Development of Electroless Deposition of Nickel from Alkaline Hypophosphite Baths Using Gluconate as Complexing Agent

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Abstract– **In the present paper, electroless deposition of nickel from alkaline hypophosphite baths on copper substrates, using gluconate, as complexing agent, were studied. The dependence of the deposited Ni-P alloy on various operating parameters and solution components were examined. The deposited Ni-P coatings was characterized using different techniques such as energy dispersive X-ray (EDX), X-ray diffraction (XRD), scanning electron microscope (SEM), and the hardness, corrosion resistance for the coated substrates were measured. The coated substrate from these baths shown high deposition rate (unexpected from alkaline hypophosphite), and lower activation energy beside good appearances and enhancement in the hardness and corrosion resistance for the deposited layer were observed.**

Keywords– **Complexing Agent, Ni-Palloy, Electrolessdeposion, Corrosion Resistance and Polarization Curves**

I. INTRODUCTION

Electroless nickel coatings, commonly referred to as simple EN, are chemically deposited alloys containing nickel and phosphorus. Since the discovery of electroless, or autocatalytic nickel plating by *Brenner and Riddel* [1], it has been widely used in electronic, machinery, automobile, aerospace and other industries.

The kinetic of the chemical reactions, deposition rate, and properties are closely dependent on various operating parameters and solution components [2].

Several theories are given in the literature to explain the mechanism of the electroless nickel process with hypophosphite as reducing agent [3], [4].

The effect of plating bath variables, e.g. pH, nickel and hypophosphite concentrations, on the composition of the resultant deposit was studied [5].

The composition, electronic states and structure of thin Ni-P layers deposited by the electroless method have been reported [6].

The heating effect of Ni-P as deposited alloy have been extensively studied [7], [8], and the Corrosion and erosion resistance were also studied [9].

Using of different complexing agents such as, glycine, citrate and $PbCl_2$ with Thiourea have been reported [10], [11]. A survey of literature shows that gluconate electrolytes were used to electroplate metals such as nickel [12], copper [13], tin [14] and zinc [15]. No literature survey was found upon used gluconate in electroless nickel plating, so The objective of the present study is to obtain Ni-P alloy from alkaline gluconate baths, in order to determine the dependence of coating characteristics on several electroless plating variables and characterizes the obtained coatings by using different techniques such as SEM, EDX, and XRD and examine the coatings corrosion resistance.

II. EXPERIMENTAL

A) Pretreatment and activation of copper substrate

Copper sheet substrates of dimensions 2X2 cm^2 were used. The substrates were mechanically polished with different grade emery papers and then immersed in pickling solution (300ml H_2SO_4+100ml HNO_3+5ml HCl+595ml doubly distilled water) for 1min, washed with distilled water, rinsed with acetone. After treating the copper substrate, it was immersed for 20 seconds in a dilute acidic solution of $PdCl_2$ (0.1 g/L $PdCl_2$ and 0.2 ml/L HCl 36%), followed by thorough rinsing, after that the substrates were dried and finally weighed [16].

B) Experimental procedure of nickel electroless deposition

Solution bath listed in Table 1 used was freshly prepared from Analar chemicals and doubly distilled water. The electrochemical cell was connected by holding only the copper substrate immersed into 250 ml of the electroless solution for 60 min. The pH was measured using Microprocessor pH/mV/^{0}C Meter (Model CP 5943-45USA) and adjusted by NH_4OH solution addition, the temperature was controlled by using thermostatic controlled bath. From the change in weights of the substrates before and after the electroless process, the deposited weight was calculated; the composition of coatings was examined using the following procedures:

1. The coating layer is stripped using 10% H_2SO_4 solution. The object is then put as anode in an electroplating cell by which the coating layer will be dissolved in the solution, which is then diluted to 250 ml with bi-distilled water.
2. The analysis was done using Atomic absorption Spectrophotometer (Perkinelner3100, Germany).

3. The solution obtained is further diluted by dissolving 5ml in bi- distilled water to 250ml.
4. Nickel standard solutions for the elements to be detected were prepared (1g Ni metal in (1+1) HNO_3. Diluted to 1 L with 1 %(v/v) HNO_3) , Ni, Air-Acetylene flame gases, wavelength of 232 nm.
5. The Phosphorus weight was calculated by subtracting the obtained nickel weight from the total deposited weight.

The results are confirmed for some samples with EDX analysis.

The deposited mass of nickel m on the unit surface during the plating time represents the deposition rate [17]:

$$DR = dm/dt \qquad (1)$$

The surface of the as-deposited Ni-P alloy on copper substrates was morphologically inspected using scanning electron microscopy (SEM). (JEOL-5410 attached to an EDX unit), phases of surface and phase changes of the different coated substrates investigated by using an X-Ray Diffractometer (Broker AXS-D8 X-ray diffractometer, ADVANCE, Germany), with a copper target ($Cu_\lambda = 1.5406^0A$) and Nickel filter, Vickers microhardness of the deposits was measured under 50 gm. load microhardness of the specimen material by using a Shimdzu Hardness tester. The electrochemical experiments were performed using A VOLTA LAB 40 (Model PGZ301) with the aid of commercial software (Volta Master 4 version 7.08). A saturated calomel electrode (SCE) and a platinized platinum black were used as the reference and auxiliary electrodes, respectively with different deposited plates as the working electrode and the electrochemical cell was filled by 3.5% NaCl. Volta Master 4 calculates and displays the corrosion rate, Corr. in μm/year: this rate is calculated from the i_{corr} the corrosion current density found, the D density and the M atomic mass and V valence entered in the Tafel dialogue box. The calculation is performed as follows:

$$Corrosion \ \mu m/year = \ (i_{corr}. \ (A/cm^2) \ x \ M \ (g)) \ / \ (D \ (g/cm^3) \ x \ V) \ X \ 3270 \qquad (2)$$

With: 3270 = 0.01 x [1 year (in seconds) / 96497.8] and 96497.8 = 1 Faraday in Coulombs (3)

III. RESULTS AND DISCUSSION

A) Optimization of Ni-P alloy electrolessdeposion parameters

Effect of Nickel g/L on the deposition rate

Fig. 1, show that the deposition rate (DR) ($mg/cm^2.hr$) increased as the nickel ions concentration increases from 5 to 35g/L. The behavior of nickel ions in alkaline medium accompanied by hydrogen evolution and the oxidation of hypophosphite ions.

Effect of Sodium hypophosphite g/L on the deposition rate

The effect of sodium hypophosphite g/L as a function of the deposition rate was shown in Fig. 2, the deposition rate increased as the sodium hypophosphite concentration increases from 5 to 30 g/L. After that no increase in the DR was observed, this is due to the fact that even though the available electrons for metal ion reduction increases with increase in concentration of hypophosphite, the rate at which the availability of the metal ion is limited by the amount of complexing agent present in the bath.

Effect of Sodium gluconate (complexing agent) g/L

The deposition rate increased as the sodium gluconate concentration increases from 10 to 50 g/L and decreases after that due to the inhibiting effect of the gluconate as shown in Fig. 3.

Effect of pH on the deposition rate

The effect of pH on DR is illustrated in Fig. 4. The deposition rate increased as the pH increases up to pH9 and decreased sharply after that due to precipitation of nickel hydroxide and phosphate ions.

Effect of temperature on the deposition rate and calculation of the activation energy (E_a)

Deposition rate of electroless nickel is increased as the bath temperature increases and this was shown in Fig. 5 and from the relation between the log DR ($mg/cm^2.hr$) one can calculate the activation energy (E_a) according to:

$$log \ DR = loga - E_a/2.3RT \qquad (4)$$

From the slope D of the log DR/T straight line, the activation energy E_a can be calculated according to the following formula:
$E_a = -2.3 \ RD(5)$, Where R is the gas constant.

From the calculation the obtained activation energy was 38.44 KJ/mol which

Show that gluconate decreases the activation energy of EN reaction in comparison with the results obtained early for halide effect and cysteine effect in electroless nickel deposition (76.6 [18], 68.5 [19] K j/mol, respectively); the decrease in the activation energy indicates the formation of the more stable reactive intermediate. Thus it can be inferred that gluconate may be involved in the formation of the reactive intermediate in the EN reaction.

Effect of time on the deposition rate

Fig. 7 shows that the deposition rate (DR) ($mg/cm^2.hr$) increased as the plating time increasing throughout 60 minute plating, and this due to autocatalytic nature of the electroless plating process. However, the increase in thickness is not the same throughout the entire duration of plating.

B) Characterization of Ni-P electroless deposits

Phosphorus content % on Ni-P alloy

Increasing the hypophosphite concentration in the plating bath increases the phosphorus content of the deposits as indicating from Fig. 8.

Fig. 9, shows the phosphorus % as a function of bath pH, the P% increased with the solution pH up to pH 9 and after that the P% decreased as results of precipitation of phosphate and nickel salts. Fig. 10 and Fig. 11 show the EDX pattern of $Ni_{96}-P_4$ and $Ni_{82}-P_{18}$ alloy respectively. The XRD pattern of the Ni-P deposits was shown in Fig. 12, where only one broad

peak with a weak intensity appeared at about $2\theta = 45°$ implying that the deposits were amorphous. This result is in agreement with result obtained by *GaoRongjie et.al* [20] which studied Ni-P deposits from bath containing malic acid, butyric acid as stabilizing agent. The crystal size was 16.84nm.

Micro structure of Ni-p alloy

SEM results, Fig. 13, indicate that the Ni-P as plated deposits is amorphous structure.

Microhardness

The hardness of Ni-P alloy decreased as the phosphorus content in the alloy increased, the heat of the deposits is also increased the hardness as mentioned before in the literature [5], [7], [8], the observed hardness fore Ni_{96}-P_4 coating without heat treatment was $490HV_{50}$.

Corrosion behavior of Ni-P alloy

The potentiodynamic polarization curve Fig. 14, and data from Table 2, indicating that the Ni-P deposits had positive effects on reducing the corrosion rate in the active corrosion region, the Corrosion rate μm/Y for the uncoated cu-substrate was 72.40 and for coated one by Ni-P alloy was 3.296 which inhibited the corrosion behavior of cu-substrate to 95.45%. Generally, nickel electroless plating improve the corrosion resistance due to formation of protective layer of metallic

nickel and nickel phosphide that act as barrier to oxygen diffusion to the metal surface.

IV. CONCLUSION

Electroless deposition of nickel from alkaline gluconate baths exhibits good properties, high deposition rate (unexpected from alkaline hypophosphite), and lower activation energy beside good appearances and finally enhance the hardness and corrosion resistance for the deposited layer.

Table 1: Bath composition and operating conditions of Nickel-phosphorus electrolessdeposion

Nickel sulfate	5-30 g/L
Sodium hypophosphite	5-40 g/L
Sodium gluconate	10-60 g/L
Succinic acid	3 g/L
Sodium dodecyl sulfate	0.5g/L
Lead acetate	2 mg/L
Time	20-100 min
Temperature	$50-100^0$ C
pH	5-10
Stirring speed	150 rpm

Table 2: Data of Potentiodynamic curve of Ni_{96}-P_4 alloy

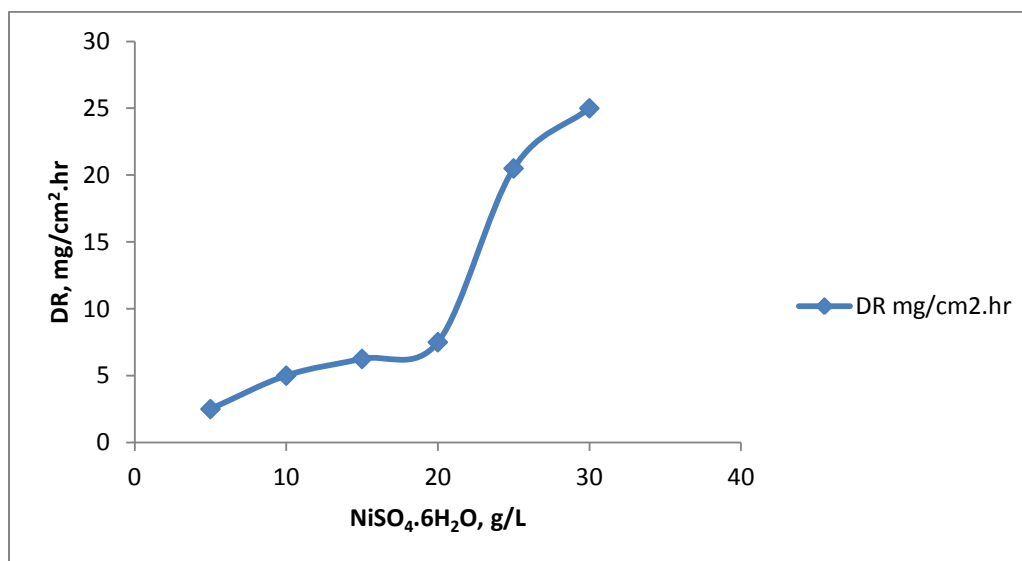|	E(i=0) corr. mV	i corr. μA/cm²	Rp kohm.cm²	Beta a mV	Beta c mV	Corrosion μm/Y
Cu Base	-315.0	6.2359	1.93	73.4	-82.7	72.40
Ni_{96}-P_4	-225	0.2848	57.64	72.7	-89.7	3.296

Fig. 1. Effect of NiSO₄.6H₂Og/L on DR from bath containing Sodium hypophosphite 15 g/L, Sodium gluconate 15g/L, Am.Sulfate 15 g/L, sodium dodecyl sulfate 0.1g/L, Succinic acid 0.3g/L, pH9, temperature 90^0C,time 60 min
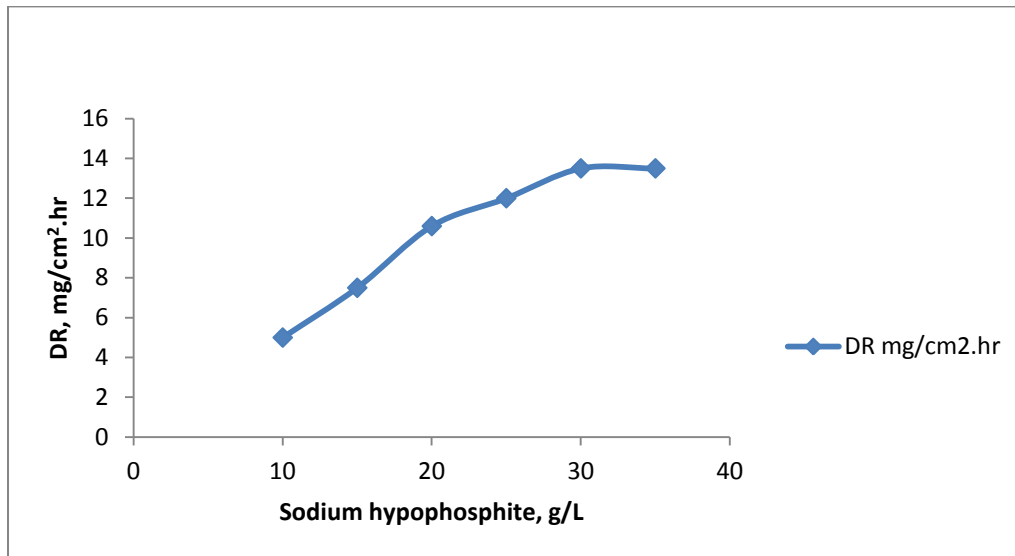
Fig. 2. Effect of Sodium hypophosphite g/L, on DR from bath containing $NiSO_4.6H_2O$ 25g/L, Sodium gluconate 15g/L, Am.Sulfate 15 g/L, sodium dodecyl sulfate 0.1g/L, Succinic acid 0.3g/L, pH9, temperature 90^0C, time 60 min
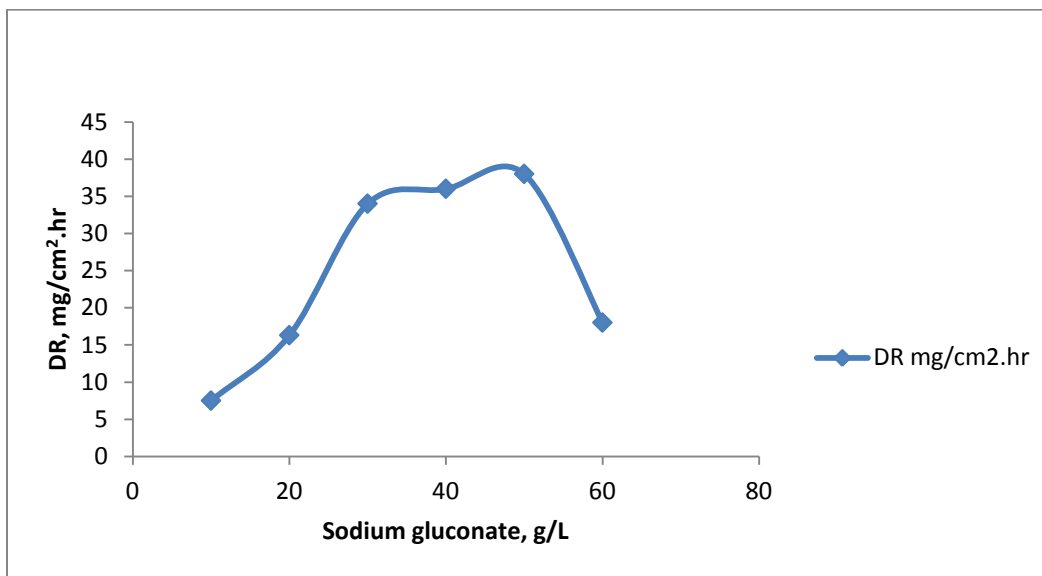

Fig. 3. Effect of Sodium gluconate g/L, on DR from bath containing $NiSO_4.6H_2O$ 25g/L, Sodium hypophosphite 15g/L, Am.Sulfate 15 g/L, sodium dodecyl sulfate 0.1g/L, Succinic acid 0.3g/L, pH9, temperature 90^0C, time 60 min
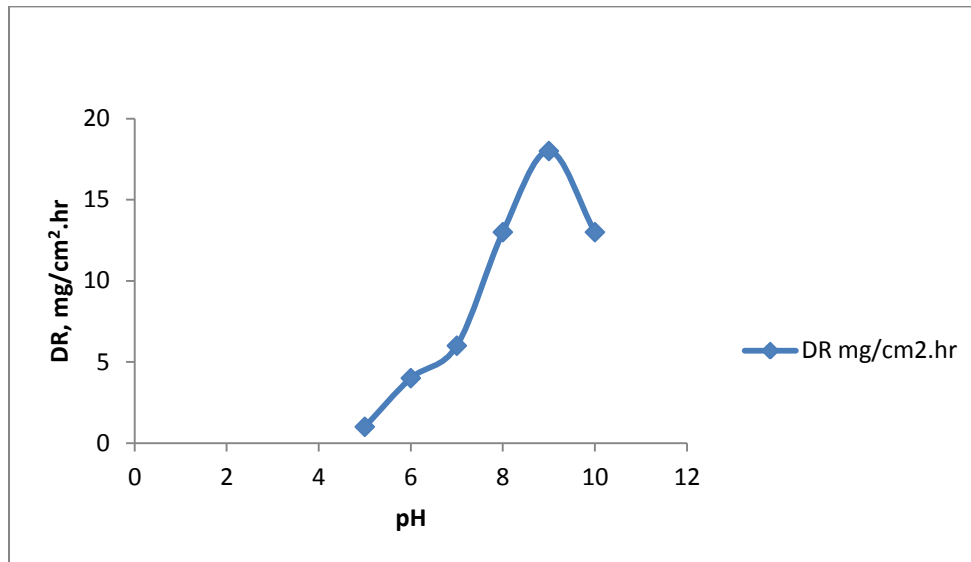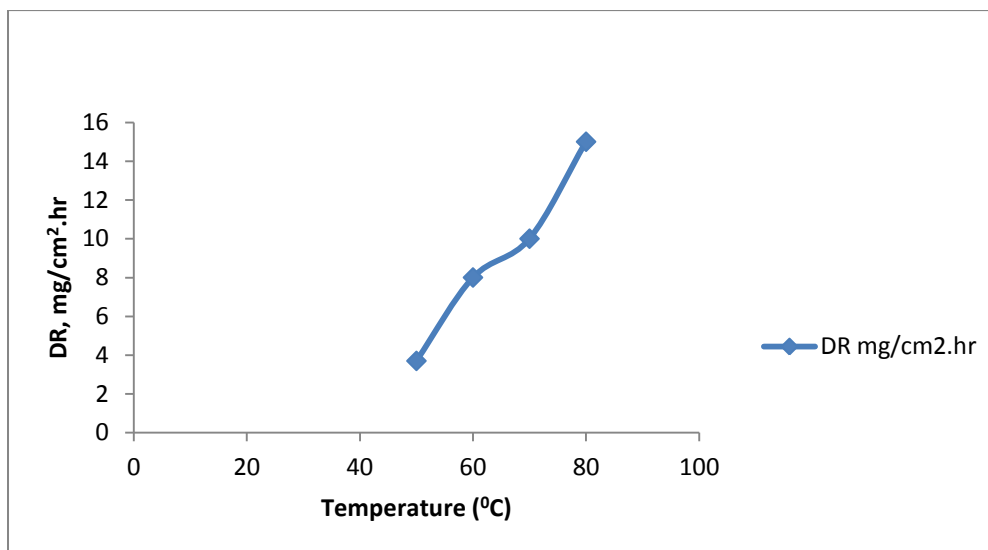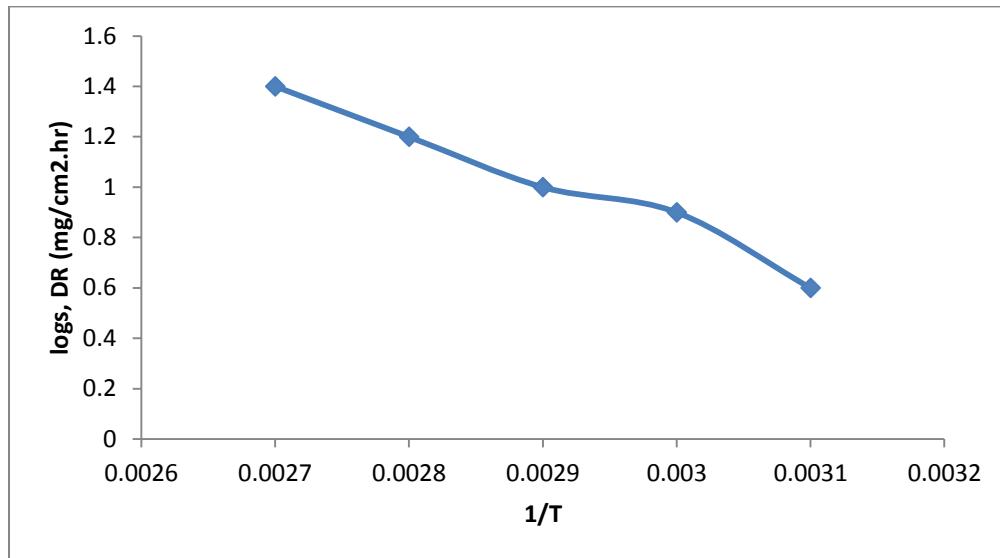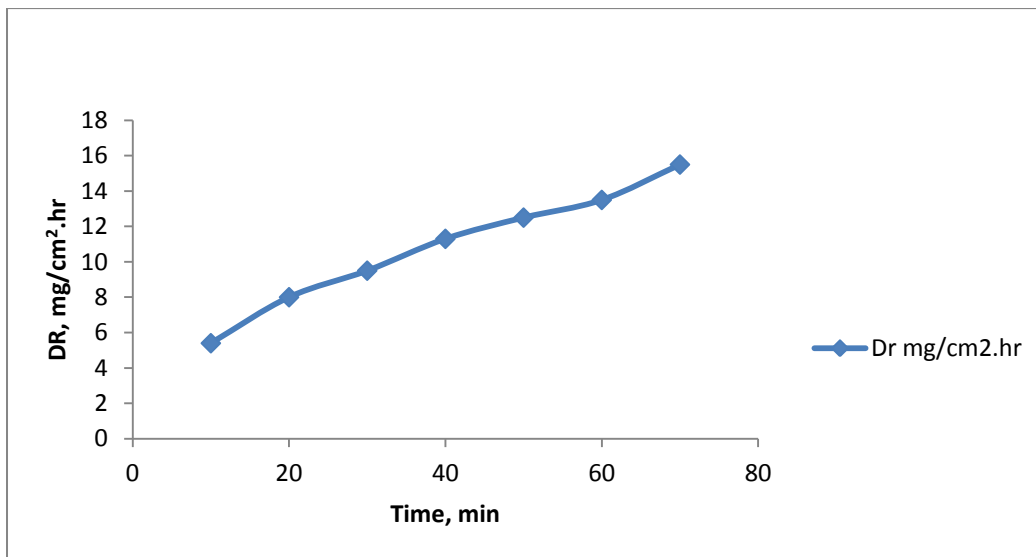
Fig. 4. Effect of pH on DR from bath containing NiSO$_4$.6H$_2$O 25g/L, Sodium hypophosphite 15g/L, Am.Sulfate 15 g/L, sodium dodecyl sulfate 0.1g/L, Succinic acid 0.3g/L, Sodium gluconate 15g/L, temperature 90^{0}C,time 60 min
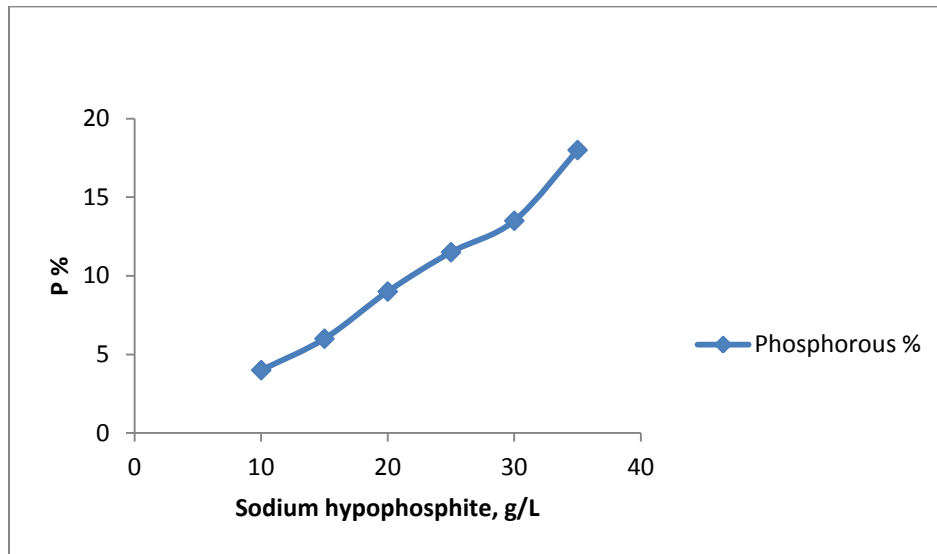

Fig. 5. Effect of temperature(^{0}C) on DR from bath containing NiSO$_4$.6H$_2$O 25g/L, Sodium hypophosphite 15g/L, Am.Sulfate 15 g/L, sodium dodecyl sulfate 0.1g/L, Succinic acid 0.3g/L, Sodium gluconate 15g/L, pH 9,time 60 min

Fig. 6. Relation between logs, DR with the reciprocal of temperature (K).Unmoved sample; air-free solution

Fig. 7. Effect of time, min on DR from bath containing $NiSO_4.6H_2O$ 25g/L, Sodium hypophosphite 15g/L, Am.Sulfate 15 g/L, sodium dodecyl sulfate 0.1g/L, Succinic acid 0.3g/L, Sodium gluconate 15g/L, pH 9,temperature 90^0C

Fig. 8. Effect of Sodium hypophosphite g/L, in phosphorus % from bath containing $NiSO_4.6H_2O$ 25g/L, Sodium gluconate 15g/L, Am.Sulfate 15 g/L, sodium dodecyl sulfate 0.1g/L, Succinic acid 0.3g/L, pH9, temperature 90^0C, time 60 min
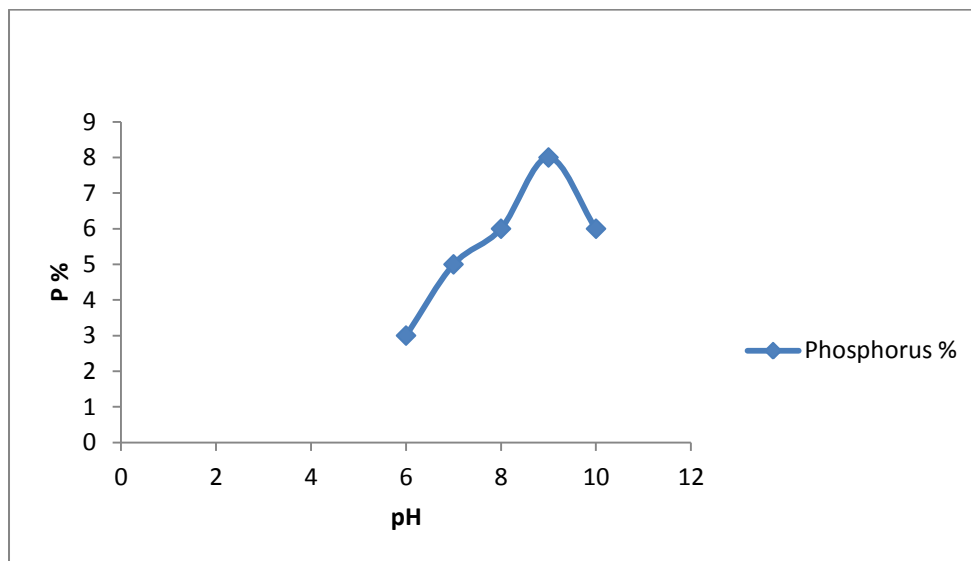

Fig. 9. Effect of pH in phosphorus % from bath containing $NiSO_4.6H_2O$ 25g/L, Sodium hypophosphite 15g/L, Am.Sulfate 15 g/L, sodium dodecyl sulfate 0.1g/L, Succinic acid 0.3g/L, Sodium gluconate 15g/L, temperature 90^0C, time 60 min
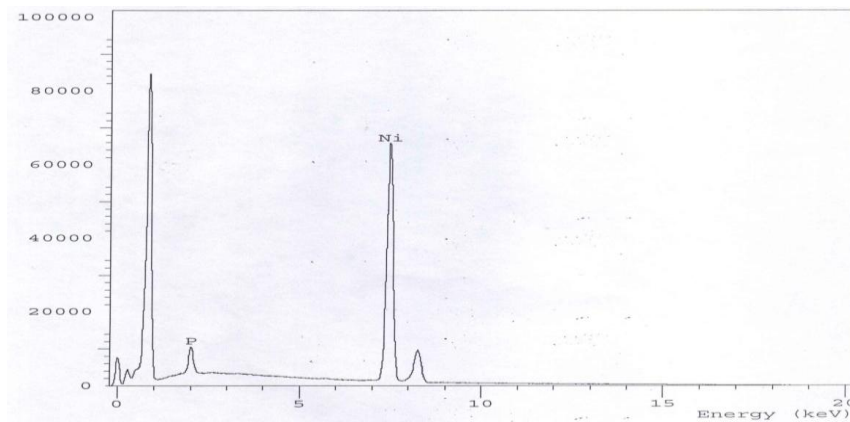
Fig. 10. EDX chart of Ni_{96}-P_4 from bath containing $NiSO_4.6H_2O$ 25g/L, Sodium gluconate 15g/L, Sodium hypophosphite 10 g/L, Am.Sulfate 15 g/L, sodium dodecyl sulfate 0.1g/L, Succinic acid 0.3g/L, pH9, temperature 90^0C,time 60 min
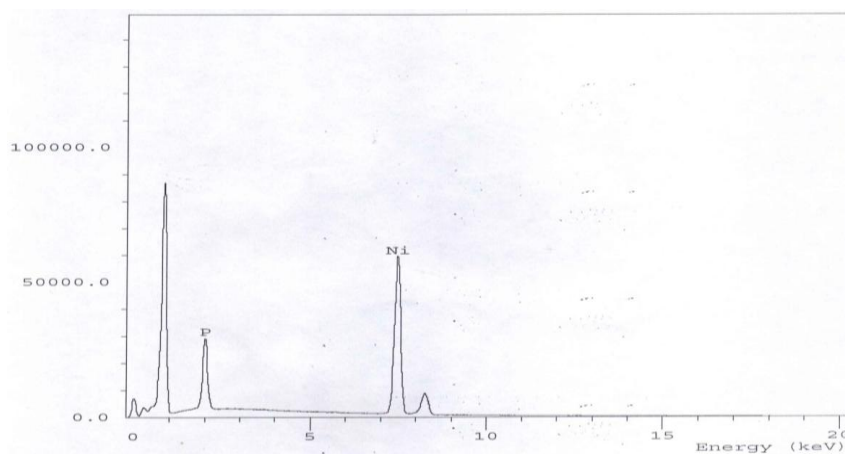
Fig. 11. EDX chart of Ni_{82}-P_{18} alloy from bath containing $NiSO_4.6H_2O$ 25g/L, Sodium hypophosphite 35g/L, Am.Sulfate 15 g/L, sodium dodecyl sulfate 0.1g/L, Succinic acid 0.3g/L, Sodium gluconate 15g/L, temperature 90^0C,pH9,time 60 min
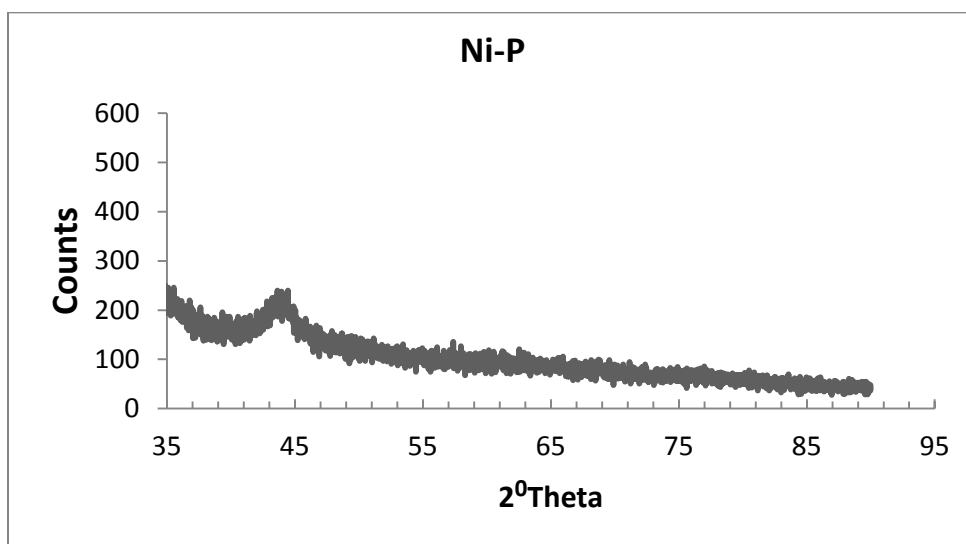
Fig. 12. XRD chart of Ni_{82}-P_{18} alloy from bath containing $NiSO_4.6H_2O$ 25g/L, Sodium hypophosphite 35g/L, Am.Sulfate 15 g/L, sodium dodecyl sulfate 0.1g/L, Succinic acid 0.3g/L, Sodium gluconate 15g/L, temperature 90^0C,pH9,time 60 min
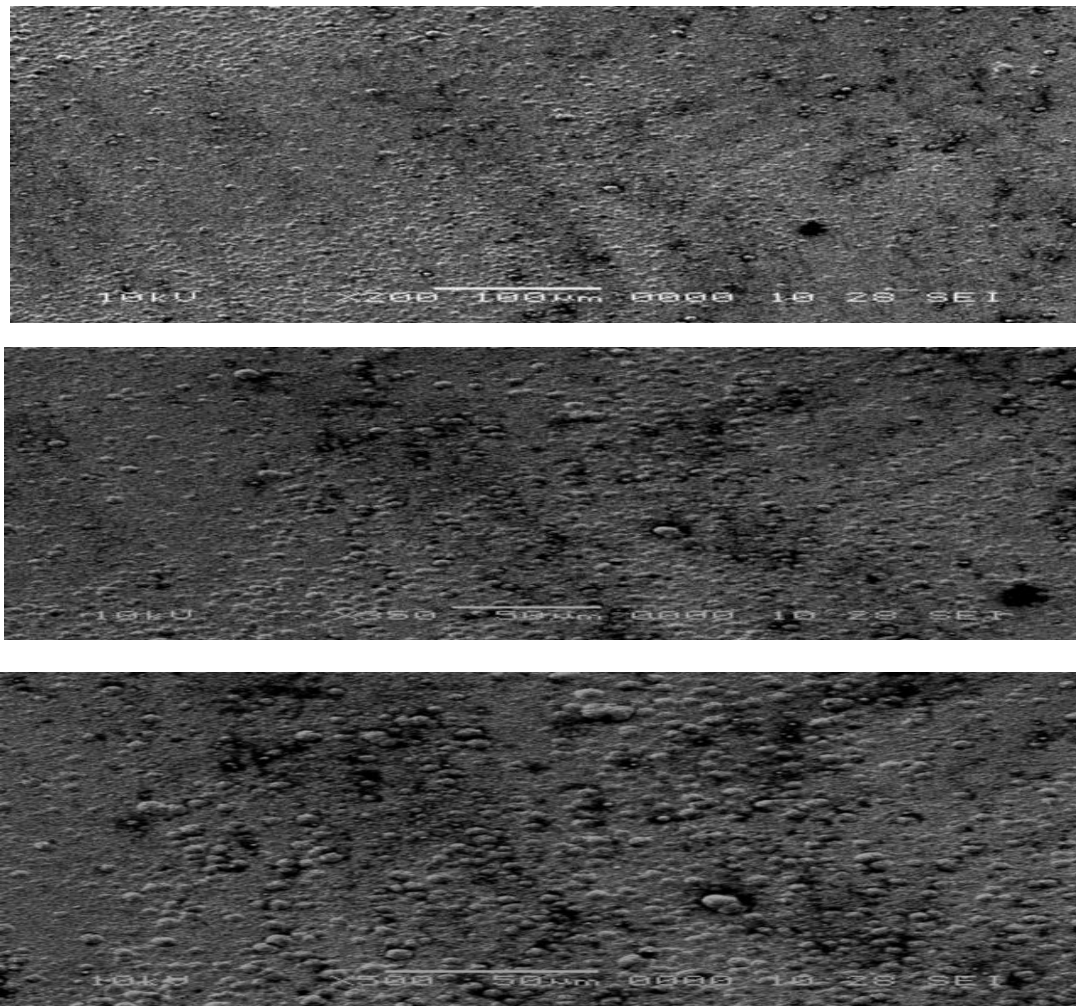
Fig. 13. SEM of Ni_{82}-P_{18} alloy from bath containing $NiSO_4.6H_2O$ 25g/L, Sodium hypophosphite 35g/L, Am.Sulfate 15 g/L, sodium dodecyl sulfate 0.1g/L, Succinic acid 0.3g/L, Sodium gluconate 15g/L, temperature 90^0C,pH9,time 60 min
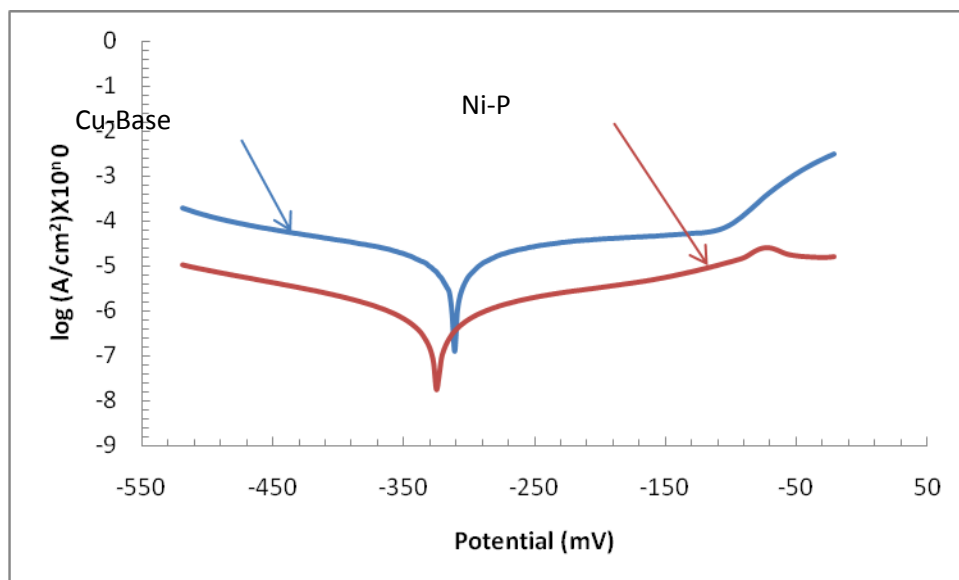

Fig. 14. Potentiodynamic curve of Ni_{96}-P_4 alloy

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