

Morphology and Corrosion Performance of Chromate Conversion Coatings on Different Substrates

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Received September 12, 2008; accepted November 14, 2008

Abstract. The aqueous corrosion resistances of galvalume (Fe-Al+Zn) and steel galvanized (Fe-Zn) alloys, passivated by immersion in chromating solution with different immersion times (0, 10, 30 y 60 s) are compared. The electrochemical behaviour of various chromated and non-chromated coatings was investigated in 3 wt-% NaCl solution using polarization techniques. For comparison, AISI 1010 carbon steel substrates were also analyzed. The characterization measurements and polarization curves revealed that textural properties of Fe alloys influence the growth of the films and both the cathodic and anodic reactions. An optimum anticorrosive protection was obtained at 30 s. CCCs treatments inhibited the corrosion of zinc to a significant degree, but less effectively than coatings formed with aluminium-zinc alloys. The difference in the corrosion protection given by the two substrates types was attributed to the structural properties, thickness coating, grain size and roughness observed, which affect oxygen diffusion.

Keywords: CCCs, Fe alloys, textural properties, adhesion.

1. Introduction

Zinc coatings are predominantly used to improve the aqueous corrosion resistance of steel by two methods, barrier protection and galvanic protection. In the barrier protection, the zinc coating which separates the steel from the corrosion environment will first corrode before the corrosive environment reaches the substrate [1]. In addition, aluminium is added to provide an enhancement in the protective properties [2]. In general, aluminium coating offers better protection than zinc coating since aluminium itself carrying protective oxide attacked very slowly [3]. However, under certain mild conditions the attack of aluminium is too slow to provide cathodic protection to steel and in such circumstances zinc coating is preferred [4]. In view of limited galvanic protection by aluminium, zinc alloyed with Al is used to enhance the corrosion resistance of zinc coating on the steel surfaces. It is clear that considerable efforts are being made to improve the corrosion resistance of zinc coatings by alloying and often by applying a compatible conversion coating treatments. Chromate conversions coatings have been widely used for many engineering materials to provide improve corrosion resistance, desirable surface finishes and paint adhesion characteristics. In spite of the fact, the composition, structure and protective mechanism of such coatings are not well known up to now [5-8]. The morphology

Resumen. En este trabajo se analizó el efecto de la composición superficial de dos aleaciones de hierro (Fe-Al+Zn, Fe-Zn) y su desempeño contra la corrosión al aplicar tratamientos de conversión química con cromo hexavalente y diferentes tiempos de inmersión (0, 10, 30 y 60 s). El desempeño electroquímico de los materiales se evaluó utilizando técnicas de polarización en una solución al 3 % en peso de NaCl. Como referencia se sintetizaron y compararon películas de cromo en muestras de acero al carbono comercial (AISI-1010). Los recubrimientos obtenidos mostraron un crecimiento no uniforme, con poros y grietas superficiales. Los recubrimientos obtenidos en tiempos de 30 s mostraron las propiedades de protección más eficaces para este tipo de sustratos. Las propiedades texturales de las aleaciones evaluadas juegan un papel muy importante en el tipo de crecimiento de las películas de conversión y afectan las propiedades de protección en medios agresivos.

Palabras clave: Tratamientos de conversión, recubrimientos, aleaciones de hierro, impedancia electroquímica, adherencia.

and the composition of a conversion coating play an important role in corrosion protection. The properties of these coatings depend on the kind of substrate metal, the composition and structure of the coatings. On the other hand, the composition and structure of the coatings depend on the method chromating the bath composition and parameters of the process [9, 10]. In our knowledge, there is little information concerning the composition and characteristics of the coatings on the Fe-Zn and Fe-Zn+Al alloys and there are many literatures on the various applications of the chromate conversion coating [11-14]. In the present article, an analysis of the effect of textural properties in the formation of chromate conversion films on galvanized steel and galvalume substrates was realized. The corrosion resistance and electrochemical behaviour for both substrates after different immersion times was evaluated and compared with the performance of commercial carbon steel AISI-1010.

2. Results and Analysis

2.1 Characterization of Films

Figures 1a-e show the SEM images for chromate coatings on zinc with dipping time of 10, 30 and 60 s. Galvalume substrates displayed an irregular film formation with plates that

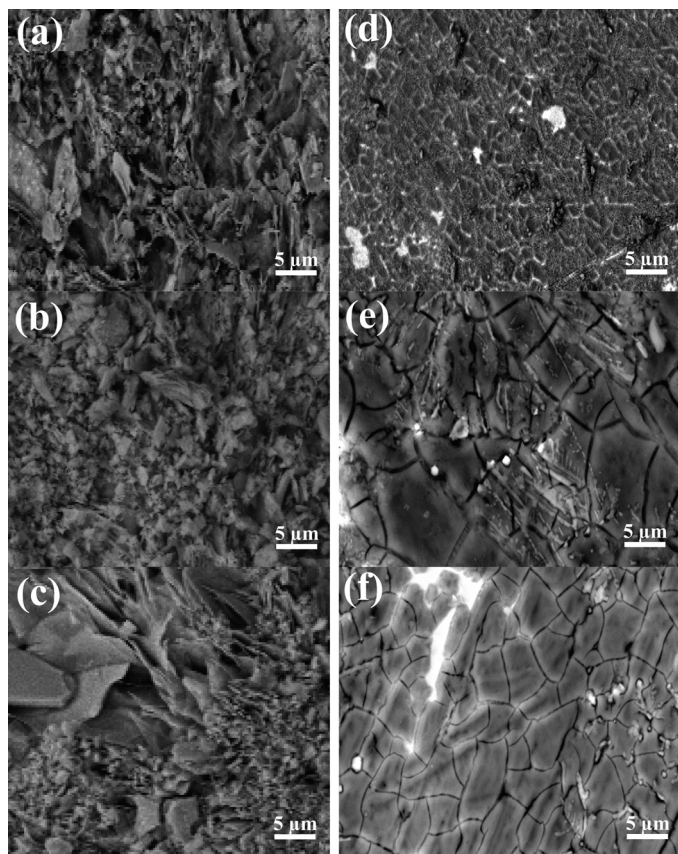


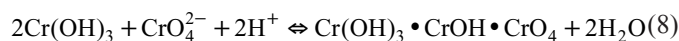
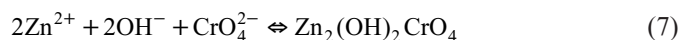
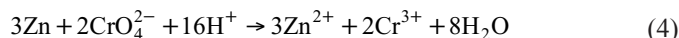
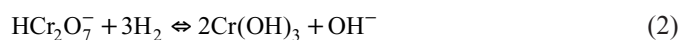
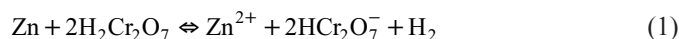
Fig. 1. SEM images for Fe-Zn+Al and Fe-Zn treated in chromate bath with different dipping times (a, d) 10 s, (b, e) 30 s, and (c, f) 60 s.

increase with immersion time while galvanized steel sheets displayed evident cracks which seem to decrease with dipping time. As it was noted in the figures (1d-f), the texture of the conversion film depends strongly on the chemical composition of substrate surface and immersion time. Hexavalent chromium with low concentration than that reported for black chromate also existed in the coatings and this composition was one of the reasons to result in the pale yellow colour of the coating [9]. From these micrographs, the semiquantitative measurements of the chromate film thicknesses ranged from 900 to 1500 nm, which are higher than those reported in the literature, and could explain the high light dispersion [14, 15]. Specially, for galvanized steel, the SEM micrographs show «dried riverbed» cracks on the coating surface. These cracks look like platelets with sharp and well defined edges. In the preparation of the coating it was known that the coating before drying was gel-like structure. In the stage of drying, the coating would shrink and the shrinkage processing result in the formation of microcracks with «dried riverbed» patterns [16]. The mechanism of the crack formation is mainly due to the internal stress in the coating, if the crack penetrates through the coating it may allow corrosive ions access to the substrate metal. The film tensile stress has usually a tendency to increase as a function of the coatings thickness [14]. However, in this case the light or crack areas also show an important quantity of chromium, which is indicative of the film quality. In addition, Galvalume

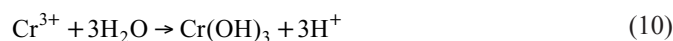
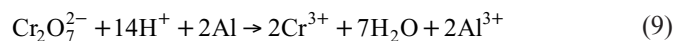
show interesting differences comparing to galvanized steel. In that case, low magnifications (100 μm) two zones can be distinguished. The first region consists of dispersed islands; and the second area, where a lower thickness film covers some zones of the alloy; in these zones, the substrate microstructure is visible because the layer is very thin and no crack is observed in the area. The comparison with AISI-1010 commercial carbon steel using different immersion times is shown in figure 2. Even though the microstructure of the treated steel displayed changes with the time of immersion and textural properties of the substrate, it is well known that the improvement in corrosion resistance of steels by added chromium films mainly result by the inner resist ion and electron migration better than FeO, which is formed immediately when the steel electrode is immersed in aqueous media. However, an optimal immersion time is desirable due to the conversion bath can attack the surface substrate. In fact, important differences can be observed for carbon steel with 5 and 10 s of immersion at room temperature which affect growth and adhesion properties of the films. The EDS analysis of Fe-Zn and Fe-Zn+Al specimens has revealed that the composition of the film ranged of 8-16 atomic % of chromium with remaining contribution coming from Fe, Zn, Al, C and O and XRD patterns (not shown here) displayed that the presence of $\text{Cr}_2\text{O}_7^{2-}$, Cr_2O_3 or CrO_3 , and their intensity increased with dipping time. Then, CCCs growth was strongly affected by substrate surface. Specially, the coating formed on Fe-Zn consisted of small crystals randomly distributed on the surface and whose size was larger than those obtained on the Fe-(Al+Zn) matrix. These results also suggested that is easier to form a uniform film on galvanized steel than on galvalume samples, which is in good agreement with other researches using different substrates [17]. In addition, it is necessary to consider that maybe occur dissolution of Fe-Zn and Fe-(Al+Zn) substrates during coating growth, which can cause locally defects or pores.

The mismatch in the growth of the film can be explained in terms of the mechanism of the reaction, which depends of the substrate surface composition and affects crystal shape forming the film.

The overall electrochemical reactions in the chromate solution may be described for galvanized steel as [9,18, 19]:



Aluminium and its alloys have been extensively investigated in presence of dichromate ions, which induce a redox reaction between dichromate ions in solution and aluminium according to the following reactions [20-24]:



On the other hand, for carbon steel, the researchers indicated that CCCs formation consisting of a mixture of iron and chromium hydroxides and oxides. The Cr/Fe-ratio in the film depends on the passivation procedure, but possible reactions can be written as follows [25,26]:

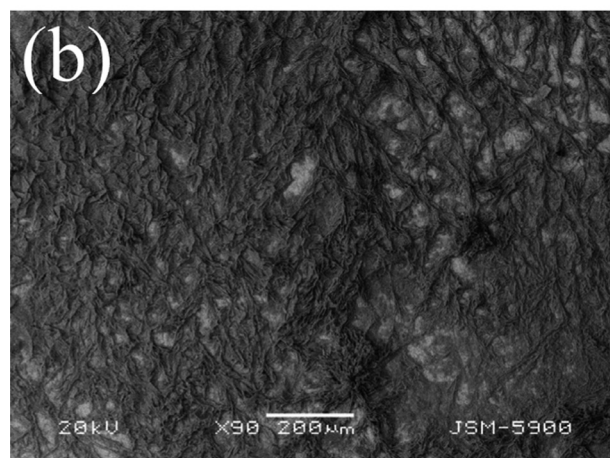
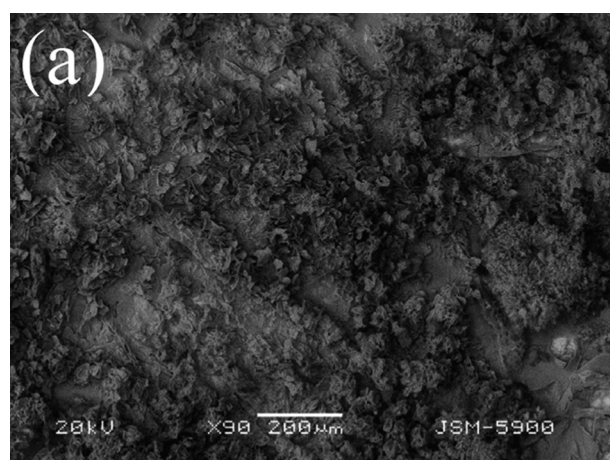
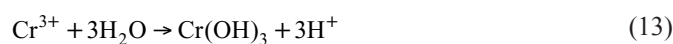
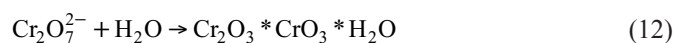
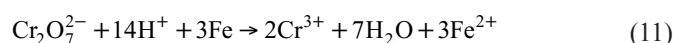


Fig. 2. SEM images for AISI 1010 commercial carbon steel treated in chromate bath with different dipping times (a) 5 s and (b) 60 s.

It is clear that the surface composition affects film growth formation and maybe, adhesion properties and corrosion performance as will be discussed below.

2.2 Electrochemical Measurements

The change in the E_{corr} for different specimens with immersion time is shown in Figure 3a. The displayed values correspond to an average of the samples after 10 min of immersion in a solution of NaCl. AISI-1010 commercial carbon steel substrates are also displayed in that figure. In general, the E_{corr} for untreated specimens increased a little with immersion time but after remains constant, -1020 mV and -1083 mV for galvalume and galvanized steel samples, respectively; while for bare steel was about -700 mV. A shift of E_{corr} to more positive values was found with the time. The E_{corr} of galvalume samples showed a higher displacement than that observed for galvanized steel sheets and is maintained at -980, -947, -956 mV. Carbon steel

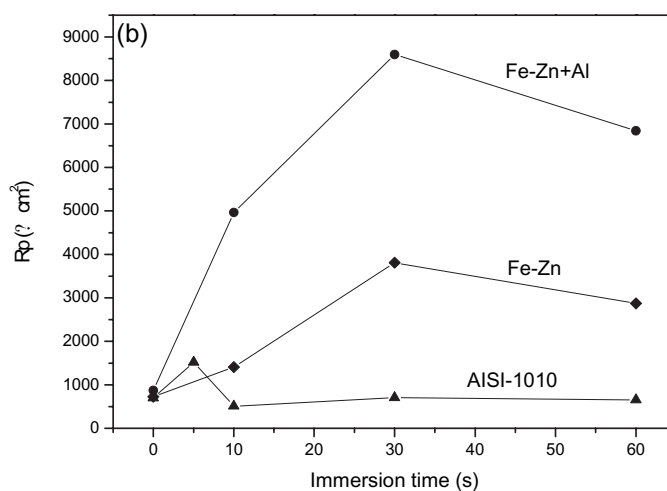
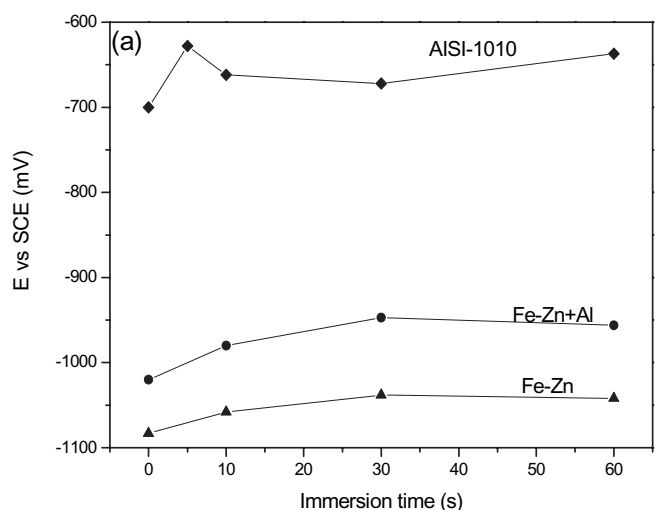


Fig. 3. (a) Open circuit potential and (b) polarization resistance with dipping time for the bare and chromate Fe-Zn, Fe-Zn+Al and AISI-1010 commercial carbon steel.

displayed strong differences with the immersion time without any trend. The potentials of chromate coatings are slightly higher than those for the bare samples, which is the result of the chromate layer.

The polarization resistance R_p of the treated and untreated samples also shows the influence of the surface characteristic of the substrate and immersion time (Figure 3b). The value of R_p was determined in each case by analyzing an interval of polarization of ± 30 mV around the corrosion potential. In terms of the R_p the maximum level of the protection was achieved by treatment the Fe-Zn, Fe-Zn+Al samples for a period of 30 s. The values obtained indicated that an increase in the polarization resistance by a factor close to 8 and 5 can be reached for galvalume and galvanized steel, respectively. On the other

hand, carbon steel displayed a maximum value only after 5 s of immersion and after decrease drastically.

The figures 4 a-b show the effect of chromating on the polarization behaviours of galvalume and galvanized steel samples. It is worth to emphasize that the anodic and cathodic polarization curves shifted toward positive values of corrosion potential and lower values of current densities. The higher displacement was observed for samples with dipping time of 30 s. The behaviour points to the presence of protective barrier layer. Comparison of galvalume and galvanized steel indicated the shape of anodic branches is quite similar. The cathodic polarization curves, however, were different, which is more noticeable in galvanized steel. The bare galvalume and galvanized showed the largest cathodic current density, while Cr^{6+} -treated specimens showed the smallest current density. These results can again be explained in terms of tensile stress inside the coating when the chromate layer is growing.

2.3 Adhesion Properties

Adhesion to the metal substrate can be considered in some practical situations as the most important property of an organic coating [27]. Such a property has a particular significance when painted metals work in humid environments or in electrolytes, because the presence of polar molecules such as water can greatly affect the chemical bonds between the metal and the coating. Pull-off measurements were then performed on samples protected with the polyester coating in order to evaluate the adhesion between polyester and pretreated substrates. In Figure 5 the adhesion strength calculated from the maximum adherence (pull-off) forces upon withdrawal the top-coat from treated substrates are presented. For all cases, the mean values of five identical specimens with detached area close to 100% are given (see inset figure). It can be seen that the bond strength of the coatings after CCCs was increased of 77-108 and 60-108 for lb in^{-2} galvalume and galvanized steel, respectively. From the results above discussed is pointed out

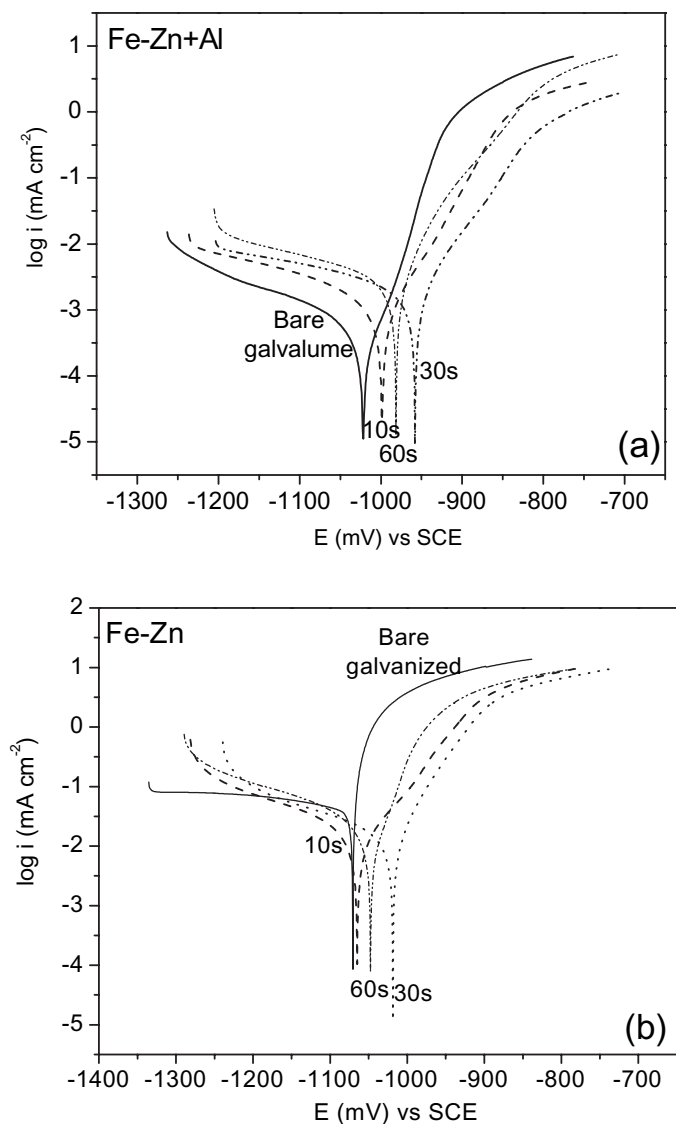


Fig. 4. Anodic and cathodic potentiodynamic polarization curves of (a) galvalume (b) galvanized steel with and without chromate layers after immersion in a deaerated 3 wt-%, NaCl solution, scan rate 1 mV s^{-1} and room temperature.

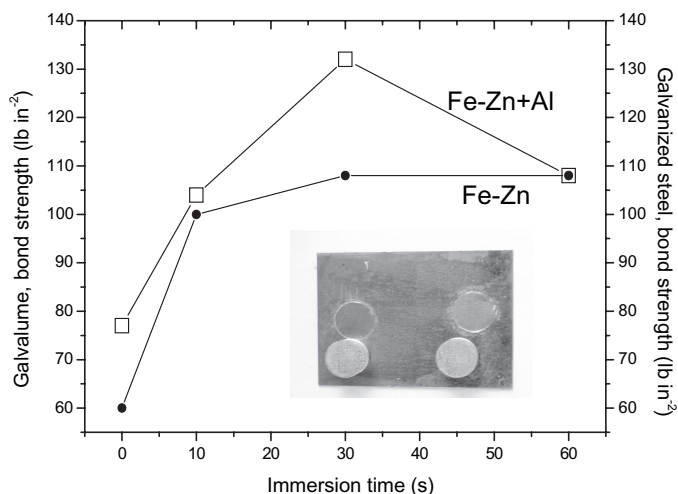


Fig. 5. Bond strength from pull-off test for galvalume and galvanized steel.

the importance of the morphology and chemical composition on surface substrate and influences the mechanism of the growth film. Even the coating morphology after coating/drying treatments could be important because condition the type of corrosion.

Conclusions

CCCs were grown on two substrate types of steel (galvalume and galvanized) and their protection against corrosion was determined. The coatings obtained on both galvalume and galvanized steels developed different morphology and crystal shape forming the film, which is attributable to the surface composition of the substrates. These textural properties of the substrate, also affects the growth mechanism and film tensile stress, which increases as a function of the coatings thickness. From electrochemical measurements, it can be drawn that when galvalume and galvanized steels are coated, their protective properties are enhanced; in general, coated galvalume showed a better behaviour than the coated galvanized, and the maximum level of protection and adhesion properties were obtained when an immersion time of 30 s is applied.

3. Experimental

3.1 Material and CCCs Processes

Hot dip galvalume and galvanized steel sheets (zinc and zinc+aluminium coating) with the average thickness of 22 and 14 μm , respectively was used as starting materials. The coating layers of galvanized steel were composed of three phases: η phase (Zn), ζ phase (Fe-Zn_x) and steel, while the microstructure of the galvalume coating has four principal phases; one phase is the primary aluminum-rich dendritic phase that begins to grow initially during the solidification, an interdendritic zinc-rich region that forms when the zinc concentration in the solidifying liquid reaches a high level, an intermetallic (Fe-Al-Si-Zn) phase and steel. It should be emphasized that this study did not intend to prepare the alloy layer but to investigate the influence of surface characteristics of the substrate on film growth during chromate conversion treatments and its corrosion behaviour in aggressive media. In this regard the CCCs were carried out as follows:

Fe-Zn and Fe-Al+Zn sheets, 2.25 cm^2 and a thickness of 2 mm were used as samples. Before immersion, metallic samples were degreased using acetone, then ethanol and finally dried in air. The chemical conversion coatings (CCCs) were obtained by dipping the commercial samples in the conventional Chronak solution (200 g L^{-1} $\text{K}_2\text{Cr}_2\text{O}_7$ and 10 g L^{-1} H_2SO_4) at room temperature and $\text{pH} = 1.1$ [18], for 10, 30 and 60 s. The coatings were then rinsed, air-dried and aged for 24 h before any further handling or analysis. For comparison, chromate conversion coatings were also deposited on AISI-1010 carbon steel specimens with similar experimental conditions.

3.2 Characterization of Sample

The samples thus obtained at the different immersion times were analyzed for their composition using and X-ray diffractometer operated at 35 kV and 25 mA (Siemens 5000). Surface morphology was examined by using Scanning Electron Microscope (SEM/EDS) JEOL JSM-35C equipped with an EDS voyager Tracor Northern Spectrometer.

3.3 Electrochemical Measurements

The electrochemical behaviour of the samples coated with chromate films was investigated by means of potentiodynamic polarisation measurements, open circuit potential measurements and electrochemical impedance spectroscopy (EIS) a 3 wt % NaCl aqueous solution at room temperature. The counter electrode was a large-area graphite bar and the reference electrode was a saturated calomel electrode (0.2415 V vs NHE). The measurements were carried out at room temperature in a standard electrochemical cell of an acrylic rectangular box (60*80*100 mm) and the area exposed was 0.785 cm^2 (100 ml electrolyte). The scan rate was 10 mV min^{-1} for potentiodynamic polarization measurements. Five potentiodynamic polarization measurements were repeated for each sample investigated in this work. Tafel polarisation curves were measured from cathodic to anodic area. Scans were started at -250 mV vs SCE with a sweep rate of 1 mV s^{-1} .

3.4 Adhesion Properties

In order to test the adhesion properties of the CCCs, non-chromate and chromate specimens were painted with polyester type coating. The thickness of the top coat was between 80 and 100 μm for all samples, which was measured with a surface profiler (digital coating thickness gauge, C. C. Elcometer 106 series), according to ASTM D-4541 standard. The specimens for each test were glued onto an aluminium stud of 21 mm in diameter with epoxy resin, followed by drying process at room temperature during 24h.

Acknowledgements

The authors wish to thank the financial support from SIP-IPN and SEP-CONACYT trough the projects SIP-20080805, SIP-20080654 and 2006-01-61354, respectively. The authors are also grateful to Javier Zapata Torres and Ivan Puente L., for their technical support.

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