

# Influence of Heat Treatment on the Autocatalytic Ni-P and Ni-Co-P Deposits

A. Ahmad<sup>1</sup>, K.M.Ghauri<sup>1</sup>, L.Ali<sup>1</sup>, A. A. Noshahi<sup>1</sup> and J. P. G. Farr<sup>2</sup>, E-mail: drakhlaq@uet.edu.pk

1. Department of MME
2. University of Engineering and Technology Lahore
3. Department of Metallurgy & Materials, University of Birmingham, UK.

## Abstract

*Autocatalytic or electroless deposition is the process of depositing a coating by means of a reducing agent in solution without using electric current. Deposits so produced are primarily alloys of metal(s) with a non-metal like phosphorus or boron. Addition of a non-metal in the metallic lattice may change the metallic crystalline structure to amorphous or microcrystalline that in turn affects the properties such as wear resistance, hardness and corrosion resistance. This paper presents the electroless deposition of Ni-P and Ni-Co-P films using hypophosphite-based baths. The effects of plating parameters like bath composition, temperature, pH and heat treatment at different temperatures have been discussed. The deposits were explored for their magnetic and electrochemical behaviour. The chemical analysis of the deposits was carried out using energy dispersive X-ray analysis (EDX) and TEM. The crystal structure was determined using X-ray diffraction analysis (XRD). The magnetic properties were measured with the help of a vibrating sample magnetometer (VSM). A potentiostat was used to carry out linear sweep voltametry. The results showed that the bath temperature and the pH strongly affect the chemical composition and characteristics of the deposits. The deposits are microcrystalline in the as-deposited condition and recrystallize at 300-3500 °C. However, the corrosion resistance of the deposits decreased after the heat treatment due to formation of different anodic phases.*

**Key Words:** Autocatalytic deposition, Electroless Ni-P and Ni-Co-P deposits, Electrochemical potential

## 1. Introduction

Electroless Nickel deposits are functional coatings credited mainly to Brenner & Riddell who invented the process in 1946 [1]. Since then the process has experienced a number of modifications such as addition of metal ion complexants and stabilizers etc to avoid homogeneous decomposition of the bath and to meet the requirements of various industrial applications such as chemical engineering, mechanical and industrial engineering, automobile engineering, electronics and aerospace industry etc [2, 3]. The deposits are uniform in composition regardless of geometries and possess excellent corrosion resistance, high wear resistance, low coefficient of friction, adequate magnetic properties, lubricity, solderability and bondability [4-6]. The coatings formed by electroless deposition also contain phosphorus or boron, derived from the

reducing agent. The deposition rate, structure and properties of coated components mainly depend upon the constituents of the plating bath, the concentration and type of the reducing agent, stabilizer, pH and bath temperature [7, 8]. The properties of Ni-P and Ni-B alloy deposits can be further improved by the development of autocatalytic Ni ternary deposits. Cobalt is an important alloying addition for imparting magnetic properties in the electroless deposits [9, 10]. Being ferromagnetic, cobalt can improve the coercivity of Ni-Co-P deposits and reduce residual magnetic induction [3, 9]. The Ni-Co-P alloy films are therefore used in high density disk and as electromagnetic shielding film. Reducing agents used for industrial deposition of electroless coatings are sodium hypophosphite, sodium borohydride, aminoboranes and hydrazine. About 90% of the electroless Ni deposition is based on reduction by sodium hypophosphite. This is due to its good

corrosion and wear resistance [4]. In the present study Ni-P and Ni-Co-P deposits were produced by using hypophosphite based baths. The effect of heat treatment on the microstructure, magnetic properties and corrosion resistance of the deposits has been investigated.

## 2. Experimental Technique

Hypophosphite based baths prepared from analytical grade chemicals were used for electroless Ni-P and Ni-Co-P plating on copper strips. The copper sheets having dimensions 3x2.5x0.5cm approximately were cleaned in an alkaline cleaner followed by rinsing, pickling in 10 % HCl and rinsing again before electrolytic Ni strike.

Electrolytic Ni strike for 30-40 seconds was used to make the samples catalytically active because copper is classified as non-catalytic metal for electroless deposition. The pretreated samples were lacquered on one side and plating was done on the other side. Table-1 shows composition of the plating baths used for electroless plating. The pH of the solution was adjusted with NH<sub>4</sub>OH. The substrates were weighed by an electronic weighing balance before and after plating to assess the deposition rate.

**Table-1** Compositions of electroless plating baths with operating conditions

Constituents	Electroless Plating Baths	
	1	2
Nickel Sulphate (gms)	15	30
Cobalt Sulphate (gms)	15	-
Sodium Hypophosphite(gms)	22	21
Tri-Sodium Citrate(gms)	75	75
Ammonium Sulphate(gms)	65	65
pH(NH <sub>4</sub> OH)	9	8
Temperature (°C)	90±3	90±3

JEOL 6300 SEM equipped with energy dispersive x-ray analyzer (EDX) was employed to determine the chemical compositions of the deposits. The copper substrate samples were grounded and polished down to 1 μm. X-ray diffraction was carried out using Vanadium filtered Cr K<sup>α</sup> radiation (2.291Å). Full-width at half-maximum (FWHM)

data was analyzed by using Scherer's formula to determine average grain size. The transmission electron microscopy was carried out using JEOL FX 4000 TEM. The electron diffraction patterns were indexed using standard patterns and maps.

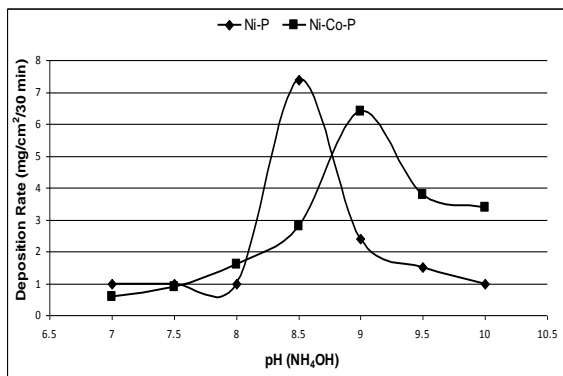
The magnetic measurements on the as-plated and heat treated samples were carried out using a vibrating sample magnetometer (VSM). The results were drawn as hysteresis curves for these samples. Electrochemical properties of the deposits were studied by linear sweep voltametry. In this technique the electrochemical properties of the deposits were studied by the application of a linearly swept potential and measuring the corresponding current. Electrochemical measurements were done in 35 g/l NaCl (pH 7) using a Solartron 1286 electrochemical interface. A PVC sample holder of surface area 0.636 cm<sup>2</sup> was used and the measurements were made against a saturated calomel electrode (SHE = +0.2420V). A platinum piece was used as the counter electrode. Typically the linear sweep potential varied between OCP (open circuit potential) -100 mV to +1V versus SCE at a sweep rate of 1mv/sec. The results are plotted as potential versus current density curves.

## 3. Results and Discussion

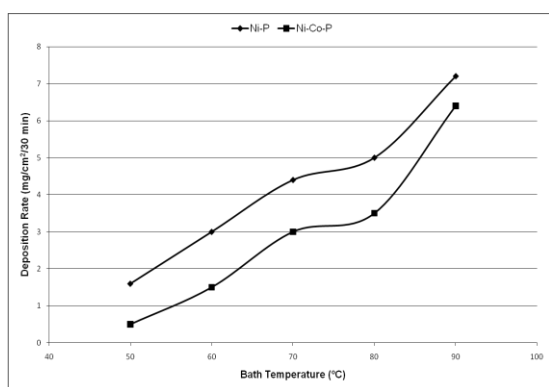
Fig.1 shows the deposition rate of Ni-P and Ni-Co-P deposits as a function of plating bath pH. Coating was carried out at 90±2 °C temperature and deposition rates were measured as weight gain/cm<sup>2</sup>. Fig.2 shows the deposition rate of Ni-P and Ni-Co-P deposits at optimum pH as a function of plating bath temperature. Table 2 summarizes the optimized conditions for Ni-P and Ni-Co-P platings. As evident from Fig.1, Ni-P shows maximum deposition rates at pH 8.5 while Ni-Co-P shows maximum deposition rate at pH 9.0. Both systems show maximum deposition rates at 90 °C. It is assumed that electroactive complexes are formed under operating conditions that increased the deposition rates.

**Table-2:** Optimized Conditions for plating baths

Deposit	pH	Temp. °C	Deposition rate mg/cm <sup>2</sup> /30min
Ni-P	8.5	90	7.3
Ni-Co-P	9.0	90	6.5

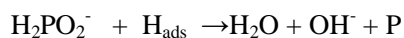


**Fig.1** Deposition rate as a function of plating bath pH



**Fig.2** Deposition rate as a function of plating bath temperature

Results indicate that Ni-Co-P exhibits a lower deposition rate than Ni-P. This may be due to the fact that Ni has a higher catalytic activity than cobalt. A decrease in deposition rate with the increase in cobalt content in the electroless plating bath has been reported by Matsubara et al. [11] and Kim et al. [12]. Alberts et al.[13] suggested that Co forms a stable oxide with the dissolved oxygen that reduces effective Co ion concentration in the solution. They also reported that the electroless deposition of Co is diffusion controlled. Probably these two factors reduced the deposition rate of Ni-Co-P. Table-3 shows the EDX analysis of the deposits plated at varying bath pH values. The results indicate that in both types of deposits, P content decreased with increasing pH of the bath. This is probably related to the following reaction, which under equilibrium conditions indicates a decrease in elemental P with the increase in OH<sup>-</sup> ions [14]:

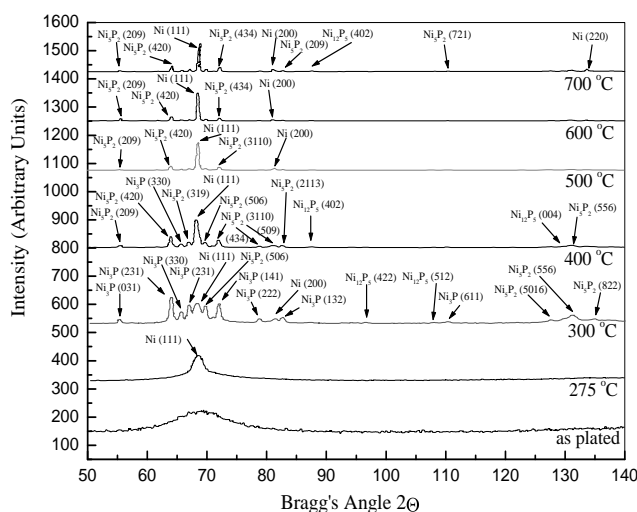


In binary Ni-P coating, Ni content in the deposit is increased with the increase of bath pH. In case of ternary Ni-Co-P coatings, there is a mixed behavior up to pH 8.5, Ni content is increased and Co content is decreased but at pH 10, Ni is decreased and Co is increased. Furthermore P content in Ni-P deposits is more as compared to Ni-Co-P deposits. Tarozaita et.al [15] has also reported a comparatively higher phosphorus co-deposition with Ni than with cobalt.

**Table-3** EDX analysis of the deposits plated at varying bath pH values

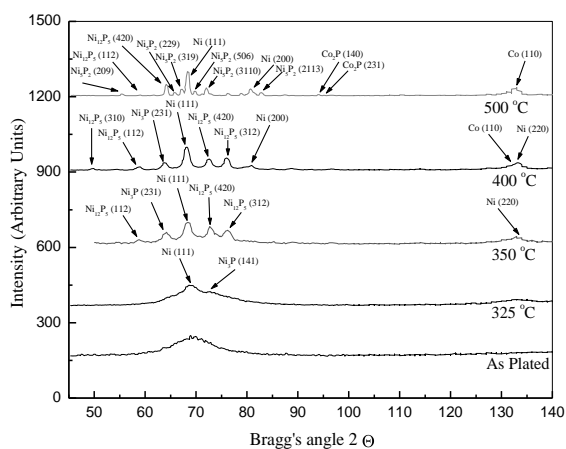
Deposits	Ni-P		Ni-Co-P		
	Elements (atomic %)				
pH	Ni	P	Ni	Co	P
7.0	82.2	17.8	35.5	47.5	17.0
7.5	82.0	18.0	-	-	-
8.0	82.5	17.5	36.5	49.7	13.8
8.5	85.9	14.1	49.0	39.0	12.0
9.0	93.3	6.7	56.9	34.4	8.7
10.0		--	39.5	53.4	7.1

Fig. 3 shows the XRD patterns for as-plated and annealed Ni-P deposits. The deposits were annealed at different temperatures i.e. 275°C, 300°C, 400°C, 500°C, 600°C and 700°C respectively. The diffraction pattern of as plated sample shows one broad hump at 2θ, 60-80° with a large amorphous band. The background is quite high. This kind of diffraction pattern is characteristic of microcrystalline or amorphous material.



**Fig.3** XRD pattern for as-plated and annealed Ni-P autocatalytic deposits.

Peaks No. 1, 2 and 3 have been labeled as Ni(111), Ni<sub>3</sub>P(202) and Ni<sub>2.55</sub>P(426) respectively because the closest d-spacing correspond to these phases but the peaks overlap and this evidence is not enough to assign these phases to the peaks with certainty. The grain size of the deposit is ~10 Å indicating that probably the material is in an amorphous or microcrystalline state. H. Ashassi et al. [7] have also reported that as-plated Ni-P deposits are amorphous in nature. The broadening of the peaks can be attributed to the presence of micro-stress in the deposited film being supersaturated with respect to phosphorous [15]. Sample annealed at 275°C shows one sharp peak with a broad base at  $2\theta = 68.55^\circ$ . The grain size is ~39 Å. The shape of the pattern and the grain size indicate that the material is probably in transition between amorphous to crystalline state. The peak has been labeled as Ni(111). The XRD pattern for the sample annealed at 300°C indicates the appearance of quite sharp peaks corresponding to various phases. The pattern shows that the re-crystallization temperature lies between 275-300°C. Main peaks in the pattern correspond to f.c.c Ni, tetragonal Ni<sub>3</sub>P and hexagonal Ni<sub>5</sub>P<sub>2</sub>. The grain size for the various phases lies between 36-316 Å. At 400 °C probably the proportion of Ni<sub>5</sub>P<sub>2</sub> is increased and this phase becomes dominant in place of Ni<sub>3</sub>P. At annealing temperature of 500°C the deposit crystallizes to mainly two phases i.e. metallic Ni and Ni<sub>5</sub>P<sub>2</sub>. The main peak for Ni(111) has moved to slightly to higher angle ( $2\theta = 68.6^\circ$ ). The peaks are quite sharp with less broad bases indicating grain growth and increase in crystallinity of the deposits. The grain size of the deposit lies between 92-337 Å. The heat treatment at higher temperatures does not produce any further visible change in the structure.



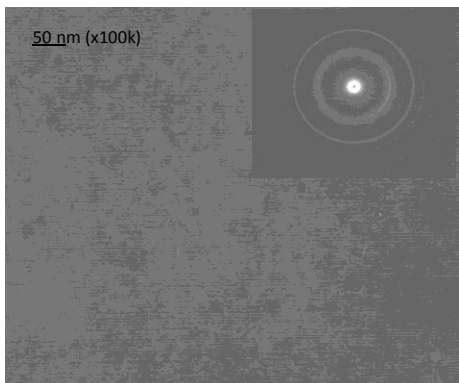
**Fig.4** XRD pattern for as-plated and annealed Ni-Co-P autocatalytic deposits

Fig. 4 shows XRD pattern for as-plated and annealed Ni-Co-P deposit. The XRD pattern for as-plated sample, shows one broad peak with a large amorphous band at  $2\theta = 62-75^\circ$  with a high background. The d-spacing at  $2\theta = 68.3^\circ$  corresponds to both f.c.c Ni(111) and cubic Co(100) and it is difficult to distinguish between these phases because of overlapping of the peaks. The grain size of the deposit was calculated using Scherrer formulae and found to be 23 Å. The data indicates that material is probably in a microcrystalline or amorphous state. The heat treatment at varying temperatures indicate that crystallization occurs at 325-350°C which is higher than that of Ni-P deposits and the deposit crystallizes to a matrix of metallic Ni and Ni<sub>2</sub>P<sub>5</sub> instead of Ni<sub>3</sub>P as observed in Ni-P with Ni(111) parallel to the deposit. This is consistent with the crystallization temperature reported by Sankara et al. that lies between 329-337°C [9]. The XRD pattern for annealing at 325°C shows overlapping peaks for Ni<sub>3</sub>P and hexagonal Ni<sub>5</sub>P<sub>2</sub>. The peak for hexagonal Ni<sub>5</sub>P<sub>2</sub> at the same temperature is also observed by Lee et al.[16] and Hur et al.[17]. The peaks for tetragonal Ni<sub>2</sub>P<sub>5</sub> are evident in XRD pattern for sample annealed at 400°C. This is again consistent with the results reported by Sankara et al.[9]. The patterns for the deposits annealed at 500-700°C show the appearance of strong peaks for Ni<sub>5</sub>P<sub>2</sub> in place of Ni<sub>12</sub>P<sub>5</sub> indicating a phase transformation in the deposits. Peaks for Co<sub>2</sub>P, CoP and Ni<sub>3</sub>P in these patterns are weak.

The bright field transmission electron micrograph with electron diffraction pattern as an inset of the as plated Ni-P is shown in Fig 5. The bright field image shows that the deposit is composed of very fine crystallites while the electron diffraction pattern indicates a series of rings corresponding to various Ni planes. These planes proceeding from the center are (111), (200), (220), (222), (311) and (420).

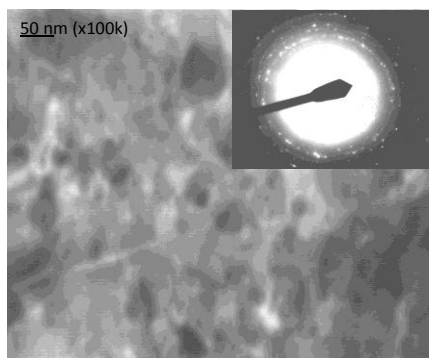
The bright field electron micrograph with electron diffraction pattern as an inset of the as plated Ni-Co-P deposit is given in Fig. 6. The bright field image shows very fine crystals while the diffraction pattern reveals a series of rings corresponding to various planes of Ni and Co. These planes proceeding from the center are Ni (111), Ni (200)/cubic Co(200), cph Co(102), cubic Co(220), cph Co(200), Cubic Co(222), Ni(311), and Ni(420).

These results indicate that the matrix is a mixture of fcc Ni, cph and cubic Cobalt.



**Fig.5** Bright field TEM micrograph with electron diffraction patterns of as-plated Ni-P deposits

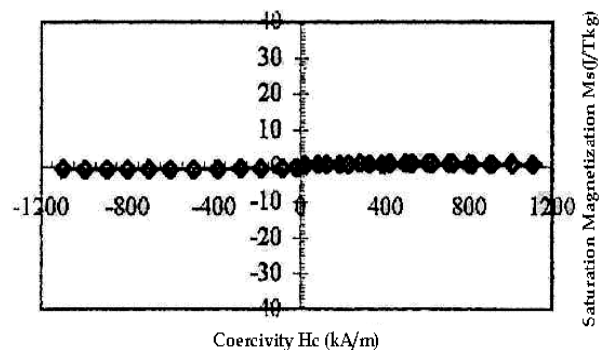
The bright field electron micrograph with electron diffraction pattern as an inset of the as plated Ni-Co-P deposit is given in Fig. 6. The bright field image shows very fine crystals while the diffraction pattern reveals a series of rings corresponding to various planes of Ni and Co. These planes proceeding from the center are Ni (111), Ni (200)/cubic Co(200), cph Co(102), cubic Co(220), cph Co(200), Cubic Co(222), Ni(311), and Ni(420). These results indicate that the matrix is a mixture of fcc Ni, cph and cubic Cobalt.



**Fig.6** Bright field TEM micrograph with electron diffraction patterns of as-plated Ni-Co-P deposits

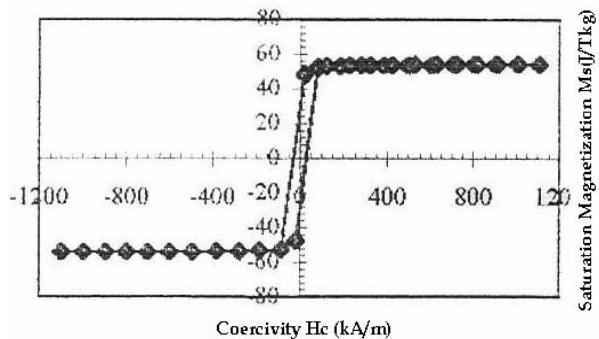
Fig.7 shows the curve for magnetic measurement on as plated Ni-P deposit. These results indicate that Ni-P deposit is almost non-magnetic in the as deposited condition. This result is consistent

with the work of Fields et al. [18] who reported that electroless Ni-P deposits with >10 wt % P (17 at %) are non magnetic in the as deposited condition. Bogenschutz et al [19] has reported that heat treatment at 400°C increased the magnetizability of electroless Ni-P deposits probably due to the formation of metallic Ni and weakly ferromagnetic phosphides.



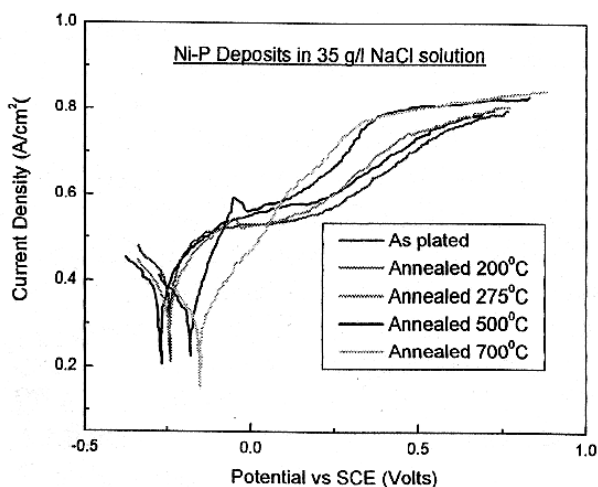
**Fig.7** Hysteresis curves for as-plated Ni-P deposit.

Fig.8 shows the curves for magnetic measurements on as plated Ni-Co-P deposit. Ni-Co-P deposit contains 57.154 at % Ni, 32.975 at % Co and 11.018 at % P. This deposit shows a saturation magnetization of 50 J/Tkg, coercivity close to 30 kA/m and a remanence nearly 30 J/Tkg in the as deposited condition. These values are higher than Ni-P deposits. Sankara et.al [9] has also reported a rise in saturation magnetization and remanence with the increase in Co content. Our results are consistent with the results reported by Rivero et al [20] who observed a linear rise in magnetic moment with the increase in Co content for Ni-Co-P amorphous ribbons obtained by electrodeposition.

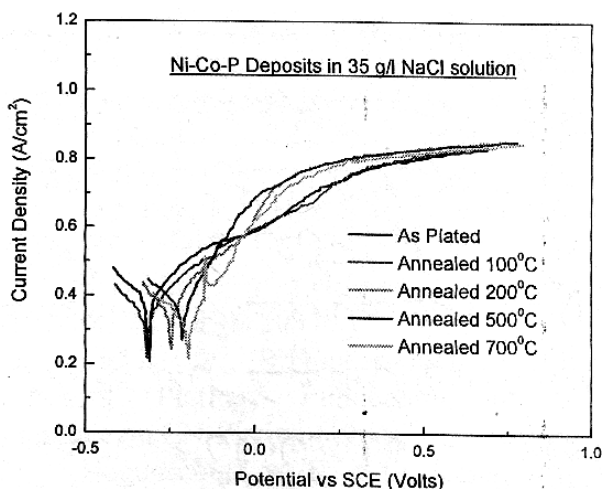


**Fig.8** Hysteresis curves for as-plated Ni-Co-P deposit.

Linear sweep voltammetry was carried out in 35 g/l NaCl at a sweep rate of 1 mV/sec to compare the electrochemical properties of the Ni-P and Ni-Co-P deposits. The current density-voltage curves are shown in Figs.9 and 10 respectively. The results show that Ni-P deposit is passive up to 200 mV in the as plated condition and after heat treatment up to 200°C. This passive behavior is assumed to be due to the formation of a stable oxide film nickel oxide or phosphorous oxide on the deposits during the potential sweeps. The deposits show a less passive behavior after annealing at 275-500°C which is assumed to be due to re-crystallization at these temperatures. A little peak appears in the curves at 275-600°C which indicates that some phase is formed which is active initially but quickly becomes passive.



**Fig.9** Electrochemical measurements of Ni-P deposits in 35 g/l NaCl solution



**Fig.10** Electrochemical measurements of Ni-Co-P deposits in 35 g/l NaCl solution

At 700°C the material is more active showing a rapid corrosion. These results are consistent with the work of Salvago et. al [21] who reported that the electroless Ni-P deposits passivate in 3.5 % NaCl up to 600 mV more anodic than the rest potential. We have achieved passivation up to 500 mV more anodic than the rest potential.

The current density-voltage curves for Ni-Co-P deposit show that in the as-deposited condition the deposit is passive up to + 300 mV than the rest potential and then it becomes active. The passive behavior is probably due to the formation of a passive film of nickel oxide/cobalt oxide/phosphorus oxide. The deposits annealed at 200-700°C showed little passivation which is assumed to be related to the re-crystallization of these deposits. It is evident that corrosion resistance of as plated Ni-Co-P deposit is better as compared to Ni-P as plated deposit. This is in agreement with the findings of Abdel et.al [22].

#### 4. Conclusions

1. Ni-Co-P exhibits a lower deposition rate as compared to Ni-P. This may be due to the fact that Ni possesses a higher catalytic activity than cobalt. Co forms a stable oxide with the dissolved oxygen that reduces effective Co ion concentration in the solution.
2. The P content in both type of deposits decreased with an increase of the pH. In Ni-P deposits Ni content is increased with the increase of the pH. In Ni-Co-P deposit Co content is increased and Ni content is decreased with the increase of the pH.
3. X-ray diffraction studies revealed that Ni-P and Ni-Co-P deposits are amorphous in the as plated conditions. Ni-P deposit crystallizes to a tetragonal Ni<sub>3</sub>P and metallic Ni after annealing at 275-300 °C. Ni-Co-P deposit crystallizes at 325-350 °C to tetragonal Ni<sub>12</sub>P and metallic Ni. This deposit re-crystallizes around 500 °C and Ni<sub>5</sub>P<sub>2</sub> appears in place of Ni<sub>12</sub>P.
4. The comparison of the magnetic properties revealed that Ni-P deposit is almost non-magnetic in the as deposited condition and remain non magnetic after annealing up to 100°C. However Ni-Co-P is fairly magnetic in

the as deposited conditions. This is consistent with the results reported by Rivero et al [20] who observed a linear increase in magnetic moment with increase in Co content for electrodeposited Ni-Co-P amorphous ribbons.

5. The electrochemical studies revealed that corrosion resistance of as plated Ni-Co-P deposit is better as compared to Ni-P as plated deposit.

## References

- [1] A. Brenner, G.E.Riddell, J.Res. NBS 37(1), (1946) 31
- [2] C.Y.Huang, W.W.Mo, M.L.Roan. Surf.Coat.Technol.184 (2004) 163-169
- [3] Y.Gao, L.Huang, Z.J.Zheng, H.Li, M.Zhu, Applied Surface Science 253 (2007) 9470-9475
- [4] Changdong Gu, Jianshe Lian, Guangyu Li, Liyuan Niu and Zhonghao Jiang, Surface & Coating Technology 197 (2005) 61-67
- [5] M.Bin-Sudin, A.Leyland, A.S.James, A.Matthews, J.Housden, B.Garside, Surf. Coat.Technol.81 (1996) 215-224
- [6] R.E.Miller, Plating Surf.Finish.74 (1987) 52-55
- [7] H.Ashassi-Sorkhabi, S.H.Rafizadeh, Surface and Coating Technology 176 (2004) 318-326
- [8] G.Lu, G.Zangari, Electrochem. Acta 47 (2002) 2969-2979
- [9] T.S.N Sankara Narayanan, S.Selvakumar and A. Stephen, Surface and Coating Technolgy, 172 (2003) 298-307
- [10] T.Osaka, Electrochim. Soc.139 (1992) 1311-1314
- [11] Takayuki Homma, Mitsuru Suzuki, and Tetsuya Osaka, J.Electrochem.Soc. 145(1) (1998) 134-138
- [12] D.H.Kim, K.Aoki, O.Takana, J.Electrochem.Soc. 142(11) (1995) 3763-3767
- [13] G.S.Alberts, R.H.Wright and C.C.Parker, J.Electrochemical Soc.113, (1997) pp113-117
- [14] A.Ahmad, S.Akhtar, A.A.Noshahi, Proceedings of International conference on frontiers of Advanced Engineering Materials, Lahore, Pakistan, (2004) 261-269
- [15] R.Tarozaitė, Z.Jusys, chemija (Vilnius) 10(1) (1999) 5
- [16] D.N.Lee, K.H.Hur, Scripta Mater. 40 (12) (1999) 1330
- [17] K.H.Hur, J.H.Jeong, D.N.Lee, J.Mater.Sci.26 (1991) 2037
- [18] Fields, W., R.Duncan and J.r.Zickraff: Electroless Plating. Publication of ASM Committee on EN-Plating (1984)
- [19] Bogenschutz, A.F., J.L. Joston and W. Mossinger: Galvanotechnik, 60 (1969) pp 507-510
- [20] G. Rivero, M. Multigner, J. M. Garcia, P. Crespo, A. Hernando, J. Magn. Magn. Mater. 177-181 (1998) 119
- [21] G.Salvago,D.Sinigaglia, G.Fumagalli, D.Continzenza and G.Taccani. Proc Interfinish 80, Tokyo, (1980) 162
- [22] A.Abdel Aal, A.Shaaban, Z.Abdel Hamid, Applied Surface Science 254 (2008) 1966-1971