A comparative study between Cr(VI)-containing and Cr-free films for coil coating systems

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Abstract

In this work, the protection conferred by Cr(VI)-containing and Cr-free pre-treatments and primers used in hot dip galvanized steel (HDG) coated systems were studied. The EIS results showed a differentiated behaviour for the specimens with Cr(VI) compared to the chromium-free ones. The samples with Cr(VI), both in the pre-treatment and in the primer, presented a better corrosion performance when compared to the Cr-free ones.

Moreover, it can be said that the pre-treated and primed samples without Cr(VI) presented lower resistive properties and higher delamination fractions throughout the immersion time. The amount of Cr in the primer also influenced the coating resistance for shorter periods of immersion, but for long periods the passivating effect of Cr seems to be determinant.

When topcoat was applied, i.e. for a complete system, the Cr-free specimens performed better than the Cr(VI)-containing ones, perhaps due to a better adhesion of the topcoat to the primer in the former case. This leads to the conclusion that there is a risk in assessing the behaviour of a paint scheme on the basis of the individual behaviour of each layer.
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1. Introduction

Corrosion resistance is one of the basic requirements for a coil coating pre-treatment. The corrosion of galvanized steel is one of the major problems in industry. The material could become more resistant to corrosion if a chromatation layer is applied on top of the zinc layer.

The chromatation layer has several functions: it acts like an anodic inhibitor, forming a passive layer, lowering the rate of zinc dissolution and it is also an efficient cathodic inhibitor, lowering the rate of the oxygen reduction reaction on the metal surface, avoiding the formation of blisters [1]. A healing effect has also been reported [2].

Most of the research has been done for aluminium alloys and steel. Kendig and Bucheit [3] describe a series of hypotheses to explain the role of chromate on aluminium alloys (e.g. chromatation provides an hydrophobic Cr(III) oxide barrier with good adhesion, promoting the mechanical properties and a slowly released oxo-Cr(VI) species that actively heals defects and damage in the coating; Cr(VI) and its oxy-hydroxide reduction product inhibit the oxygen reduction and the metal dissolution). For steel, the formation of a passive layer containing a mixture of Fe_2O_3 and Cr_2O_3 oxides and with possible formation of a $(Fe_{1-x}Cr_x)_2O_3$ oxide layer has been reported [4–6].

There is less research published concerning the formation of this protective layer on zinc. It was demonstrated that the passive layer contains Zn(II) and Cr(III) oxides [7]. However Gabrielli et al. [1] state that the chromate layer does not contain significant amount of zinc, and it is permeable to zinc dissolution. The main composition of the film is $Cr(OH)_3 \cdot 2H_2O$.

The Cr-containing products are being progressively replaced by chromium-free ones, because of the suspected

* Corresponding author. Tel.: +351 243 370354; fax: +351 234 425300.
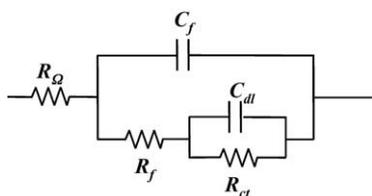*E-mail address:* mgferreira@cv.ua.pt (M.G.S. Ferreira).

Fig. 1. Standard equivalent circuit for organic-coated substrates with corrosion underneath the paint.

Table 1
Specimens preparation

Pre-treatment	Polyester primer	Topcoat
Cr-containing	High Cr content (18.5% Cr)	Polyester topcoat
	Low Cr content (0.5% Cr)	Not applied
Cr-free	Cr-free	Polyester topcoat

carcinogenic effects of Cr(VI). The coil wastewaters originated in the industry have to be expensively worked up and disposed off. The handling of Cr(VI)-containing chemicals during production, transportation and application demand important safety measures. For development of new products, ecological compatibility is nowadays an issue of paramount importance [8].

Phosphates are one of the many possible alternatives. This process is based on an acidic solution containing titanium and fluoride. It may be assumed that the metallic surface is first partly etched by the acidic solution with oxidation of the metal surface. The metallic ions are dissolved in the solution. In a second step of the process, these metal ions form poorly soluble compounds with the ions existing in the treatment solution [8].

Electrochemical impedance spectroscopy (EIS) is widely used in the investigation of organic coatings degradation. The paint degradation process can be studied by this technique that it is able to provide quantitative results on the protection afforded by these materials [9–11].

The equivalent circuit commonly used is based on a previous proposal by Michailovskii et al. [12] (Fig. 1). In this circuit, the solution, charge transfer and coating (pore) resistances, R_Ω, R_{ct} and R_f, respectively, are present. The dielectric parameters correspond to the double-layer and film capacitance, C_{dl} and C_f, respectively. A more complete equivalent circuit appeared in a work published by Walter [13], in which the diffusion process was also considered.

There are several other circuits proposed that are more complex and less used than the previous ones. Among them the most important are those proposed by Geenen [14–16] and van Westing [17,18]. Nevertheless, the first one remains the most extensively used for the interpretation of EIS results of coated steel systems under corrosion.

Several methods to estimate the values of the circuit elements were proposed and are described in published reviews [19–23].

2. Experimental

2.1. Specimens

The specimens used in this work consisted of hot-dip galvanized steel (HDG) prepared in different ways.

Some of them were only pre-treated samples. They were degreased and treated with two types of commercial products: a Cr(VI)-containing one and a Cr-free one (phosphate-based).

Other specimens were prepared with the above pre-treatments and then were coated with polyester primer. This polyester primer could be either Cr-free or Cr(VI)-containing. In this latter case, primers with two Cr contents were used: high Cr content with 18.5% (w/w) of Cr(VI) and low Cr content with 0.5% (w/w) of Cr(VI).

The third batch of samples, after pre-treatment and primer were coated with a polyester topcoat. Table 1 resumes the specimens' preparation.

The average thicknesses of the topcoat and primers are 20 and 10 μm, respectively.

2.2. Electrochemical measurements

EIS measurements were carried out at room temperature with a Frequency Response Analyser (Solartron 1255) coupled to an electrochemical interface (Solartron 1286). For the samples treated with the topcoat, due to the high impedance of the system, EIS spectra were performed with a Gamry FAS1 femtostat and a PC4 Controller Board equipment. In all cases, a three-electrode arrangement was used with a saturated calomel electrode as reference electrode and a platinum counter electrode. The cells were made by sticking a PMMA tube to the surface of the sample using an epoxidic glue (Araldite®). The exposed area was 3.80 cm², and for each specimen three replicates were made. The electrolyte used to fill the cylinders was for the samples with primer and topcoat 0.5 M NaCl solution, while 0.1 M NaCl and 0.25 M Na_2SO_4 solutions were used for the samples only pre-treated. The measurements frequency range was 50 kHz to 5 mHz and the amplitude of the a.c. signal was of 10 mV rms. With the aim of verifying the applicability of the proposed equivalent circuits, the EIS spectra were fitted with EQUIVCRT software [24,25].

2.3. SVET analysis

Scanning vibrating electrode technique (SVET) measurements were performed with Applicable Electronics equipment, using the ASET program (Sciencewares). The vibrating electrode was made of platinum–iridium covered with polymer, leaving only an uncovered tip. These electrodes were made at the Instituto Superior Técnico and were based

on Micropobe, Inc. electrodes. The electrode diameter was 40–50 μm and the distance of the tip to the surface was 200 μm. The samples under study were 2 mm × 2 mm and were immersed in 0.1 M NaCl solution.

3. Results and discussion

3.1. Pre-treated specimens

The pre-treated samples without primer were tested aiming at understanding the chromium action at the substrate. The results presented in Fig. 2 were obtained for the pre-treated samples immersed in NaCl solution. For the Cr(VI)-containing pre-treatment, the results (Fig. 2a) showed two time constants in the intermediated frequencies region, while for Cr-free pre-treatment (Fig. 2b) a time constant appears in addition at lower frequencies, probably due to a diffusion process associated to localized corrosion. These results
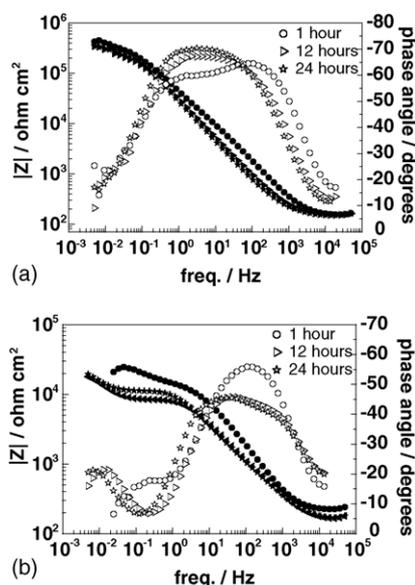

Fig. 2. EIS spectra for samples with (a) Cr(VI)-containing pre-treatment and (b) Cr-free pre-treatment in 0.1 M NaCl solution.

indicated different processes for each sample, with higher protection level for the Cr(VI)-containing samples. The low-frequency resistance values were 10 times higher than the ones obtained for the Cr-free samples. This indicates that the protective film for the Cr(VI)-containing samples was more efficient for substrate protection. This result is in accordance with the results of the immersion tests showed in Fig. 3. After 7 days of immersion, the Cr(VI)-containing sample (Fig. 3a) is much less corroded than the Cr-free sample (Fig. 3b). In the latter case, the surface is heavily corroded whereas in the former case only a few pits are visible on the surface. This is an indicator that a passivation process had occurred for the Cr(VI)-containing specimen and it is coherent with the previous result (Fig. 2).

In real conditions the pre-treatment is never used by itself, being the ultimate protective barrier between substrate and solution. Consequently, the previous tests were excessively aggressive for the pre-treatment role. With the objective of testing the samples with a milder solution and also trying to avoid pitting effects, a 0.25 M Na_2SO_4 solution was used. Fig. 4 shows the EIS spectra for these samples. The chromium-free sample presented a drop in the low-frequency resistance after 7 days of immersion. The samples with chromium showed also the same trend for that parameter, but followed by a rapid recovery after 7 days of immersion. This could be ascribed to the chromate action, causing the passivation after corrosion has started. These results are according to the previous ones in NaCl solution, since in both cases a more protective film was obtained for the Cr(VI)-containing samples, with the differences resulting from the mildest action of the sulphate solution.

Fig. 5 shows the ionic current map over the surface of pre-treated samples obtained by SVET measurements. In the specimens without chromium, some activity was observed after 30 min of immersion whereas the activity on the Cr(VI)-containing samples was negligible. This difference was more evident for 1 week of immersion. In this case, the activity of the Cr-free samples increased considerably, with areas where intense anodic activity could be observed. For the Cr(VI)-containing samples, no surface activity continues to be detected, which indicates that the chromium
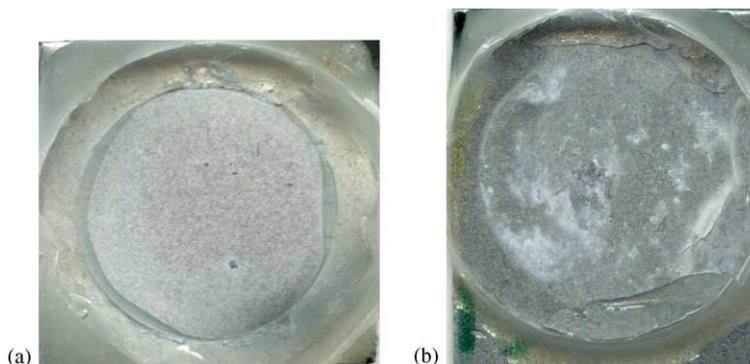

Fig. 3. Image of samples after immersion in 0.1 M NaCl solution for 7 days: (a) Cr(VI)-containing pre-treatment and (b) Cr-free pre-treatment.
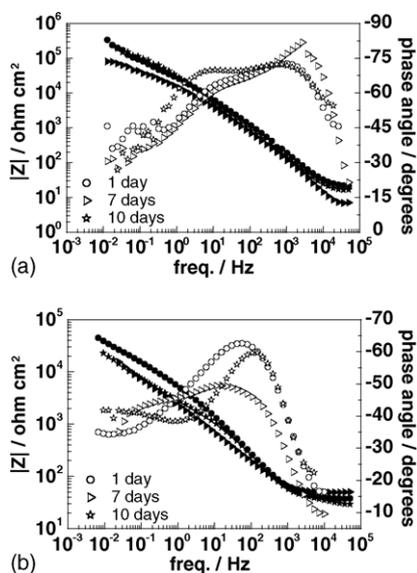
Fig. 4. EIS spectra for samples with (a) Cr(VI)-containing pre-treatment and (b) Cr-free pre-treatment in 0.25 M Na$_2$SO$_4$ solution.

Fig. 6. EIS spectra for samples with both Cr-free pre-treatment and primer.

protected the surface as expected from the previous results.

3.2. Specimens with pre-treatment and primer

The EIS results showed a differentiated behaviour for the specimens with chromium compared to the chromium-free ones.

The samples without chromium, both in the pre-treatment and in the primer, presented the typical response of a coated substrate (Fig. 6) with corrosion underneath. The equivalent circuit shown in Fig. 1 is applicable, in which the dielectric properties of the coa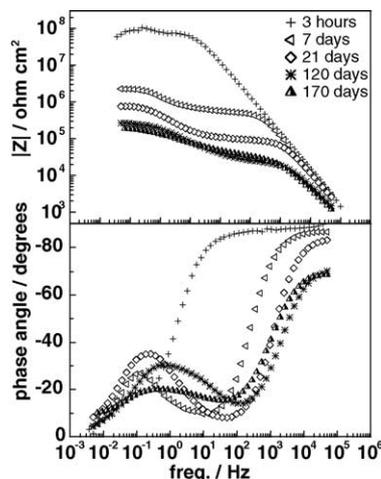ting could be identified at the high-frequency range, with C_f and R_f corresponding to the coating capacitance and the pore resistance, respectively. The double layer ascribed to the corrosion processes was apparent in the low-frequency range of the spectrum, with C_{dl} and R_{ct} corresponding to the double-layer capacitance and the charge transfer resistance, respectively. The fitting obtained with this circuit was very good as expected (Fig. 7).

Similar analysis was carried out for the samples with chromium content (in the primer and in the pre-treatment). A third time constant was detected at the intermediate frequency range (Fig. 8) for longer immersion times. The results obtained for the beginning of immersion was fitted with the standard equivalent circuit (Fig. 1), showing good agreement with the experimental curve (Fig. 9a). However, after 42 days of immersion, a third time constant seems to appear in the spectra. This was quite clear when the results for longer immersion periods were fitted, and a more com-
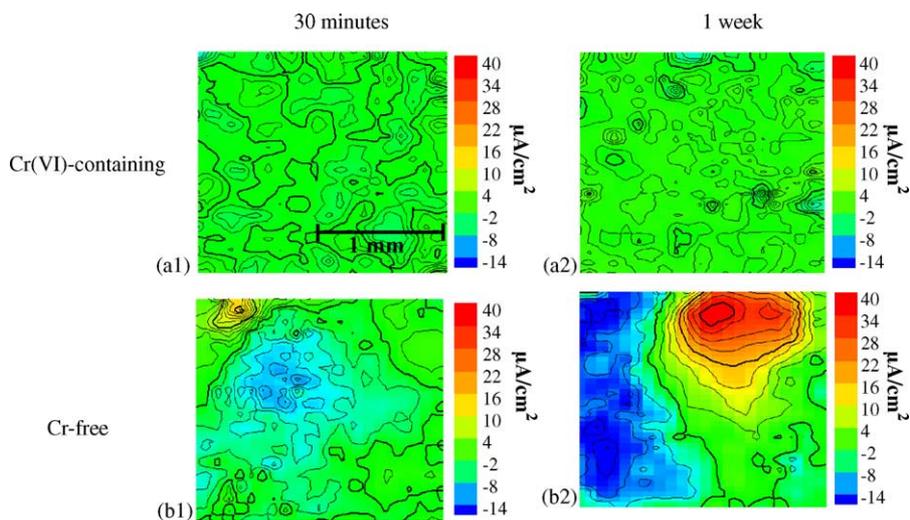

Fig. 5. SVET current maps for samples with Cr-containing and Cr-free pre-treatment after (a$_1$ and b$_1$) 30 min and (a$_2$ and b$_2$) 1 week of immersion in 0.1 M NaCl solution (darkest (positive) areas correspond to anodic activity, brightest (negative) areas correspond to a cathodic activity).
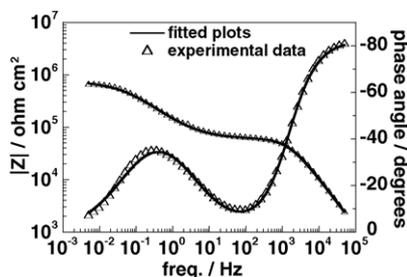
Fig. 7. Fitting of EIS experimental data for the samples with Cr-free pre-treatment and primer after 42 days of immersion in 0.5 M NaCl solution.
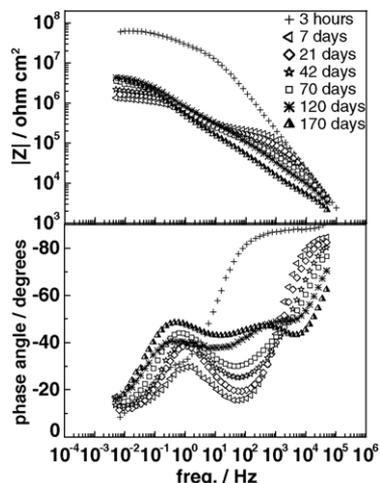

Fig. 8. EIS spectra for the samples with Cr(VI)-containing pre-treatment (high Cr content) and Cr(VI)-containing primer.

plicated equivalent circuit (Fig. 9b) was necessary to use to have a good fitting.

Mertens et al. [26] proposed an equivalent circuit that differs from the commonly used by adding an extra *RC* network.
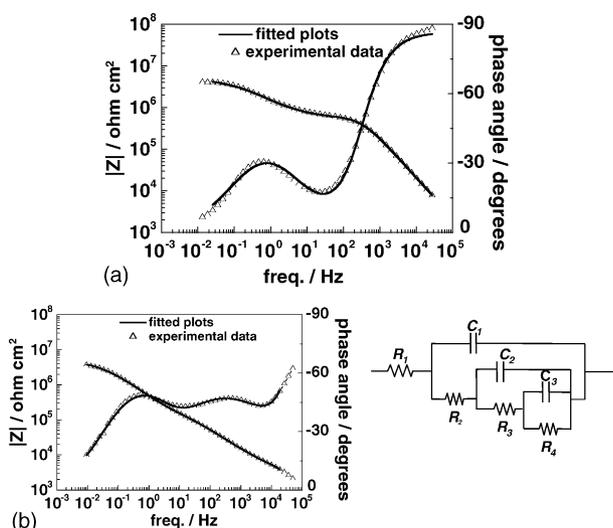

Fig. 9. Fitting of EIS experimental data for the samples with both Cr(VI)-containing pre-treatment and primer (a) for short immersion time (3 days) and (b) for long time of immersion (170 days) in 0.5 M NaCl solution (equivalent circuit also showed).
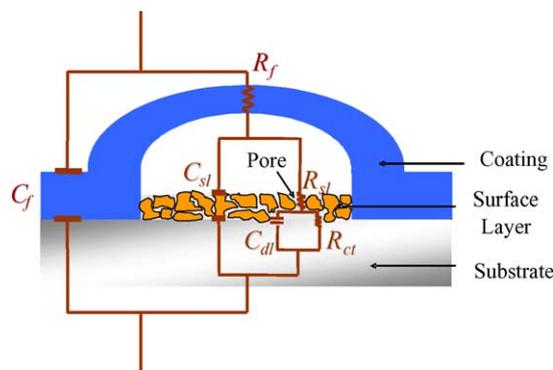

Fig. 10. Microscopic model for the three time constants circuit.

This assumes a surface layer between the metal and the coating (Fig. 10). The equivalent circuit presents, as before, the time constants of the coating and the corrosion process at the highest and the lowest frequency range, respectively. For the intermediate frequency range, the dielectric properties (C_{sl}) and the resistive properties (R_{sl}) of this surface layer are showed.

Estimation of the resistive parameters was made using the value of the impedance modulus for the minima phase angle in the region of the frequency spectra ascribed to this parameter. The results are presented in Fig. 11a and c, where the evolution with immersion time for the coating resistance R_f and the total low-frequency resistance $R_{f \to 0}$ are shown.

The estimation of delamination fraction was made using the Haruyama et al. [27] method, and was based on the effect in the double-layer capacitance of the increase of area suffering corrosion. The equation used was

$$D = \frac{C_{dl}}{C_{dl}^0}$$

in which C_{dl} is the estimated double-layer capacitance for the coated sample, C_{dl}^0 the estimated double-layer capacitance for the bare substrate (3×10^{-5} F/cm^2) and D the delamination fraction. The double-layer capacitance values can be estimated using the imaginary part of the impedance corresponding to the phase angle maximum in the spectra region where this parameter manifests. The results are presented in Fig. 11b.

Generally speaking it can be said that the samples without chromium content presented lower low-frequency resistance ($R_{f \to 0}$) and higher delamination fraction throughout the immersion time (Fig. 11). These results indicate that the chromium-free samples were less protected than the other ones.

An apparent interesting result was obtained by comparing the samples with different chromium contents in the primer. In this case, the delamination fraction (Fig. 11b) showed similar behaviour between the samples for longer periods of time. The sample with higher chromium content had initially a lower pore resistance compared to the lower chromium content one, but with time this parameter stabilizes in about the
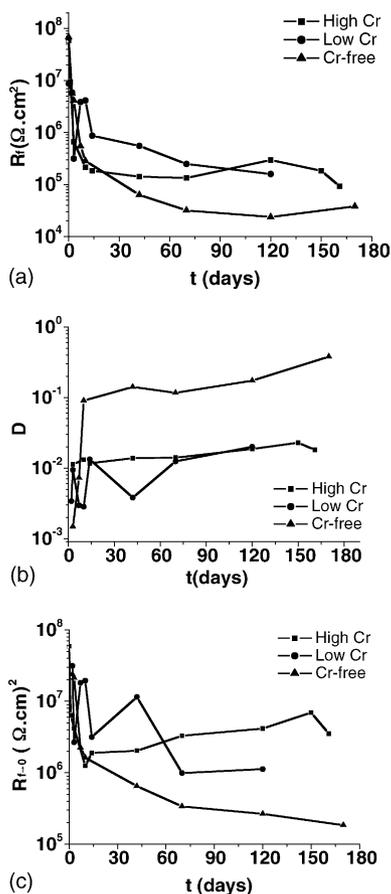
(a)

(b)

(c)

Fig. 11. Evolution with time of estimate parameters for samples with pre-treatment and primer: (a) resistance of the film, (b) delamination fraction and (c) resistance at low frequency.

same value for both samples (Fig. 11a). However, a different result is obtained by comparing the low-frequency resistance (Fig. 11c). In this case, the lower chromium content samples presented lower resistance values for long periods of time. The explanation for this discrepancy could be found considering the nature of the analysed parameters and the amount of pigments in the primer. The R_f is related to the permeability of the coating, while the low-frequency resistance indicates the global corrosive behaviour. The microscopic observation of the samples (Fig. 12) revealed that high chromium content and Cr-free samples had larger quantity of inorganic particles than the lower Cr-content specimens.

Knowing that the interfaces particles–matrix (porosity) are preferential solution penetration paths and that inorganic oxides, like the chromium pigment, depicted hydrophilic properties [28], it is likely to find lower values for R_f in the high chromium content and Cr-free sample, at least for initial immersion times. For longer periods (when coating saturation is reached), and since the coating is essentially similar for both Cr(VI)-containing types of specimens, the values of R_f tend to be similar. The corrosion protection becomes then at least identical for both specimens (considering D) or even higher for the high chromium content samples (considering the low-frequency resistance). The lower chromium content
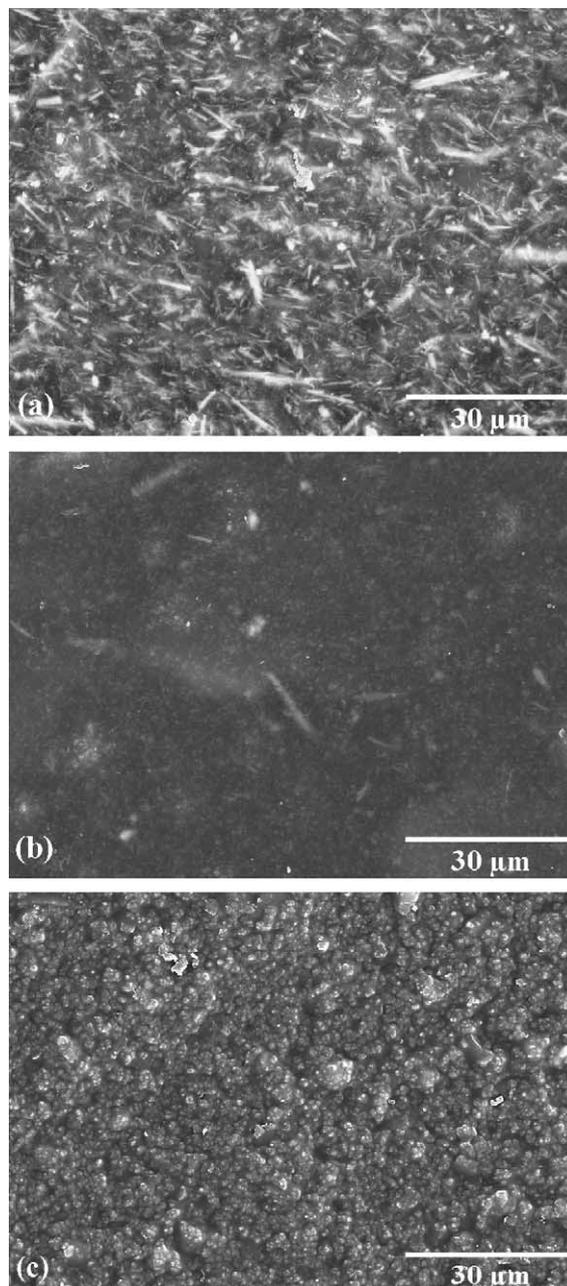

Fig. 12. SEM images for the pre-treated samples with primer: (a) high Cr content, (b) low Cr content and (c) Cr-free.

samples reveal a high rate of continuous change in the last 50 days, also suggesting a more rapidly deterioration of the corrosive protection.

3.3. Specimens treated with the complete system

Fig. 13 shows the EIS spectra for the specimens with a complete system: pre-treatment, primer and topcoat. The pre-treatment and primer are as before, i.e., both Cr(VI)-containing or both Cr-free. According to the results, the Cr-free samples show more elevated impedance values than the Cr(VI)-containing ones. A capacitive behaviour can be ob-
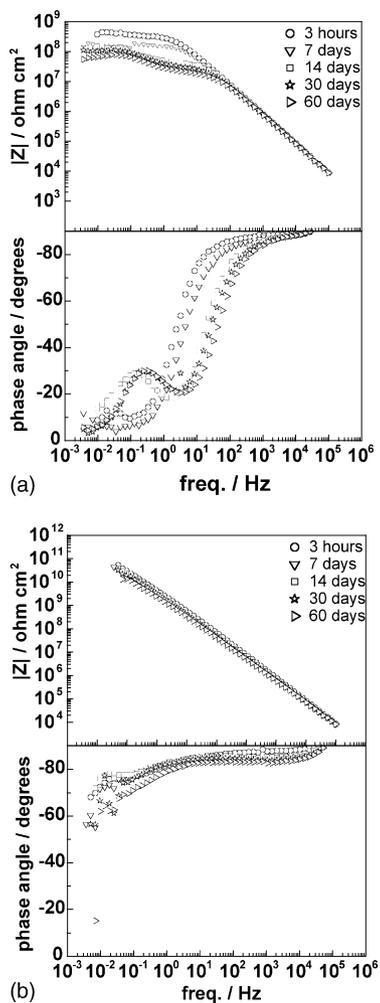
Fig. 13. EIS spectra for the complete system (pre-treatment, primer and topcoat): (a) Cr containing and (b) Cr-free.

served after 60 days of immersion for the Cr-free specimens, with no corrosion underneath the coating. This indicates an extreme resistive coating film. For the Cr(VI)-containing specimens, corrosion is apparent after a few days of immersion.

The previous tests made on pre-treated or in pre-treated and primed specimens concluded for a worst performance for the Cr-free specimens and it was expected that this result extended to the complete system behaviour. This was not the case and the explanation could rely on a better compatibility of the whole system, probably related to a good adhesion established between topcoat and primer. Another explanation could be that Cr(VI)-containing specimens were damaged. However, surface analyses (SEM, optical microscopy) showed no defects or pores in the topcoat. More tests should be made to understand this behaviour, although it is not the first time that similar results have been reported [29]. In this case, the apparent anomalous result was explained on the basis of the presence of a chromate pigment more hygroscopic than the pigment existing in the Cr-free primer.

4. Conclusions

The chromium-containing pre-treatment and primer conferred more protection to hot dip galvanized steel than the Cr-free ones, with indication that a passive layer formed on the surface.

The EIS spectra for the samples with Cr(VI)-containing pre-treatment and primer showed a third time constant that could be associated with a protective surface layer originated by the presence of Cr.

The film resistance of the primer, for short immersion times, seems to be related with the film permeability, which depends on the amount of inorganic particles in the primer.

The Cr-free complete system seems to be more protective than the Cr(VI)-containing one and this could be related to the adhesion of the topcoat to the primer.

Conclusions about the performance of a complete paint scheme based on the behaviour of each protective layer must be taken with precaution, since the interaction effect between the different layers could be determinant.

Acknowledgments

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