



## Effect of heat treatment on electroless ternary nickel–cobalt–phosphorus alloy

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### Abstract

Ternary Ni–Co–P and binary Ni–P alloy coatings were deposited on mild steel panels from an alkaline bath in the presence and absence of cobalt sulfate using an electroless process. The effects of heat treatment on surface topography and crystal orientation of Ni–Co(11.17%)–P(3.49%) alloy coatings were studied in contrast to that of Ni–P ones. It was found that the as plated Ni–Co–P alloy is a supersaturated solid solution of P and Co dissolved in a microcrystalline Ni matrix with  $\langle 111 \rangle$  preferred direction. Heat treatment induces structural changes. The formation of Ni<sub>3</sub>P phase precipitates and recrystallization of nickel occur when the sample is treated at >400 °C for one hour. It is observed that the Ni diffraction lines of treated Ni–Co–P alloy at >400 °C are shifted to lower angles as compared to those of treated Ni–P or as plated Ni–Co–P alloys. The surface topography of Ni–Co–P alloy also changes with heat treatment temperature. The surface topography and crystal orientation were characterized by means of scanning electron microscopy and X-ray diffraction, respectively. The hardness and corrosion resistance, in 5 wt % NaCl solution, of heat treated Ni–Co–P samples were studied.

### 1. Introduction

Electroless Ni–P alloy coatings have been widely used in many industrial sectors [1–3]. For many applications, the most important properties are high hardness and good wear and corrosion resistance. The microstructure and, consequently, the properties of this alloy are dependent on the phosphorus content and can be further improved by appropriate heat treatment [4, 5]. The effects of heat treatment on the structure of Ni–P deposits with respect to hardness have been well documented [6–9]. It is suggested that the initial structure of the as deposited Ni–P alloy is metastable. Upon heat treatment of these deposits, a gradual phase transformation to a more stable state takes place. To extend the range of electroless nickel coating applications in industry, it is necessary to develop ternary or quaternary alloy deposits. This is a practical and effective method of obtaining superior electrochemical and physical properties in comparison to those of binary Ni–P deposits [10–12]. Electroless ternary Ni–Co–P alloy deposits have been studied for soft magnetic properties [13] and for solar control properties [14].

The present work is an extension of our investigations of electroless Ni–Co–P alloys [15]. It was carried out to study the changes in crystal structure and surface

topography of ternary Ni–Co–P thin films with heat treatment. The hardness and corrosion resistance of heat treated Ni–Co–P samples were also studied. Electroless Ni–P alloy coatings were prepared under similar conditions for use as a reference.

### 2. Experimental procedure

The electroless Ni–Co–P electrolyte with a pH 9 was prepared with the composition given in Table 1. The binary Ni–P alloy was deposited as a reference, under the same plating conditions, in the bath composition of Table 1 without cobalt sulfate. The deposition was carried out in a 100 cm<sup>3</sup> of plating bath, maintained at 80 ± 1 °C for one hour.

The deposition experiments were usually performed onto mild steel panels (40 mm × 25 mm × 1 mm) except for the deposit analysis experiments which were performed on pure aluminum panels having the same exposed area to the electroless plating solution. For corrosion test experiments, the deposition was carried out on a mild steel disc (5 mm × 15 mm dia), which fitted in the working electrode hole of the electrochemical cell, in a 50 cm<sup>3</sup> plating bath with the above plating conditions. The steel samples were pretreated as follows:

Table 1. Typical composition of the basic electroless nickel-cobalt-phosphorus bath

Ingredient	Concentration/M
Nickel sulfate hexahydrate	0.15
Cobalt sulfate heptahydrate	0.03
Sodium hypophosphite monohydrate	0.20
Sodium citrate	0.10
Lactic acid	0.20

degreasing by organic solvent (acetone), water rinsing, alkaline soaking in 6% NaOH, water rinsing, neutralization and activation for 60 s in 10% (v/v) HCl and finally double rinsing with distilled water. However, aluminium substrates were degreased by acetone, water rinsing, dipping in 10% NaOH for 3 min for activation, to remove the surface oxides, and finally double rinsing with distilled water. The deposits were heat treated in an electrical oven at various temperatures in the presence of nitrogen atmosphere for one hour; then the samples were allowed to cool in the oven.

The nickel and cobalt contents of the alloys deposited on pure aluminium, after dissolution in 20% (v/v) nitric acid, were analysed by means of atomic absorption spectrophotometry and the phosphorus content was calculated by difference. Two samples of alloys deposited on mild steel were also examined by means of EDX analysis.

The crystal orientation was characterized by X-ray diffraction using  $\text{CuK}_\alpha$  radiation ( $\lambda = 0.154$  nm). The surface topography of the deposits was examined by means of scanning electron microscopy (SEM), (model Philips XL 30) attached to an EDX unit. The microhardness of the coatings was determined by means of a Vickers microscope with a pneumatic microhardness tester. The hardness of deposits was measured with a diamond pyramid indenter under 50 g load. The samples for aqueous corrosion tests were mounted in an electrode holder of area  $1 \text{ cm}^2$  exposed to the electrolyte. The anodic currents and potentials for the different deposits were measured by the potentiodynamic polarization technique using a scanning potentiostat connected to a recorder. The corrosion experiments were performed in a conventional three-electrode cell containing 5% analytical grade sodium chloride at 23–25 °C with  $5 \text{ mV s}^{-1}$  scanning rate. The potential was measured against a saturated calomel electrode (SCE), while the counter electrode was a platinum wire.

### 3. Results and discussion

#### 3.1. Deposit composition

The effect of  $\text{Co}^{2+}$  concentrations in the bath on Ni–Co–P alloy composition deposited on aluminium substrate is shown in Table 2. It can be seen that the alloy cobalt content increased and the nickel content decreased with increasing cobalt sulfate concentration in the bath when

Table 2. Effect of  $\text{Co}^{2+}$  concentration on the chemical composition of the Ni–Co–P alloy deposited on aluminum substrate

$\text{Co}^{2+}$ conc./M	Deposit composition/wt%		
	Ni	Co	P
0.00	95.09	00.00	4.91
0.01	92.63	03.07	4.30
0.02	88.98	07.13	3.89
0.03	85.34	11.17	3.49
0.04	81.80	15.12	3.08
0.05	77.97	19.03	3.00

the other plating conditions were constant. The alloy phosphorous content decreased slightly with increase of cobalt sulfate in the bath. This may be due to the increase in the ratio of metal ions to hypophosphite ions. Also, the deposits prepared in the plating bath without and with 0.04 M cobalt sulfate on mild steel were analysed by EDX as shown in Figure 1. It can be seen that the electroless alloy composition deposited on mild steel substrate is very close to that prepared on aluminum.

#### 3.2. Crystal microstructure

The crystal orientation of heat treated electroless deposited Ni–P and Ni–Co–P alloys at different temperatures for one hour were characterized by means of X-ray diffraction analysis. The typical X-ray diffraction patterns of Ni–P(4.91 wt %) and Ni–Co(11.17 wt %)–P(3.49 wt %) alloys are shown in Figures 2 and 3, respectively. The value of the angles corresponding to the peaks and the indexes of the crystallography planes of the phases identified are given in Table 3.

The as plated Ni–P alloy exhibited a strong Ni (1 1 1) preferred orientation in the diffraction patterns as shown in Figure 2(curve a). Also, the position of the peak corresponding to Ni (1 1 1) of as plated Ni–P alloy is slightly shifted to a lower angle as compared to that of pure nickel, as shown in Table 3. This indicates that the as plated Ni–P alloy is a supersaturated solid solution of P dissolved in a microcrystalline Ni matrix with (1 1 1) preferred direction. However, changes in the crystal structure orientation of this alloy occurred after heat treatment at 400 °C for one hour. The heat treatment caused the recrystallization of nickel and formation of a nickel phosphide ( $\text{Ni}_3\text{P}$ ) phase, as shown in Figure 2(curve b). These results are confirmed by those of other authors [16], who studied the effect of annealing temperatures on the structure of binary Ni–P alloy and found that the formation of the  $\text{Ni}_3\text{P}$  phase started at 350 °C for a one hour treatment. Increasing treatment temperature also caused recrystallization of nickel and coarsening of the  $\text{Ni}_3\text{P}$  phase.

The diffraction pattern of as plated Ni–Co–P alloy also showed only the peak of Ni (1 1 1) preferred orientation as shown in Figure 3(curve a). However, the position of this peak was shifted to lower angle of  $2\theta$  as compared to that of as plated Ni–P alloy, as shown in

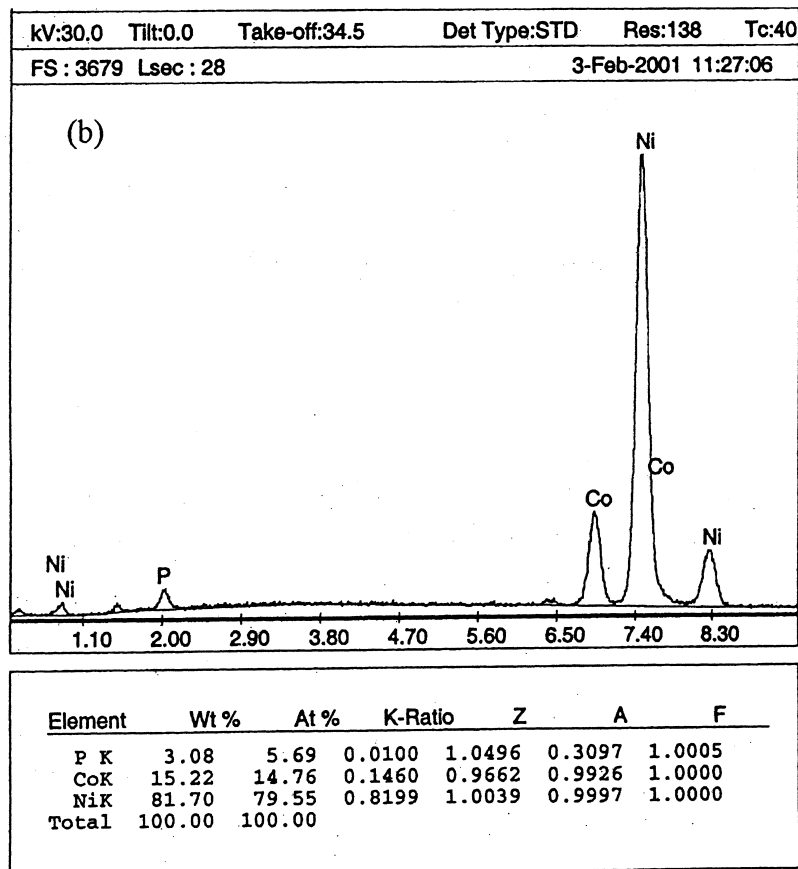
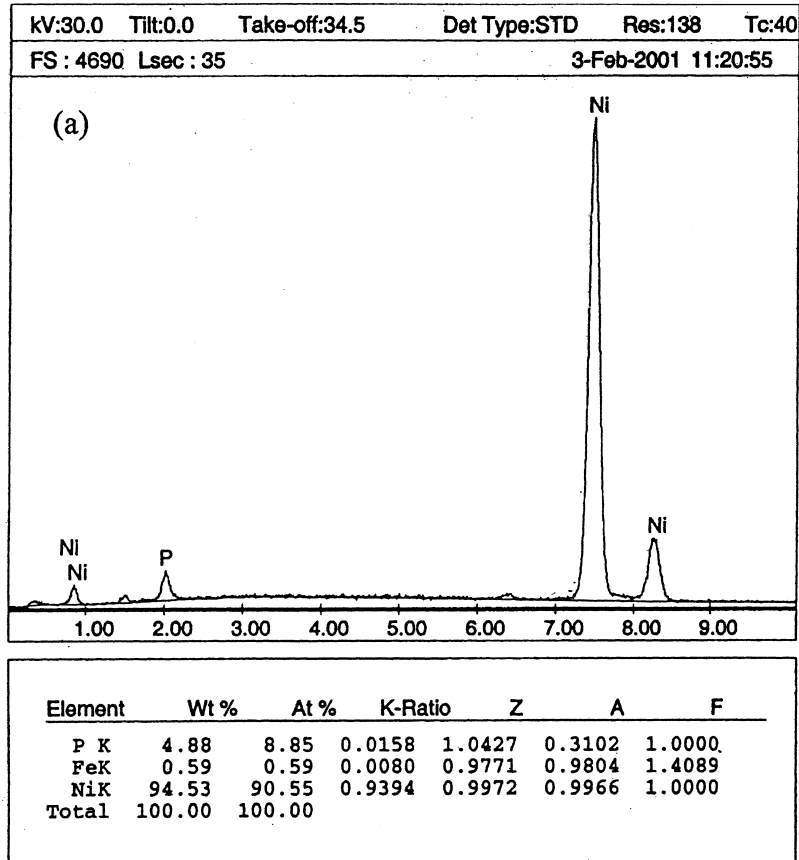


Fig. 1. EDX analysis of electroless Ni-Co-P alloys obtained on mild steel substrate, under the same conditions, in the bath containing: (a) without and (b) with 0.04 M cobalt sulfate.

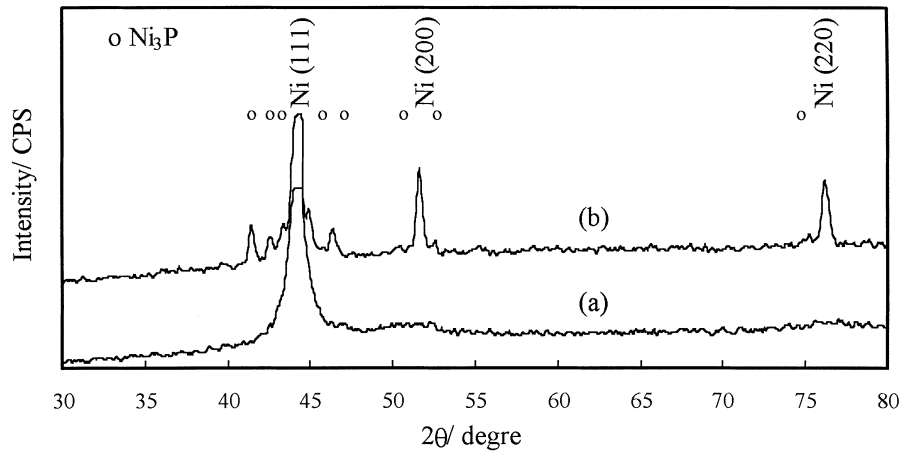


Fig. 2. X-ray diffraction patterns of electroless Ni-P deposits: (a) as plated and (b) 400 °C for one hour heat treatment.

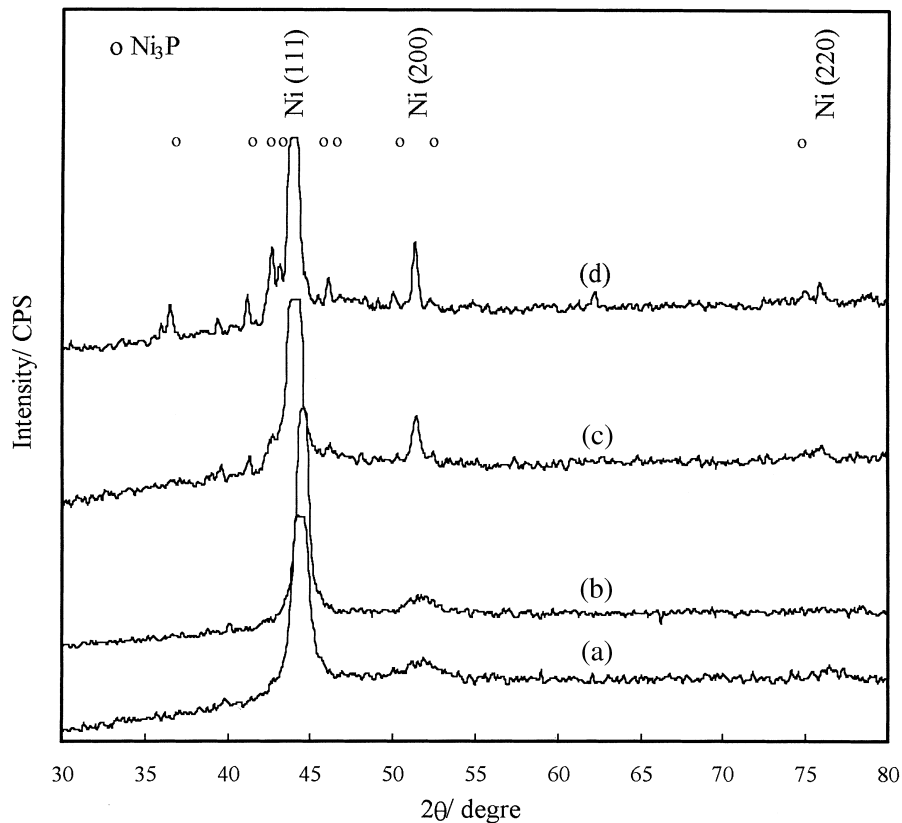


Fig. 3. X-ray diffraction patterns of electroless Ni-Co-P deposits: (a) as plated, (b) 350 °C, (c) 400 °C and (d) 550 °C for one hour heat treatment.

Table 3. This means that the interplanar distance of nickel metal is widened by cobalt codeposition and indicates that the as plated Ni-Co-P alloy is a supersaturated solid solution of P and Co dissolved in a microcrystalline Ni matrix with  $\langle 111 \rangle$  preferred direction. When heat treated for one hour at 350 °C, the diffraction pattern is similar to that of as plated alloy, exhibiting no evidence of formation of a new phase, as shown in Figure 3 (curve b). However, the structure of Ni-Co-P alloy changed from P and Co dissolved into microcrystalline Ni to crystalline structure with forma-

tion of a Ni<sub>3</sub>P phase and recrystallization of nickel when the sample was treated at 400 °C for one hour. Increasing the annealing temperature to 550 °C increased the recrystallization of nickel and the growth rate of the Ni<sub>3</sub>P phase.

Lee and Hur [17, 18] studied the texture of electroless Ni-Co-P alloy films deposited on 5086 aluminium alloy panels. They concluded that the as plated ternary alloys containing up to 13.4 wt % Co and 7.6 wt % P were solid solutions having a grain size of 6 to 7 nm and strong  $\langle 111 \rangle$  texture. On annealing these alloys

Table 3. Crystallographic orientation of nickel and nickel phosphide alloy obtained (in this work) by X-ray diffraction

Phase	<i>k h i</i>	2 $\theta$ /degree					
		Ni-P alloy		Ni-Co-P alloy			
		As plated	400 °C	As plated	350 °C	400 °C	550 °C
Ni	(1 1 1)	44.3	44.4	44.2	44.2	44.0	43.9
	(2 0 0)	–	51.6	–	–	51.4	51.3
	(2 2 0)	–	76.2	–	–	76.0	75.8
Ni <sub>3</sub> P	(3 0 1)	–	–	–	–	36.6	36.6
	(3 2 1)	–	41.5	–	–	41.4	41.2
	(3 3 0)	–	42.6	–	–	42.6	42.6
	(1 1 2)	–	43.4	–	–	43.1	43.1
	(4 2 0)	–	46.4	–	–	46.1	46.1
	(2 2 2)	–	50.5	–	–	50.0	50.0
	(3 1 2)	–	52.6	–	–	52.4	52.2
	(3 2 3)	–	75.3	–	–	75.0	75.0

for 2 h at  $>400$  °C, the formation of a Ni<sub>3</sub>P stable phase occurred and the nickel texture changed from  $\langle 1\ 1\ 1 \rangle$  to  $\langle 2\ 0\ 0 \rangle$  with no changes in the  $2\theta$  peak position. However, in the present work, it is clear that the diffraction line of Ni (1 1 1) of treated alloy samples at  $>400$  °C is shifted to a lower angle as compared to that of samples treated at 350 °C or as plated, as shown in Figure 3. Also, the diffraction lines of Ni (1 1 1), (2 0 0) and (2 2 0) of treated Ni-P alloy had sharper peaks than that of treated ternary alloy at  $>400$  °C, as shown in Figures 2 and 3, respectively. Also, cobalt codeposition in the treated alloy at  $>400$  °C shifted the diffraction lines of Ni to lower angles as compared to those of treated binary alloy and decreased the relative intensity of Ni (2 0 0) and (2 2 0). This phenomenon was also observed in electroless Ni-Mo-P alloy [19]. The changes in crystal orientation of treated Ni-Co-P alloy at  $>400$  °C are due to cobalt codeposition. This can be attributed to absorption of cobalt atoms, with heat treatment, into recrystalline nickel matrices, which widened the interplanar spacing of nickel metal.

Concomitant changes in the structure with heat treatment can be observed from SEM analysis. Fig-

ures 4 and 5 show the effect of heat treatment on surface topography of electroless Ni-P and Ni-Co-P alloys, respectively. The grain size and shape of the Ni-P alloy does not change with heat treatment, except that the grains of the heat treated sample are cracked, as shown in Figure 4(b). Earlier studies showed that the grain size of Ni-P deposits decreased with increase in P content [4, 20]. However, the as plated Ni-Co-P deposit had finer and more compact grains than that of the Ni-P deposit, as shown in Figures 5(a) and 4(a), respectively, even though the ternary deposit contains lower P content. The surface topography of ternary Ni-Co-P alloys changed with annealing temperature and was quite different to that of as plated, as shown in Figure 5. With 350 °C treatment for one hour, the grains became dense and attached to each other due to the volume increase. As the heat treatment increased to 400 °C, very fine particles formed on the surface, which may be due to changes in crystal orientation due to cobalt codeposition, as shown in Figure 5(c). When the sample was treated for one hour at 550 °C, the grains are attached to each other. This phenomenon may be attributed to the increase in volume of precipitated particles, as already reported [21, 22].

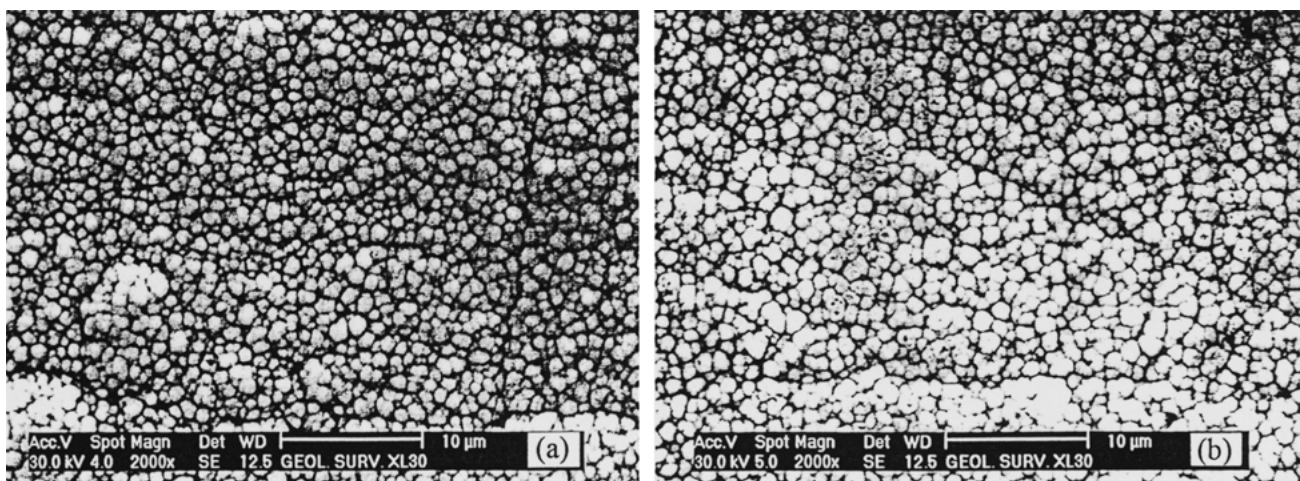


Fig. 4. SEM microphotograph of electroless Ni-P deposits: (a) as plated and (b) 400 °C for one hour heat treatment.

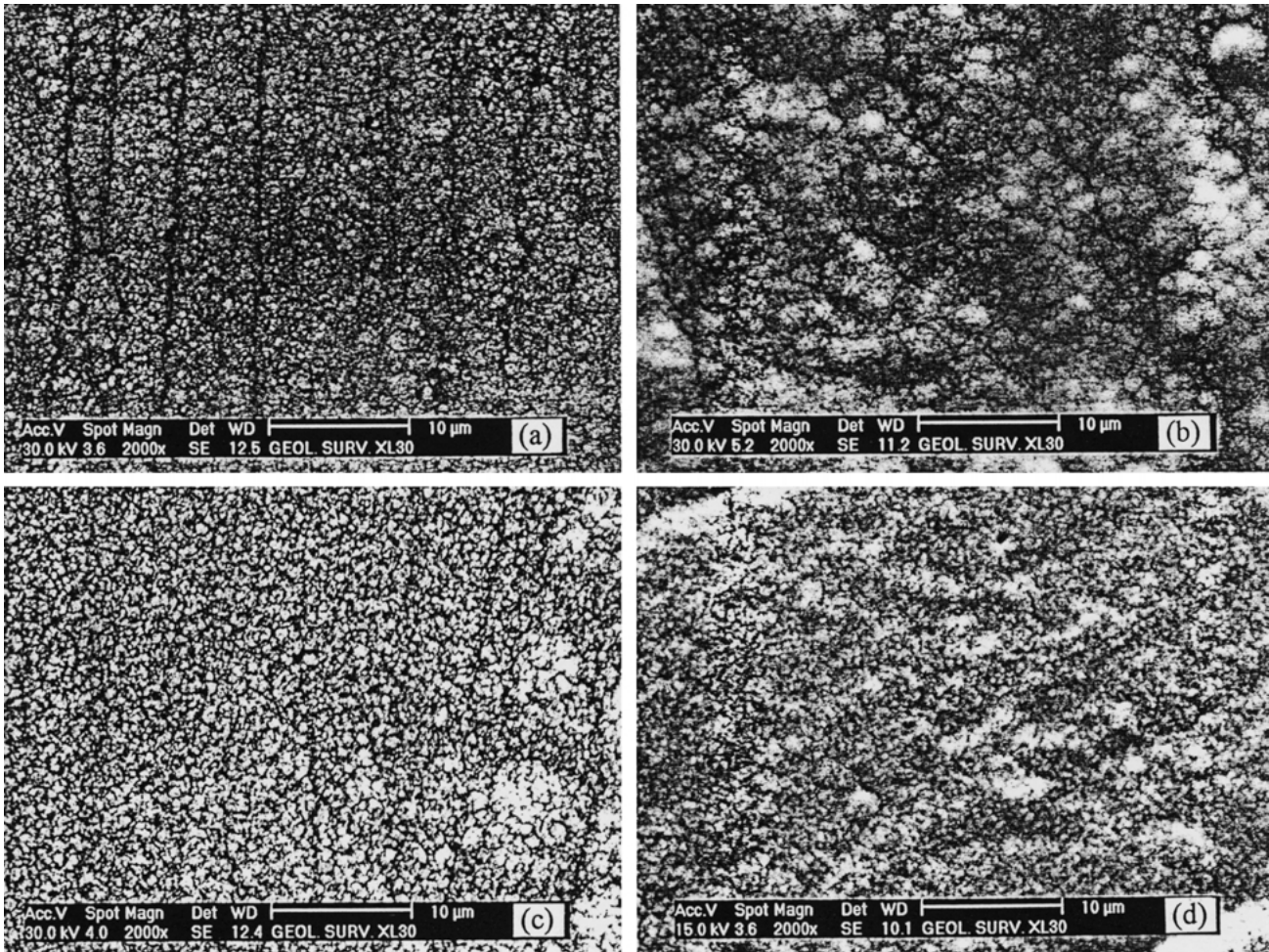


Fig. 5. SEM microphotographs of electroless Ni-Co-P deposits: (a) as plated, (b) 350 °C, (c) 400 °C and (d) 500 °C for one hour heat treatment.

### 3.3. Hardness study

It is well known that the hardness of Ni-P thin films increases with heat treatment and reaches a maximum value with annealing at 400 °C for one hour. The increase in hardness was attributed to the formation of hardened  $\text{Ni}_3\text{P}$  particles as already studied by several authors [18–21, 23]. Also, in this work, it was found that

the hardness of Ni-P thin film increases from about 686 to 1050  $\text{VHN}_{50}$  with one hour heat treatment at 400 °C. Moreover, increase in hardness was observed for one hour heat treated Ni-Co-P alloy at 400 °C.

Figure 6 shows the variation of hardness of electroless Ni-Co-P alloy with heat treatment temperature. It can be seen that the hardness increases with increase in annealing temperature up to 400 °C after which it

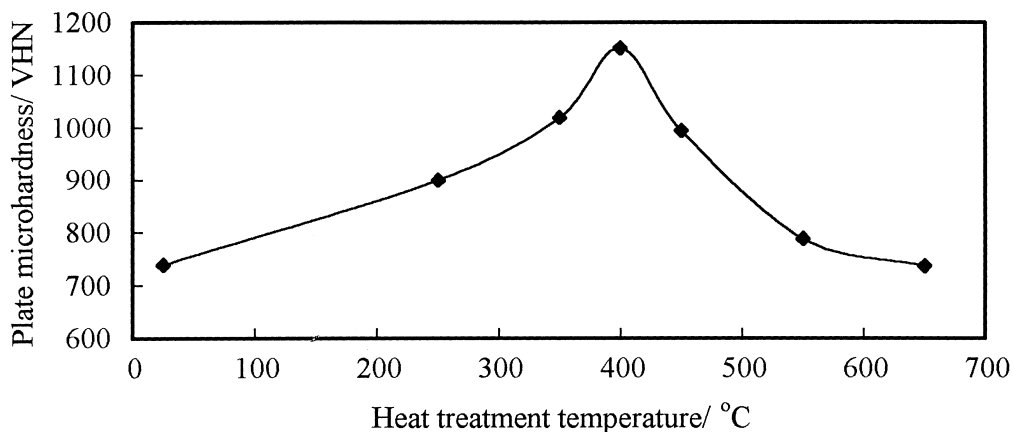


Fig. 6. Variation of electroless Ni-Co-P alloy hardness with heat treatment temperature.

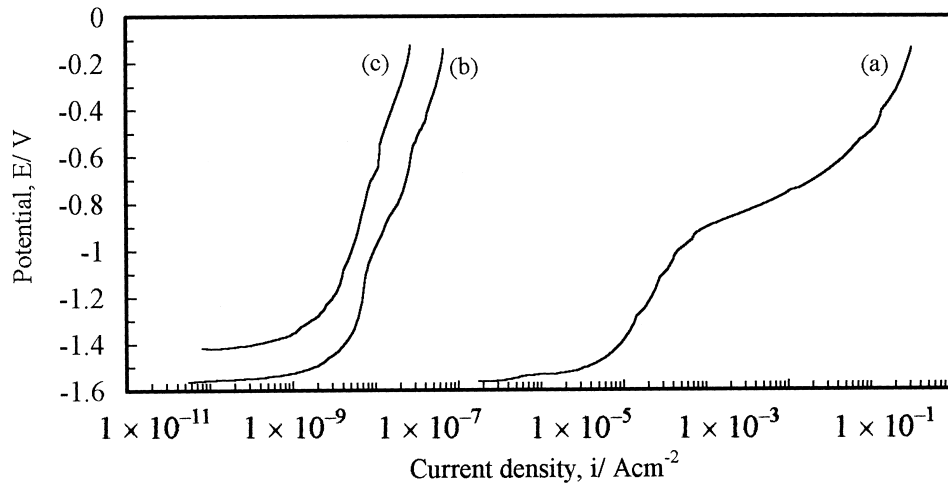


Fig. 7. Anodic polarization curves in 5% NaCl solution, of electroless Ni-Co-P alloy treated for one hour at (a) 350 °C, (b) 400 °C and (c) 550 °C.

decreases. The maximum hardness achieved at this temperature was 1152 VHN<sub>50</sub>.

In this work, there appears to be a strong relation between microhardness and the structure changes in Ni-Co-P deposits with annealing temperature. In general, three factors appear to influence the deposit microhardness; the fineness of the grains, the dislocation density and the dislocations by impurities [24]. The deposits with the smallest grain size and the highest strains had the highest hardness values. The increase in microhardness of treated Ni-Co-P deposits at 400 °C may be attributed to the formation of hardened Ni<sub>3</sub>P phase and inclusion of cobalt atoms in the crystalline nickel lattice and also to the formation of fine particles, as already observed by SEM. The decrease in hardness of treated samples after 400 °C was due to the increase in the volume of precipitated particles, which increases grain size.

#### 3.4. Corrosion resistance

One of the most important factors affecting the corrosion of an electroless nickel coating is heat treatment. The corrosion resistance of the deposits was evaluated by measuring the anodic current density with overpotential. Figure 7 shows the potentiodynamic polarization data of heat treated Ni-Co-P samples in 5% neutral sodium chloride solution. It can be seen that, with increasing annealing temperature, the passive range of the treated deposits increases.

For the sample treated at 350 °C for one hour, although no new phase formation could be detected, the P and Co congregate. Galvanic coupling develops different potentials due to P content variations. This causes the low passive range, which extends from the open circuit potential to about -940 mV, and the anodic current density (at -940 mV) was  $1 \times 10^{-4}$  A cm<sup>-2</sup> (curve a in Figure 7). On the other hand, the passive range of the deposits treated at >400 °C extends from the open circuit potential to over -200 mV. The anodic current densities (at -200 mV) were  $8 \times 10^{-8}$

and  $2.7 \times 10^{-8}$  A cm<sup>-2</sup> for the same sample treated at 400 and 550 °C, respectively (curves (b) and (c) in Figure 7).

The increase in corrosion resistance of treated Ni-Co-P deposits at high temperature is not only due to the formation of large particles of Ni<sub>3</sub>P phase, which is easy for passivation [20], but also may be attributed to the absorption of cobalt atoms in the recrystalline nickel matrices that causes a clear shift of nickel diffraction lines to lower angles at >400 °C heat treatment. Also, the formation of a hard protective and tenacious oxide film at the interface between the coating and substrate yields a significant improvement in corrosion resistance [21].

#### 4. Conclusion

Ternary Ni-Co-P alloy coatings have been successfully deposited on mild steel and aluminium substrates from alkaline baths containing sodium citrate and lactic acid as complexing agents. The following conclusions can be drawn.

- (i) The alloy phosphorus content decreased and the alloy cobalt content increased with increasing cobalt sulfate concentration in the plating bath and the composition of deposited alloy on aluminium and mild steel substrates are similar.
- (ii) The X-ray diffraction analysis of Ni-(11.7 wt %) Co-(3.49 wt %) P alloy showed that the as plated film is a supersaturated solid solution of P and Co dissolved in a microcrystalline Ni matrix with  $\langle 111 \rangle$  preferred direction.
- (iii) The structure of the Ni-Co-P alloy changed to a crystalline structure with formation of a Ni<sub>3</sub>P phase and recrystallization of nickel when the sample was treated at >400 °C for one hour. Also, cobalt co-deposition in the treated alloy at >400 °C shifted the diffraction lines of Ni to lower angles, in comparison with those of treated binary alloy, and de-

creased the relative intensity of Ni (2 0 0) and (2 2 0).

- (iv) Heat treatment at 400 °C formed very fine particles on the surface. When the treatment temperature was increased to 550 °C, the grains were attached and no cracks were found in contrast to treated Ni–P alloy.
- (v) The maximum hardness (1152 VHN<sub>50</sub>) was obtained for the sample treated at 400 °C for one hour.
- (vi) In 5 wt % NaCl solution, the Ni–Co–P samples treated at >400 °C showed much better corrosion resistance in comparison to that treated at 350 °C.

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