be seen a slight difference that the boundary between nodes increases gradually with increasing amount of current density and also with the presence of cracks at a current density of 3.7 and 9 A·m^{-4}.
3. The results showed that the P content in Ni-P coatings decreases with increasing current density.
4. Based on the effective polarization curve, weight loss measurements and the microhardness test, it is shown that 5 A·m^{-4} is the best current density value which gives the best protection coating against corrosion and high microhardness.

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Механічна характеристика електроосадженого покриття із сплаву Ni-P

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Процес електроосадження відіграє вирішальну роль у формуванні тонких плівок на інших матеріалах, зокрема, електроосадження сплаву нікель-фосфору, через його важливі властивості. У дослідженні покриття Ni-P були нанесені на сталеві (X52) підкладки методом електроосадження з розчину, що містить сульфат нікелю, гіпофосфіт натрію (NaH_2PO_2). Склад, морфологія поверхні та механічні властивості покриттів Ni-P вивчалися за допомогою методів SEM, EDAX, методу Віккерса, методів вагових втрат та потенціодинамічної поляризації. Досліджували вплив густини струму на морфологію поверхні, вміст фосфору, мікротвердість та корозію покриттів. Було помічено, що як вміст фосфору, так і мікротвердість залежать від густини струму. Результати морфології електроосаджених сплавів Ni-P показують, що зерна мають сферичну форму для усіх зразків. Було виявлено, що вплив густини струму на вміст фосфору в покриттях зв'язаний зворотним співвідношенням. Крім того, сформовані покриття при густині струму 5 А·м$^{-4}$ виявляють гарну мікротвердість. Корозійні випробування показують, що величина 5 А·м$^{-4}$ є найкращим значенням густини струму, яке дає найкраще захисне покриття від корозії.

Ключові слова: Покриття із сплаву Ni-P, Мікротвердість, Корозія, Густина струму, Потенціодинамічна поляризація, Електроосадження.