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Black passivated pulsating plated ZnCo coatings: Electrodeposition and characterization

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Abstract : ZnCo alloys (0.4 to 1.2% Co) were electrodeposited using pulsating or direct current in a chloride bath, and then chromated from a chromate conversion bath. The corrosion behavior of these coatings in aerated 0.6 N NaCl solution was investigated by Electrochemical Impedance Spectroscopy. The experimental findings showed that if the structure and proper-

ties of the metallic layer are considered the pulsating current process was more effective than the direct one, but no major difference in their corrosion behavior was observed. © Global Scientific Inc.

Keywords : ZnCo alloys; Pulsating current; Corrosion; EIS; Coatings.

INTRODUCTION

Electrodeposition of metallic coatings is currently carried out using direct current (DC). However, the nucleation and growth of deposited grains may create crystalline defects that can produce cracks in the coating^[1]. In the last decade there is an increasing interest to use pulsating current (PC) as an alternative process due to it provides better properties, like the smaller porosity and enhanced adherence and uniformity, exhibited by the coatings prepared using the latter technique^[2]. Ductility, hardness, corrosion and wear resistances are additional properties that can be improved by the use of the pulsating process. In addition, when pulsating

current is used the internal stresses are smaller, thus reducing the number of defects in the coating. An improvement in the chemical purity of the deposits is also observed^[3]. Finally, in the case of the ZnCo alloy deposition, the pulsating current process allows better control of its composition and structure^[4].

In the direct current process, the current density (or potential) is the only electrical parameter that can be varied to get changes in the deposit composition and microstructure^[4,5]. However, in pulsating current there are four independent parameters that can be used to obtain metallic coatings with the required properties. These parameters are intensity and extent ("on" or "off" times) of the cathodic or anodic current density pulses^[5]. Several

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combinations of these variables are, thus, possible for a given value of the mean current density that can lead to deposits with different properties and structure.

In the last decade has arisen an increasing demand of metallic coatings based on alloys, like ZnNi, ZnCo and ZnFe, that provide better corrosion resistance than and comparable cost with- the electrodeposited pure Zn^[6]. Several authors found that the corrosion rate of the ZnCo coating obtained with direct current is three times lower than the exhibited by the electrodeposited Zn^[7-10], and also that it can be further decreased by a subsequent chromating process^[7,9,11,12].

This paper addresses an experimental investigation on the electrochemical and corrosion behavior of chromated ZnCo alloy obtained by using direct or pulsating current. The electrochemical behavior was investigated by Electrochemical Impedance Spectroscopy (EIS). When EIS technique is employed to evaluate the corrosion resistance of coatings, the values of the charge transfer resistance, R_{ct} , at the metal/solution interface can be easily obtained and related to the corrosion rate. High values of R_{ct} are representative of protective coatings^[13].

EXPERIMENTAL

Deposits of the ZnCo alloys were obtained at 30 °C using the following bath composition: 3.0 g.L⁻¹ CoCl₂.H₂O, 77.2 g.L⁻¹ ZnCl₂, 220 g.L⁻¹ KCl, 26 g.L⁻¹ H₃BO₃, 15 mL of the additive “Zn-base”, 2 mL of the additive “Zn-brightener” under stirring provided by air bubbling. Solutions were prepared with doubly distilled water and analytical grade reagents, the pH was 5.3.

The electrodeposition was carried out under galvanostatic conditions with direct (DC) or pulsating (PC) current by using a 1 dm³ capacity PVC cell and pure Zn as anode. The current density in both DC and PC processes was in the range 3-40 mA.cm⁻². In addition, the PC process was performed with the following parameters: peak current density (i_p) = 250 mA.cm⁻², off-time (t_{off}) = 16.8 ms, and on-time (t_{on}) = 3.2 ms. The electrodeposition time was long enough as to obtain a deposit thickness of 15 μm.

Before deposition, the zinc anode was immersed for 3 h in the plating solution at 40 °C for allowing the chemical deposition of an adherent Co layer. This layer prevents the zinc dissolution reaction during the elec-

trodeposition process.

The DC deposits were accomplished with a 549 AMEL potentiostat and the PC ones with a 2055 AMEL potentiostat coupled to a programmable function generator (568 AMEL). The applied signal shape was observed through a digital oscilloscope and the current transients were recorded on a XY plotter.

The electrodeposits were produced on mild steel disks with an exposed area of 4 cm². Before electrodeposition, the disks were polished with emery paper and any grease was removed from their surface by anodic and cathodic electrolysis for 2 min in an aqueous NaOH (60 g.L⁻¹) solution at 4 V against graphite anodes. The samples were then immersed in a 2% HCl solution and finally rinsed with distilled water.

To evaluate the Zn, Co, Cr and P content into the coating, the deposits were stripped in a minimum volume of HCl solution (1 vol. of HCl at 37% by weight and 3 vol. of distilled water), which was analyzed by means of inductively coupled plasma spectroscopy (ICPS). The morphology of the deposits was characterized by SEM.

After the ZnCo alloy electrodeposition, the specimens were subjected to a black passivation process consisting of the samples immersion in two solutions free from Ag⁺. The first solution was prepared from the commercial product “zincifix 20” (100 mL.L⁻¹, pH 1.0, 25 °C) and the exposure time was 60 and 120 s for PC and DC process, respectively. The second solution was prepared by using the commercial product “seal zincifix 20” (7 mL.L⁻¹, pH 1.8, 25 °C) and the exposure time was 20 s in both processes. Finally, the samples were dried at 50 °C.

EIS measurements were performed in the 10⁻²-10⁵ Hz frequency range using a Solartron 1260 Frequency Response Analyzer coupled to a Solartron 1286 Electrochemical Interface. The sinusoidal signal amplitude was 3 mV. All the measurements were performed in aqueous aerated 0.6 N NaCl solution at 25±1 °C. The exposed area was 3.14 cm². A three-electrodes electrochemical cell was obtained by sticking a plastic cylinder on the sample sheet and filling it with the test solution. A Saturated Calomel Electrode (SCE) as reference and a platinum counter electrode were further employed. EIS measurements were carried out during a total immersion time of 24 h.

All the impedance measurements were carried out in a Faraday cage in order to minimize external interferences on the studied system. The impedance spectra were analyzed on the basis of equivalent electrical circuits using the software (EQUIVCRT) proposed by Boukamp^[14].

RESULT AND DISCUSSION

Figure 1 shows the Co content in the deposit as a function of current density (i) for PC and DC processes. As can be seen, the Co content in the DC produced samples is smaller than that in the PC ones, for all current densities investigated. It is well documented in the scientific literature that brilliant black chromating can

be obtained with alloys having a Co content into the coating from 0.4 to 1.3%^[15]. Thus, results showed in Figure 1 suggest that the PC is more effective than the DC process. In the latter case, a current density as high as $30 \text{ mA}\cdot\text{cm}^{-2}$ was necessary in order to coatings with the required minimum Co were obtained.

Figures 2 to 5 show the surface and the cross section of black passivated ZnCo coatings prepared by PC or DC using a current density of $30 \text{ mA}\cdot\text{cm}^{-2}$.

Figures 2 and 4 show that the surface of both deposits is entirely cracked. As well that the number of cracks formed at the passive DC films (Figure 4) is less than those exhibited by the PC ones (Figure 2). At this respect, it should be taken into account as an important detail that the depth of the cracks did not overcome the

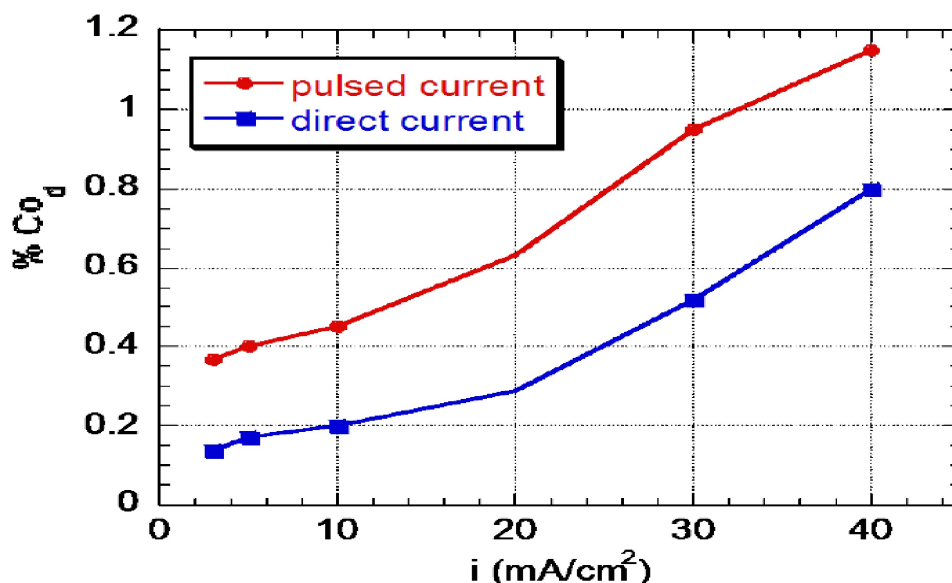


Figure 1 : Cobalt content in electrodeposited ZnCo alloys vs. current density.

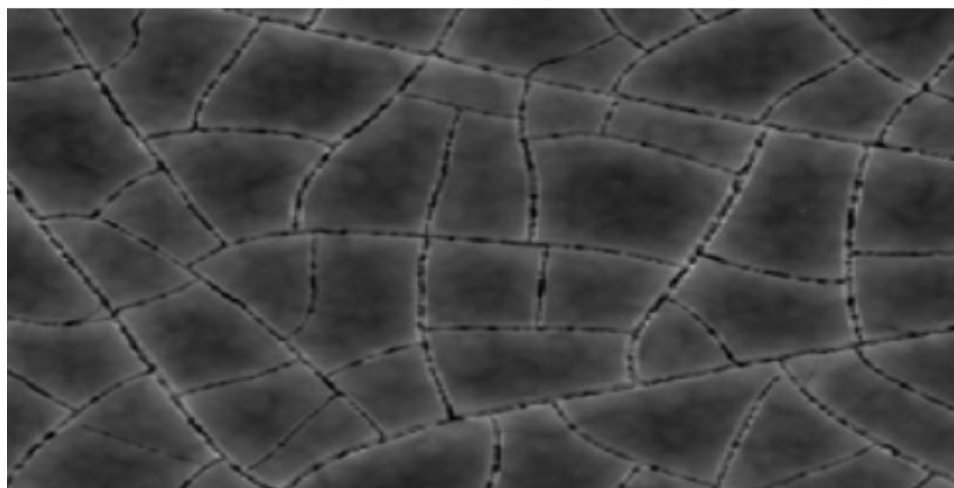


Figure 2 : Micrograph of black ZnCo coating (PC). $i = 30 \text{ mA}\cdot\text{cm}^{-2}$. Magnification: 2500X.

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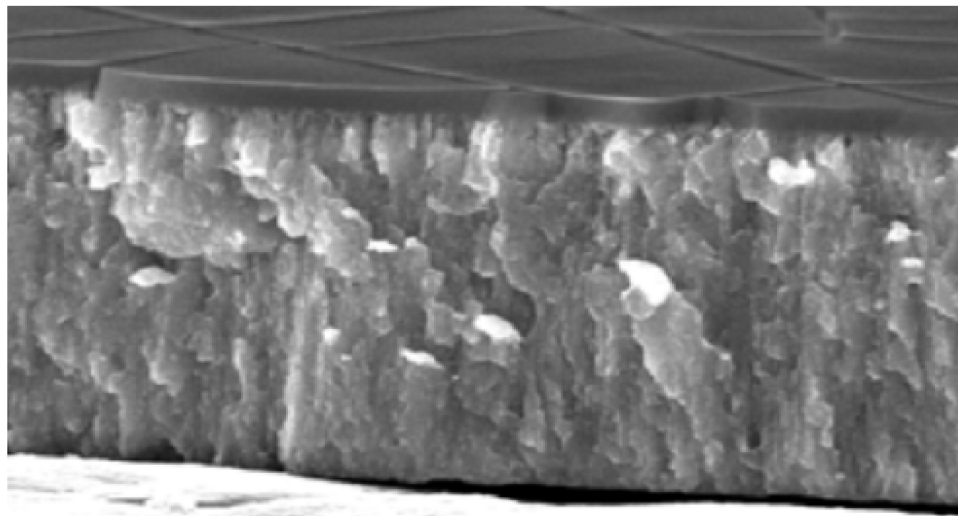


Figure 3 : Cross section of black ZnCo coating (PC). $i = 30 \text{ mA.cm}^{-2}$. Magnification: 5000X.

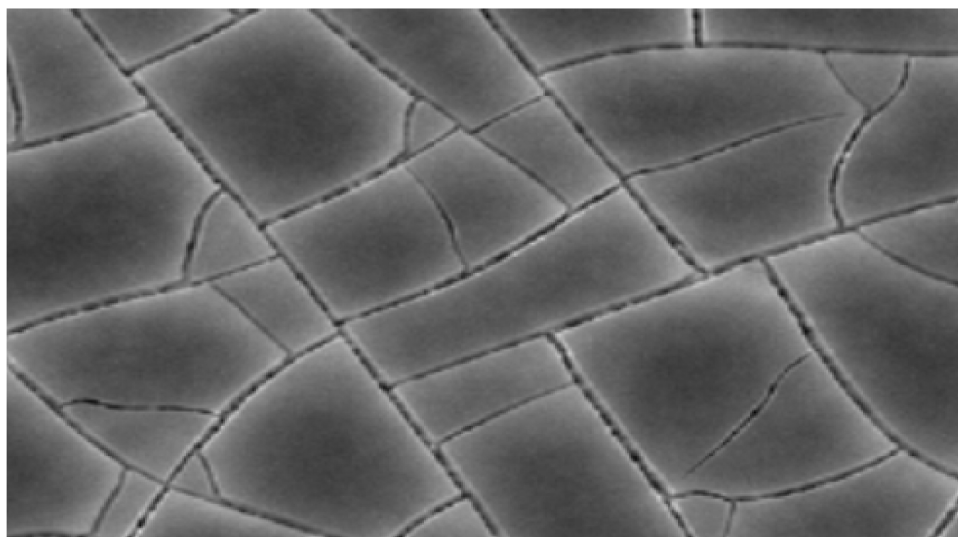


Figure 4 : Micrograph of black ZnCo coating (DC). $i = 30 \text{ mA.cm}^{-2}$. Magnification: 2500X.

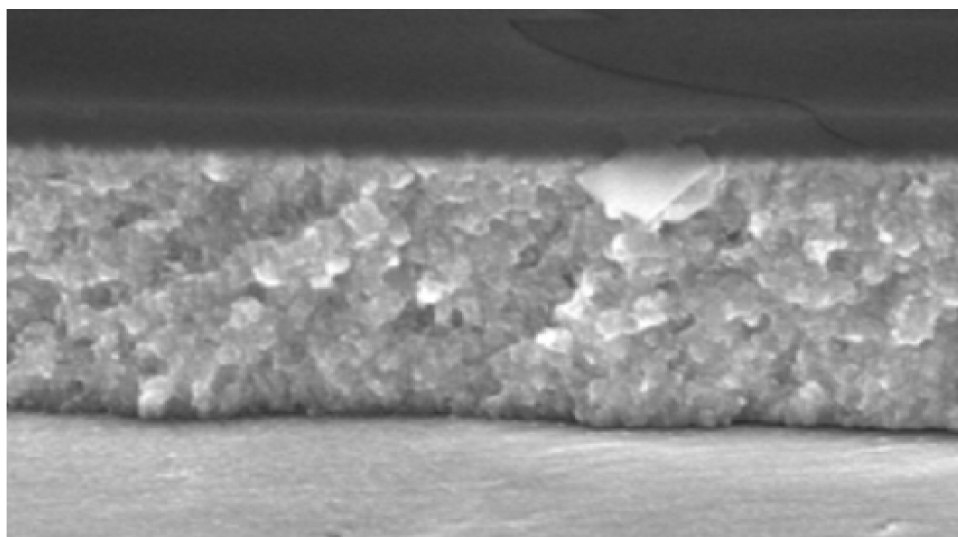


Figure 5 : Cross section of black ZnCo coating (DC). $i = 30 \text{ mA.cm}^{-2}$. Magnification: 5000X.

passive layer thickness. Related with the same films, Figures 3 and 5 depict that the ZnCo deposits were uniform and, as it is reported in TABLE 1, they exhibited comparable thicknesses.

EDXS analysis performed on both deposits, but not shown here, revealed the presence of P, Cr and S, while the chemical analysis (ICP) evidenced the presence of only Cr and P in the coating layer (see TABLE 1). This result, thus, suggests that S is present only on the surface on the deposit.

The time dependence of the corrosion behavior of chromated PC and DC samples was evaluated in aerated NaCl (3.5% wt) solution by EIS until macroscopic corrosion products appeared on the samples

surface. These samples were obtained using a current density of $30 \text{ mA}\cdot\text{cm}^{-2}$ because under this operation condition the Co content was greater than 0.5%, it is to say, the required amount as to obtain a uniform black passivation layer^[15].

Figures 6 (a - b) and 7 (a - b) exhibit the Bode and phase angle plots at several exposure times for the PC

TABLE 1 : Composition and thickness of black ZnCo coatings

Coating	Coating thickness (μm)	Passive film thickness (μm)	Cr (mg/cm^2)	P (mg/cm^2)
Black ZnCo (PC)	10	0.85	0.05	0.01
Black ZnCo (DC)	7.5	1.00	0.08	0.02

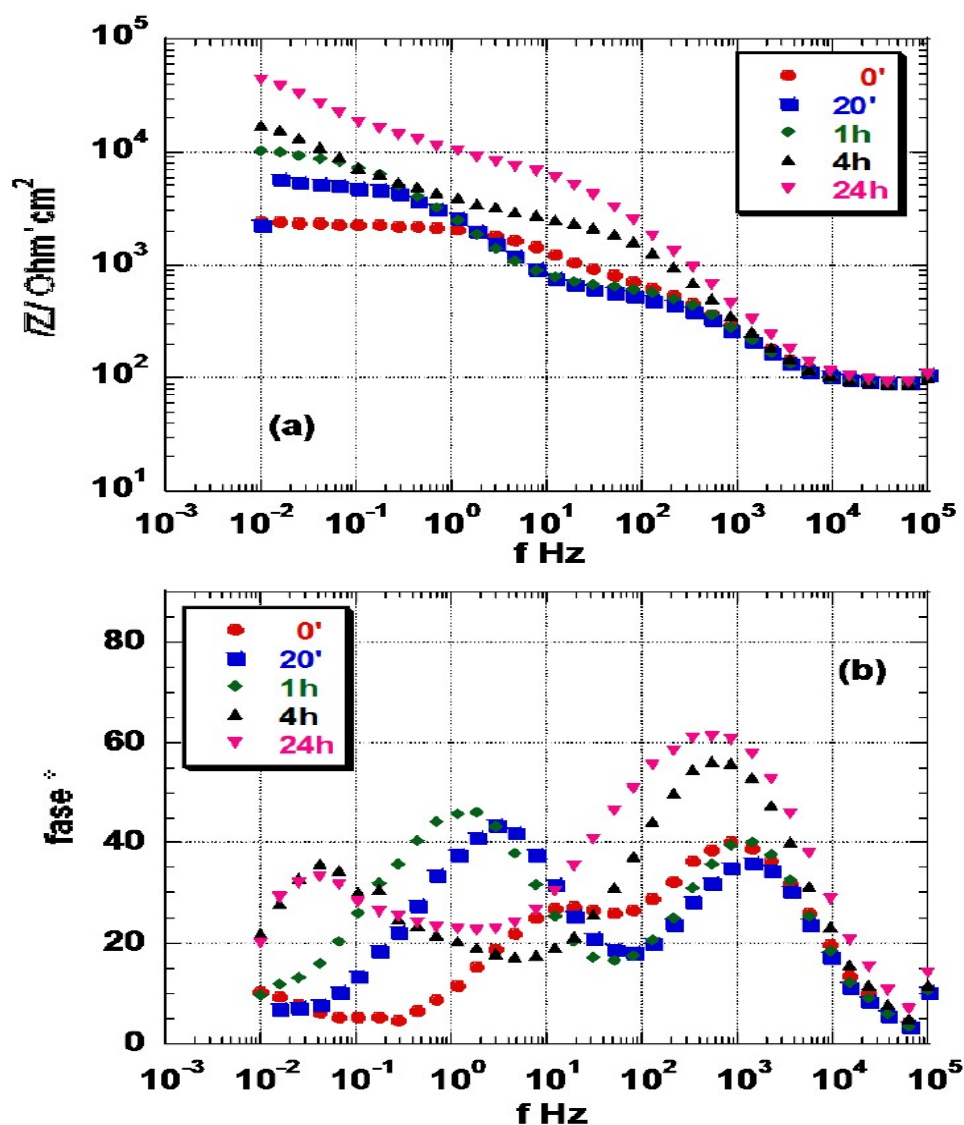


Figure 6 : Bode (a) and phase angle (b) plots as a function of the immersion time, for black ZnCo coating obtained with the DC process.

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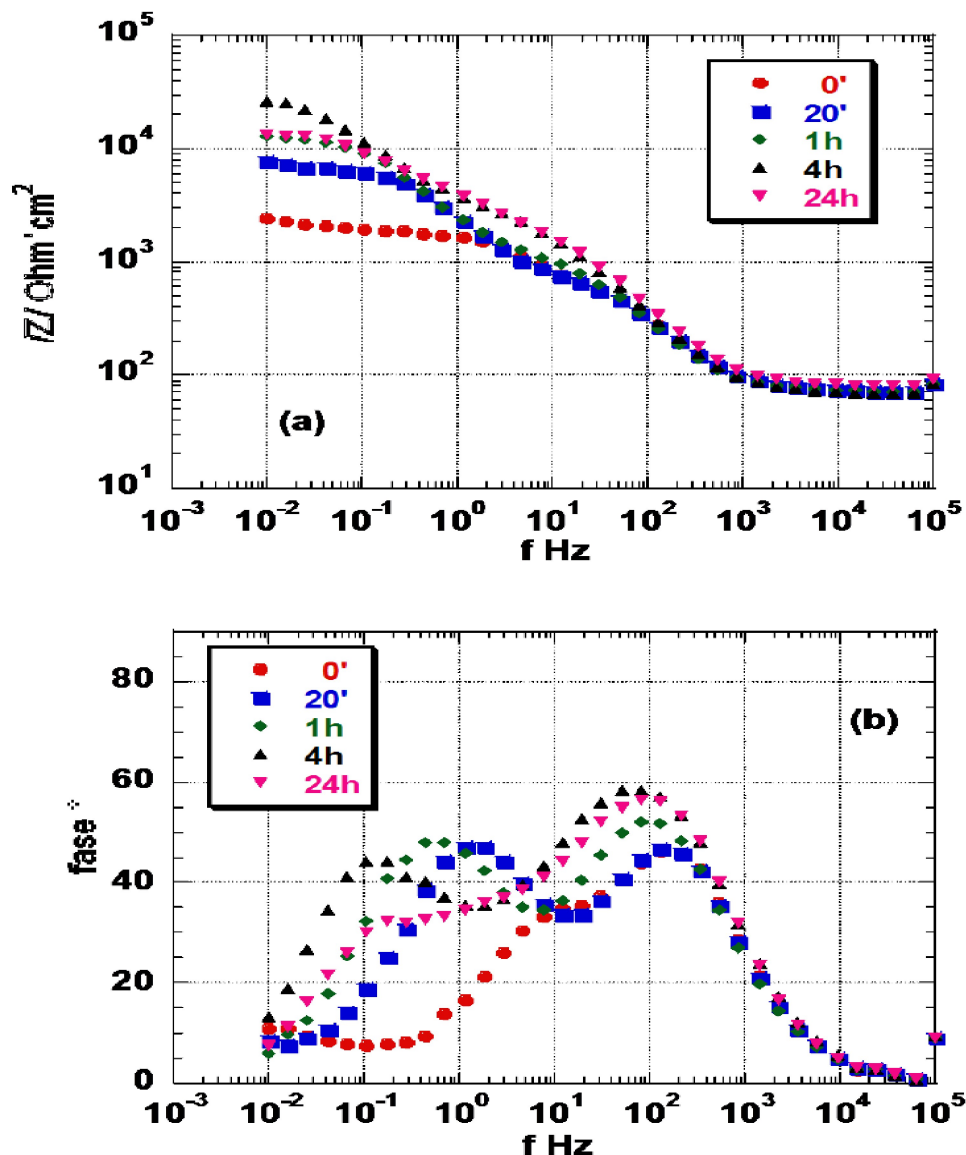


Figure 7 : Time dependence of (a) Bode and (b) phase angle plots for the black ZnCo coating obtained with the PC process.

or DC coated samples, respectively.

From the phase angle plot of Figure 6b the following interesting observations can be drawn. Upon the samples immersion in the test solution, three time constants could be observed.

Such a result may suggest a non-homogeneous structure of the passivation layer. After 1 h and up to 24 h of immersion, however, only two time constants were defined in the same frequency range; this change was attributed to the sealed of the coating defects by the corrosion products. Finally, white rust was visually observed on the sample after 3 days of exposure. Similar conclusions can be drawn from the visual inspection of

the PC samples EIS spectra. It must be pointed out, however, that at each immersion time the phase angle values were higher for specimens processed with pulsating current than those processed with direct current. This result may be attributed to a more homogeneous structure of the chromated layer of PC specimens.

EIS spectra shown in Figures 6 and 7 were analyzed on the basis of the equivalent circuit presented in Figure 8 as suggested in the literature^[16], because it describes properly the experimental findings obtained in this investigation for all the exposure times. The Warburg impedance was added to the equivalent circuit in order to fit the data obtained at the lower fre-

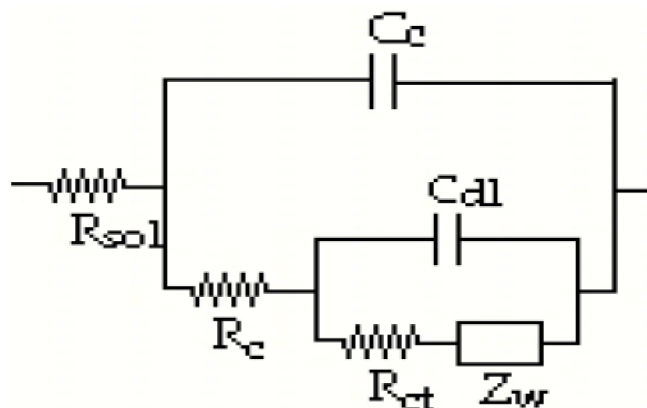


Figure 8 : Equivalent electrical circuit.

quency range^[17]. In this circuit R_{sol} represents the solution resistance, C_c and R_c are associated to the chromated layer, C_{dl} is the electrochemical double layer capacitance, R_{ct} is the charge transfer resistance, related to the ZnCo coating/solution interface, and Z_w is the Warburg impedance^[18].

Figure 9 a-b shows a comparison between experimental and simulated data for chromated ZnCo coatings obtained through PC or DC processes upon immersion in the test solution. Similar data were obtained for all exposure times and were omitted for the sake of simplicity.

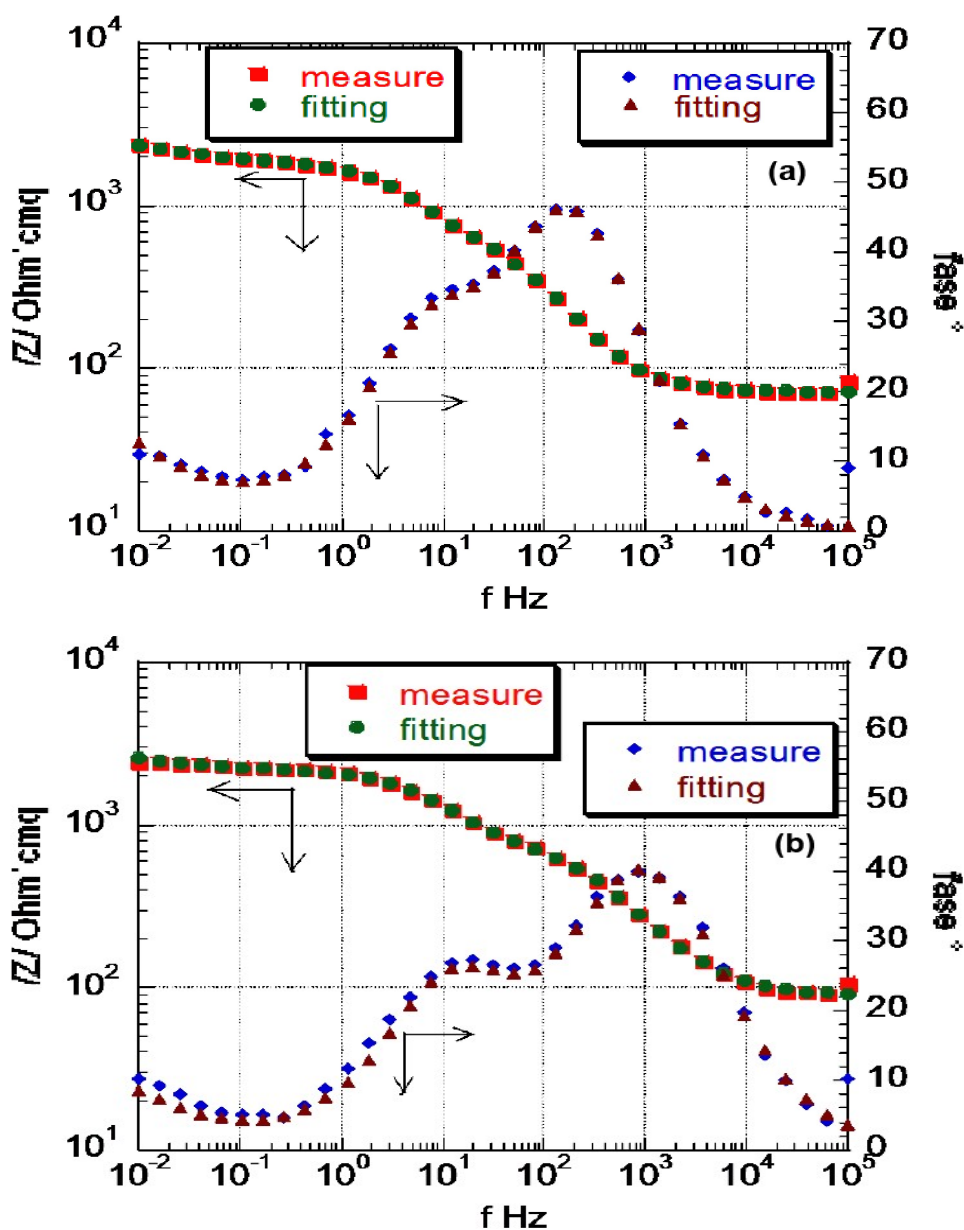


Figure 9 : Bode and phase angle plots of experimental and simulated data for the black ZnCo coatings obtained with (a) DC and (b) PC processes just after immersion in the test solution.

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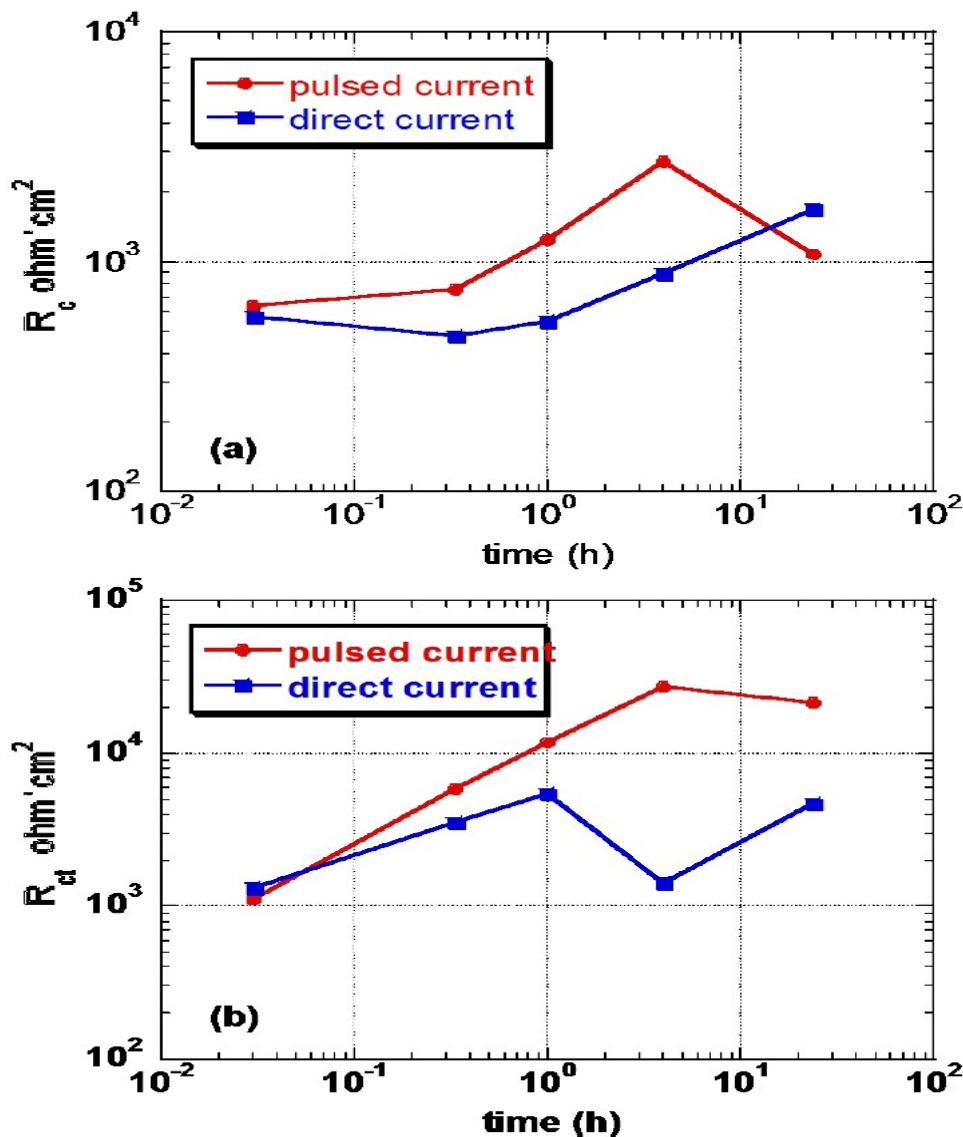


Figure 10 : Time dependence of the (a) R_c and (b) R_{ct} values for the chromated ZnCo coatings obtained using PC or DC processes.

From the equivalent circuit presented in Figure 8, the values of its resistive and capacitive elements could be easily evaluated. In this sense, the estimated R_c and R_{ct} values are reported in Figure 10 a-b, respectively. As can be seen, the chromated layer on the ZnCo coating obtained by means of the PC process exhibited slightly better coating resistance properties than that obtained by the DC one. As well, that the R_c values showed that the PC samples provided an also slight higher corrosion resistance than the DC ones.

CONCLUSION

From the results attained in this investigation the

following conclusions could be drawn:

1. Deposits of ZnCo prepared using pulsating current showed great Co content than those obtained using direct current. This is to say, the coatings generated through the PC process were more protective than those coming from the DC process; and
2. A slightly higher corrosion resistance was exhibited by ZnCo coatings obtained with the PC process.

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REFERENCES

- [1] G.Perger, P.M.Robinson; *Met. Finish*, **77**, 17 (1979).
- [2] C.M.A.Freire, M.Ballester; *Tratamento de Superficies*, **9-10**, 30 (1998).
- [3] T.Pearson, J.K.Dennis; *Plating Surf. Finish*, **76**, 64 (1989).
- [4] G.Devaraj, S.Guruviah, S.K.Seshadri; *Mat.Chem. Phys.*, **25**, 439 (1990).
- [5] J.C.Puippe, F.Leaman; 'Theory and Practice of Pulse Plating', AESF Publication, 247 (1986).
- [6] T.E.Sharples; *Products Finish*, 5438 (1990).
- [7] N.R.Short, A.Abibsi, J.K.Dennis; *Trans.Inst.Met. Finish*, **67**, 73 (1989).
- [8] R.Sard; *Plating Surf. Finish*, **74**, 30 (1987).
- [9] A.P.Shears; *Trans.Inst.Met. Finish*, **67**, 67 (1989).
- [10] W.Siegert; *Metalloberfläche*, **42**, 259 (1987).
- [11] M.Joy; *Galvano-Organo-Traitements de Surface*, **55**, 352 (1986).
- [12] G.Nikolova; *Galvanotechnick*, **82**, 2321 (1991).
- [13] L.De Rosa; *La Metallurgia Italiana*, **3**, 23 (1999).
- [14] B.A.Boukamp; *Solid State Ionics*, **20**, 31 (1986).
- [15] R.Fratesi, G.Roventi; *Mat.Chem.Phys.*, **23**, 529 (1989).
- [16] C.Delouis, M.Duprat, C.Tournillon; *Corros.Sci.*, **29**, 13 (1989).
- [17] P.L.Bonora; *Atti della Scuola-Convegno sull'Impedenza Elettrochimica*, Padova, 15-17 Aprile, 161 (1991).
- [18] G.W.Walter; *Corros.Sci.*, **26**, 681 (1986).