



THE EFFECT OF OPERATING CONDITIONS DURING PLATING ON THE ELECTROCHEMICAL BEHAVIOR AND MORPHOLOGY OF TRIVALENT SOLUTION-DERIVED CHROMIUM COATINGS

EL EFECTO DE LAS CONDICIONES DE FUNCIONAMIENTO DURANTE EL CULTIVO SOBRE EL COMPORTAMIENTO ELECTROQUÍMICO Y LA MORFOLOGÍA DE LOS RECUBRIMIENTOS DE CROMO TRIVALENTES DERIVADOS DE SOLUCIÓN

O.J Suarez¹, J.J Olaya^{1*} and S. Rodil²

¹Universidad Nacional de Colombia, Bogotá, Colombia. Ciudad universitaria edificio de posgrado de materiales. Bogotá-Colombia.

²Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, México D.F.-Mexico.

Received 28 of February of 2012; Accepted 17 of January of 2013

Abstract

Trivalent electrolyte-based chromium plating represents an alternative for the major problems associated with traditional hexavalent plating. Response surface methodology was chosen in this work for designing experiments. Chromium coatings were obtained from trivalent solutions in a chloride-based bath using different operating conditions. Three concentrations (0.19, 0.38 and 0.57 mol L⁻¹ as Cr(III)), three pH (2.0, 3.0 and 4.0) and temperature (25°C, 32°C, 40 °C) was varied during the experiments. Scanning electron microscopy and energy dispersive X-ray analysis were used for examining the coatings surface morphology and composition; the coulometric method was used for thickness measurement and potentiodynamic and impedance tests on 3% NaCl were made on a three-electrode cell for studying chromium film electrochemical behavior. Large differences in morphology, thickness and corrosion resistance were observed, mainly due to variations in chromium concentration and pH solution. Crack patterns were observed on films obtained at high pH values independently of process temperature.

Keywords: trivalent chromium, plating, microstructure, corrosion, electrochemical impedance.

Resumen

Los electrolitos basados en el cromo trivalente presentan una alternativa a los problemas asociados con los recubrimientos tradicionales basados en cromo hexavalente. En este trabajo se empleo un diseño de experimentos de superficie de respuesta para observar el efecto de las variables. Los recubrimientos de cromo se obtuvieron a partir de soluciones de cloruro de cromo modificando las condiciones de electro deposición. Tres concentraciones (0.19, 0.38 y 0.57 mol L⁻¹ de Cr(III)), tres valores de pH (2.0, 3.0 y 4.0) y tres temperaturas (25°C, 32°C y 40 °C) se variaron durante los experimentos. La morfología y composición de los recubrimientos se analizó por medio de microscopia electrónica de barrido y la sonda de análisis de dispersión de rayos X acoplada al microscopio; el espesor de los mismos se midió por titulación coulombimétrica y el comportamiento electroquímico a la corrosión se estudio por medio de polarización potenciodinámica y espectroscopia de impedancia electroquímica en NaCl 3%. Se observaron grandes diferencias en la morfología, espesor y resistencia a la corrosión debido principalmente a la variación en la concentración de cromo y al pH de la solución. Se observaron patrones de agrietamiento cuándo el deposito se obtuvo a altos valores de pH independientemente de la temperatura del electrolito.

Palabras clave: cromo trivalente, electro plateado, microestructura, corrosión, impedancia electroquímica.

*Corresponding author. E-mail: jjolaya@unal.edu.co

1 Introduction

Modern society's population growth and industrialization have resulted in improvements in people's quality of life, but the cost to be paid for this has resulted in a major environmental impact on air, water and soil. Chromium deposits obtained by electrolysis are of great importance in the field of decorative and industrial coatings; however, the conventional process using hexavalent chromium solutions presents serious drawbacks from environmental and occupational health view-point (European Commission, 2006), that fact has caused different physicochemical alternatives have been proposed to deal with Cr(VI) solutions (Barrera *et al.*, 2003, 2004).

Alternatively, processes have been based trivalent chromium chemistry to reduce some hexavalent-chromium associated problems. They have not fully implemented in an industrial environment because of such technology's higher maintenance cost and incomplete knowledge (Suarez, 2006; Suarez *et al.*, 2009).

Chromium metal cannot be obtained directly from trivalent chromium sulfate or chlorides solutions, since they form stable and inert complexes with $[\text{OH}]^-$, $[\text{SO}_4]^{2-}$, $[\text{Cl}]^-$ ions, and oxides during electro-deposition interfering cathodic reaction. Chromium should then be used as a complex with a compound (ligand) that can easily glide the Cr(III) ion and reduction to Cr(s) thus occurs (Szyncarzuk *et al.*, 1988, 1989; Song and Chin 2002; Vinokurov *et al.*, 2005). The main complexing agents are: sodium hypophosphite and glycine, as well as other chelating agents such as carboxylic acids or salts, urea, thiourea, thiocyanates, dimethylformamide, hydrazine or hydroxylaminophosphates (Baral and Engelken, 2005; Surviliene *et al.*, 2007; Boasong, 2006). Also they found that using chromium chloride solutions with formates and acetates as complexant agents, obtaining chrome surfaces and experimentally showing that complexing agents were actively involved in Cr(s) reduction reactions and the elements presents as compounds in the solution, such as oxygen, carbon and phosphorus are incorporated into the coating, thereby modifying its structure.

Other researchers (Surviliene and Nivinskiene, 2006) have studied the effect of operating conditions (i.e. pH, temperature, current density and adding agents) on cathodic efficiency, morphology and structure of the deposits; finding is a strong response variable dependence in all cases.

For example, the effect of reaction conditions during Cr(III) complex formation, as well as the effect of compounds present in solution, on chromium film morphology and corrosion resistance have already been reported (Suarez, 2006; Suarez *et al.*, 2009; Suarez, 2010). These studies have indicated that a mixture of sodium formate plus sodium acetate with the addition of boric acid and sodium lauryl sulfate (with no other salts as additives) has shown better performance regarding corrosion pattern.

The electrochemical behavior of chromium films obtained at different values for chromium concentration, pH and temperature during plating was studied in this work through a response surface experiment. This kind of experiment has been used for examining the effect of operating conditions during plating in trivalent and hexavalent baths (Baral and Engelken, 2005; Bayramoglu, 2008). Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were used to study the chromium deposits electrochemical behavior. Morphology and composition were studied by scanning electron microscopy (SEM) and energy dispersive X-rays (EDX) and films thickness was measured by using a coulometric method current cathode efficiency was thus calculated (ASTM, 1995).

2 Experimental details

2.1 Experimental design

The underlying goal of this study was to correlate corrosion resistance of a chromium coating with a set of factors such as pH, bath temperature and chromium concentration. Statistical software was used for designing and analyzing the experiments. Response surface methodology was chosen for designing the experiments; this method provides information on direct effects, pair-wise interaction effects and curvilinear variable effects. It also needs fewer combinations than a fully factorial experiment. Central composite design (CCD) of response surface methodology using a three-level factorial design with axial and central points was thus used where the response variable was the corrosion resistance obtained from electrochemical experiments and three factors having three levels: concentration (0.19, 0.38 and 0.57 mol L⁻¹ as Cr(III)), pH (2.0, 3.0 and 4.0) and temperature (25, 32, 40 °C) as input variable. The order of the experiments was randomized to ensure against the effect of time-related variables

Table 1. Experimental design showing the set of conditions for chromium plating

No	Treatment	Concentration of Cr ⁺³ /(mol L ⁻¹)	pH	Temperature /(°C)	Replicates
1	S1P1T2	0.19	2.0	32.5	2
2	S3P1T2	0.57	2.0	32.5	2
3	S1P3T2	0.19	4.0	32.5	2
4	S3P3T2	0.57	4.0	32.5	2
5	S1P2T1	0.19	3.0	25	2
6	S3P2T1	0.57	3.0	25	2
7	S1P2T3	0.19	3.0	40	2
8	S3P2T3	0.57	3.0	40	2
9	S2P1T1	0.38	2.0	25	2
10	S2P3T1	0.38	4.0	25	2
11	S2P1T3	0.38	2.0	40	2
12	S2P3T3	0.38	4.0	40	2
13	S2P2T2	0.38	3.0	32.5	4

Table 2. Composition of chromium baths for chromium plating

Compound	Concentration /(mol L ⁻¹)		
	Solution 1 (S1)	Solution 2 (S2)	Solution 3 (S3)
CrCl ₃ ·6H ₂ O	0.19	0.38	0.57
H ₃ BO ₃	0.80	0.80	0.80
HCOONa	0.095	0.19	0.285
CH ₃ COONa 3H ₂ O	0.095	0.19	0.285
C ₁₂ H ₂₅ NaO ₄ S	3.5 × 10 ⁻⁴	3.5 × 10 ⁻⁴	3.5 × 10 ⁻⁴

and also to satisfy independence of observation statistical requirement. Each experiment required two replications and four replications were made for central point, until experiments were completed according to the design layout; adding of central points (as shown in Table 1) led us detecting nonlinearity in responses.

2.2 Electroplating

All chemicals used were reagent grade. Chromium solutions were formulated with chromium chloride as chromium source in the quantities shown in Table 2; sodium formate and acetate were used as complexing agents in equal molar concentration in 1:1 ratio regarding chromium in solution. 50g L⁻¹ boric acid was used as buffer and 0.1 g L⁻¹ sodium lauryl sulfate as wetting agent. Solutions were heated up to 60°C for three hours as in (Suarez, 2006).

The coatings were deposited on a 2 × 2 cm² mild steel (AISI 1008) flat sample. All experiments were prepared as follows: firstly, the surface was

mechanically polished using up to 600 grade emery paper (to simulate an industrial condition) and then manual and anodically degreased in sodium hydroxide (5% w/v), after having been activated in sulfuric acid (5% w/v) for 2 minutes and then plated in a nickel Watts bath until a 6 micron thickness was reached. Deionized water was used for rinsing between all steps. Nickel bath composition is listed in Table 3. Conditions during nickel plating were pH 4.5, 55°C and 3 A cm⁻² cathode current density.

Samples were coated with chromium immediately after nickel plating. Chromium plating was done at constant 8 A dm⁻² cathodic current for 2 minutes using graphite as anode. The set of conditions used during chromium plating are presented in Table 1. Nickel and chromium were plated separately but in similar cathodic device. Figure 1 shows the cell used for nickel and chromium plating.

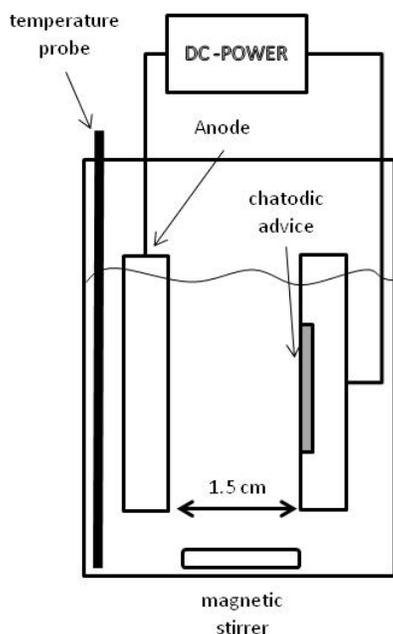


Fig 1. Nickel and chromium plating cathodic device.

Table 3. Composition of Watts bath for nickel plating

Compound	Concentration / (g L ⁻¹)
NiSO ₄	250
NiCl ₂	60
H ₂ BO ₃	40
C ₁₂ H ₂₅ NaO ₄ S	1
(NH ₂) ₂ CS	0.25
C ₇ H ₄ NnaO ₃ S·2H ₂ O	1

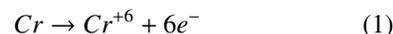
2.3 Corrosion measurement

Electrochemical experiments were performed in 100mL volume three-electrode cell with. A 0.2 cm² area of every sample isolated with an o-ring was used as working electrode. A graphite bar and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively.

Corrosion pattern was evaluated after 1 and 24 hours exposure to neutral 3% NaCl at room temperature (20 ± 1°C) using a GAMRY potentiostat. EIS measurements were conducted at open circuit potential (OCP) over a 10³ Hz to 5×10⁻³ Hz frequency range with 10 mV AC amplitude. Potentiodynamic polarization curves were measured between 0.25 V to 0.25 V vs. open circuit potential (OCP) at 0.2 mV s⁻¹ scan rate.

2.4 Thickness measurement

Chromium film thickness was measured by the coulometric method using the three-electrode cell in a 100 g L⁻¹ sodium sulfate solution (neutral pH) with 0.1 A dm⁻² current density, at this conditions potentials close to 1.10V vs SCE were registered on work electrode. The amount of mass dissolved was calculated assuming that the only oxidation reaction occurring on the electrode was (ec 1), this could be concluding by analysis of Pourbaix and predominance zone diagrams (Barrera *et al.*, 2003):



Average current cathode efficiency was calculated on the other side as the stripped to deposition charge ratio; three points were measured on any sample.

2.5 Morphology and composition

Composition and surface morphology were examined by EDX analysis and SEM. QUANTA 200 microscope was used with a 20KeV electron beam.

3 Results and discussion

3.1 Morphology, thickness and composition

Fig. 2 shows the morphology of representative chromium coatings produced using different operating conditions. Smooth surfaces were observed in all cases (all samples not shown); however, pH was the parameter mainly affecting surface morphology. When comparing deposits a crack pattern was found for coatings obtained at higher pH values, 3.0 and 4.0 (Fig. 2 c.e.f). while this did not occur for pH 2.0 (Fig. 2 a.b.d). Such effect was seen to be independent of Cr(III) temperature and concentration in the plating bath. Cracks in electrolytic chromium have been explained as being due to incorporating chromium hydride in the coatings which breaks down, thereby causing film cracking (Snyder and Mandic, 2000; Snyder and Jones, 2004).

Fig 3, shows chromium coatings thickness measured by coulometric method, chromium atomic percentage measured by EDX and average current cathode efficiency. Good correlation was found between thickness measured by coulometric method and Cr at% obtained by EDX. Data in Fig. 3 shows that thickness was very low for diluted solutions (S1) having 0.19 mol L⁻¹ of Cr⁺³, while both thickness and cathode efficiency increased greatly for more

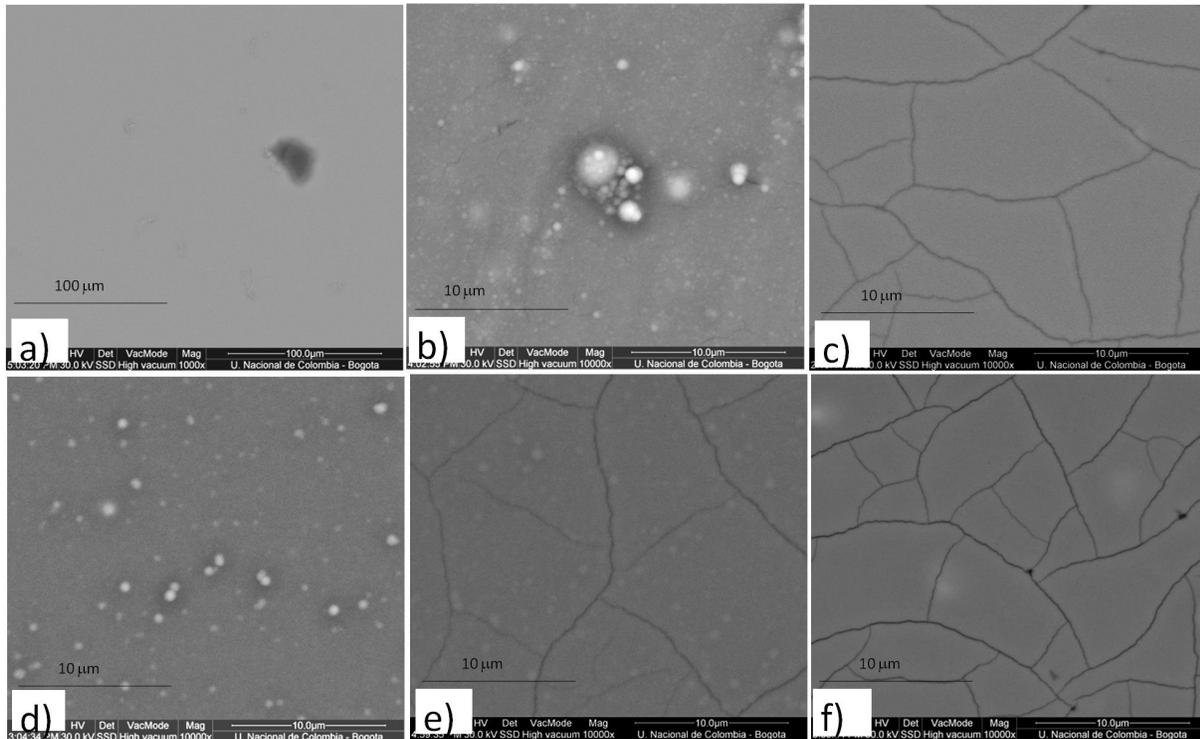


Fig. 2. SEM micrographs of chromium films plated in different operating condition; (a) S1P1T2 1KX; all others 10KX (b) S2P1T1, (c) S2P2T2, (d) S3P1T2, (e) S3P2T1, (f) S2P3T2.

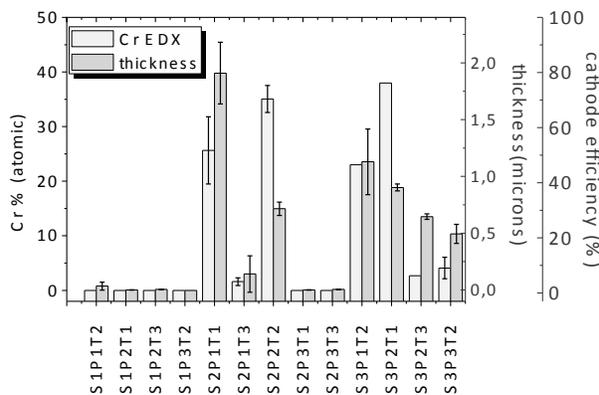


Fig 3. Right axis: thickness measured by coulometric method and equivalent current efficiency; Left axis: EDX analysis of chromium in atomic percentage.

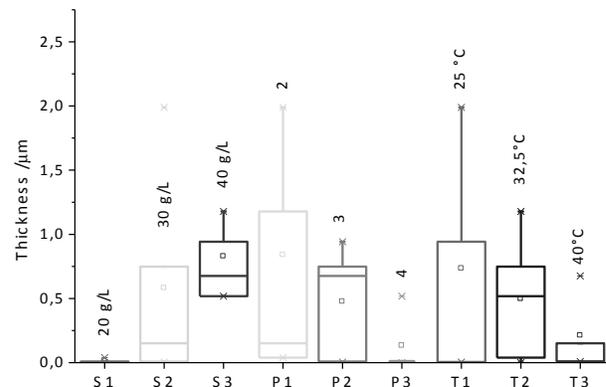


Fig 4. Box plots for thickness measured by coulometric method grouped by factor: concentration (S), pH (P) or temperature (T).

concentrated solutions (S2 and S3). Fig. 4 shows box plots of thickness grouped by variable and this explained the partial effect of every operating condition (concentration, pH and temperature). Average thicker chromium coatings were obtained at high chromium concentration and variation due to other parameters was less, while increased solution

pH and temperature caused decreased thickness and cathode efficiency. These results were similar to those presented in previous work (Baral and Engelken, 2005; He *et al.*, 2007); however, the efficiency values obtained were higher compared to those obtained for hexavalent chromium, ranging from 15% to 25% (Snyder and Mandic, 1974; Snyder and Jones, 2004).

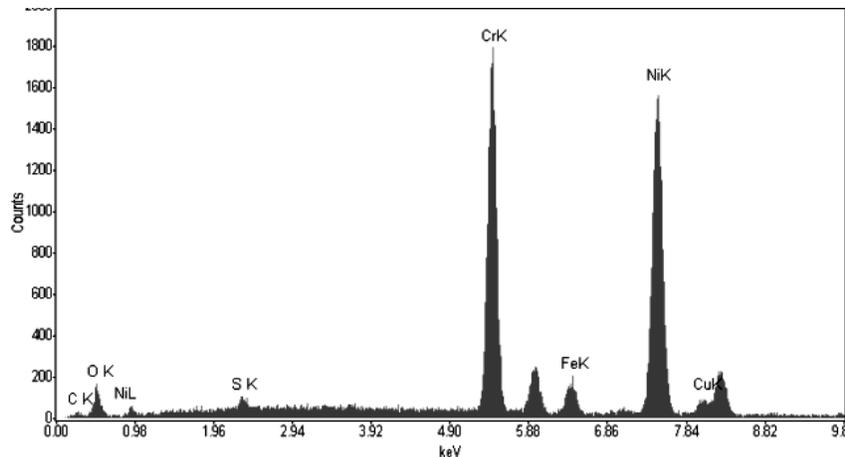


Fig. 5. EDX spectrum for sample plated with S2P1T1 (0.38 mol L⁻¹ Cr(III), pH 2.0, T=25°C).

Table 4. EDX analysis for chromium coatings

Sample	at%						
	Cr	Ni	O	C	S	Fe	Cu
S1P1T2	0.6	96	–	–	–	3.4	–
S1P2T1	0.5	97	–	–	–	2.5	–
S1P2T3	0.6	97	–	–	–	2.4	–
S1P3T2	0.3	97	–	–	–	2.7	–
S2P1T1	31	34	15	15	0.8	2.2	2
S2P1T3	2.3	82.7	2.1	8.8	0.7	3.4	–
S2P2T2	33.3	55	8.7	–	–	3	–
S2P3T1	0.8	95.5	–	–	–	3.7	–
S2P3T3	0	97	–	–	–	3	–
S3P1T2	23	60.7	4.2	6.8	0.6	2.9	1.8
S3P2T1	39	50.1	8	–	0.4	2.5	–
S3P2T3	2.7	42.2	18.2	30.5	2.1	2.4	1.9
S3P3T2	2.7	69.6	8.9	1.6	2.6	4.6	–

Such important influence of concentration coating thickness could have been due to diffusional control during chromium reduction; the effect of pH and temperature were due to the reaction between Cr(III) and [OH]⁻ to form [Cr(OH)]⁻², [Cr(OH)]⁻¹, and [Cr(OH)₃] to form bridge hydroxyl, which can obstruct Cr(III) from electrode (Baral and Engelken, 2005).

EDX spectra for one of the films obtained are shown in Fig. 5. Table 4 shows the composition results for the other coatings. The Elements presents were: iron from substrate, sub-nickel layer nickel and sulfur (sulfur due to the brightener system used) and upper film chromium. Peaks corresponding to carbon and oxygen were also observed for coatings

having high chromium quantity. These elements can be co-deposited during plating, as previously observed (Survilliene *et al.*, 2007; Boasong *et al.*, 2006). A copper peak appeared in some coatings; this element was not part of chromium plating solution formulation, meaning that it might have resulted from chromium solution contamination with this metal due to accumulation and drag-in from previous solutions.

3.2 Potentiodynamic polarization tests

Fig. 6 shows potentiodynamic polarization curves for chromium electrodeposited coatings immersed in 3%

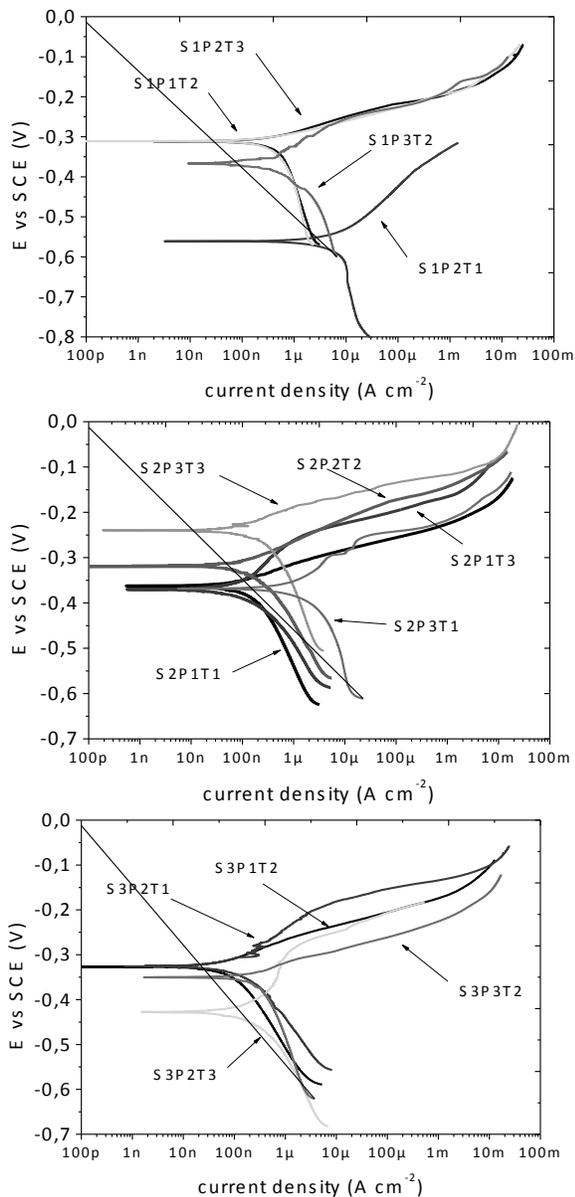


Fig 6. Potentiodynamic curves for electrodeposited chromium obtained at different operating conditions in 3% NaCl electrolyte, $v=0.2\text{mV s}^{-1}$.

NaCl. All curves showed active behavior up to OCP and no passivation occurred. The main difference between chromium coatings was in the potential where pitting began. Current density increases rapidly when potential increased in coatings obtained from more dilute solution ($S1=0.19\text{ mol L}^{-1}$ as Cr(III)) while, for some thicker coatings (thicker chromium films) obtained from concentrated solutions ($S2=0.38$ and $S3=0.57\text{ mol L}^{-1}$ as Cr(III)), an area of little current density increase was observed until close to 100mV

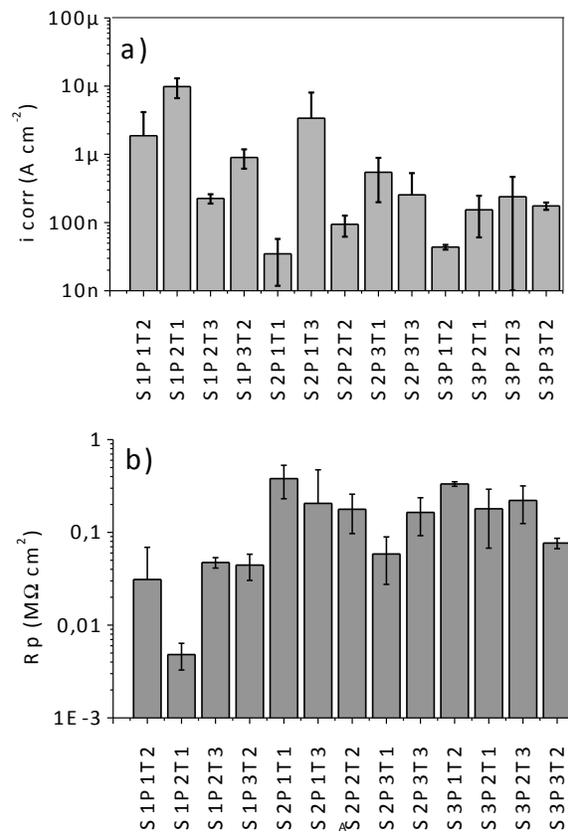


Fig 7 Polarization curve results for electrodeposited chromium coatings; a) corrosion current density (i_{corr}). b) polarization resistance (R_p).

up to the OCP, meaning these coatings perform high polarization resistance in this area. A higher increase in current density with low polarization resistance could be observed due to the beginning of pitting (Kaesche, 2003). Fig 7 shows corrosion current density (i_{corr}) and polarization resistance (R_p) at OCP calculated for Tafel extrapolation of polarization curves. Differences close to one order of magnitude were found between coatings obtained from dilute to concentrate solutions. No differences in behavior due to pH and plating temperature were observed.

3.3 Electrochemical impedance spectroscopy tests

Fig 8 shows spectrums in Nyquist diagrams for electrodeposited chromium, after one and twenty-four hours immersed in 3% NaCl. The impedance plots showed depressed semicircles which decreased in size after 24 h.

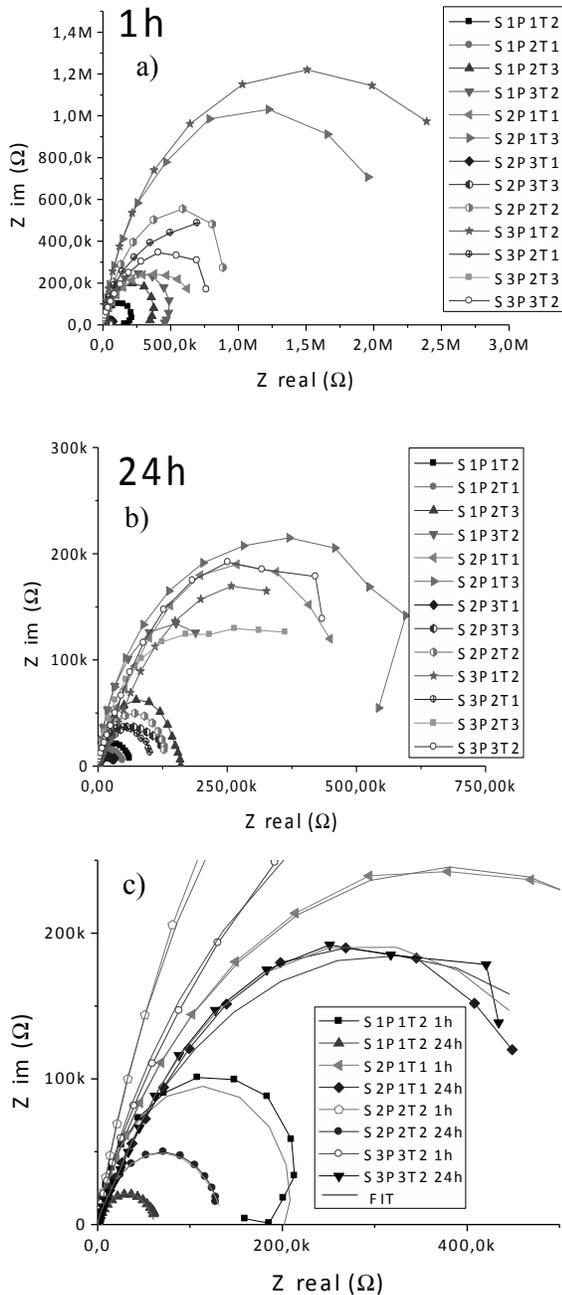


Fig 8 Nyquist diagrams for electrodeposited chromium obtained in different operating conditions in 3% NaCl at OCP after: a)1h; b) 24 hours and c)selected fit data 1 and 24h.

These were modeled by using the circuit presented in Fig 9. An inductive effect was also observed in coatings obtained from low chromium concentration (S1); this effect appeared even with short time immersion, indicating that the chromium and nickel

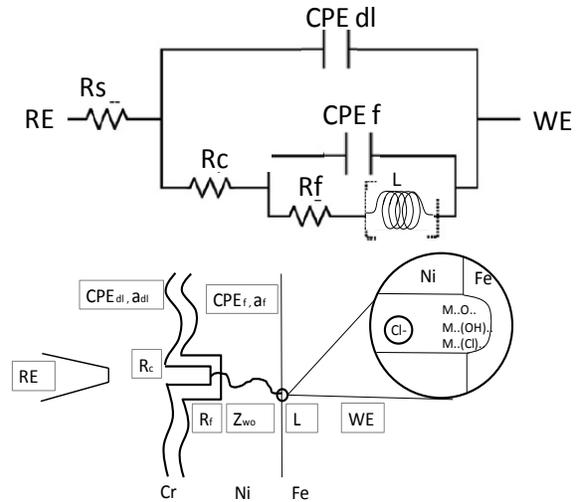


Fig 9. a) Equivalent circuit used to fit corrosion resistance parameters in EIS tests. b) physical equivalent.

layers presented defects (as pores) which were rapidly penetrated by the solution and a small area of steel substrate was constantly exposed to the chloride solution during the corrosion test.

The circuit shown in Fig 9, is the usual type of circuit used for multi layer coatings (Kaesche, 2003; Tapan; 2007) where R_s represents the circuit's total ohmic resistance, R_c porous resistance and CPE_{dl} (constant phase element) double layer capacitance with correction for the surface roughness and R_f and CPE_f , respectively, the film resistance and coating capacitance. Only for thinner films, inductive element L appears as can be seen in Fig 8c (parentheses representation in Fig 9). Inductive element represents corrosion products adsorption in electrode surface or interaction between active and passive areas (Kaesche, 2003). Table 5 shows parameters of proposed equivalent circuit. Values for equivalent resistance R_f are always at least one order of magnitude greater than R_c resistance, this means to R_f is the control resistance in the corrosion process. Diminution of overall resistance corrosion of the coating after 24 hours then can be attributed to decreasing in R_f . It can be observed to exponents for CPE_{dl} elements are between 0.76-1.00 which means no regular surfaces are presents in all cases, for the exponents of CPE_f it can be seen to values as low as 0.15 are obtained in some cases, this could indicate to diffusion phenomena can be occurring in these coatings. Inductive parameter (L) was observed only for coating obtained from diluted solutions S1 and

Table 5. Parameters for equivalent circuit corrosion for chromium coatings obtained at different operating conditions.

Treatment	Time (h)	R_s ($\Omega \text{ cm}^2$)	CPE_{dl} ($S^*s^a \text{ cm}^{-2}$)	a_{dl}	R_c ($\Omega \text{ cm}^2$)	CPE_f ($S^*s^a \text{ cm}^{-2}$)	a_f	R_f ($\Omega \text{ cm}^2$)	L(H)
S1P1T2	1	15.1	3.40E-05	0.88	4.62E+04	—	—	1.69E+05	1.55E+07
	24	14.2	3.74E-05	0.87	4.00E+02	5.45E-05	0.60	1.28E+04	—
S1P2T1	1	11.8	2.84E-05	0.89	4.60E+03	—	—	1.43E+04	5.61E+06
	24	16.8	4.77E-05	0.84	1.24E+03	9.10E-05	0.60	8.90E+03	—
S1P2T3	1	15.1	2.76E-05	0.88	9.54E+04	—	—	3.46E+05	1.45E+07
	24	15.2	2.02E-06	0.75	1.26E+01	3.18E-05	0.88	3.14E+04	—
S1P3T2	1	12.8	2.49E-05	0.82	8.20E+01	1.03E-05	0.74	1.15E+05	—
	24	13.6	5.76E-05	0.75	4.20E+02	6.36E-05	0.88	6.40E+04	—
S2P1T1	1	11.3	2.30E-05	0.86	8.08E+01	1.34E-05	0.54	1.66E+05	—
	24	12.2	3.97E-06	1.00	7.06E+00	4.66E-05	0.67	1.25E+05	—
S2P1T3	1	13.0	2.69E-05	0.90	2.10E+03	5.40E-06	1.00	7.72E+05	—
	24	11.9	2.65E-05	0.87	3.14E+04	1.82E-04	0.25	9.20E+04	—
S2P2T2	1	12.4	2.77E-05	0.84	6.44E+02	6.30E-05	0.84	4.50E+04	—
	24	13.2	6.40E-05	0.78	1.63E+01	7.15E-06	0.92	2.74E+04	—
S2P3T1	1	11.6	5.10E-05	0.82	7.00E+01	4.13E-05	0.75	9.50E+05	—
	24	13.4	5.60E-05	0.78	8.40E+02	8.74E-06	0.82	5.23E+04	—
S2P3T3	1	14.6	4.25E-05	0.89	7.70E+01	8.27E-05	0.73	6.73E+04	—
	24	14.0	7.16E-05	0.83	3.50E+02	1.74E-05	0.66	1.12E+04	—
S3P1T2	1	8.8	5.70E-06	0.76	6.52E+00	1.29E-05	0.93	6.14E+05	—
	24	12.9	2.29E-05	0.81	3.32E+03	7.95E-05	0.52	1.61E+05	—
S3P2T1	1	12.9	2.79E-05	0.87	3.54E+03	1.02E-06	0.15	5.24E+05	—
	24	12.3	3.64E-05	0.86	1.45E+04	1.17E-04	0.66	1.85E+04	—

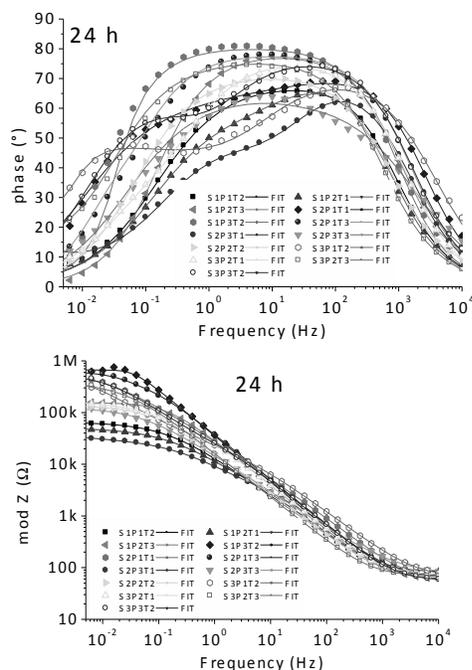


Fig. 10. Bode plots for electrodeposited chromium obtained at different operating conditions. after 24

hours immersed in 3% NaCl.

corresponds to thinner chromium coatings obtained.

Fig 10 shows Bode diagrams after twenty-four hours immersed in 3% NaCl. The general behavior observed was the same for all coatings, meaning two time constants; however, one of these decreased rapidly after 24 hours for the less resistant coatings. A large difference of about two orders of magnitude in total impedance was observed between films obtained from diluted to concentrate solutions; chrome surfaces obtained at low pH values presented the highest resistance.

3.4 Corroded surface morphology

Fig 11 shows SEM images obtained for representative coatings after EIS experiments. No pits were observed after 24 hours' immersion in 3% NaCl; however, the crack pattern which had only been observed for deposits obtained from solutions with pH 3.0 or 4.0, was then observed for all coatings, including those obtained at pH 2.0 (Fig 10 a. b). Attack on the cracks' edges with an incipient delaminating of the film was observed for some coatings.

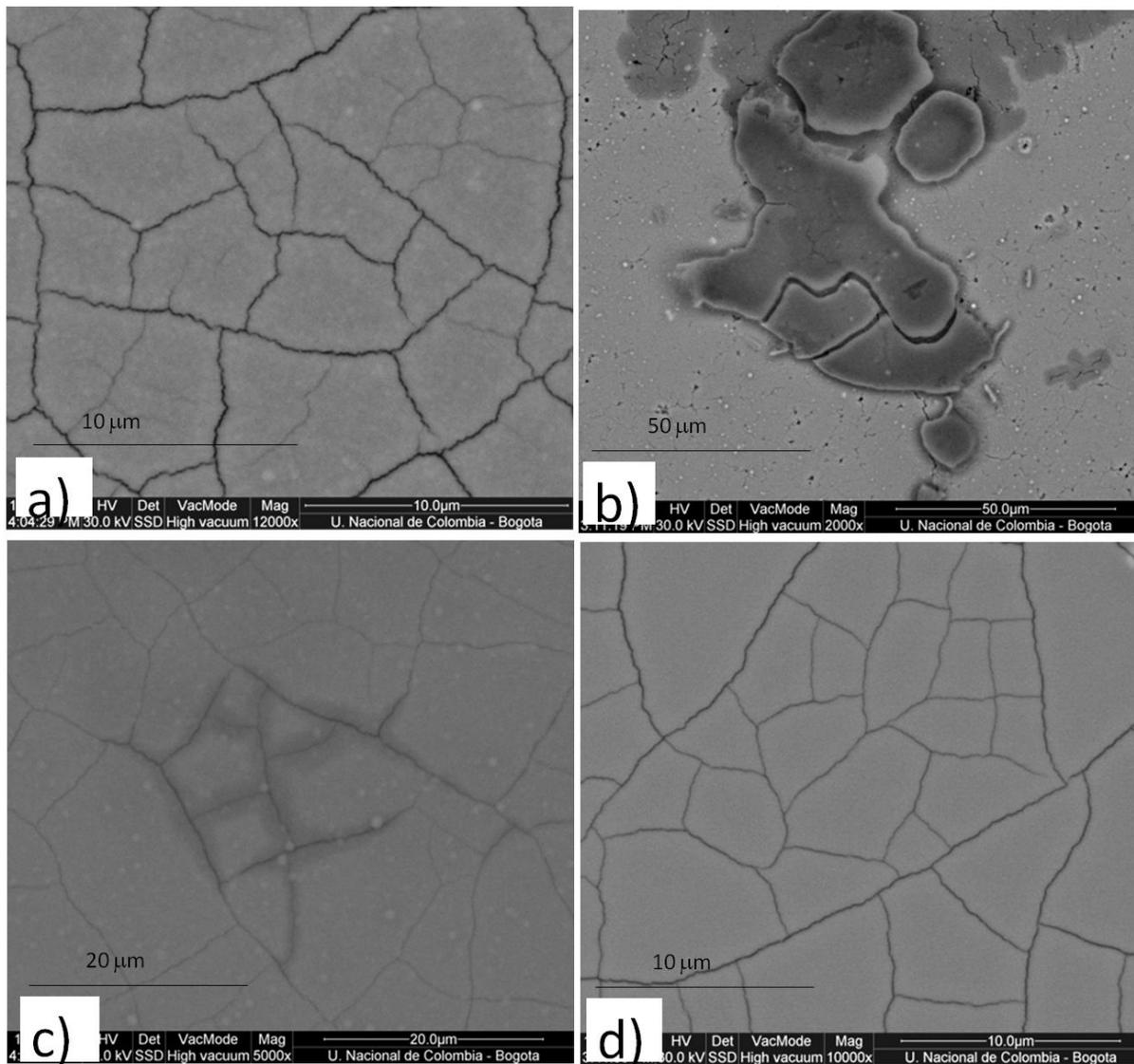


Fig 11. SEM micrographs of chromium films corroded after 24 hours in 3% NaCl; (a) S2P1T1. (b) S3P1T1. (c) S3P2T1. (d) S3P3T2.

Table 6. ANOVA ($\alpha = 0.05$) analysis for $\text{Log}(i_{corr})$

Factor	Coeff	Dev Coeff	T	P
Constant	-2.349	0.943	-2.49	0.020
Concentration	-0.054	0.017	-3.25	0.003
pH	0.144	0.166	0.87	0.394
Temperature	-0.016	0.022	-0.74	0.466

S = 0.66; $R^2 = 33.1\%$; R^2 (adjusted) = 24.7%

Table 7. ANOVA ($\alpha = 0.05$) analysis for $\text{Log}(R_p)$

Factor	Coeff	Dev Coeff	T	P
Constant	-2.296	0.699	-3.28	0.003
Concentration	0.049	0.012	3.94	0.001
pH	-0.104	0.123	-0.82	0.418
Temperature	0.015	0.016	0.92	0.366

S = 0.49; $R^2 = 41.6\%$; R^2 (adjusted) = 34.3%

3.5 Statistical analysis of results

Tables 6 to 9 show ANOVA analysis for i_{corr} , R_p and R_f derived from potentiodynamic and impedance tests

for 1 and 24 hours' immersion in 3% NaCl. EIS test values were obtained from the fixed model presented in Fig 9. R_c was not analyzed because it was close to an order of magnitude less than R_f and the highest

Table 8. ANOVA ($\alpha = 0.05$) analysis for $\text{Log}(R_{f1h})$

Factor	Coeff	Dev Coeff	T	P
Constant	-5.055	2.365	-2.13	0.044
Concentration	0.292	0.064	4.54	0.000
pH	1.727	0.643	2.68	0.014
Temperature	0.357	0.002	4.97	0.000
Conc x Temp	-0.009	0.002	-4.48	0.000
pH x Temp	-0.063	0.019	-3.24	0.004

$S = 0.4146$ $R^2 = 65.6\%$ R^2 (adjusted) = 57.7%

Table 9. ANOVA ($\alpha = 0.05$) analysis for $\text{Log}(R_{f24h})$

Factor	Coeff	Dev Coeff	T	P
Constant	4.285	2.147	2.00	0.059
Concentration	0.063	0.101	0.63	0.537
pH	-1.177	0.404	-2.92	0.008
Temperature	0.137	0.053	2.56	0.018
Conc x Temp	-0.006	0.002	-2.12	0.046
Conc x pH	0.040	0.019	2.12	0.046

one would that which control the corrosion. In all cases, data was analyzed as Log scale for obtaining normal parameter distribution and met the statistical requirements. The tables show coefficients for the associated regression model with associated standard deviations and also T (T-student distribution) and P values for statistic validation of the hypothesis.

ANOVA analysis of i_{corr} and R_p (Tables 6 and 7) showed that only chromium concentration in plating solution affected the coatings' corrosion resistance (less than 0.05 P value); this could have been due (as seen before) to concentration greatly affecting the thickness of the chromium coating obtained. Chromium thickness has been directly related to coating/substrate system corrosion resistance; however, due to pitting caused by chloride ions, no other effects such as porosity or surface effects, were easily detected by this technique. Analysis of R_f after 1 and 24 hours' immersion (Tables 8 and 9) showed that all parameters (concentration, pH, temperature and interaction between some of them) influenced electrodeposited chromium corrosion resistance due to the sensitivity of EIS measurement for detecting differences in complex systems such as coatings/substrate, as in this case [13].

Fig 12 shows contour plots for $\text{Log}(R_{f1h})$ obtained from the surface response experiment for coatings obtained from solutions of different chromium (III) concentration regarding pH and temperature during plating. The relationship between different parameters

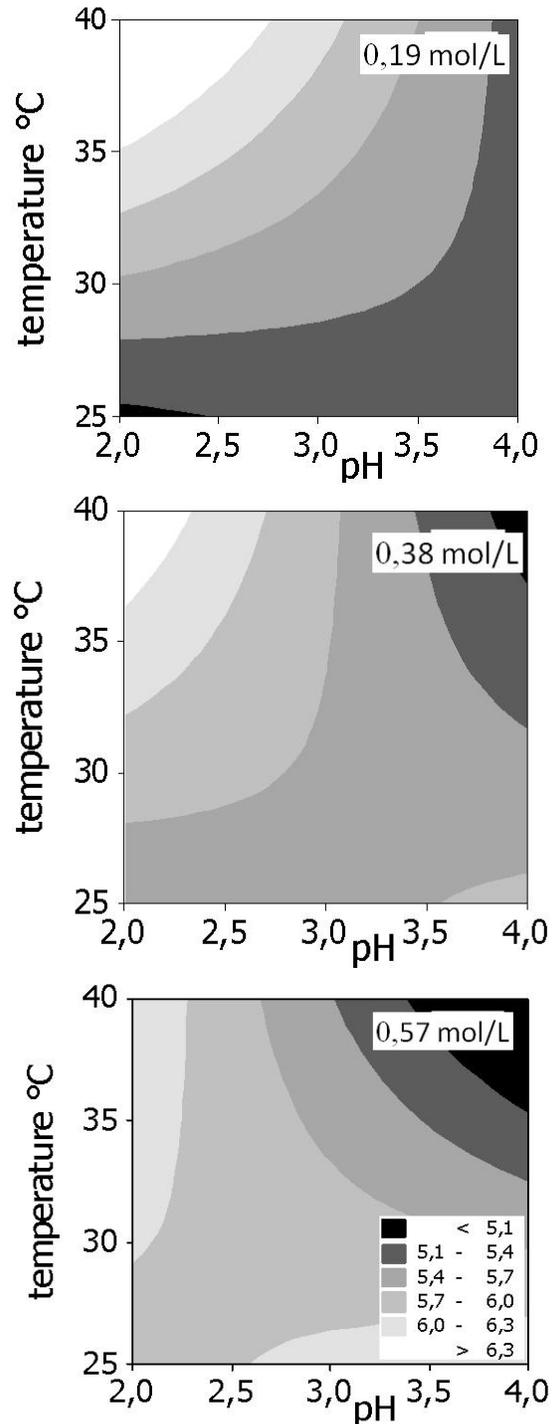


Fig. 12. Contour plots for $\text{Log} R_{f1h}$ for electrodeposited chromium in different operating conditions, $\alpha = 0.05$.

during plating can be seen concerning coatings' corrosion resistance after 1h in 3% NaCl (R_{f1h}). Areas with log R_{f1h} from 5.7 to 6 had greater than 500k Ω impedance; these were the more resistant coatings and were only obtained from diluted solutions at high temperatures and low pH values. The operation area where resistant coatings could be obtained were greater for more concentrated solutions and a wide pH and temperature window conditions could be used for S3 (0.57 mol L⁻¹) for obtaining major corrosion resistance. The contour profiles also that low pH values provided the most favorable conditions for obtaining high corrosion resistance values (R_{f1h}).

Conclusions

Electrodeposited chromium coatings were obtained by modifying operating conditions such as concentration, pH and temperature during plating.

Differences in morphology were observed, mainly depending on plating bath pH; a crack pattern was observed in high pH conditions.

The coulometric method was used for measuring chromium films thickness. This method had good correlation with chromium amount detected by EDX measurements. Difference in chromium coatings thickness was mainly due to chromium solution concentration.

Chromium coatings' electrochemical behavior of was studied by potentiodynamic and EIS experiments in 3% NaCl. The results were analyzed by ANOVA finding that potentiodynamic curves only detected differences due to plating concentration solution greatly affecting coatings thickness while EIS experiments led to seeing all effects and interaction ships between process conditions. Chromium films morphology after the EIS corrosion test showed to that no pitting occurred, but corrosion flow increased in the edges of cracks thereby initiating coating delaminating.

High chromium concentration in solution led to obtaining coatings having good corrosion resistance in a wide window of pH and temperature conditions.

Acknowledgements

Division de Investigación Universidad Nacional de Colombia, project 202010010654, Red de Macrouiversidades de America Latina y el Caribe, CONACYT projects P45833 and DGAPA IN102907 and ALFACROM LTDA.

References

- ASTM B 504-90. (1995). Standard Test Method for Measurement of Thickness of Metallic Coatings by the Coulometric Method.
- Baral, A. y Engelken, R. (2005). Modeling, optimization, and comparative analysis of trivalent chromium electrodeposition from aqueous glycine and formic acid baths. *Journal of The Electrochemical Society* 152 (7), C504-C512.
- Barrera, C., Palomar- Pardavé, M., Romero-Romo, M. and Martínez, S. (2003). Chemical and electrochemical considerations on the removal process of hexavalent chromium from aqueous media. *Journal of Applied Electrochemistry* 33, 61-71.
- Barrera, C. Colín, F. et al. (2004). Cr(VI) removal from wastewater using low cost sorbent materials: roots of *Typha latifolia* and ashes. *Environmental Technology* 25, 907-917.
- Bayramoglu, M. Onat, B. y Green, N. (2008). Statistical optimization of process parameters to obtain maximum thickness and brightness in chromium plating. *Journal of Materials Processing Technology* 203, 277-286.
- Boasong, L., Lin A., Wu, X., Zhang, Y. y Gan F. (2006). Preparation and characterization of Cr-P coatings by electrodeposition from trivalent chromium electrolytes using malonic acid as complex. *Surface and Coating Technology* 201, 2578-2586.
- European Commission. (2006). Applied processes and techniques. In: *Integrated Pollution Prevention and Control - Surface Treatment of Metals and Plastics*, 48-51.
- He, X.K., Qiu, G.Z., Chen B.-Z., Zhou, N.-B., Wu L.-Y. y Xu L.J. (2007). Process of pulse electrodeposition of nanocrystalline chromium from trivalent chromium bath. *Transactions of Nonferrous Metals Society of China* 17, s685-s691.
- Kaesche, H. (2003). Electrode Impedance Spectroscopy. En: *Corrosion of Metals Physicochemical Principles and Current Problems*, 562-581. Springer, New York.

- Snyder, D. y Mandic, N.V. (2010). Electrodeposition of Chromium. In: *Modern Electroplating* (S. Mordechay y P. Milan, eds), Pp. 205-248. John Wiley & Son, New Jersey.
- Snyder, L.D. (2004). Decorative and Functional. Trivalent chromium electroplating. *Surface Finished*, 215-216.
- Song, Y.B. y Chin, D.T. (2002). Current efficiency and polarization behavior of trivalent chromium electrodeposition process. *Electrochimica Acta* 48, 349-356.
- Suarez, O.J. (2006). Obtención de un recubrimiento de cromo decorativo a partir de soluciones de cromo trivalente. *Ingeniería e Investigación* 26, 75-83.
- Suarez, O.J. (2010). Obtención y caracterización electroquímica y estructural de recubrimientos de cromo decorativo a partir de soluciones de cromo trivalente. Tesis de maestría en Ingeniería - Materiales y Procesos, Universidad Nacional de Colombia, Colombia.
- Suarez, O.J., Olaya, J.J., Rodil S., Suarez M.F. y Zarco H. (2009). Obtención y caracterización electroquímica y estructural de recubrimientos de cromo decorativo a partir de soluciones de cromo trivalente. *Revista Latinoamericana de Metalurgia y Materiales SI 4*, 1575-1583.
- Surviliene, S. Jasulaitiene, V. Nivinskiene, O. y Cesuniene, A. (2007). Effect of hydrazine and hydroxylaminophosphate on chrome plating from trivalent electrolytes. *Applied Surface Science* 253, 6738-6743.
- Surviliene, S. Nivinskiene, O., ?e?unien?, A. y Selskis, A. (2006). Effect of Cr(III) solution chemistry on electrodeposition of chromium. *Journal of Applied Electrochemistry* 36, 649-654.
- Szyncarzuk, J. Drela I., Kubicki J. (1989). Electrochemical behaviour of chromium III in the presence of formica acid ?I. *Electrochimica Acta* 34, 589-592.
- Tapan, K.R. (2007). Electrochemical impedance spectroscopy study on multilayered coated steel sheets. *Corrosion Science* 49, 794-817.
- Vinokurov, E.G. Demidov, A.V. y Bondar, V.V. (2005). Physicochemical model for choosing complexes for chromium-plating solutions based on Cr(III) compounds. *Russian Journal of Coordination Chemistry* 31, 17-21.