

Study of the Magnetic Field Effect on the Electrochemical Behavior of a Ni Electrodeposit

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In this work, using a Watts bath, nickel electroplating on AISI 1018 steel were obtained in the presence, and absence, of a magnetic field of 0.15 T, at 30 °C and 60 °C, during electrodeposition times of 7, 12 and 17 minutes. The coatings were characterized by X ray diffraction (XRD), Scanning Electron Microscopy (SEM), Vickers Microhardness (HV), Atomic Force Microscopy (AFM) and roughness measurements. The anticorrosion properties of the Ni coating were studied by electrochemical techniques of direct current (Linear polarization resistance, LPR) and alternating current (Electrochemical Impedance Spectroscopy, EIS). In general, for both temperatures, the magnetic field showed an influence in the grain size and hardness of the electrodeposits; it has also an influence in the preferential orientation of electrodeposited Ni particles at 30 °C, for the different times studied, however the anticorrosive properties decreased as a function of the electrodeposition time in the Watts bath. At 60 °C, it has not been observed a significant effect of the magnetic field on the orientation of the electrodeposited Ni particles, but it has been observed a strong effect on anticorrosion properties from impedance diagrams and capacitance behavior.

Keywords: AISI 1018 steel, magnetic field, corrosion, electrodeposit, nickel.

1. INTRODUCTION

Due to their high hardness, wear resistant and anticorrosive properties, Nickel and its deposits are very important in several industries (e.g. automotive, manufacturing, chemical, electronic, etc)[1]. The physical, chemical and mechanical properties of the electrodeposits depend on, among other factors, the interaction between the substrate and the electrolyte, the surface finish and, to some extent, on the molecular order at the moment of the electrodeposition[2]. Many disciplines that have experimented with the magnetic field effects, present this phenomenon as a particle arranger. For

having a better fuel efficiency and to reduce the production of contaminants, the automotive industry has implemented a magnetic device placed before the combustion chamber in order to orient the molecules before the combustion[3]. In heat exchangers it has been demonstrated that the use of a magnetic field has the peculiarity of modifying the crystalline structure of the calcareous deposits[4], which are very harmful for such systems, resulting in a loss of hardness of these deposits. In the field of the metallic coatings by using electric current, there are some unique phenomena when magnetic fields are superimposed to electrodeposition process due to the Lorentz forces, one is called the magnetohydrodynamic (MHD) effect, which has been reported by Calivar [5] as a convection phenomenon during the electrodeposition of copper thin films, explaining in that way an additional contribution to the material transport in aqueous media; other is the magnetocrystalline anisotropy effect, which is known as anisotropy of magnetization energy for different crystallographic axis[6], thus crystal orientation could be determined by crystal anisotropy factors when a magnetic field of sufficient strength is applied during an electrodeposition process.

AISI 1018 steel is a low carbon steel that is widely used in the industry because of its good machinability, weldability and low cost, despite its low corrosion resistance in various aggressive environments[7]; it is used for forged motor shafts, hydraulic shafts, and pump shafts as well as machinery parts, thus it is very important to protect this steel from the corrosive environments.

In this work it is studied the effect of the magnetic field, temperature and electrodeposition time on the physical (roughness, particle size, hardness and crystalline orientation) and electrochemical properties of Ni electrodeposition on an AISI 1018 steel.

2. EXPERIMENTAL PROCEDURE

The nickel electrodeposits were carried out on 10 cm x 2 cm plates of AISI 1018 steel. The steel plates were chemically cleaned following the procedure of the standard ASTM G1[8], then they were polished using SiC abrasive paper from 180 to 600 grit sizes.

For the electrodeposition, with and without magnetic field, it was used a power source GW Instek model GPR-3510HD, it was applied a constant voltage of 4 V in a Watts bath [9] with the following composition: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 340 g/l, $\text{NiCl}_2 \cdot 5\text{H}_2\text{O}$ 60 g/l, H_3BO_3 45 g/l. The electrodeposition was conducted in a pH of 3.0 at 30 and 60 °C during electrodeposition times of 7, 12 and 17 minutes for each temperature. All electrodepositions were carried out at static conditions.

The magnetic field was generated by Nd magnets with a flux density of 0.15 T each one, the north pole was placed near to the anode (nickel, purity 99.9 %) and the south pole near to the cathode (AISI 1018 steel).

The average thickness of the obtained electrodeposits were calculated by[9]:

$$T = \frac{W}{A \cdot D} \quad (1)$$

where T is the thickness in cm, W is the deposited mass in g, A is the area on which the deposit was performed (cm^2) and D is the density of the deposited material, in this case, for nickel corresponds

to 8.9 g/cm³.

The obtained electrodeposits were electrochemically evaluated in a 3 % wt. NaCl solution by DC and AC electrochemical techniques such as Linear Polarization Resistance (LPR) and Electrochemical Impedance Spectroscopy (EIS) with a potentiostat Bio-logic model SP-150 coupled to a desk station. LPR electrochemical measurements were carried out according to ASTM G59-91. EIS measurements were carried out at open circuit potential, (E_{corr}), in a frequency range from 100 KHz to 10 mHz with a 10 mV/rms signal perturbation and 7 points per decade. Both DC and AC techniques were carried out in a three electrode electrochemical cell at room pressure and temperature to Veracruz City. As working electrode a nickel electrodeposited plate was used in static conditions and as a counter electrode a graphite bar (large 10 cm x 0.6 cm diameter). All over potentials were referred to a Ag/AgCl saturated reference electrode.

The surface of the electrodeposits was studied with a SEM Jeol JSM 6610LV and with an AFM Asylum Research model Cypher; the roughness was obtained with a roughness tester Mitutoyo model SurfTest-402.

The XRD characterization was carried out using a Siemens D-5000 diffractometer, with a Cu K α ($\lambda=1.54178$ Å) radiation at 35 KV and 25 mA. The crystallite, or grain, size for nickel electrodeposits was calculated using the Scherrer's equation[10]:

$$D = \frac{K\lambda}{FWHM \cos \theta} \quad (2)$$

where D is the crystallite size in nm, $FWHM$ is Full Width at Half Maxima in 2θ radians, K is a constant with a value of 0.94, and λ is the X-ray wavelength (0.154 nm). The preferred orientation of the deposits was obtained by the following texture coefficient ($TC_{(hkl)}$)[11]:

$$TC_{(hkl)} = 100 \cdot \frac{\frac{I_{(hkl)}}{I_{0(hkl)}}}{\sum_{i=1}^n \frac{I_{(hkl)}}{I_{0(hkl)}}} \quad (3)$$

where $I_{(hkl)}$ and $I_{0(hkl)}$ represent the X-ray diffraction intensities of (hkl) planes of nickel electrocoatings and the standard nickel powder, respectively, n is the number of diffraction peaks. In this case, n is 4 for (111), (200), (220) and (311) crystal planes. When TC values of each plane are the same, it indicates a preferred-free orientation.

Microhardness was tested on the surface of nickel coatings by a Mitutoyo Vickers hardness machine with a load of 10 g during 20 s, the average microhardness was calculated from five test values.

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM images of the Ni deposits obtained at 30 °C (a, b, e, f, i, j) and 60 °C (c, d, g, h, k, l) in the presence (WMF) and absence (NMF) of the magnetic field as a function of the

electrodeposition time (7, 12 and 17 minutes). Independently of the time and temperature, it is seen that in the presence of the magnetic field the nickel deposited films are more homogeneous than absence magnetic field. It is seen some traces of possible bubbles (Figure 1 and l) produced during the electrodeposition process by the hydrogen evolution reaction ($2H^+ + 2e^- \leftrightarrow H_2 \uparrow$) as a result of pH solution.

The AFM images (Figure 2) shows clearly that at 30 °C the shape of the electrodeposited particles is very well defined in the presence of the magnetic field, however at 60 °C this effect is not observed suggesting a negative effect at this temperature. In this figure, it seems that the particle size is a function of the electrodeposition time, this is corroborated by the grain size obtained by the XRD analysis, as it is seen in Figure 3 where it is noted that the magnetic field at both temperatures, 30 °C and 60 °C, has an effect in reducing the grain size with respect to the electrodeposits obtained at the same temperature, during the same period of time but in absence of the magnetic field.

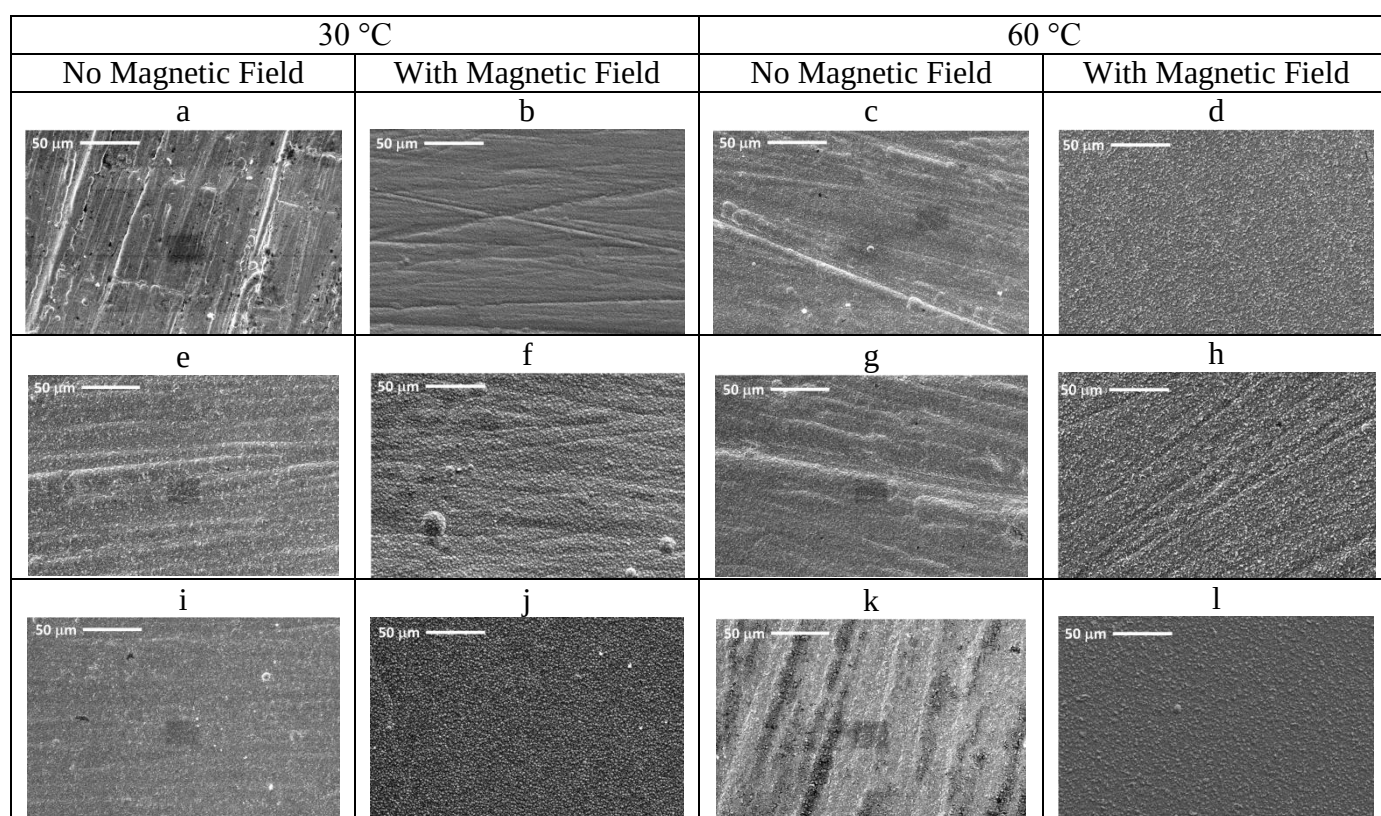


Figure 1. SEM Micrographs of the electrodeposits obtained at 30 °C and 60 °C during 7 minutes (a, b, c, d), 12 minutes (e, f, g, h) and 17 minutes (i, j, k, l).

In general, at 30 °C and 60 °C, particle size increase with electrodeposition time as it can be seen in Figure 3. This effect is better observed at 30 °C (with and without magnetic field) than at 60 °C maybe due to the rise of entropy of molecules involved giving an erratic behavior. It is important to note, a similar decrease in the grain size reported by Matsushima et al. in electrodeposition of iron and copper[12], where Magnetic field effect in the grain size decrease has been also observed. Nasirpour

[13] obtained, in absence of a magnetic field, grain sizes of 30, 36 and 41 nm, depending on the electrodeposition current flows, on Ni films electrodeposited from Watts bath with a pH of 3.7 at 45 ± 0.5 °C, thus, it seems that also the pH of the Watts solution has an effect, even if it appears slight, on the grain size; in the present case, the electrodeposits were performed at pH of 3.0 and the larger crystallite size, 38 nm, was obtained at 60 °C during 12 minutes in absence of the magnetic field.

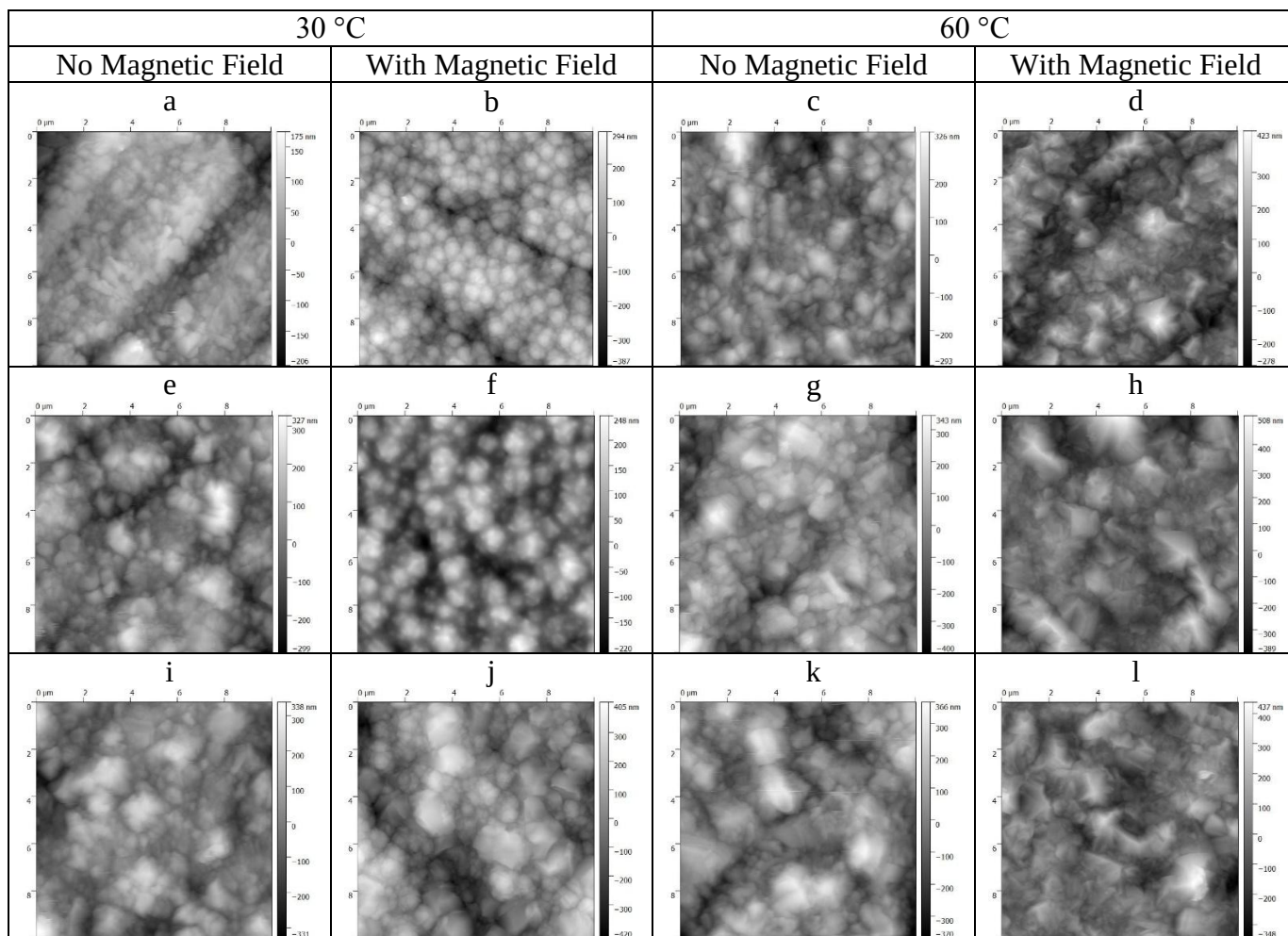


Figure 2. AFM images of the electrodeposits obtained at 30 °C and 60 °C during 7 minutes (a, b, c, d), 12 minutes (e, f, g, h) and 17 minutes (i, j, k, l).

Figure 4 shows hardness behavior (NMF and WMF) of the electrodeposits of nickel as a function of time at both, 30 °C and 60 °C. It is clearly noted a lower hardness when magnetic field is present, this applies for both temperatures tried.

It seems that the evolution of the HV does not follow a specific pattern, the exception is the case of the electrodeposits obtained at 30 °C in presence of the magnetic field, where the hardness decreases as the electrodeposition time increases, thus it seems that in this condition it is a relation between the hardness and the grain size, since the grain size increase (Figure 3) lead to the HV decrease, however, the relation does not appear to be linear as the Hall Petch relation[14]. It is important to note that in all the cases the HV obtained is higher than that of the conventionally electrodeposited nickel coating (130-200 HV)[9].

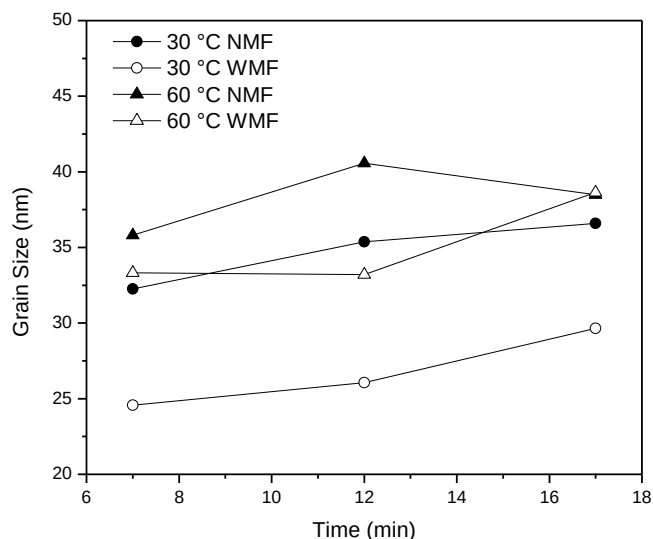


Figure 3. Grain size the electrodeposits as a function of the electrodeposition time at 30 °C and 60 °C in absence (NMF) and presence (WMF) of a magnetic field.

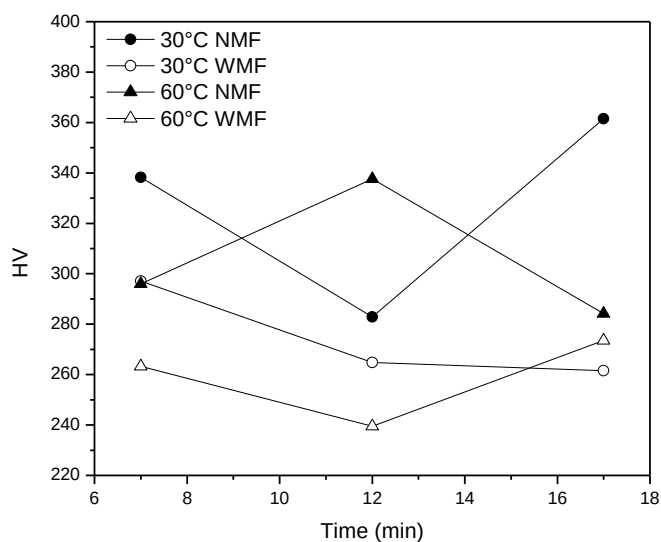
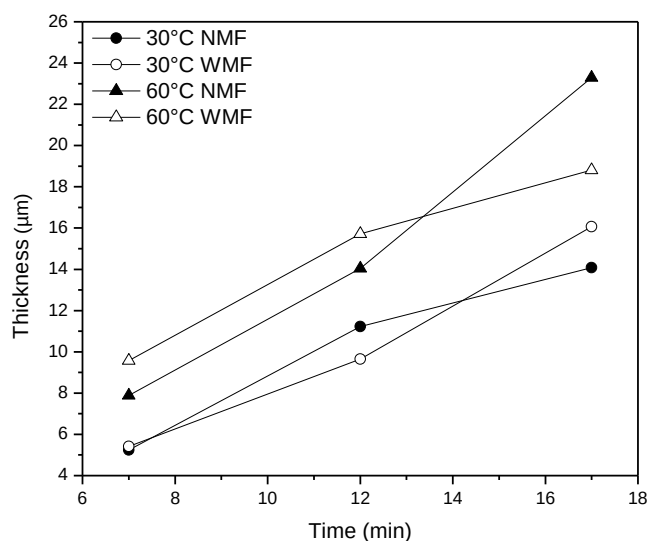


Figure 4. Vickers Microhardness (HV) as a function of the electrodeposition time at 30 °C and 60 °C in absence (No MF) and presence (With MF) of a magnetic field.

Analyzing experimental data presented in Table 1 (roughness and thickness), in general it could be said that the electrodeposits made in presence of the magnetic field are less rough than the ones made in the absence of the magnetic field at the same temperature and electrodeposition time; it is also observed that the thickness is a function of the electrodeposition time and the temperature of the electrodeposit, being thicker the ones obtained at 60 °C during an electrodeposition time of 17 minutes (see Figure 5). The thickness increase of a electroplating as a function of the electrodeposition time is an expected behavior that has been largely reported in the literature[15].

Table 1. Roughness and thickness of the electrodeposits obtained at 30°C and 60°C in presence and absence of magnetic field.

Time (min)	30 °C				60 °C			
	No Magnetic Field		With Magnetic Field		No Magnetic Field		With Magnetic Field	
	Roughness (μm)	Thickness (μm)	Roughness (μm)	Thickness (μm)	Roughness (μm)	Thickness (μm)	Roughness (μm)	Thickness (μm)
7	0.4	5.24	0.3	5.42	0.7	7.89	0.4	9.58
12	1.3	11.23	0.5	9.65	1.8	14.05	0.6	15.72
17	1.1	14.08	1.6	16.07	0.8	23.29	0.5	18.81

**Figure 5.** Thickness of Ni electrodeposit as a function of the electrodeposition time at 30 °C and 60 °C in absence (NMF) and presence (WMF) of a magnetic field.

The EIS measurements were acquired in order to relate the thickness with the corrosion protection capacity of the electrodeposits obtained. Additionally, this technique allows determining the capacitor formed at the interface metal-electrolyte[16],[17]. The capacitance values, reported in Table 2, were determined from the Brug's equation[18]:

$$C = Q^{1/\alpha} [R_s^{-1} + R_{ct}^{-1}]^{\alpha-1/\alpha} \quad (4)$$

where:

C = Capacitance (Farads)

Q = Brug constant

α = Linear parameter from log f vs log Z_{im}

R_s = Electrolyte resistance (Ohms)

R_{ct} = Charge transfer resistance (Ohms)

Impedance experimental data at NMF and WMF are presented in Figure 6 and in Figure 7, respectively, as Nyquist diagrams. High impedance corresponds to better corrosion properties. Generally speaking, as a function of electrodeposition time, both 30 and 60 °C at NMF condition show

an increase in impedance explained by an increase in thickness (see Table 1). At the same time, according to equation (5), an increase in thickness leads to a decrease in capacitance values. Focusing us in Table 2, we observe a decrease of capacitance, as a function of time, for NMF condition. This could be explained considering the deposit thickness increment as a function of the electrodeposition time, as reported in Table 1 and as per equation (5).

$$C = \frac{\varepsilon \varepsilon^0 A}{\delta} \quad (5)$$

where:

ε^0 = Vacuum permittivity

ε = Dielectric material

A = Area of the Plates

δ = Thickness

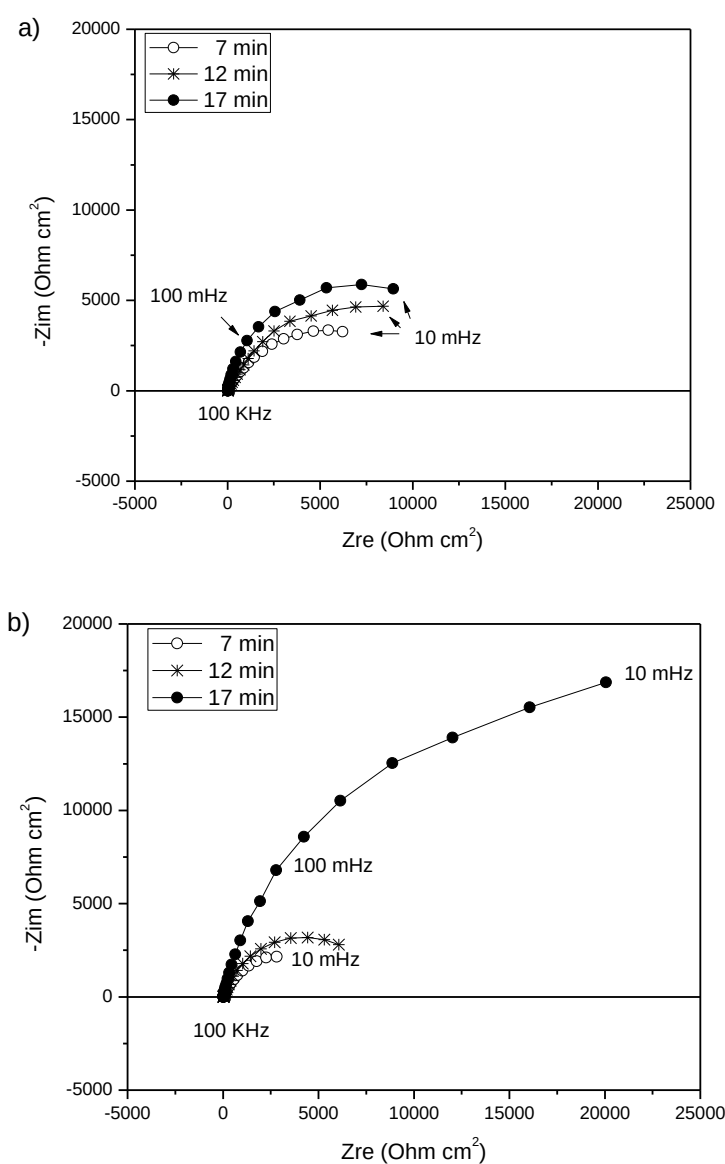


Figure 6. EIS diagrams at NMF condition of nickel electrodeposits as a function of electrodeposition time at a) 30 °C, b) 60 °C

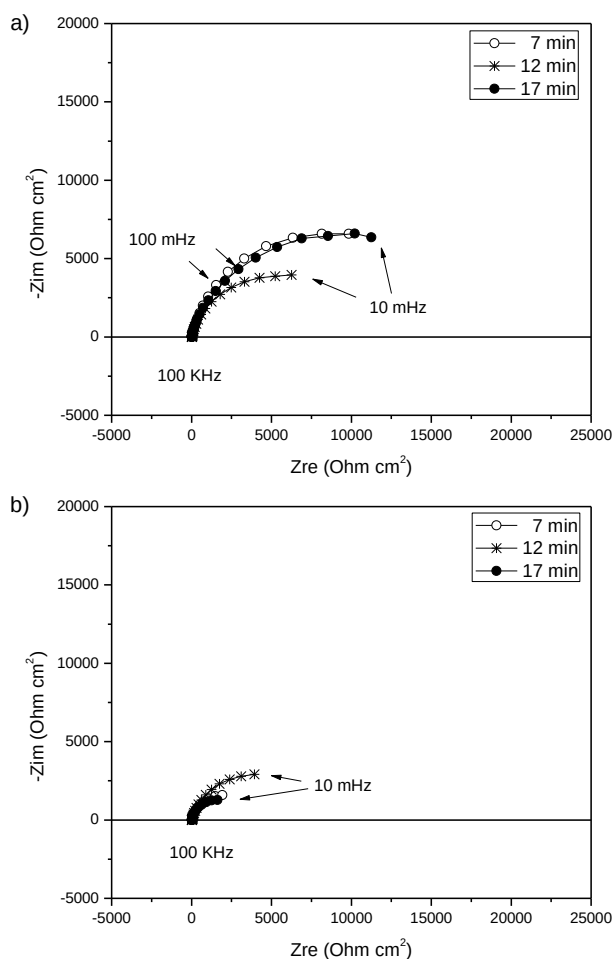


Figure 7. EIS diagrams at WMF condition of nickel electrodeposits as a function of electrodeposition time at a) 30 °C, b) 60 °C.

Table 2. Capacitance of the electrodeposits obtained at 30°C and 60°C in presence and absence of magnetic field.

Time (min)	30 °C		60 °C	
	No Magnetic Field	With Magnetic Field	No Magnetic Field	With Magnetic Field
	Capacitance (μF)	Capacitance (μF)	Capacitance (μF)	Capacitance (μF)
7	33.0	30.9	59.9	75.4
12	27.5	46.8	37.8	91.5
17	21.5	36.2	31.4	43.8

By the other side, from equation (6), decreasing the capacitance values leads to higher impedance. Regarding Table 2, capacitance values at NMF decrease when electrodeposition time increase leading to impedance increase as can be seen in Figure 6a and Figure 6b. Considering Figure 7 and Table 2, WMF at 60°C condition has a random impedance behavior that could not be explained

with the capacitance behavior expressed by equation (6).

$$Z(\omega) = \frac{R}{1+j\omega CR} \quad (6)$$

where:

Z = Impedance (Ohms-cm²)

ω = Angular frequency (Radians per second)

R = Resistance (Ohms)

j = Complex number

C = Capacitance (Farads)

Figure 7 shows that EIS diagrams obtained at 60 °C in WMF condition (Figure 7b) presents a significant decrease with respect to NMF condition (Figure 6b). It is generally known from literature [19] that the impedance decrease indicates that Corrosion Rate (CR) has increased. The literature recognizes that the mass transfer experiments an increase in presence of a magnetic field [20]. Wang et al. [21] state that in presence of a magnetic field the Ni dissolution is function of the applied potential. At the activation region, the dissolution current decreases whilst at higher potentials the current increases; this suggests that the magnetic field exerts a convection force that promotes or facilitates the oxidation reaction of the system.

As it has been said before, for the same period of time, we observe a hardness decrease in presence of magnetic field. This behavior could be explained by the increase of the porosity in presence of the magnetic field as a result of the electroplating process. In absence of the Magnetic field (NMF condition), at 30 °C and 60 °C we clearly observe that capacitance decreases as a function of the electrodeposition time (or the thickness increase), however, in WMF condition capacitance presents a random behavior at both temperatures, nevertheless, it seems to be a mixed function of both, thickness and hardness. It is well know that an increase of area or /and of the dielectric material could be also the responsible of the capacitance increase. In our case, it could be possible an increase of the electroplated area if magnetic field would have an effect on the polarization for covering a higher area. Wang et al [21] state that magnetic field may affect both, mass and electric charge transport. In our case, it seems that magnetic field affects both process, and its effect is stronger at 60 °C, where we could have a higher exposed area due to the porous evidenced by the decrease of hardness. This suggests that the anticorrosive properties do not only depend on the thickness that was gained during the electrodeposition but also in the arrangement of the cations during the electrodeposition step. The results of Ferreira et al [22] using a magnetic field for cooper electrodeposition shows that magnetic fields of low intensity allow more ordinated atomic arrangements than high intensity magnetic fields.

From EIS measurements it is possible to determine the Corrosion Rate (CR), only if the experimental response intersects at the real impedance axe when the frequency tends to zero ($f \sim 0$). However, in the present work is not possible to determine CR from EIS data because experimental response not intersects real impedance axe. In order to determine CR's, LPR electrochemical technique

was used. In Figure 8 and Figure 9 we present the experimental results obtained from the LPR technique for NMF and WMF conditions respectively. In Table 3 we report the E_{corr} and R_p values determined from Figure 8 and Figure 9; the CR and R_p values were computed using Ec-Lab® electrochemistry software.

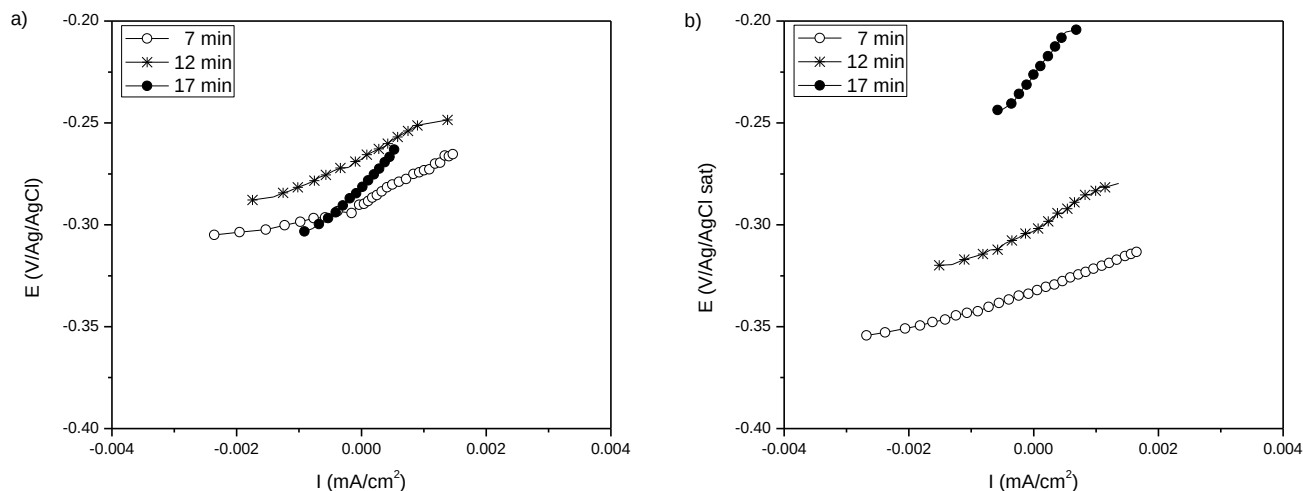


Figure 8. LPR experimental data at NMF condition of nickel electrodeposits as a function of electrodeposition time at a) 30 °C, b) 60 °C.

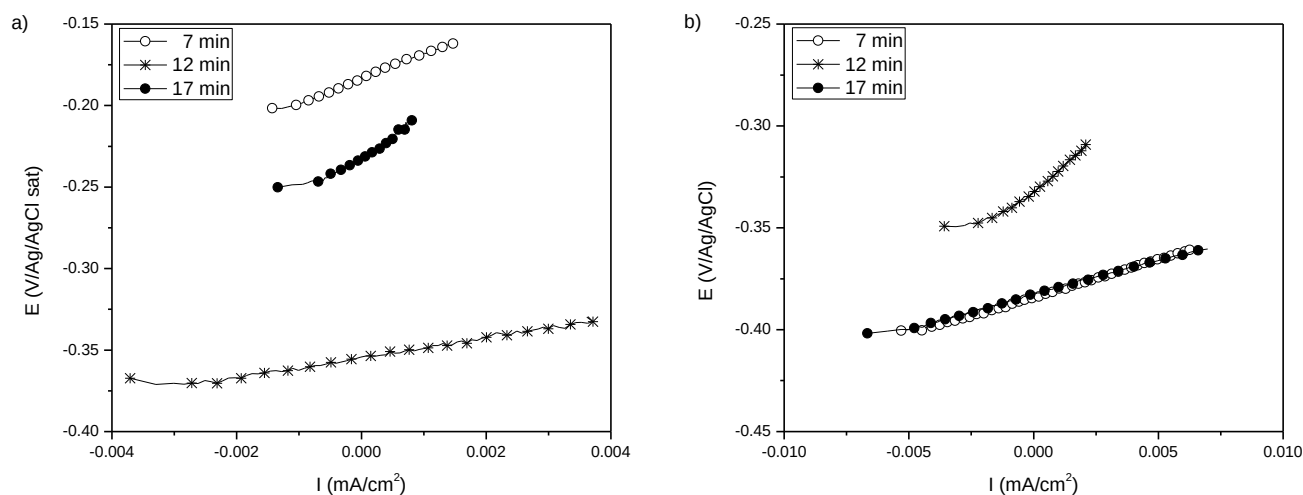


Figure 9. LPR experimental data at WMF condition of nickel electrodeposits as a function of electrodeposition time at a) 30 °C, b) 60 °C.

Table 3. Potential and Polarization Resistance experimental values at 30 °C and 60 °C in presence and absence of magnetic field.

Time (min)	30 °C				60 °C			
	No Magnetic Field		With Magnetic Field		No Magnetic Field		With Magnetic Field	
	E_{corr} (VAg/AgCl)	R_p (KΩ)	E_{corr} (VAg/AgCl)	R_p (KΩ)	E_{corr} (VAg/AgCl)	R_p (KΩ)	E_{corr} (VAg/AgCl)	R_p (KΩ)
7	-0.290	10.799	-0.183	17.116	-0.334	6.735	-0.384	3.990
12	-0.268	14.960	-0.355	10.823	-0.303	8.435	-0.332	8.150
17	-0.281	15.010	-0.233	18.015	-0.226	49.061	-0.383	3.586

In Figure 8 and Table 3 we observe for NMF condition an increase of the R_p value as a function of electrodeposition time for both temperatures, similarly to the increase of impedance observed in Figure 6 as a function of electrodeposition time. By the other side, in Figure 9, corresponding to WMF condition, we do not observe such tendency, however, the slope, as a function of time, has the same behavior observed in Figure 7, which is an aleatory behavior. The increase of slope in LPR graphs means an increase in CR. Focusing us in the R_p values reported in Table 3, we observe that they are the lower ones.

In general, Figure 10 shows that CR increases in the presence of the magnetic field, which is the same observed before in the impedance diagrams presented in Figure 6b and Figure 7b.

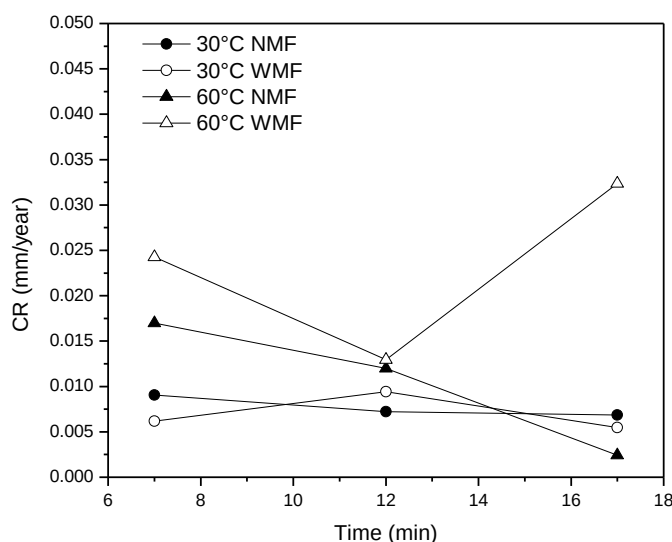


Figure 10. Corrosion rate (CR) as a function of the electrodeposition time of nickel at 30 °C and 60 °C in presence (WMF) and absence (NMF) of a magnetic field.

Figure 11 shows the XRD patterns (in relative intensity) and the TC of the electrodeposits obtained at 30 °C; it can be seen that in this conditions and in presence of a magnetic field the higher intensity corresponds to the plane (111), having also the higher TC, which means that the electrodeposits produced in the presence of the magnetic field has this preferred orientation, whilst the samples prepared in absence of the magnetic field even if they present the higher intensity either in the plane (111) or in the plane (200), the TC shows that they have a (200) preferred orientation; it is also noticeable that in presence of the magnetic field the plane (220) has higher TC values than the electrodeposits obtained in absence of the magnetic field during the same period of time.

Figure 12 presents the XRD patterns (in relative intensity) and the TC of the electrodeposits obtained at 60 °C; it can be seen that the higher intensity peak or TC is not a function of the magnetic field or the deposition time, however it is seen a slight effect of the magnetic field in the decrease of (220) and (311) TC's with respect to the coatings obtained during the same electrodeposition times in absence of the magnetic field.

According Hu [1], the plane (111) of Ni presents more active sites/activities for both the hydrogen responses and the Ni (III)/ Ni (II) transition, thus it is inferred that the (111) preferred

orientation induced by the magnetic field at 30 °C promotes the corrosion of the Ni electrodeposit, which is corroborated by the CR results presented in Figure 10.

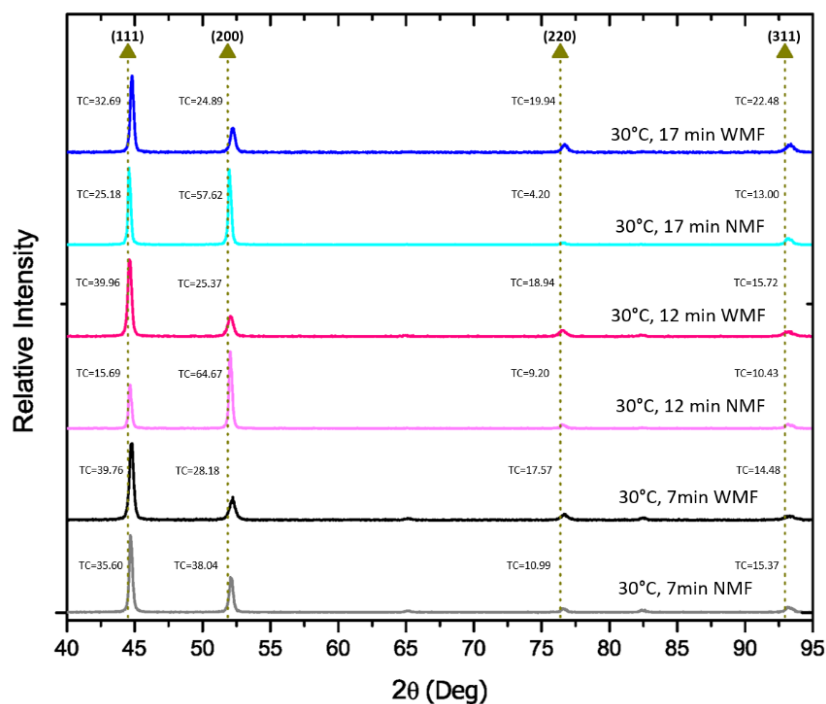


Figure 11. X ray Diffraction patterns and Texture coefficients (TC) of the electrodeposits made at 30 °C in absence (NMF) and presence (WMF) of a magnetic field.

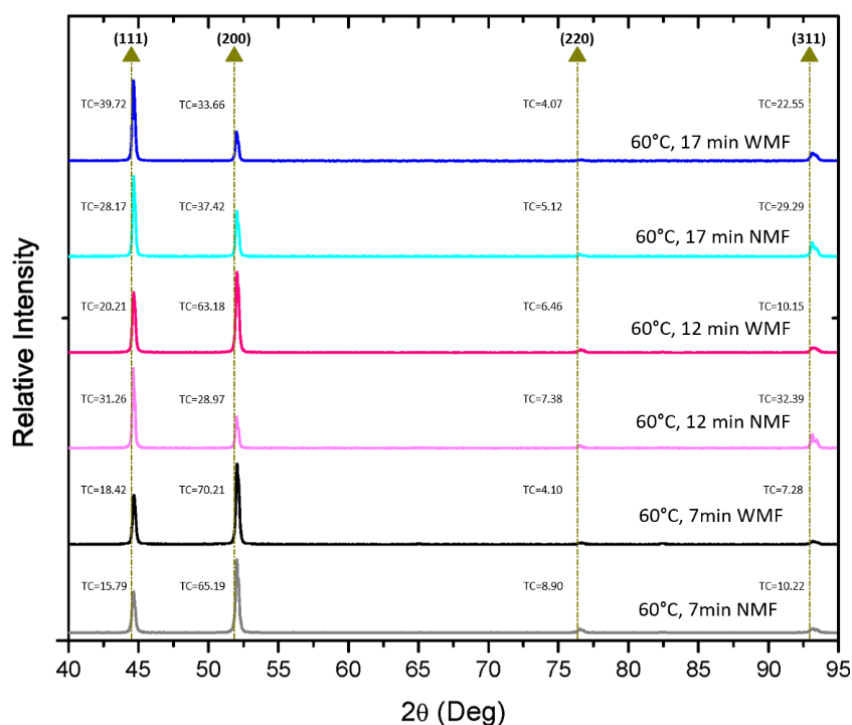


Figure 12. X ray Diffraction patterns and Texture coefficients (TC) of the electrodeposits made at 60 °C in absence (NMF) and presence (WMF) of a magnetic field.

By the other side, Hu [1] also shows that the activation energy of the hydrogen evolution reaction is greater for the (111) preferred orientation than for the (200) orientation; in our case, for the electrodeposits produced at 60 °C it is observed in the Figure 10 that the (200) preferred orientation is present in the deposits with the higher CR (7 minutes with and without magnetic field and 12 minutes with magnetic field), having the greater CR the electrodeposit obtained in presence of the magnetic field during 7 minutes, which coincide with the higher TC of the plane (200). This behavior could be explained by the hydrogen evolution reaction, which is promoted in the course of the electrodeposition when Ni is deposited preferentially on the (200) plane, which produce bubbles during the process, leading to a porous coating; in the case of the electrodeposits obtained at 30 °C, as we saw before, it is not observed the same CR behavior in the deposits that have the higher TC for the plane (200), which could be due to the fact that the hydrogen evolution reaction is a thermally activated process, that is more facilitated at 60 °C than at 30 °C, thus it is probable that the deposits obtained at 30 °C are less porous than the ones produced at 60 °C, which agree with the previous observations on hardness and capacitance.

4. CONCLUSIONS

It has been observed that in NMF condition the anticorrosion properties of the electrodeposits are essentially dependent of thickness whilst in WMF, the anticorrosion properties are independent of thickness, quantity of electrodeposited mass.

In WMF conditions, it was observed an increase of the mass transport; however, it was not related with an improvement of the anticorrosive properties of the electrodeposit. Thus, in this work the magnetic field had an effect in both, the mass transport and the electric properties of the deposits obtained.

Magnetic field produces a reduction of grain size, roughness and hardness of electrodeposits of Ni.

At 30 °C, magnetic field induces a (111) preferential orientation, which is more vulnerable to corrosion.

At 60 °C, magnetic field produces an impedance decrease which leads to Corrosion Rate (CR) increase.

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References

1. Chi-Chang Hu, Chiou-Yi Lin, Ten-Chin Wen, *Materials Chemistry and Physics*, 44 (1996) 233-238.

2. Biao Lv, Zhenfeng Hu, Xiaohe Wang, Binshi Xu, *Surface & Coatings Technology*, 270 (2015) 213-131.
3. J. Torres, “Sistemas de ahorro de energía marca FES ®”, Slide, México, 25 slides (2000).
4. A. González, *Revista Cubana de Física*, 25 (2008) 101-105.
5. L. Calivar, G. González, A. Soba, G. Marshall, *Revista de la Asociación Física Argentina*, 23 (2011) 56-59.
6. H. Matsushima, T. Nohira, I. Mogi, Y. Ito, *Surface and Coatings Technology* 179 (2004) 245–251
7. F. Depenyou Jr., A. Doubla, S. Laminsi, D. Moussa, J.L. Brisset, J.-M. Le Breton, *Corrosion Science*, 50 (2008) 1422- 1432.
8. ASTM G1. Standard practice for preparing, cleaning and evaluating corrosion test specimens. Anexo A1: Chemical cleaning procedures (2011).
9. G.A. Di Bari, “Electrodeposition of Nickel” in *Modern Electroplating*, 5th edition, S. Mordechay, M. Paunovic Eds., John Wiley & Sons. EUA (2010) 79-114.
10. B.D. Cullity & S.R. Stock, *Elements of X-Ray Diffraction*, 3rd Ed., Prentice-Hall Inc., 2001, p 167-171.
11. E.A. Pavlatou, M. Raptakis, N. Spyrellis, *Surface & Coatings Technology*, 201 (2007) 4571-4577.
12. H. Matsushima, A. Bunda, W. Plieth, S. Kikuchi, Y. Fukunaka, *Electrochimica Acta* 53 (2007) 161–166.
13. F. Nasirpouri, M.R. Sanaeian, A.S. Samardak, E.V. Sukovatitsina, A.V. Ognev, L.A. Chebotkevich, M.-G. Hosseini, M. Abdolmaleki, *Applied Surface Science*, 292 (2014) 795- 805.
14. M. K. Cho, J. W. Cho, J. H. Wu, J. U. Cho, Y. J. Choi, Y. K. Kim, *Current Applied Physics*, 10 (2010) 57-59.
15. W. Blum, G. Hogaboom, *Galvanoplastia y galvanotecnia*, McGraw Hill. México (1992).
16. R. Cottis, S. Turgoose, *Electrochemical Impedance and Noise*, NACE International (1999).
17. S. Tait, *An introduction to electrochemical corrosion testing for practicing engineers and scientists*, PairODocs Publications. Wisconsin, EUA (1994).
18. G. Brug, G. Van den Eeden, M. Sluyters-Rehbach, J. Sluyters, *Journal Electroanalytical Chemistry*, 176 (1984) 275-295.
19. K. Hladky, L. M. Callow, J. L. Dawson, *British Corrosion Journal*, 15 (1980) 20-25.
20. Z. Lu, D. Huang, W. Yang, J. Congleton, *Corrosion Science*. 45 (2003) 2233.
21. L. Li, W. Wang, C. Wang, S. Chen, *Electrochemistry Communications* 11 (2009) 2109–2112.
22. L Ferreira, B. y Colnago, *Copper electrodeposition studies using in situ time domain NMR*, lecture presented at the XXVI Congress of the International Society of Electrochemistry (2013) Queretaro, Qro., Mexico.