Effect of Ni-P electroless coating and heat treatment on tribological and corrosion properties of copper substrate

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ABSTRACT

Copper is relatively soft metal and its wear and corrosion are considered to be a major factors of degradation of this metal. For this reason, when the higher wear and corrosion properties are needed, surface properties should be improved with different surface treatments. One of these methods is the applying of Ni-P electroless coating due to good mechanical properties, suitable corrosion resistance and its ability of heat treatment on Cu. In this research after the surface preparation of Cu, which included grinding, degreasing and surface activation, the specimens were dipped into commercial electroless nickel bath (SLOTONIP 70A) for 60 minutes. SEM images and the results of the EDS test confirmed the formation of Ni-P electroless coating (with 10.83 wt.% phosphorus) with a spherical structure. Applying the heat treatment increased the hardness of the coatings from 495 to 880 Vickers. XRD results showed this hardening is due to the formation of Ni crystal and Ni_3P phases at this temperature in the coating. The study of wear resistance and corrosion property of coatings was also done using pin-on test and polarization tests, respectively. The results showed that the heat treatment improved the wear resistance of the coating, and the weight loss in the presence of the heat treated coating reduced to 76% due to increasing hardness and roughness of the coating by performing heat treatment. This effect was also quite noticeable in the SEM images of the wear surfaces. The corrosion results illustrated the Ni-P electroless coating significantly improved the Cu substrate corrosion performance, due to the dense spherical structure and without any pores of the coating, and in particular the amorphous phase of the coating, but the heat treatment reduced the corrosion property of the as deposited coating.

1-Introduction

Cu due to its unique properties, including attractive colors, excellent electrical and thermal conductivity and ductility in cold and heat, is widely used in various industries [1]. But an important problem with the use of Cu equipment is the low wear resistance of this metal [2]. On the other hand, in many applications, such as marine industries, higher corrosion resistance is also required [3]. For this purpose, various surface treatments such as laser surface cladding, plasma surface process, thermal spraying, chemical, and physical deposition are used[4-7]. Among them, the electroless coating, which was invented by Brenner and Riddel in 1946, is the most important method for coating

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with a uniform surface morphology due to no need of electrical current and the deposition occurs as the result of the reduction of metal ion into metal atoms in the presence of reducing agents and the required electron is provided by chemical reactions inside the bath [8,9].

Ni electroless coatings have high hardness, wear resistance, corrosion resistance and also the ability to coating of non-conductive and semi-conductive surfaces such as plastics and ceramics, which has made these coatings a suitable choice for use in aerospace, automotive, chemical, oil and gas industries [10]. Ni-P coatings are most examined in Ni electroless coatings, which based of their phosphorus amount, they are divided into three categories of low phosphorus (1-5wt. %), moderate phosphorus (5-9wt.%) and high phosphorus (more than 9wt.%)[11]. The effect of the heat treatment has always been considered to improve the surface properties of these coatings [12-14]. Most studies have shown that heat treatment with temperatures of 400°C for 1 hour are appropriate for these coatings to enhance the surface properties, especially the hardness and wear resistance [14-16]. Therefore, the application of Ni-P electroless coatings with suitable heat treatment can be a great idea for increasing the surface properties of Cu.

In this paper, after the surface preparation of substrate, electroless Ni-P plating was performed on Cu and then the effect of Ni-P coatings on the hardness, wear resistance and corrosion resistance of Cu substrate were examined.

2. Experimental procedure

Disc shaped specimens with chemical composition of 0.01Al, 0.02Mn, 0.03Fe, 0.09P, 0.11Si, 0.14Sn, 0.25Pb and 99.35 wt.% Cu and 5 cm diameter and 1 cm thickness were used as the substrate. Then the specimens were ground using 80 to 1200 abrasive papers. In order to remove contaminations and increase the adhesion of the final coating, they were rinsed in solution containing 50 g/l sodium hydroxide (NaOH) at a temperature of 50 ºC for 3 min. Finally, they were immersed in a solution of HCL (10 wt. %) for 1 min at room temperature to activate the surface for the electroless process. For deposition, the substrates were dipped into commercial electroless nickel bath (SLOTONIP 70A that was prepared from Schlotter Company) for 60 min. Coating temperature was 87 ° C and pH =4.6. In order to stirring and uniformly distribution of the ions in the bath during the plating process, a magnetic stirrer system was used at a speed of 500 rpm. The heat treatment of the specimens was carried out for 1 hour at 400 ° C in a Naber therm N7/H electric furnace. The surface morphologies of the coated specimens were studied using scanning electron microscopy (SEM, model Philips XL30). The chemical composition analysis was performed to determine the amount of Ni and P in the coatings by EDS analysis. The phase composition of the coatings was detected by a X-ray diffractometer (XRD, model Philips X'pert MPD) using Cu Kα (1.5405 °A). The scan rate was 1 deg/min.

The hardness of coatings was measured using a microhardness tester (Wilson model 402MVD) with Vickers diamond indenter at a load of 50 g. The average of four repeated measurements is reported. The surface roughness of the coatings was determined using a stylus roughness tester (model Mitotoyo SJ.210) in length of 5 mm. To examine the wear resistance of the specimens, a Pin on disk test was used.

Pin-on-disc wear tests were conducted at a normal load of 15N and a sliding speed of $0.1ms^{-1}$ to evaluate the wear resistance of the coatings. The wear tests were performed against AISI 52100 steel pins for a sliding distance of about 1000m without lubrication at 25 °C and in an air with 30% relative humidity.

In order to investigate the effect of Ni-P electroless coatings on the corrosion resistance of Cu substrate, a potentiodynamic polarization test was performed with IVIUMSTAT potentiostat/galvanostat in 3.5 wt% NaCl solution. The polarization tests were applied after 30 min exposure and stabilization of open circuit potential (OCP) condition at scan rate of $1\ mV.s^{-1}$. A three-electrode cell with a platinum plate as the counter electrode, a saturated calomel as the reference electrode and coated specimens as the working electrodes was used.

3. Results and Discussion

3.1. The coating's characterization

In figure 1, SEM images of the surface and cross-sectional of the coating with a thickness of 17 µm are shown. The spherical pattern with a cauliflower structure is observed in images,

which this structure is the common features of the Ni-P electroless coating [17].
The morphology of the Ni-P electroless coating is spherical, which with the combination of these spheres, the structure similar to cauliflower is achieved. According to other researcher's reports, this form of the morphology causes the inherent lubrication properties of the electroless coatings [17,18]. Also, it is not observed any cracks in the coating specimens, which indicates the proper coating on the Cu. The EDS analysis (figure 2) shows that the coating contains 10.83 wt.% P and therefore is considered as a high phosphor coating.

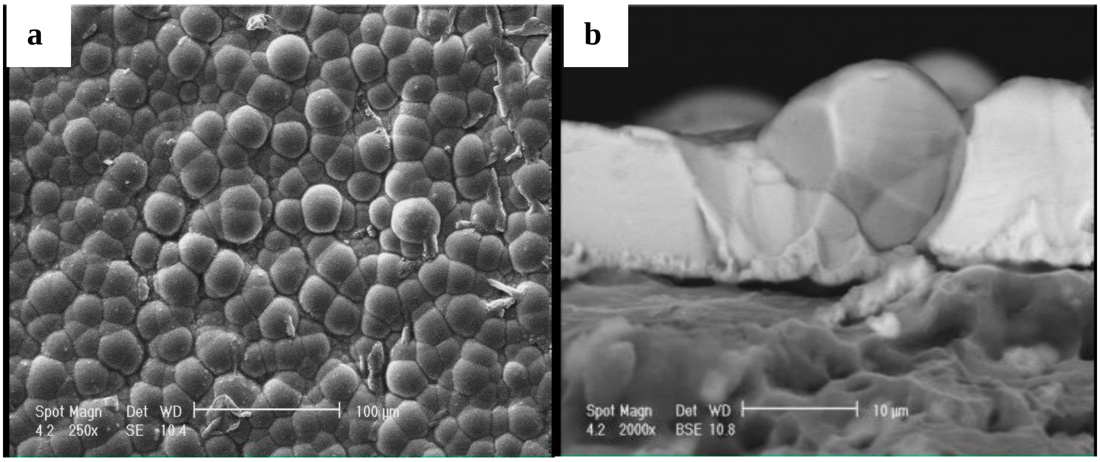
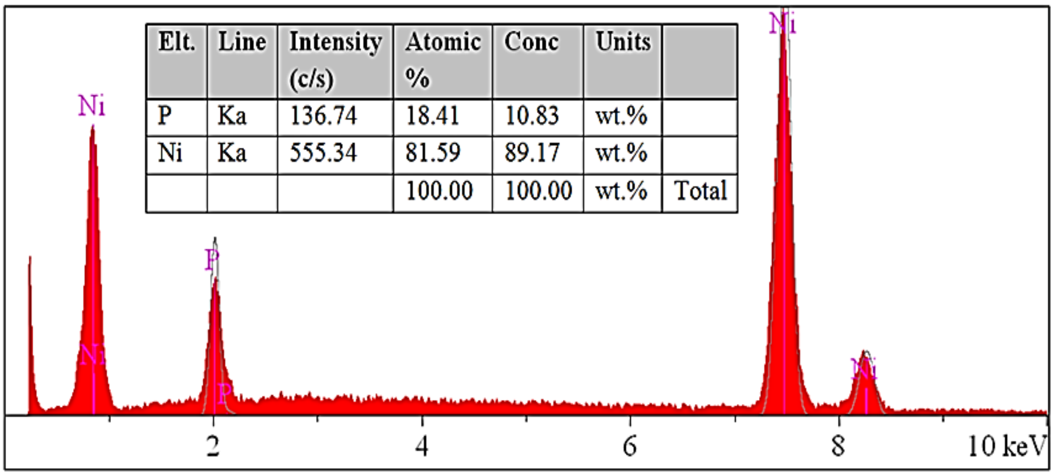


Fig. 1. SEM morphology images of a) surface and b) cross section of Ni-P electroless coating.



Elt.	Line	Intensity (c/s)	Atomic %	Conc	Units	
P	Ka	136.74	18.41	10.83	wt.%	
Ni	Ka	555.34	81.59	89.17	wt.%	
			100.00	100.00	wt.%	Total

Fig. 2. EDS analysis of coated specimen.

Figure 3 indicates the XRD patterns of the as deposited and heat treated Ni-P electroless coated specimens in optimum temperature (400 °C). Ni-P coatings are thermodynamically unstable and can be crystallized by heat treatment. XRD pattern of as deposited specimen has a wide peak at 2θ of 40 to 50°, indicating the non-crystalline (amorphous) structure of the coating before the heat treatment [7, 19, 20]. After heat treatment at 400 ° C, it is observed that the wide peak was disappeared and the structure has completely crystallized, so that instead of the effects of amorphous wide peak, new XRD peaks corresponding to crystalline FCC Ni and Ni_3P with a tetragonal structure appeared.

3.2. The roughness and hardness of the coatings

The results of the roughness of the specimens are shown in table 1. It is noted that the surface roughness increases about 0.983 µm after coating, which is due to the spherical morphology of the coating and shows that the adhesion properties of the coating will increase as a result of increased roughness. Heat treatment also increases the coating's roughness, which is due to the disappearance of the boundary between these spheres and the growth of new spheres of electroless Ni-P coatings [11,21].

The hardness of the Ni-P (as-deposited) coating was 495 Vickers, which increased to 880 Vickers by heat treatment. This hardness for a Cu substrate with a hardness of 61 Vickers can be very suitable and increases the wear properties. The hardness enhancement is mainly due to precipitation of the intermetallic structure of Ni_3P and Ni in the coating, which the presence of these particles is shown in the XRD pattern after heat treatment in Figure 3. The mechanism of increasing hardness at 400 °C may be due to the precipitation hardening of a typical supersaturated solid solution [22]. In fact, when electroless coatings are heated at suitable temperatures, precipitation of phosphides occurs, which acts as barriers for dislocation movement, thereby causes increasing the hardness. This unique feature causes the widespread application of these coatings where they face the challenge of wear [23].

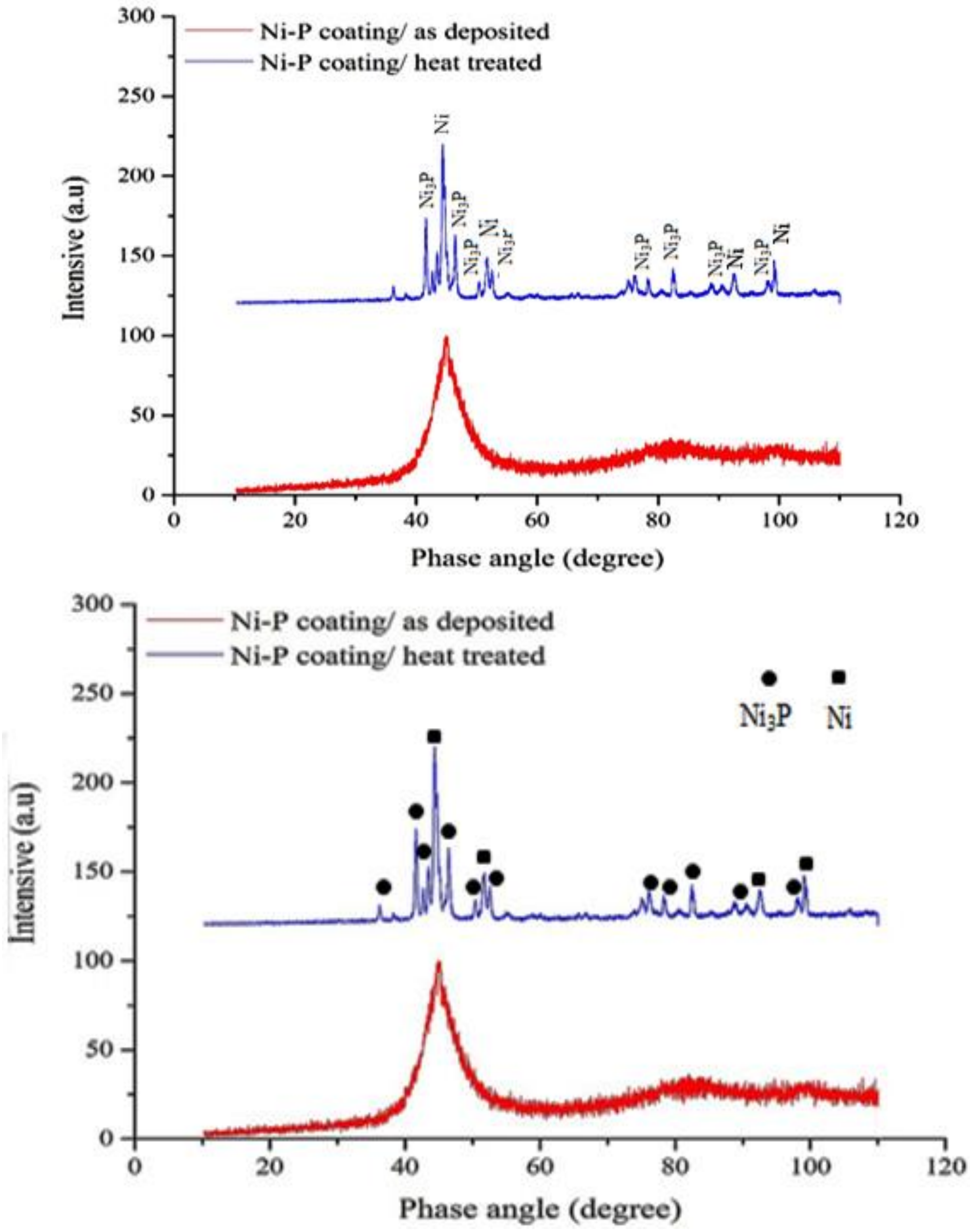


Fig. 3. XRD patterns of as deposited and heat treated Ni-P electroless coating.

Table 1. Roughness results of the coatings

specimens	R_a(μm)	R_q(μm)	R_z(μm)
Cu substrate	0.253	0.387	5.713
Ni-P coating/as-deposited	1.236	1.603	11.495
Ni-P coating/heat-treated	1.908	2.527	16.185

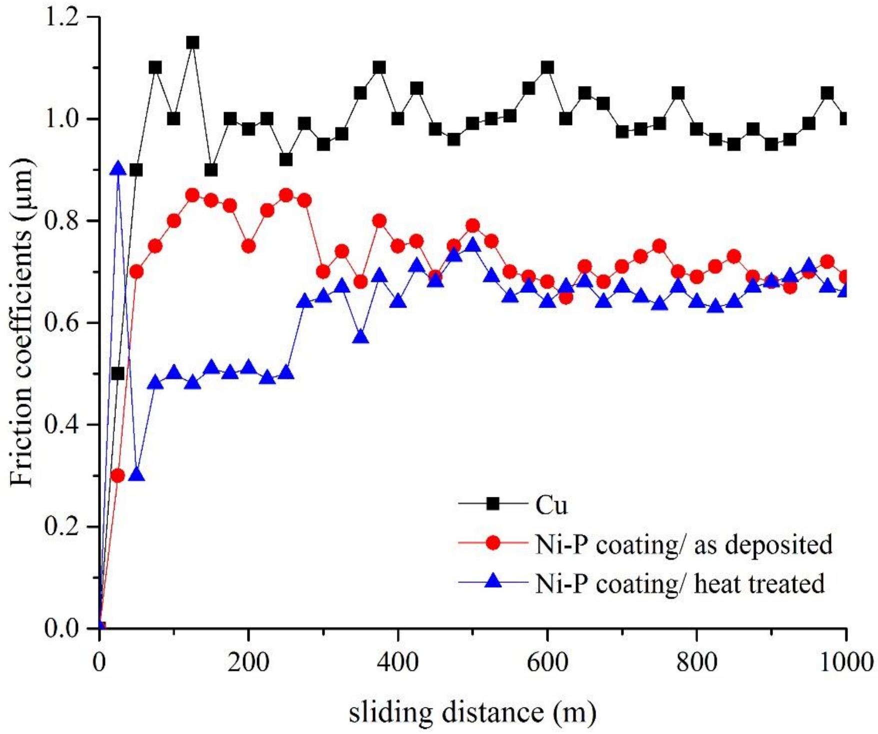


Fig. 4. The relationship between friction coefficients and the sliding distances used in the pin-on-disc test.

3.3. Wear resistance

In the tribological contact of two solid objects, two phenomena occur, which is important: wear and friction [24]. Figure 4 presents the dependence of the average friction coefficients on the sliding distance for all conditions tested. As can be observed, with the application of Ni-P electroless coating, the coefficient of friction decreased from about 1 to about 0.6 μm, due to the lubricating properties of these coatings. Due to the low friction coefficient, coatings can reduce the friction between the two surfaces and extend the lifespans of the parts.

It is concluded that the influence of heat treatment on the friction coefficient for sliding distances higher than 300 m is not appreciable. But for sliding distances lower than 300 m, this difference becomes appreciable and the lowest friction coefficient is obtained for the heat treated coating. It is believed that this difference may be attributed to the changes in the true contact area and the shear stresses in each test condition [25]. So that, at the beginning of the test, the true contact area of the heat treated coating with high hardness is lower than other conditions, therefore the friction coefficient tends to decrease. However, it has been shown that higher ductility, which is characteristic of the coating in as deposited condition, allows the formation of debris due to the fact that this coating present smaller hardness, contributes an increase in the contact area between the tribological pair [26]. When the sliding distance is higher than 300 m, owing the higher hardness in the heat-treated coating, the wear in the pin is higher and there is an increase in the true contact area, which increases the friction coefficient until it reaches the same level as the other coating.

In figure 5, the curves of the weight loss in terms of sliding distance are shown. As it is illustrated, by applying the electroless coatings, the weight loss decreased from 79 mg to 41 mg at the end of the test. The heat treatment of the coatings also improved the wear resistance of the Cu substrate about 76% and the coating with no heat treatment up to 56%, which has three reasons: 1) Due to the hardness of the coating in presence of the hard particles such as Nickel phosphate, it can withstand against wear pin and cannot increase the wear.

2) Due to the low friction coefficient, this coating reduces friction between surfaces and prevents weight loss.

3) The adhesion of the coating to the substrate is one of the most important factors for improving the wear properties [26]. On the other hand, it is generally accepted that surface roughness improves adhesion strength due to mechanical interlocking effect induced by the protrusions at the interface [27]. This is known as the dominant mechanism of adhesion between an overlay coating and a substrate [28]. As it has been mentioned, in this research also, the roughness of coating has increased from about 0.9 to about 1.9 μm with heat treatment, which improves wear and tear resistance.

SEM images of the wear surfaces of all three samples at low magnification can help to better compare the sample property (Figure 6). As it is known, copper samples have had the most damage during wear (Figure 6-a) and surface treatment in this study have reduced surface degradation. But in the heat treated electroless coating can be said to have the least effect on wear (Figure 6-c). This effect includes the diameter of the wear pin as well as the degree of destruction along the wear lines.

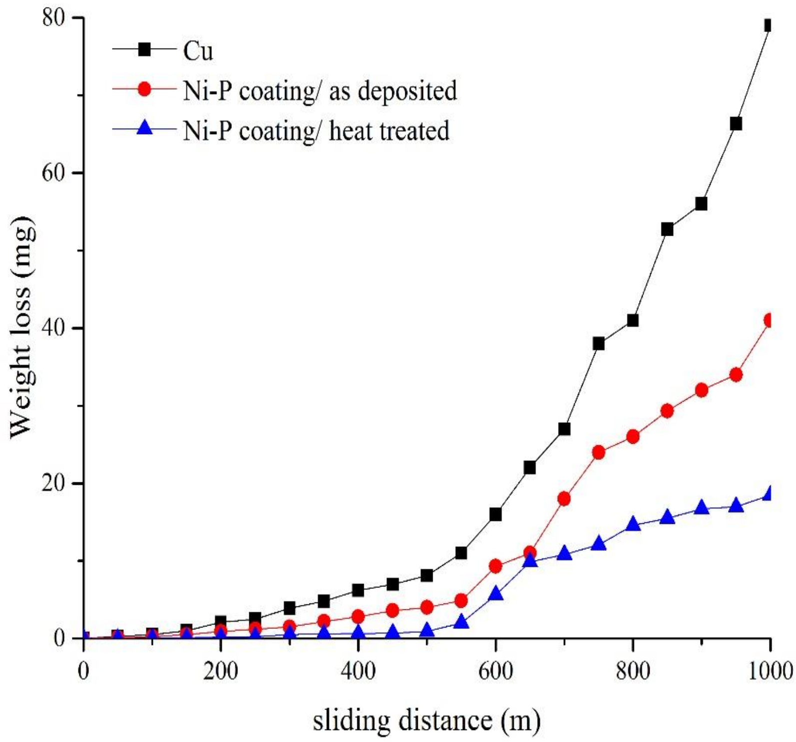


Fig. 5. Weight loss- sliding distance curves for substrate and the coatings.

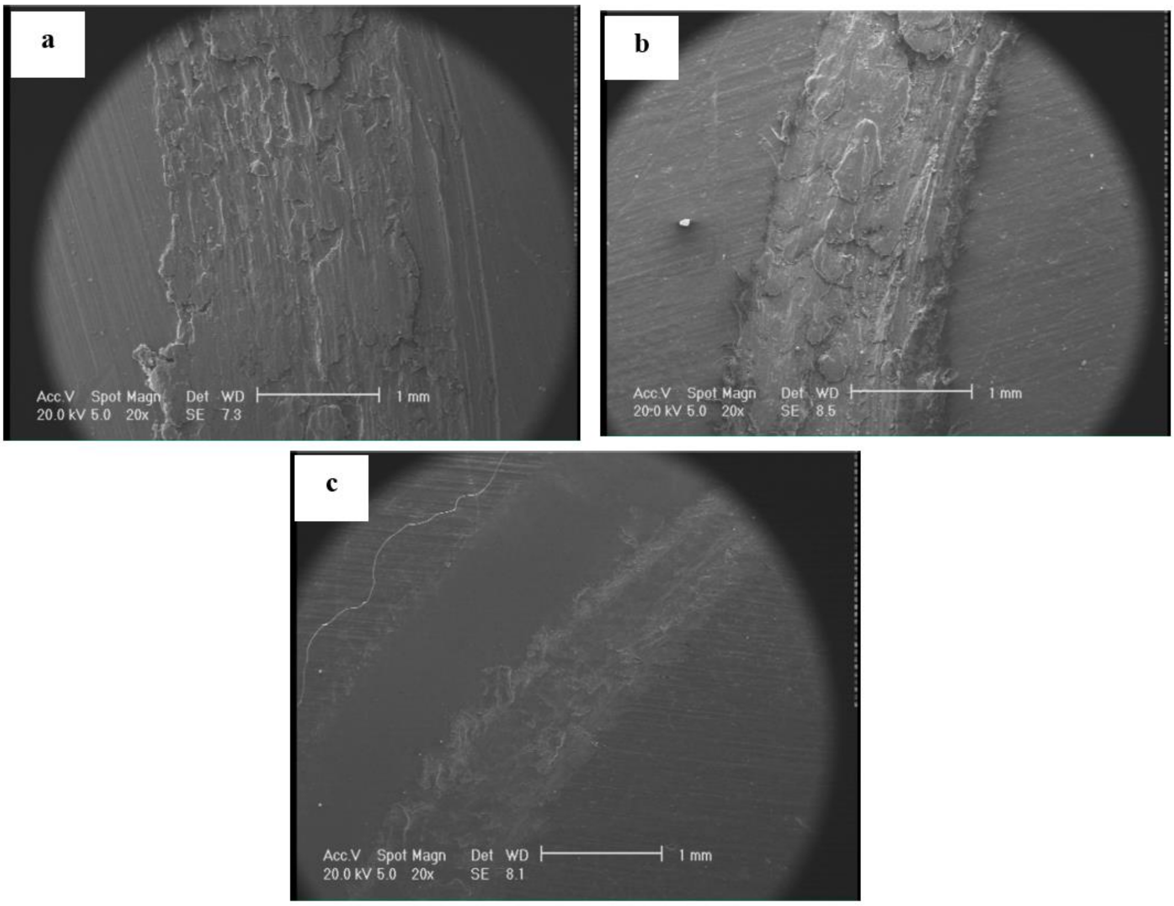


Fig. 6. The low magnification SEM images of surfaces of sample: a) Cu ,b) Ni-P coating/as-deposited and c) Ni-P coating/heat treated.

3.4. Corrosion properties

The potentiodynamic polarization curves of the uncoated Cu (substrate) and the coated samples in 3.5% NaCl solution for 30 min are shown in Figure 7. The corrosion potential (E_{corr}), corrosion current (i_{corr}), cathodic and anodic branches slope (βc and βa) estimated from the polarization curves from Stern-Geary equation (equation 1) [29] and reported in Table 2:

$$\text{Equation1:} Rp = \frac{\beta a \times \beta c}{2.303 icorr(\beta a + \beta c)}$$

In polarization curves, the cathodic response is due to the hydrogen reduction reaction and, in some cases, the oxygen gas reduction while the anodic branch indicates the dissolution of the metal, and the repassivation reactions and formation of the coating. With reference to this figure, typical anodic polarisation curves can be split into three main regions of potential [30,31]:

• Section I: a potential region of 'apparent Tafel' behavior where mixed charge transfer and mass transport controlling kinetics are usually assumed.

• Section II: a potential window of film formation leading to a maximum peak current density indicates the dissolution of the metal and the formation of the CuCl layer exposed to the chloride media in which the reaction rate of the anode is due to the formation or dissolution of the CuCl layer.

• Section III: a potential above (second peak) which any increase in current density is due to the formation of of copper oxide layer (CuO).

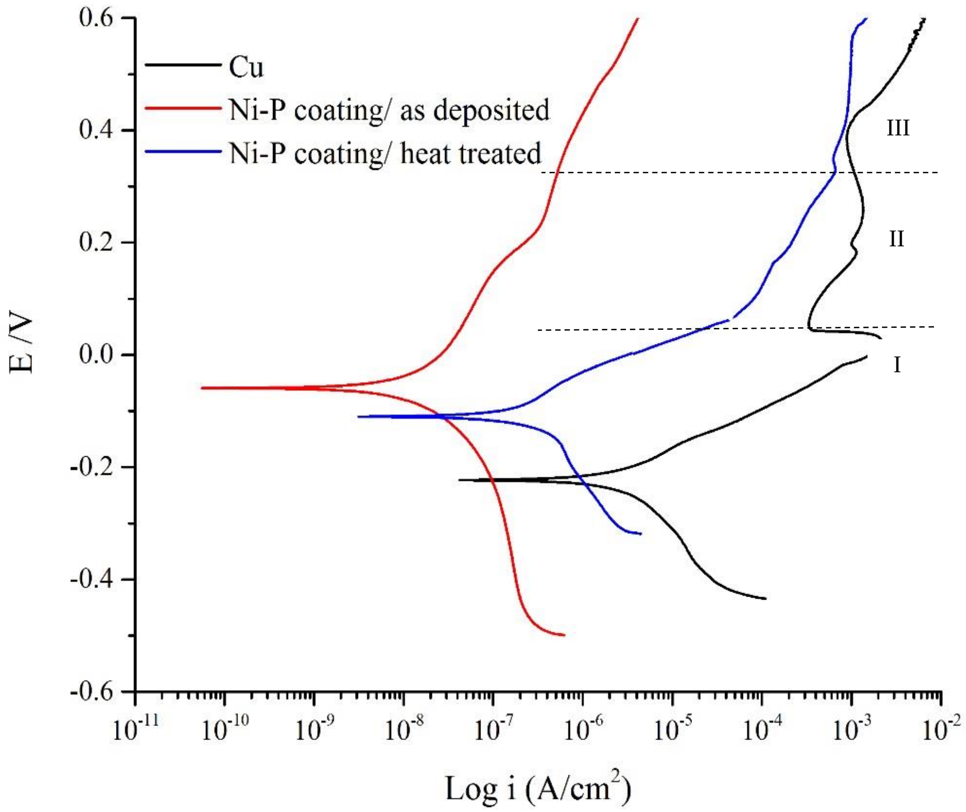


Fig. 7. Potentiodynamic polarization curves in 3.5% NaCl solution of the uncoated and coated Cu samples.

Table 2. Data extrapolated from polarization curves

Specimens	E_{corr} (mV vs. SCE)	i_{corr} (μA/cm^2)	β_a (mV.dec^{-1})	$-\beta_c$ (mV.dec^{-1})	R_p (Ω)
Cu substrate	-221.5	23.9	71	96	1.06×10^4
Ni-P coating /as deposited	-62.9	0.65	11	69	1.5×10^5
Ni-P coating /heat-treated	-127.2	1.47	52	32	3.61×10^4

By applying the Ni-P electroless coating, the corrosion performance of the Cu substrate has significantly improved, such that the Cu corrosion density is reduced from 23.9 to 0.65 μA/cm^2 and the corrosion potential is increased from -221.5 to -62.9 mV. This highly suitable corrosion behavior of Ni-P electroless coating is due to the dense spherical structure and without any pores of the coating, and in particular the amorphous phase of the coating [32]. As one of the strengths of Ni-P electroless coatings mentioned in many studies, are the high corrosion resistant of them in corrosive environments [32-34]. Also, by examining the anodic branch of the coating, the peaks on the anodic Cu branch are no longer observed, indicating a change in the mechanism of corrosion of Cu in the presence of Ni-P electroless coating. In fact, in the presence of phosphorus and amorphous phases, the passivation of the coating increases significantly, and the anodic branch shows a completely passive behavior. It should be noted that the low passive current density of this coating reflects its good protective function against pitting corrosion under test conditions. Also it is evident from literature reports on Ni–P coatings that preferential dissolution of nickel occurs at open circuit potential, leading to the enrichment of phosphorus on the surface layer. The enriched phosphorus surface reacts with water to form a layer of adsorbed hypophosphite anions ($H2PO^{-2}$). This layer in turn will block the supply of water to the specimen's surface, thereby preventing the hydration of nickel, which is considered to be the first step to form either soluble Ni^{2+} species or a passive nickel film [12,35].

With heat treatment at 400 °C, the particles of phosphide are formed, and thus the phosphorus content in the coating decreases. This phenomenon causes the corrosion resistance reduction of the coating (according to figure 7). The resulting Ni_3P particles cause active-passive corrosion cells [36]. The coating also shrinks due to heat treatment, which causes cracking the coating and contacting the metal with the surrounding environment.

On the other hand, one of the important parameters in the polarization tests is the surface roughness of the coating [11,32]. The heat treatment increases the coating roughness and by the roughness enhancement, the corrosive ion penetration are increased and the corrosion resistance of the coating is reduced.

4. Conclusions

- Ni-P electroless coating with a primary hardness of 495 Vickers with spherical surface morphology with a cauliflower structure was formed on Cu.
- The XRD pattern of the specimen before the heat treatment had a wide peak. This indicates the non-crystalline (amorphous) structure of the coating, which is justified by the presence of 10.83% phosphorus in the coating.
- By performing the heat treatment at 400 °C for 1 h, the hardness increased to 880 Vickers due to the formation of Ni and Ni_3P phases.
- By applying the electroless coating, the wear resistance of the Cu substrate improved to 56% (as-deposited) and 76% (heat-treated). This is due to the properties of lubrication, hardness and good roughness of the coatings.
- Corrosion resistance of the Cu substrate has been improved by applying of the coating due to the dense amorphous structure.
- By performing heat treatment, the corrosion resistance of the coating is reduced. The most important reason is the convert of the amorphous structure into crystalline structure and roughness enhancement.

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