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Galvanostatic Electrodeposition and Corrosion Characterization of Ni-Co Alloy Thin Films

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ABSTRACT

Electrodeposited NiCo alloy thin films on mild steel substrate were produced from sulphate baths containing citrate as complexing agent. The thin films were galvanostatically deposited at 2 mA/cm^2 for 20 min. The corrosion rate of the films was determined by tafel polarization method in three different corrosive medium i.e. NaCl, HCl and H_2SO_4. It has been found that Film composed from deposition bath having Ni^{2+}/Co^{2+} =0.33 showed the highest corrosion resistance. Scanning electron microscopy (SEM) and Energy dispersion X-Ray spectroscopy (EDAX) analysis revealed the morphology and elemental composition of thin films respectively. The XRD analysis confirmed the crystalline nature of thin films.

Keywords: Galvanostatic electrodeposition, thin film, Corrosion rate, XRD, SEM.

INTRODUCTION

Corrosion resistant alloy thin films[1] are receiving remarkable attention of researchers since a long period due to its consequential protective applications in automotive industry[2], sea water and marine industries, aviation and chemical process industry[3]. In present era, economical alloy thin film coatings are very important materials used to protect substrate from corrosion.

Iron group transition metal alloys possessed extreme corrosion resistance. Alloy of Zn-Co[4], Zn-Ni[5], Fe-Ni[6], Co-W [7] etc show higher resistance towards corrosion. When OCP applied. Few metals has been gone through preferential dealloying corrosion due to formation of oxyanions[8]. Addition of an electronegative element suppress the preferential dissolution of particular metal[9]. Ni alloys endow with excellent pitting and crevice i.e. localized corrosion resistance. They also exhibit tremendous strength[10], toughness, heat resistance properties, which makes them more suitable for practical applications[11]. Electrodeposition of Ni-Co alloy is studied by many researchers[12-14]. C.D. Grill *et al*.,[15] studied the effect of bath composition, current density and complexing agent on co-deposition process of Ni-Co. Ni-Co alloy co-deposition is anomalous[16-17] because in Co-Ni electroplating the reduction of cobalt occurs preferentially though it is less noble than nickel. This anomalous behavior of Ni-Co co-deposition is explained by the hydroxide suppression mechanism[18] and kinetic effect[19].

Present work aims to study galvanostatic co-deposition of Ni-Co alloy thin films on steel substrate and to analyze the effect of various cobalt concentrations in plating bath on the morphology, structure and corrosion parameter of deposited films.

MATERIALS AND METHOD

AR grade Nickel sulphate ($NiSO_4.6H_2O$), Cobalt sulphate ($CoSO_4.6H_2O$), Boric acid(H_3BO_3), Sodium sulphate(Na_2SO_4) and sodium citrate($Na_3C_6H_5O_7$) were used to prepare deposition solutions. The deposition solutions were prepared in deionized water. Deposition concentrations and parameters of various deposition baths are specified in table 1.

The electrochemical deposition and polarization experiments were carried out in Open circuit conventional three electrode cell galvanostatically. Mild steel plates (1cm x 1cm) were used as counter as well as working electrodes. MS plates were firstly cleaned with emery paper than washed with acetone and double distilled water consecutively. All potentials were referred to saturated calomel electrode. High precision digital multimeters were used for current and potential measurement and transistor based power supply was used for data acquisition.

Table1: Deposition bath composition and operating parameters

Composition & operating parameters	Deposition Bath I	Deposition Bath II	Deposition Bath III
$NiSO_4.6H_2O$	26.28 g/L (0.1M)	26.28 g/L (0.1M)	26.28 g/L (0.1M)
$CoSO_4.6H_2O$	26.31 g/L (0.1M)	52.62g/L (0.2M)	78.93g/L(0.3M)
H_3BO_3	12.37 g/L (0.2M)	12.37 g/L (0.2M)	12.37 g/L (0.2M)
Na_2SO_4	28.4 g/L(0.2M)	28.4 g/L(0.2M)	28.4 g/L(0.2M)
$Na_3C_6H_5O_7$	25.81 g/L(0.1M)	25.81 g/L(0.1M)	25.81 g/L(0.1M)
pH	3.0	3.0	3.0
Temperature	25° C	25° C	25° C
Ni^{2+}/ Co^{2+} ratio	1	0.5	0.33

The electrodeposition was done using galvanostatic method and the potential-time dependence for the deposition of NiCo alloy thin films on mild steel substrate obtained at constant current density 2 mA/cm^2 for 20 minutes.

The film thickness was estimated using relationship (1)

$$F.T.= (i *t * eq.wt.) / (F*D*A) \qquad (1)$$

Here, F.T . = film thickness

Eq.wt. = equivalent weight of deposited alloy
I = current density
t = time (second)
F = faraday's constant
D = density of alloy (gm/cm^3)
A = Area of substrate(cm^2)

The corrosion rate of NiCo alloy thin films was determined by Tafel Polarization curve. The corrosion rates were calculated using equation (2)

C.R. = (0.13 * Icorr * eq.wt.) / (D* A) ________ (2)

Here, C.R. = corrosion rate (MPY)
Icorr = corrosion current density (μA/cm^2)
Eq.wt.= equivalent weight of deposited alloy
D= density of alloy (gm/cm^3)
A= Area of substrate (cm^2)

The morphology and composition of thin films were investigated by FModel: JEOL JSM 5600 Scanning electron microscope (SEM) and EDS model: INCA Oxford. Crystalline phase of the deposited films were characterized by Bruker D8 Advance X-Ray Diffractometer (XRD) with a monochromatized CuKα irradiation (λ = 0.154 nm).

RESULT AND DISCUSSION

The binary alloy of Ni-Co prepared on a static current density. The co-deposition potential found out by current Vs potential graph and to achieve a smooth uniform alloy thin film galvanostatically, the suitable current for deposition was established by performing deposition at different current densities i.e. from 0.5mA/cm^2, 1 mA/cm^2, 2 mA/cm^2, 3 mA/cm^2 and 4 mA/cm^2. a uniform surface deposition was observed at 2 mA/cm^2 so all the depositions were accomplished at 2 mA/cm^2. The variation in potential with time is publicized in fig.1. The potential sharply increased in first few minutes than attained a steady value throughout the deposition with little change. The steady value indicated the nearly full surface coverage of substrate. The estimated film thickness of ni-co alloys are in μm range.

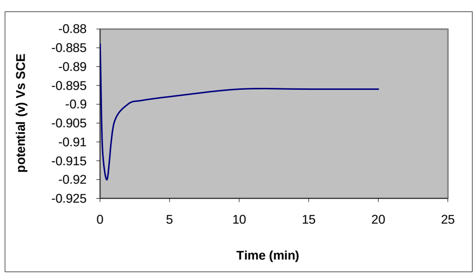


Fig. 1: Potential-Time graph of 0.10M Ni+0.20M Co alloy Thin film at 2 mA/cm^2

Polarization studies

The corrosion behavior of electrodeposited thin films on mild steel substrate was studied using Tafel polarization curve. The polarization studies were made by cathodic and anodic polarization data shown in **fig 2(a-c)**

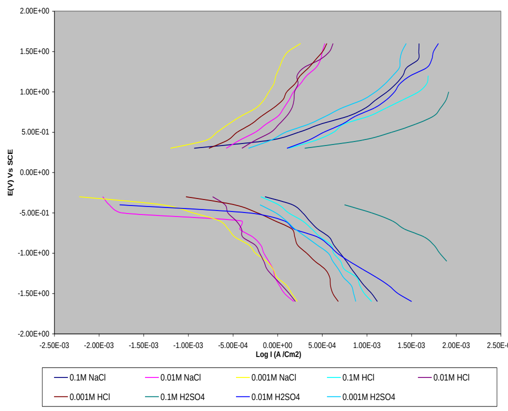


Fig.2(a) Tafel plot for 0.10M Ni-0.10M Co alloy thin Film

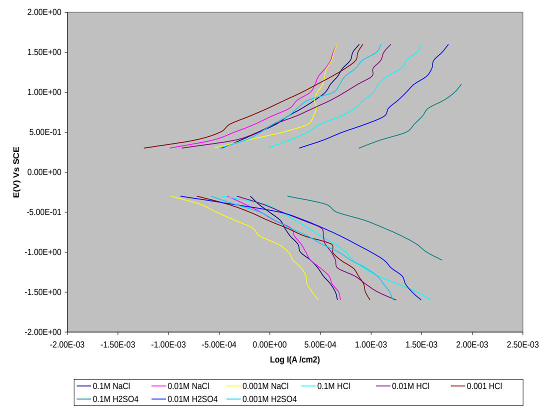


Fig.2(b) Tafel plot for 0.10M Ni-0.20M Co alloy thin film

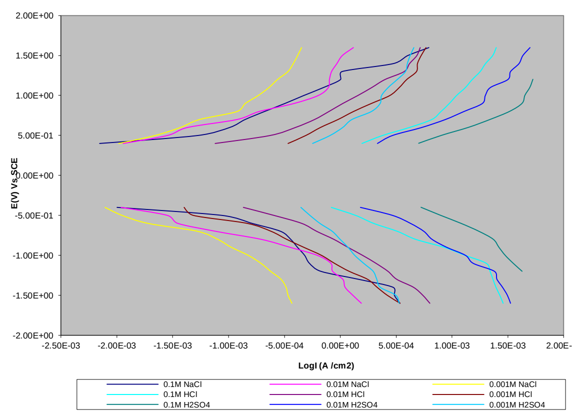


Fig.2(c) Tafel plot for 0.10M Ni-0.30M Co alloy thin film

The alloy thin films were tested in three different corrosive mediums i.e. HCl, H_2SO_4 and NaCl at three different concentrations. Table 2(a-c) shows the corrosion parameters of deposited films in different corrosive mediums respectively. It was found that as the concentration of Cobalt increased the corrosion rate is decreased in all corrosive mediums. Thus higher concentration of cobalt in alloy is beneficial for corrosion resistance.

Table 2(a): Corrosion Rate of electrodeposited NiCo alloy thin films in NaCl medium

Conc. of $NiSO_4.6H_2O$	Conc. of $CoSO_4.6H_2O$	0.1 M NaCl		0.01 M NaCl		0.001 M NaCl	
		I_{corr} (mA/cm^2)	Corrosion Rate (mm/year	I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)	I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)
0.10 M	0.10 M	0.2534	1.4541	0.1496	0.8585	0.0501	0.2875
0.10 M	0.20 M	0.2371	1.3606	0.1259	0.7225	0.0376	0.2158
0.10 M	0.30 M	0.1585	0.9095	0.1000	0.5738	0.0316	0.1813

Table 2(b): Corrosion Rate of electrodeposited NiCo alloy thin films in HCl medium

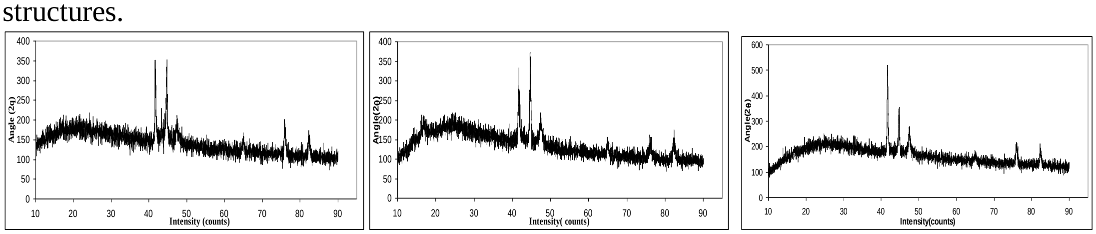
Conc. of $NiSO_4.6H_2O$	Conc. of $CoSO_4.6H_2O$	0.1 M HCl		0.01 M HCl		0.001 M HCl	
		I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)	I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)	I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)
0.10 M	0.10 M	0.5011	2.8755	0.1258	0.7219	0.0631	0.3621
0.10 M	0.20 M	0.2818	1.6171	0.0944	0.5417	0.0531	0.3047
0.10 M	0.30 M	0.1884	1.0811	0.0794	0.4556	0.0398	0.2284

Table 2(c): Corrosion Rate of electrodeposited NiCo alloy thin films in H_2SO_4 medium

Conc. of $NiSO_4.6H_2O$	Conc. of $CoSO_4.6H_2O$	0.1 M H_2SO_4		0.01 M H_2SO_4		0.001 M H_2SO_4	
		I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)	I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)	I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)
0.10 M	0.10 M	1.0593	6.0787	0.4732	2.7154	0.2113	1.2125
0.10 M	0.20 M	0.8913	5.1146	0.3350	1.9224	0.1884	1.0811
0.10 M	0.30 M	0.7943	4.5580	0.3162	1.8145	0.1413	0.8108

Structural analysis

Xrd of NiCo alloy thin films is shown in fig.3(a-c). The xrd contained sharp peaks indicated the crystalline nature of the films. the peaks obtained in xrd graphs are compared with the standard JCPDS data and found that the films are a mixture of FCC and HCP crystal structures.



(a) (b) (c)

Fig.3(a) XRD of 0.10M Ni-0.10M Co alloy thin film (b) XRD of 0.10M Ni-0.20M Co alloy thin (c) XRD of 0.10M Ni- 0.30M Co alloy thin film

It was observed that as the cobalt content increased in the films the HCP crystal structure became predominant indicated by the increased intensities of related peaks. The crystallite size is determined by Scherer equation (eq.3) which was found to be less than 25 nm.

Crystallite size

$$D = \frac{k\,\lambda}{\beta\, Cos\,\theta} \qquad (3)$$

λ = wavelength of incident beam (nm)
k= scherrer's constant
β= peak broadening (FWHM)
θ = scattering angle in radian

The dislocation density of thin films was calculated by eq 4.

$$\delta = 1/D \qquad (4)$$

here, δ= dislocation density
D=crystallite size

The crystallite size and dislocation density of electrodeposited NiCo thin films is shown in table 3.

Table 3 : XRD parameters for (111) hcp plane

S. No.	Conc. Of $NiSO_4.6H_2O$	Conc. Of $CoSO_4.6H_2O$	Ni^{2+}: Co^{2+} in deposition bath	Angle 2 θ	Interplaner spacing (d) (Å)	FWHM (β)	Crystallite size (nm)	Dislocation density (nm)
1	0.10 M	0.10 M	1:1	41.6285	2.1678	0.3192	24.8862	0.0402
2	0.10 M	0.20 M	1:2	41.7427	2.1621	0.4446	17.8697	0.0560
3	0.10 M	0.30 M	1:3	41.6666	2.1659	0.2890	27.494	0.0363

Morphology and compositional analysis

The SEM images of deposited thin films are shown in fig.4(a-c) It showed that the thin films are homogenous with smooth surface area and evenly covered the substrate surface. At higher magnification fig.4(b) showed the thorn like structured particles which agglomerated as the concentration of cobalt is increased(fig.4(c)). The EDAX analysis (Fig5(a-c)) confirmed the oxide alloy of NiCo. it is also observed that the EDAX of few thin films possessed traces of iron, sulphur and carbon which may be due to Mild steel substrate.

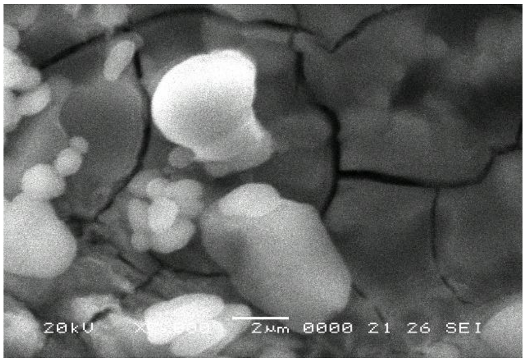


Fig.4(a) SEM of 0.10M Ni-0.10M Co Thin film

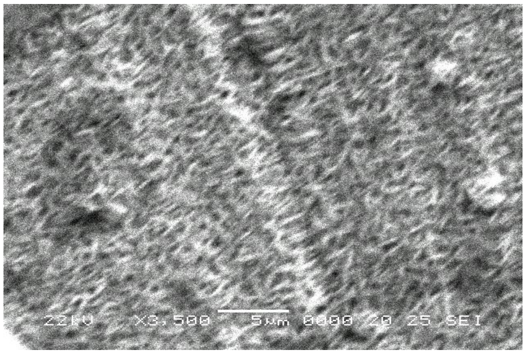


Fig.4(b) SEM of 0.10M Ni-0.20M Co alloy Thin film

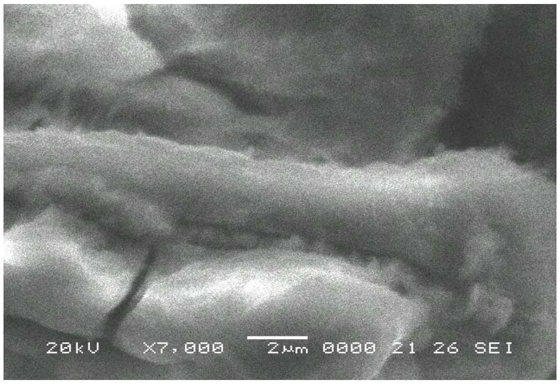


Fig.4(c) SEM of 0.10M Ni-0.30M Co alloy Thin Film

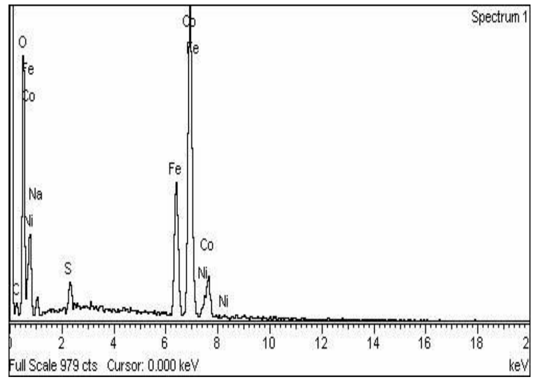


Fig.5(a) EDAX of 0.10M Ni-0.10M Co alloy Thin film

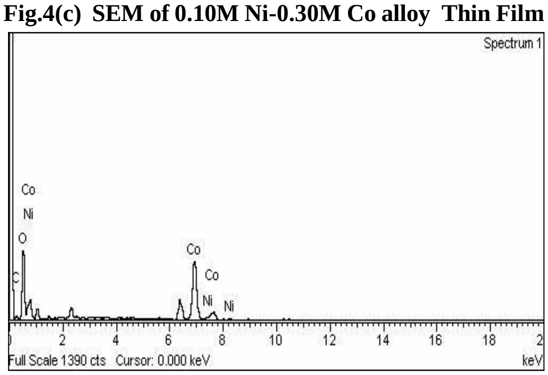


Fig.5(b)EDAX of 0.10MNi-0.20MCo alloy Thin Film

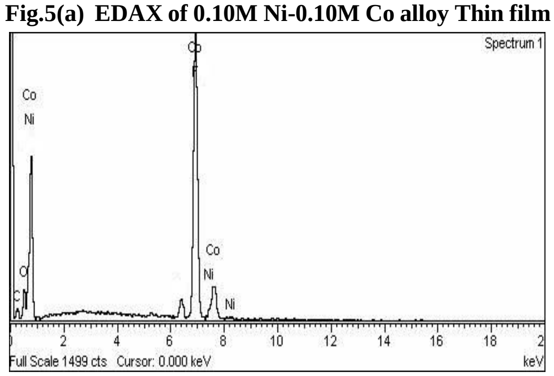


Fig.5(c) EDAX of 0.10M Ni-0.30M Co alloy Thin Film

CONCLUSION

The depositions of NiCo alloy thin films were achieved successfully from sulphate bath. The films are oxides in nature. The alloy thin films having higher cobalt content showed the best anticorrosive property in all three corrosive mediums. Deposited thin films have homogenous distribution on the substrate and have smooth surface area. With increasing concentration of cobalt in deposition bath the cobalt content in deposited film was also increased. The films contained thorn like structures which agglomerated on increasing concentration of cobalt. XRD analysis confirmed the crystalline nature of films which neither possessed pure Ni crystalline phase nor like pure Co crystalline phase but having hexagonal closed packed crystal structure along with face centered cubic phase which confirms the formation of NiCo alloy thin films.

REFERENCES

1. Lopez-Melendez,C., Bautista-Margulis, R.G., Garcia-Ochoa, E.M., Esparza-Ponce, H.E., Carreno-Gallardo, C., Gaona-Tiburcio, C., Uruchurtu-Chavarin, J.& Martinez-Villafane, A. Evaluation of Corrosion Resistance of Thin Films 304 Stainless Steel Deposited by Sputtering, *Int. J. Electrochem. Sci*., 7:1149-1159 (2012).

2. Todd, B. Nickel-Containing Materials in Marine and Related Environments, 25th annual conference of metallurgists (1986).
3. Elayaperumal, K. & Raja, V.S. Materials of Construction for Chemical Process Industry, Wiley Online Library, Retrieved from http://doi.org/10.1002/9781119043270.ch4 (1 may 2015).
4. Garcia, J.R., Logo, D.C.B. & Senna, L.F. Electrodeposition of Cobalt Rich Zn-Co alloy coating from citrate bath, *Mater. Rec.* (2014).
5. Wykpis, K., Popczyk, M. & Budniok, A. Electrolytic deposition and corrosion resistance of Zn-Ni coatings obtained from sulphate-chloride bath, *Bull. Mater. Sci*,34(4): 997-1001 (2011).
6. Alharthi, N., Sharif, E.M., Abdo, H.S. & Zein el Abedin, S. Effect of Nickel Content on the Corrosion Resistance of the Iron-Nickel alloy in concentrated hydrochloric acid picking solutions, *Adv. Mater. Sci. Eng.* 1-8 (2017).
7. Yapontseva, Y.S., Dikusar, A.L. & Kyblanovskii, V.S. Study of the composition, corrosion and catalytic properties of Co-W alloy electrodeposited from a citrate pyrophosphate electrolyte, *Surf. Eng. Appl. Electrochem.*,50(4):330-336 (2014).
8. Li, Y., Jiang, H., Huang, W. & Tian, H. Effects of peak current density on the mechanical properties of nanocrystalline Ni-Co alloys produced by pulse elecrodeposition, *Appl. Surf. Sci.*,254:6865-6869 (2008)
9. Schulz, R., Huot, J.-Y, Trudeau, M. L., Dignard-Bailey, L., Yan, Z. H., Jin, S., Lamarre, A., Ghali, E. & van Neste, A. Nanocrystalline Ni-Mo alloys and their application in electrocatalysis, *J. Mater. Res.*, 9(11):2998-3008 (1994).
10. Gopinath, K., Gogia, A.K., Kamat, S.V., Balamuralikrishnan, R. & Ramamurti, U. Tensile Properties of Ni-Based Superalloy 720Li: Temperature and Strain Rate effects, *Metallurgic Miner. Trans. A*, 39A:2340-2350 (2008).
11. Yoritaka, M., Yamamoto, Y., Hasegawa, Y. & Hokari, T. Automotive application of Advanced Superalloys, *JOM: J. Minerals met. Mater. Soc.* ,38(12):20-22 (1986).
12. Kuan-xin, H., Quan-fu, W., Xiao-gang, Z. & Xin-lei, W. Electrodeposition of Nickel and cobalt Mixed oxide/carbon nanotube Thin films and Their Charge Storage Properties, *J. Electrochem. Soc.*, 153(8):A1568-A1574 (2006).
13. Rafailovic, L.D., Minic, D.M., Karnthaler, H.P., Wosik, J., Trisovic, T. & Nauer, G.E. Study of the Dendritic Growth of Ni-Co Alloys Electrodeposited on Cu substrate, *Electrochem. Soc.*, 157(5):D295 (2010).
14. Ati, M.A., Khudhair, H., Dabagh, S., Rosnan, R.M. & Ati, A.A. Synthesis and Characterization of Cobalt doped Nickel-Ferrites Nanocrystalline by Co-precipitation Method, *Int. J. Sci. Eng. Res.*,5(9):927-930 (2014).
15. Grill, C.D., Kollender, J.P. & Hassel, A.W. Electrodeposition of cobalt-nickel material libraries, *Phys. Status. Solidi A*, 212(6):1216-1222 (2015).
16. Dolati, A., Sababi, M., Nouri, E., Ghorbani, M. A study of the kinetic of electrodeposited Co-Ni alloy thin films in sulphate solution, *Materials Chem. Phys.*,102(2-3):118-124 (2007).
17. Brenner, A. Electrodeposition of alloys, Academic press: New York,1 (1963).
18. Dahms, H. & Croll, I.M. The anomalous codeposition of Iron-Nickel Alloys, *J. Electrochem. Soc.*, 112(8):771-775 (1965).
19. Kamel, M.M. Anomalous codeposition of Co-Ni Alloys from glutamate baths, *J. Appl. Electrochem.*, 37(4):483-489 (2007).