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Influence of Magnetic Field on the Mass Electrodeposition and Investigation of Corrosion Rate on Ni and Ni-Co Alloy

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The electrodeposition of Ni and Ni-Co alloy from a nickel Watt's solution in the absence and presence of a perpendicular magnetic field applied to the cathode surface produced a depositing layer with fine grain structure. It is found that the mass deposition rate with perpendicular magnetic field was greater than the deposition in the absence of magnetic field. The difference between the mass deposition with the presence of perpendicular magnetic field (4.4T) and the absence of magnetic field was ≈ 0.08-1.22 mg cm^{-2} min^{-1}, if the current was 62 mA cm^{-2}. The deposited layers have been characterized with scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray (EDX) and electrochemistry corrosion evolution with EIS and Tafel plots.

Key Words: Magnetic-electrodeposition, Deposition rate, Corrosion rate.

INTRODUCTION

The alloy deposition carried out through depositing of two or more metal at the same time because of improve some properties such as finer grains and more corrosion resistance than the parents metal. The Ni-Co electrodeposition is one example of alloy fabrication. The deposition of face-centered- cubic (fcc) films Ni-Co alloy coating have been widely used as recording head materials in computer hard drive and mainly used in surface finishing industries for items such as printed circuit boards, wear resistant coating, corrosion resistance, electroformed laser mirrors and decorative coating[1,2].

The alloy electrodeposition anomalous point is that the metal with more noble (bigger E°) is preferential compared to lower noble metal. Emphasizing this point, Barnner[3] described and classified some of the anomalous phenomenon within alloys electrodeposition. Hessami and Tobias[4] developed a mathematical model with the mass transfer equations. They explained pH value effected on deposition rate. That means the great size metal-hydroxide can prevent the small size metal hydroxide and may be deposited faster. However, Plieth *et al.*[5] purposed deposition pioneer belonging to Kink site position. Furthermore, magnetic superimposed have main impact on mass transfer and changing the fabrication morphology. This paper presents the synthesis of Ni-Co alloy film under superimpose of perpendicular magnetic field. The perpendicular magnetic field exerted to cathode surface can effect on quantity (mass amount deposition) and quality (uniformity, corrosion resistance, *etc.*) within deposition[6-8]. In fact, the alloy composition can be control under magnetic field.

When there is no magnetic field, four forces can play roles as ion driving force, diffusion, migration and convection (natural and forced). The magnetic field causes five imposing forces such as paramagnetic force ($\vec{F}_P$), filed gradient force ($\vec{F}_B$), Lorentz force ($\vec{F}_L$), electrokinetic force ($\vec{F}_E$) and magnetic damping force ($\vec{F}_M$). Table-1 shows body magnetic forces expressed[9].

TABLE-1
TYPICAL FORCES ACTING IN AQUEOUS ELECTROLYTE

Force	Expression (N/m^3)
Driving force for diffusion	$RT\vec{\nabla}_c$
Driving force for electro migration	$zFc\vec{\nabla}V$
Driving force for forced convection	$\rho(r\omega)^2/2\delta_0$
Driving force for natural convention	$\Delta\rho\vec{g}$
Viscous drag	$\eta\nabla^2 v$
Magnetic damping force ($\vec{F}_M$)	$\sigma\vec{v}\times\vec{B}\times\vec{B}$
Field gradient force ($\vec{F}_B$)	$\chi_m cB\vec{\nabla}B/\mu_0$
Lorentz force ($\vec{F}_L$)	$\vec{j}\times\vec{B}$
Electro kinetic force ($\vec{F}_E$)	$\sigma_d\vec{E}_{II}/\delta_0$
Paramagnetic force ($\vec{F}_P$)	$\chi_m B^2\vec{\nabla}c/2\mu_0$

[T (K), c(mol m^{-3}), δ (m), z; (oxidation number), ν; (v), ρ; (kg m^{-3}), d; (m), ω; (rad s^{-1}), δ_o = 10^{-3} m, ∇p; (kg m^{-3}), η; (Ns m^{-2}), ν; (m s^{-1}), B; (T), χ_m; (m^3 mol), ∇B; (T m^{-1}), j; (A m^{-2}), σ_d; (C m^{-2}), E_{II}; (V m^{-1}), σ; (Ω^{-1} m)].

The presence of Lorentz force ($\vec{F}_L$) and electrokinetic force ($\vec{F}_E$) are due to the interaction of magnetic field with the electric current. The Lorentz force $\vec{F}_L$ = $\vec{j}\times\vec{B}$, is produced from the charge convey across line of magnetic flux radiation. The other three magnetic body forces noted in Table-1 are related to charge particle properties. Thematically, they depend on magnetic momentum (μ) and molar susceptibility (χ_m) value which arise from the number of unpaired valence electrons of elements. Table-2 shows magnetic momentum values of some metal ions[10].

The molar susceptibility for paramagnetic ($\chi_m > 0$) and diamagnetic ($\chi_m < 0$) and χ_m is maximal if magnetic field is placed perpendicular to electric current direction and *vice versa*[11]. This paper investigated the influence of cobalt and magnetic field on quantity and some quality properties of Ni-Co alloy.

TABLE-2
MAGNETIC MOMENTUM VALUE OF SOME METAL IONS WERE OBSERVED AND CALCULATED

Metal ions	3d electron	Terms symbols	μ_{eff} √(n(n+1))	μ_{eff} (obs)
Ni^{2+}	8	$^3F_4$	2.83	2.9-3.4
Co^{2+}	7	$^4F_{9/2}$	3.87	4.4-5.2
Zn^{2+}	10	$^1S_0$	0.00	0.00

EXPERIMENTAL

The deposition of Ni-Co films on copper substrate (0.001 cm × 1 cm × 2 cm) was performed using a conventional nickel Watt's solution that shown in Table-3. The pH was adjusted to 4 ± 0.1 by adding sulphuric acid. Current density operates 62 mA cm^{-2} with temperature set between 50-55 ºC. The cell made from Teflon (10 cm × 6 cm × 3 cm) which used for electrodeposition of Ni-Co in the presence and absence of magnetic field. Two copper plates held back to back as same distance to nickel anodes in which one of them was faced to magnetic zone while another one toward to the absence magnetic field zone, that shown in Fig. 1. The distance between the cathode and nickel anode was 4.5 cm. The stationary magnetic supply (4.44 T) was placed perpendicular to ions direction from anode to cathode.

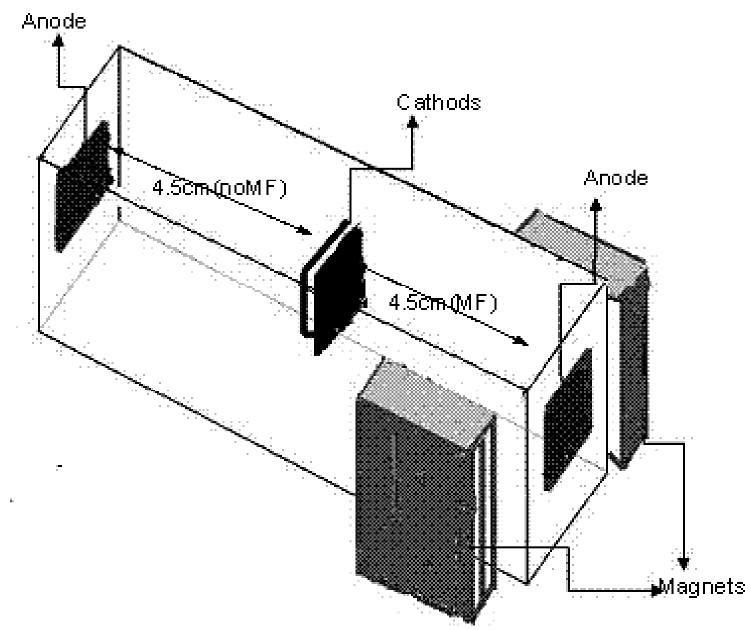

Fig. 1. Schematic diagram of the experimental set up. A Teflon cell (10 cm × 6 cm × 3 cm), consisting of two copper cathodes plate (2 cm × 1 cm) which are held apart by 4.5 cm from Ni anodes. One copper plate is perpendicular to the magnetic field (4.4T), second is perpendicular to the one without the magnetic field zone

TABLE-3
NICKEL WATT'S BATH COMPOSITION ELECTROLYTE FOR
Ni, Ni-Co DEPOSITED LAYER

Sample (g^{-1})	Component salts	Concentration	Deposition parameters			
			pH	Temp. (ºC)	Time (min)	Current density (mA/cm^2)
Ni-Co	$NiSO_4\cdot 6H_2O$	260	4	50-55	7	62
	$NiCl_2\cdot 6H_2O$	60				
	H_3BO_3	40				
	Thiourea	0.2				
	$CoSO_4\cdot 7H_2O$	X = 0, 2.3, 4.5, 6.7, 8.9, 11, 13.2, 15.3, 17.4, 19.5, 21.6				

RESULTS AND DISCUSSION

Mass deposition rate: Electrodeposition rate is the amount of metal deposited (g) per unit time (t)[12]. Many factors are imposed on the deposition rate such as electric potential, electrode parameters (material, surface state, shape, *etc.*) and electrolyte parameters (composition, concentration, conductivity, velocity, pH, *etc.*)[13]. The convection forces were used to enhance the deposition rate efficiency through stirring the electrolyte by air bubble, mechanical agitation or magnetic stirring. If magnetic field was placed during electroplating, it can also affect on ion convection. This flow is generated by Lorentz force ($\vec{F}_L$), which arises from the interaction between electrolytic current and magnetic field[14-16]. Fig. 2 shows mass deposition (g) *vs.* cobalt amount excise in nickel Watt's bath solution. Electrodeposition rate of Ni consist different amount of Co is measured through the weight addition. Cobalt is one of the elements that have excellent ferromagnetic properties[17]. Magnetic moment of Co is greater than Ni as shown in Table-2. Therefore, it can be one of the factors which pioneered cobalt deposition compared to nickel.

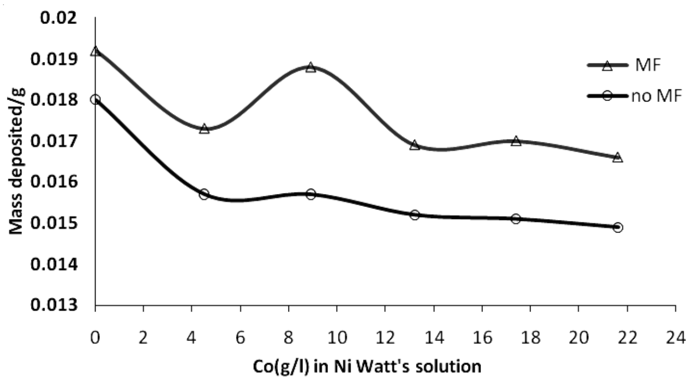

Fig. 2. Mass deposition of Ni and Ni-Co alloy on electrodeposited in the presence of magnetic field (MF) (4.4 T) and in absence of magnetic field, through different concentration of cobalt in Ni Watt's bath on copper plate (2 cm^2)

X-Ray diffraction (XRD) studies: Four representative samples were chosen for the XRD analysis, two of them were made without a superimposed magnetic field and another two samples made on superimposed magnetic field. The magnetic field was applied perpendicular (4.44 T) to electric current direction in deposition bath.

Four peaks could be seen for the range of 2θ analysis from 40° to 80°. Three are marked in the Fig. 3 which corresponds to Ni and Ni-Co structure in Fig. 3a (without superimposed magnetic field) and Fig. 3b (with superimposed magnetic field). The peak which is not marked belongs to copper (substrate).

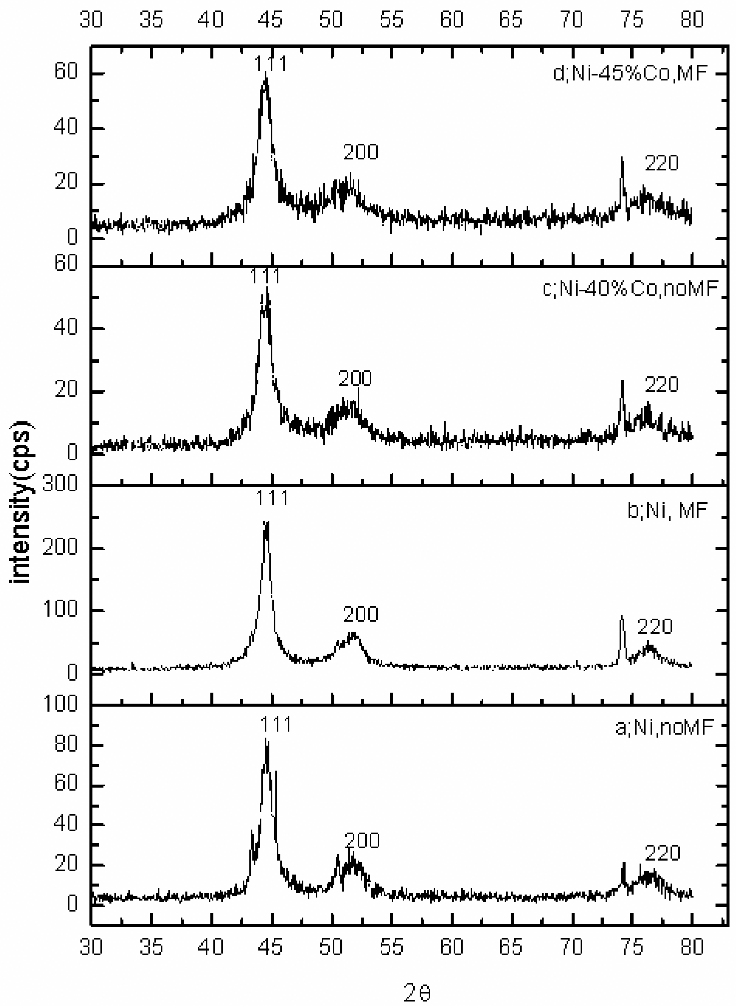

Fig. 3. X-Ray diffraction spectra; (a) electrodeposited nickel in the absence of a magnetic field (MF); (b) electrodeposited nickel in the presence of a magnetic field of 4.4T; (c) electrodeposited Ni-Co alloy in the absence of a magnetic field; (d) electrodeposited Ni-Co under magnetic field 4.4T

Comparing to intensity where obtained in Fig. 3(c,d), two factors can affect on intensity of peaks. The first is magnetic superimposed, which reduced intensity of peaks compare to absence of magnetic field. The second is amount of cobalt in Ni-Co alloys (*e.g.*, cobalt exist on alloy causes shorter signals peak on 111, 220 and 200) as shown in Fig. 3.

Each peak from the pattern is possible to evaluate the grain size with the Debye-Scherrer[18] eqn. 1:

$$l = \frac{0.9\lambda}{\text{FWHM} \cos\theta} \tag{1}$$

where λ is the wavelength, full width at half maximum (in radians). 'l' is the grain size and θ is the angle satisfying Brayy's law.

The strain was found that for our date with the eqn. 2[18]:

$$\text{Strain} = \frac{\text{FWHM}}{4\tan\theta} \tag{2}$$

Grain size and strain results are presented in Table-4 that grain size of nickel in superimposed magnetic field condition is smaller than without superimposed magnetic field. Cobalt amount reinforced to finer (smaller) grain size on (200) too. The fine grain (200) plan will induce the formation finer grain films, previously reported by Ispas *et al.*[19]. The strain value increased on finer films (200), so this can be another advantage of using superimposed magnetic field.

TABLE-4
XRD ANALYSIS OF ELECTRODEPOSITED Ni AND Ni-Co OBTAINED IN ABSENCE AND PRESENCE OF MAGNETIC FIELD OF 4.4 T

Compounds	Grain size			Strain		
	111	200	220	111	200	220
Ni	8.602	7.445	10.317	0.638	0.636	0.315
Ni (magnetic field)	8.832	4.867	12.762	0.617	0.980	0.225
Ni-40%Co	7.500	4.867	10.220	0.727	0.559	0.317
Ni-45%Co (magnetic field)	7.624	5.324	8.765	0.721	0.906	0.372

SEM and EDX analysis and characterization of Ni-Co films: Deposited films were investigated using SEM and EDX analyses which have illustrated the surface fabricated and alloy content, respectively. Interestingly, from EDX analysis, it was discovered that cobalt pioneered to deposit, compare to nickel despite concentration of Co is lower than the amount of nickel Watt's solution. The anomalous on alloy electrodeposition has been explained by Brenner[3]. Magnetic moment value of cobalt is more than nickel (Table-1), thus the more interaction could be happened between Lorentz force ($\vec{F}_L$) and electric flow on Co^{2+} and then arises the more cobalt deposition in perpendicular magnetic field. Fig. 4 shows the deposition rate of cobalt was increased compare to nickel, if the perpendicular magnetic field was applied.

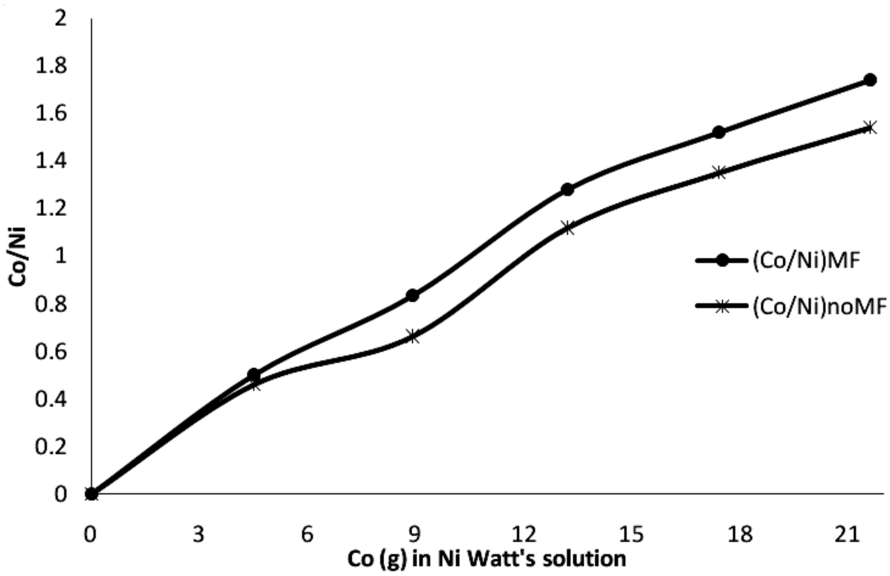

Fig. 4. Mass deposition rate of Co to Ni in the presence and absence of magnetic field (MF) (4.4 T) *via* different doses of Co in the nickel Watt's solution

Fig. 5 shows the SEM image of Ni and Ni-Co surfaces which electrodeposited at 62 mA cm^{-2} current density for 7 min using Ni Watt's solution as basic bath. Fig. 5(a) shows SEM image of Ni surface deposited in the absence and in the presence of magnetic field. It was found that Ni deposited under magnetic field becomes smoother than Ni deposited without magnetic field, in the same deposition operation condition. The presence of cobalt in nickel bath causes finer surface[20].

Fig. 5(b) shows SEM pictures of Ni and Ni-Co alloy deposit obtained by electrodeposition at 62 mA cm^{-2} current density in the presence of an applied magnetic field of 4.4 T. Interestingly, from SEM pictures, it was found uniformity and surface smoothness of fabricated layer has enhanced with the increasing cobalt salt and exert of perpendicular magnetic field to nickel Watt's bath. This results also investigated by Shannon *et al.*[20] in which the cobalt presence in nickel bath causes finer surface[21].

Corrosion studies: Dissolution of Ni and Ni-Co coated layers was investigated in 3.5 % seawater salinity[22]. The alternate current (AC) and direct current (DC) methods (Nyquist and Tafel plots, respectively) were measured by Autolab analyzer. The platinum wire and calomel (SEC) were used as counter and reference electrodes, respectively. The solution was carefully deaerated before measurement with nitrogen. In electrode impedance spectroscopy (EIS), the frequency range was set between 10 kHz-0.01 Hz. The general trend of the impedance is in agreement with expectation, as the impedance is smaller and corrosion rate is lower, as illustrated in Fig. 6(a,b). Polarization resistance (R_p) value is accessible in Nyquist and Tafel plots.

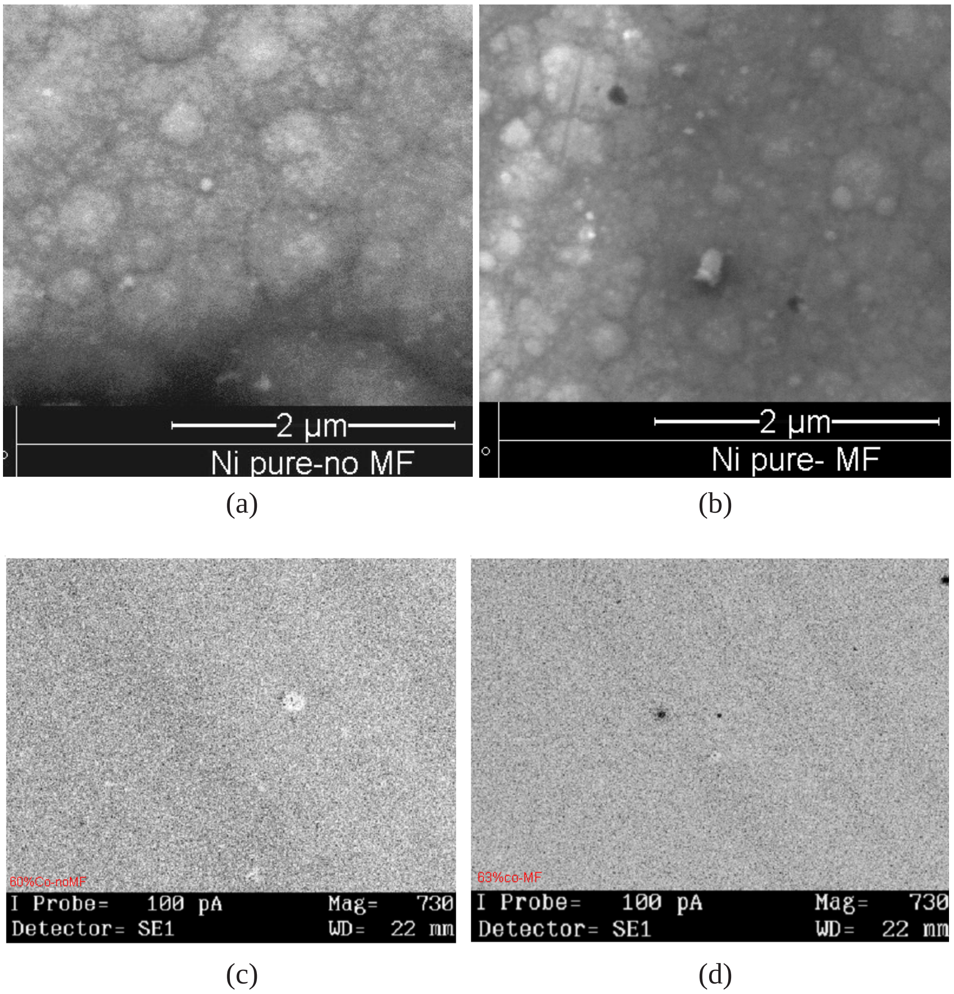

Fig. 5. SEM micrographs of Ni and Ni-Co deposits obtained at 62 mA cm^{-2} for 7 min nickel Watt's bath based on copper deposition; (a) nickel in the absence of magnetic field (MF); (b) nickel in the presence of a magnetic field of 4.4T; (c, d) Ni-Co deposited in same bath solution which; (c) Ni-Co in the absence of magnetic field; (d) in the presence of a magnetic field 4.4 T

Fig. 6(a) indicates the decreasing of the corrosion rate with increasing Co composite in deposited layer and shows that the resistance of corrosion rate on deposited layer under magnetic field is greater than fabricated layer in the absence of magnetic field. Kelley[23] has investigated the corrosion rate under magnetic field.

During the polarization of cathode (Tafel plot), the magnitude of current is controlled by diffusion of reactions towards the electrode as shown by Volmer Balter equation[24]:

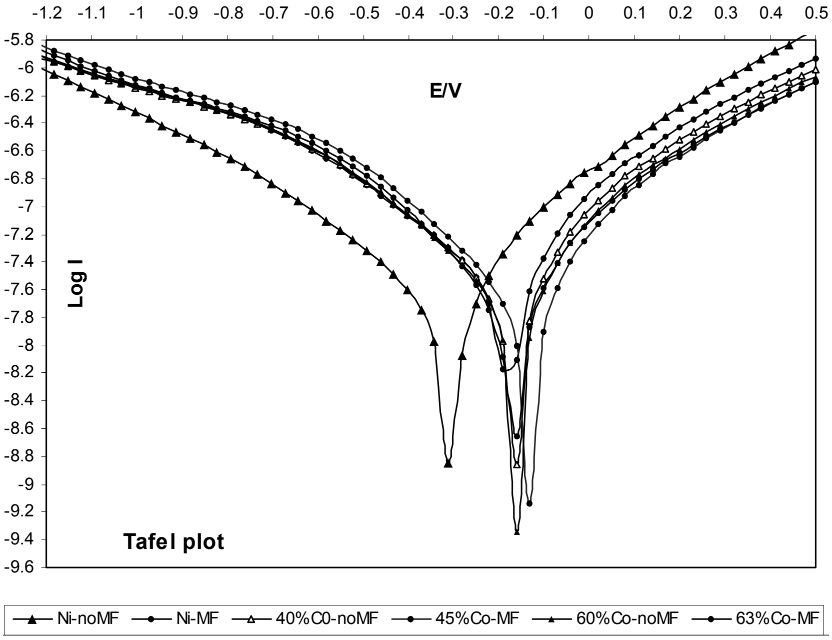

Fig. 6(A). Direct current corrosion analysis method; Tafel plots were shifted in presence and absence magnetic field. Plots were shifted through exist amount of cobalt in Ni-Co alloy

$$I_{corr} = \frac{b_a b_c}{2R_p(b_a + b_c)} \tag{3}$$

$$CR = 3.27 \times 10^{-3} \frac{I_{corr}(EW)}{\rho} \tag{4}$$

$$EW = \frac{1}{\sum \frac{nifi}{wi}} \tag{5}$$

b_a = The anodic Tafel slop, b_c = the cathodic Tafel slop. The dimension of R_p is ohm cm^2, ρ is the density of corroding material in g cm^{-3}, I_{corr} is µA cm^{-2}, Wi is the atomic weight of i^{th}, EW is equivalent weight, ni is the valance of i^{th} element of the alloy.

Fig. 6(b) shows that the R_p value is enhanced with increasing the amount of cobalt in textured layer under magnetic field. Whereas, fabricated plate without magnetic field shows more corrosion resistance in Fig. 6(b'). The Nyquist plots display both factors (Co and magnetic field) increased resistance polarization. Consequently, shows the corrosion resistance (CR) was increased in the presence of Co and perpendicular magnetic field.

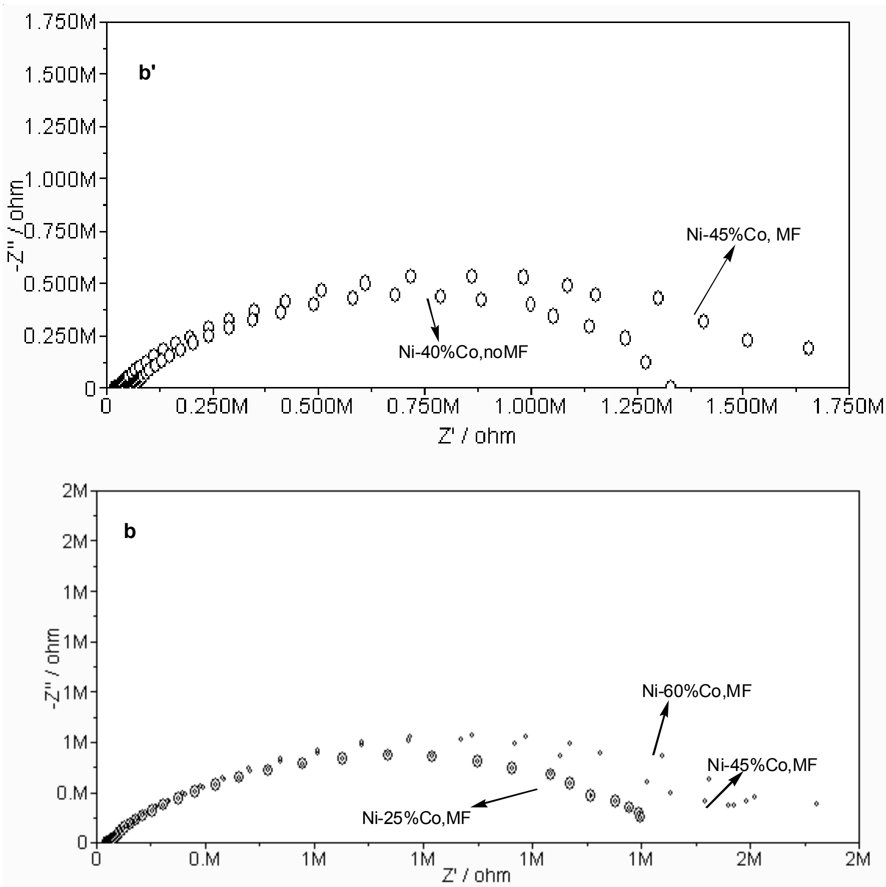

Fig. 6(b,b'). Alternative current corrosion analysis method (Nyquist plot); through polarization Resistance (R_p) *via* magnitude of semi circle diameter; (b) increasing R_p with increasing Co in Ni-Co alloy ; (b') the increasing of semi circle diameter in presence of magnetic field (MF) (4.4T) comparing the absence of MF for Ni-Co alloy deposition in same concentration of electrodeposition bath

Conclusion

The influence of a perpendicular external static magnetic field on electrodeposition of Ni and Ni-Co alloys was studied. The morphology of electrofabricated layers can be changed with both factors, increasing of cobalt in Ni-Co layers and applied perpendicular magnetic field. The morphology changing carried out from interaction between Lorentz force and electric field. The results obtained through this study can be summarized as follow: (i) The amount of metal deposition was increased with applied perpendicular magnetic field. Thus the efficiency of electrodeposition was enhanced and hydrogen revolution reaction reduced in aqueous solution. (ii) The grain size was refined in electroplated layers and then it carried out more dense layers with the presence of magnetic field. (iii) Both factors (Co and magnetic field) were created more uniform layers in Ni and Ni-Co alloys. (iv) The growth of cobalt fractal in electrodeposited layers was enhanced resistance polarization. Thus could be claimed both of the magnetic field and Co fractal were reinforced corrosion resistance in deposited layers.

The future work is influence of magnetic field on electrodeposition of Ni and Ni-Co in ionic liquids and organic solvents environment, with different doses of cobalt in nickel solution and different current density.

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