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Electrodeposition of nickel plates on copper substrates using PC y PRC

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ABSTRACT

Electrodeposition processes using direct current (DC) require the use of additives to control deposit structure and properties as well as current distribution. The Pulse Current (PC) and Pulse Reverse Current (PRC) techniques improve the properties of deposits based on an appropriate selection of the parameters involved. This research evaluates the influence of cathodic time (t_{on}), anodic time (t_{rev}), relaxation time (t_{off}), and voltage on the resistance to corrosion of nickel deposits using the PC and PRC techniques. Test were conducted in a dynamic manner, employing a rotating system with Watt's solutions as the electrolyte and copper substrate electrodeposited on zamak as cathodes. Measurement of the grain size was conducted using Atomic Force Microscopy. Protection level against corrosion was evaluated by polarization curves and Electrochemical Impedance Spectroscopy. Important results include the formation of uniform deposits showing fine grain and excellent protection against corrosion.

Keywords: Pulse Current (PC); Pulse Reverse Current (PRC); Nickel electrodeposition; Protection against corrosion.

1 INTRODUCTION

Metal electrodeposition is a process whose objective is to alter the surface characteristics of a given material. It has been used extensively to protect different types of elements from the action of corrosive agents, in order to enhance their resistance to abrasion and erosion and obtain metallic surfaces with specific finishing aspect [1, 2]. Among the wide range of electroplating materials available, nickel is widely used in processes such as steel plating and in the manufacturing of copper and zinc alloys due to its excellent protection against corrosion and to the good superficial characteristics it exhibits. Industrial processes are always in the vanguard of technological progress which, in turn, contributes to obtain outstanding improvements in all production lines. This has motivated several researchers to study the consequences of supplying Direct Current (DC) on resistance to corrosion of nickel plates compared to the use of other alternative currents such as Pulse Current and Pulse Reverse Current. A refining in size grain of crystals can be obtained by applying these latter techniques. [3, 4, 5]. Zinc nanocrystalline coatings obtained by the application of pulse current have exhibited greater resistance to corrosion than galvanized steel with Direct Current. [6, 7]. A similar effect can be found in nickel nanocrystalline deposits obtained after the application of pulse current. In this case, lower corrosion velocities and a decrease in grain size have been found. [8, 9, 10].

2 EXPERIMENTAL DEVELOPMENT

Nickel coatings were electrodeposited on zamak cathodes that were previously plated with copper measuring 8 microns thick. A Watt's-type bath was employed ($NiSO_4$*6H_2O 300g/l, $NiCl_2$*6H_2O 75 g/l, H_3BO_3 50 g/l) plus an additive that acted as a refiner of the grain size. All electrodeposition experiments were developed at 65°C, using three different techniques: DC, PC and PRC. A 30-ampere hardware controlled by a software designed by Labview was used in electroplating. This software allows the management of both anodic and cathodic voltages and their corresponding duration times. The electrodeposition time in each case was 75 minutes considering that 99%-pure nickel anodes were utilized. Conditions corresponding to each test are described in the Table 1.

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Table 1: Parameters utilized in obtaining nickel electroplates

Technique		V_{on} (V)	V_{off} (V)	Vtrev (V)	t_{on} (ms)	t_{off} (ms)
DC	1	10	-	-	-	-
	2	8	-	-	-	-
PC	1	10	2	-	100	100
	2	8	2	-	100	100
PRC	1	10	-	-2	100	10
	2	10	-	-4	100	10
	3	10	-	-2	100	40
	4	10	-	-4	100	40

Determination of grain size and surface analysis of deposits were conducted using a Scan Probe Microscope (SPM) in the mode of Atomic Force Microscopy of Contact (AFM-C) from Park Scientific Instruments, model AutoProbe CP. Different scans at a velocity of 1 Hz and 256 x 256 pixels were conducted. Electrochemical characterization was completed by using the Electrochemical Impedance Spectroscopy (EIS) and polarization measures (Tafel), at room temperature (24°C), using a cell composed by the work electrode with an exposed area of 1 cm^2, an Ag/AgCl reference electrode and a platinum wire as a counter-electrode in a solution of HCl at 1% in distilled water. Bode's diagrams were obtained by performing frequency scanning ranging from 0.1 Hz to 10 KHz, using a sinusoidal signal amplitude of 10 mV. Tafel diagrams were obtained at a scan velocity of 0.5 mV/s with voltages ranging from -0.25V to 1V using an exposed area of 1 cm^2.

3 RESULTS AND DISCUSION

3.1 Topography of Nickel Plates

Figure 1 illustrates the different topographies of nickel films obtained by the three techniques: DC (1.a), PC (1.b) and PRC (1.c). It is clearly observed that the films produced by the PRC exhibit greater uniformity, less roughness, and a finer grain size than the films obtained by using PC. The effect of PC on plates can also be observed since it induces higher nucleation velocities in grains and therefore it is possible to obtain structures with more refined grain size [5].

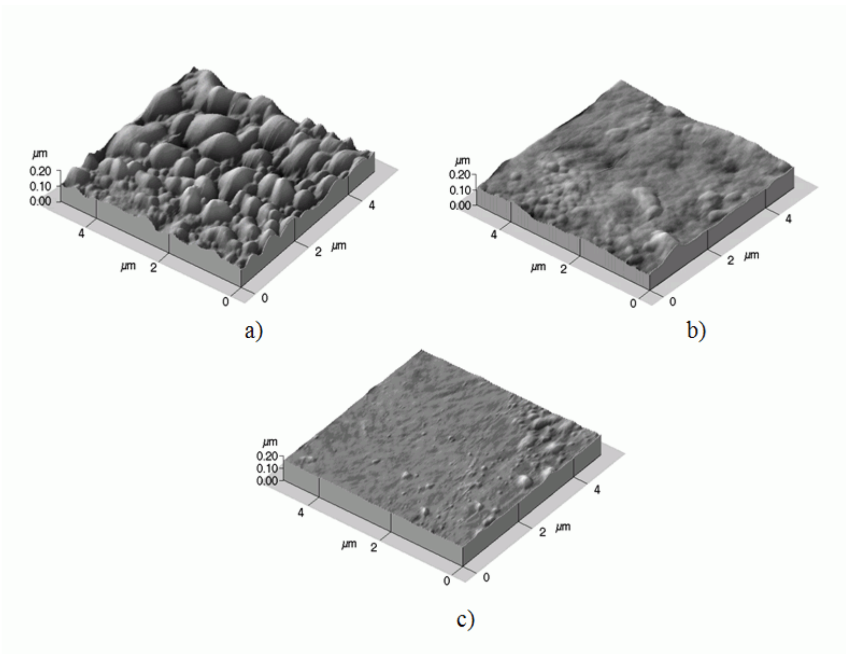

Figure 1: Topography Ni electrodeposited films obtained by the application of three techniques:
a) DC: V = 10V. b) PC: V_{on} = 10V, V_{off} = 2V, t_{on} = 100ms y t_{off} =100ms.
c) PRC: V_{on} = 10V, V_{rev} = -2V, t_{on} = 100ms y t_{rev} = 10ms.

Table 2 shows the values corresponding to the average grain size and the roughness observed in each plate obtained by the application of the different techniques. The values found corroborate the advantage of using PRC to obtain films that exhibit less roughness and a decrease in grain size. This contributes to obtain plates with a greater compaction degree.

Table 2: Measurements of grain size and roughness in nickel films

Technique	Grain size (ηm)	Roughness (Å)
DC	2250	4610
PC	824	2414
PRC	624	1673

3.2 Electrochemical Impedance Spectroscopy Diagrams

Figure 2 shows the Bode's diagrams obtained for nickel films resulting from the application of the three electrodeposition techniques.

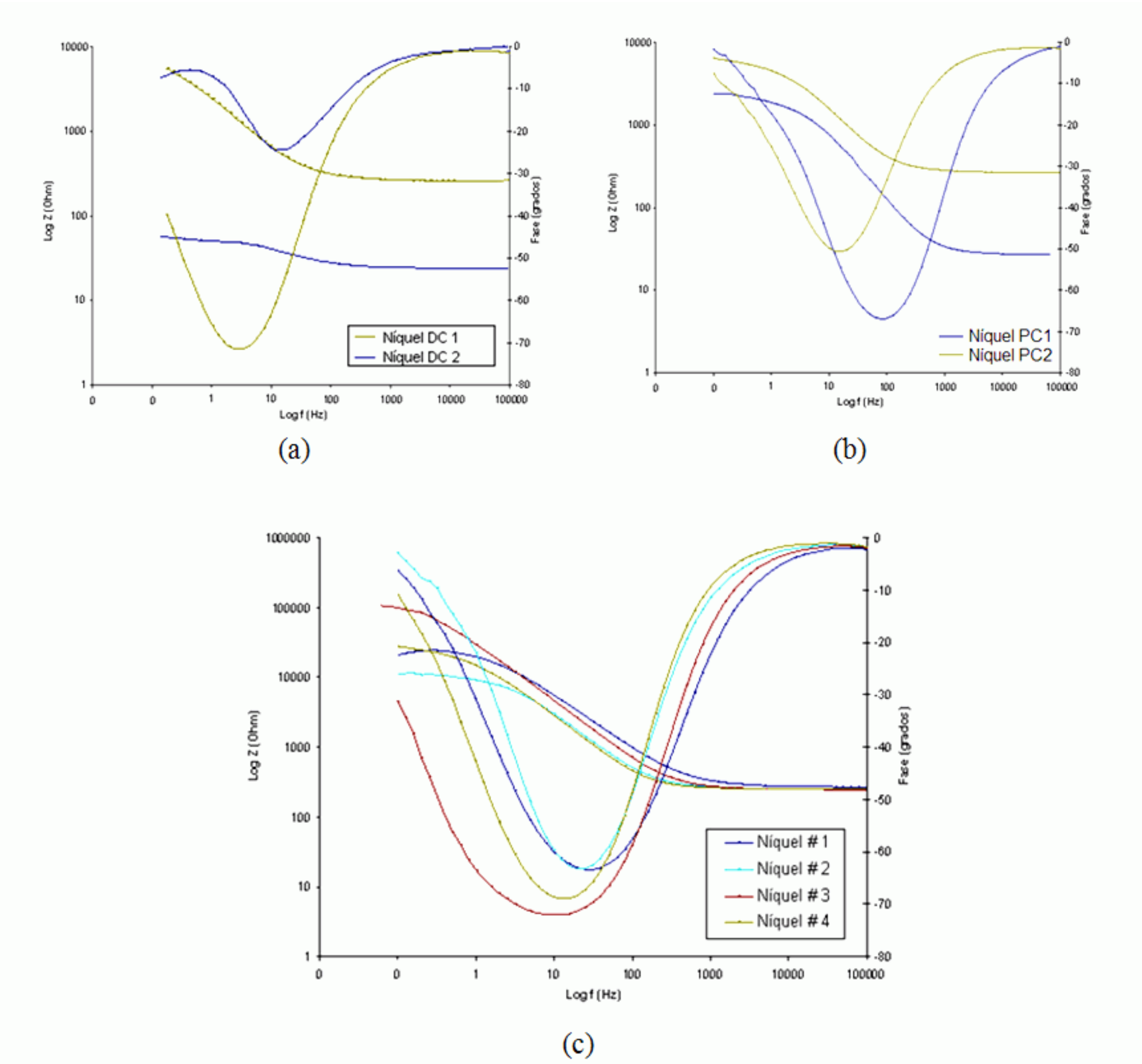

Figure 2: Bode's Diagrams for Nickel films. a) DC, b) PC y c) PRC

Figure 3 shows the equivalent circuit for electroplate impedance behavior where R_s represents the resistance to solution, R_p is the resistance to polarization and C_f is the double-layer phase element. This equivalent circuit resembles the behavior of plates obtained when using the PRC technique in which the response is associated to the reaction of nickel with the medium (one single metal). No other component is observed (copper and zamak). This indicates that the nickel obtained by this technique is sufficiently dense.

Based on the above illustrated diagrams, it is possible to calculate the values obtained by simulating the behavior with equivalent circuits. Table 3 shows the values corresponding.

Some important characteristics are inferred from the impedance diagrams. Figure 2.a. shows a second constant-phase element which is associated to the reaction of the copper film located underneath the nickel plate. Besides, small changes in the film deposition variables are observed to affect the electrochemical response in a considerable way. This statement is based on the observation that that the spectrum for the sample labeled DC2 shows a very good behavior compared to DC1. Two magnitude orders of difference are observed only in the resistance to polarization. Figure 2.b. shows the PC technique is observed to generate more homogeneous plates. No second element of constant phase is observed. The response of plates prepared under different conditions is similar. Figure 2.c. shows clearly that the spectra obtained correspond only to the nickel reaction. Therefore, this is not a porous material. It is also important to observe that these PRC obtained plates exhibit the highest resistance to polarization which indicates a high nickel stability and a high anti-corrosive capacity.

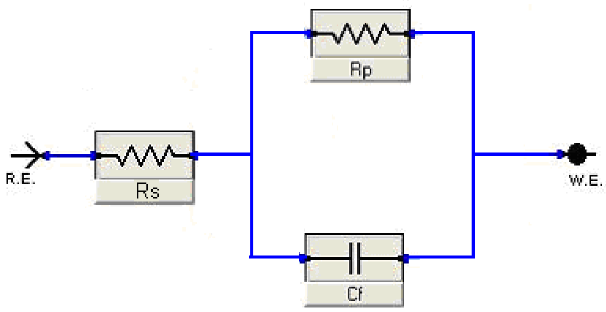

Figure 3: General equivalent circuit for electroplate impedance behavior

Table 3: Values of nickel electroplating circuit elements

Parameter	Techniques							
	DC		PC		PRC			
	1	2	1	2	1	2	3	4
resistance to solution (Ω)	278.9	235	269	215	249.2	249.1	244.2	248.8
resistance to polarization (KΩ)	2.15	0.8	4.06	8.06	25.39	10.88	49.9	16.27

3.3 Polarization Curves

Figure 4 shows the Tafel diagrams corresponding to nickel deposits obtained by using the DC, PC and PRC techniques. The polarization curves obtained support the finding of anodic and cathodic slope values in each case. These are shown in the tables 4, 5 and 6 together with current density and corrosion velocity values for each one of the cases studied.

A value of 18.52 mpy was found which indicates concordance with the results obtained during the topography evaluation that revealed that less uniform and rougher deposits were found with this technique. Regarding the PC technique, the deposition conditions employed do not reveal a significant change in the behavior against corrosion. Intermediate values of 12.43 mpy were obtained. With the PRC technique, a marked influence of the anodic voltage was observed regarding the deposit deterioration. However, an increment in anodic pulse time generates a deposit with a more refined grain size, a greater compaction and a better response to corrosive attack. Reduced corrosion velocities were found with this technique (0.055 mpy and 0.097 mpy) compared to the other two assessed techniques.

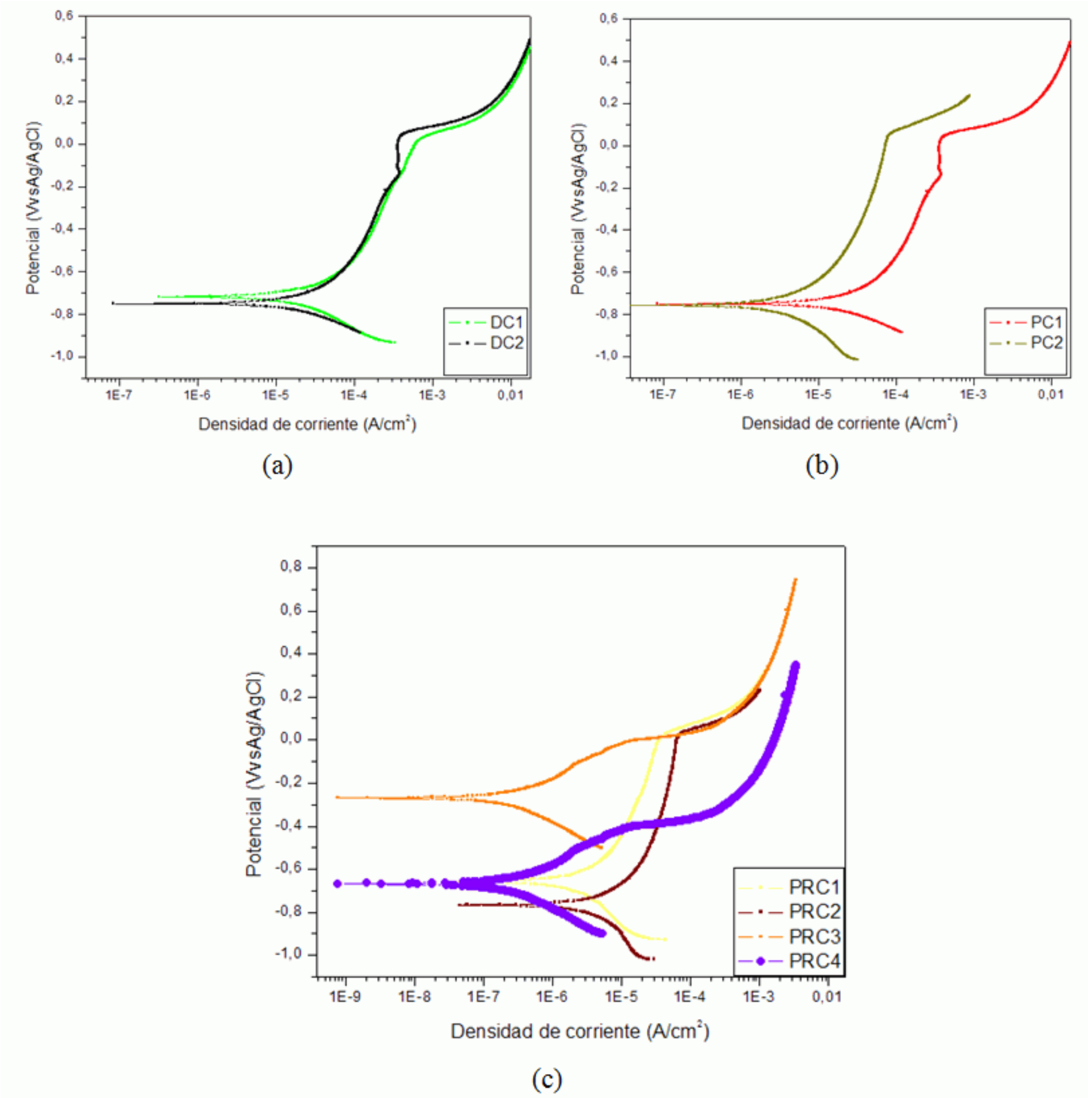

Figure 4: Polarization curves of nickel electroplating obtained by applying different techniques in HCl at 1%, at a scan velocity of 0.5 mV/s. a) DC, b) PC y c) PRC

Table 5: Current values and corrosion velocity of the DC nickel test piece

Parameter	Test	
	1	2
β_a (mV/decade)	133.9	212.9
β_c (mV/decade)	89.50	79.90
i_{corr} (μA)	60.30	8.210
Corrosion Velocity (mpy)	18.52	6.554

Table 6: Current values and corrosion velocity of PC nickel test piece

Parameter	Test	
	1	2
β_a (mV/decade)	496.6	306.3
β_c (mV/decade)	270.8	312.4
i_{corr} (μA)	40.50	34.50
Corrosion velocity (mpy)	12.43	10.61

Table 7: Current values and corrosion velocity of the PRC nickel test piece

Parameter	Test			
	1	2	3	4
β_a (V/decade)	276.6	891.1	68.20	78.92
β_c (V/decade)	239.1	890.9	73.00	86.56
i_{corr} (μA)	7.08	15.90	0.069	0.078
Corrosion velocity (mpy)	0.65	1.69	0.055	0.097

4 CONCLUSIONS

The following conclusions can be drawn from this work:

1) A decrease in the grain size and a greater uniformity of electrolytic deposits were obtained by the implementation of the PC and PRC techniques. Grain sizes of up to 624 nanometers were found.
2) Plates obtained by the application of the normal DC technique are porous. This observation results from the EIS analysis because the presence of a constant-phase second element was evident either at the copper of the zamak reaction. The PC technique improves the nickel sealing conditions which is manifested by the absence of a second constant – phase element. Furthermore, the plates obtained with different parameters show similar spectra. Finally, plates obtained by using the PRC technique exhibit the best sealing characteristics. Their spectra can be easily simulated with an equivalent circuit similar to the circuit obtained with one single metal. In other words, only the nickel behavior is observed in an aggressive media. Moreover, the highest R_p values were obtained which agrees with the excellent protection against corrosive phenomena in the evaluated medium.
3) A strong influence of the anodic pulse time was observed in the corrosion velocity of electrodeposits obtained by utilizing PRC. Values up to 100 times lower were evident.

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