



## Self-assembling molecules as corrosion inhibitors for 1050 aluminum

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### ARTICLE INFO

#### Article history:

Received 9 January 2010

Accepted in revised form 11 March 2010

Available online 17 March 2010

#### Keywords:

Self-assembling molecules

Chromating

Oxide-hydroxide

Corrosion inhibitors

Aluminum

EIS

### ABSTRACT

Whether it contains hexavalent chromium, chromium (VI), or simply Cr(VI), chromating has been largely used for surface preparation of aluminum aimed at corrosion protection due to its effectiveness and easy application. The most used among these processes are those that contain toxic and carcinogenic substances, which generate environmental backlash concerning the disposal of used baths with toxic elements. The high costs involved in the treatment of the disposal solutions prior to being discarded, besides the increasing restrictions concerning the environment, have encouraged research in the search for alternatives with lower toxicities than chromating processes but with high effectiveness for corrosion protection. Surface treatments with alkane diphosphonate molecules (ADM) have been investigated as potential substitutes for chromating. However, their effectiveness in the corrosion protection of aluminum alloys still needs further investigation. In the present study, the corrosion resistance of 1050 aluminum with various surface treatments was investigated by electrochemical techniques and salt spray testing. The corrosion performance of 1050 aluminum samples with a surface treatment that consisted of immersion in ADM was compared with that of the same alloy chromated by immersion in baths of Cr(III) or Cr(VI). The results showed that surface treatment with ADM was effective on samples that had been exposed to boiling water for oxide growth prior to treatment with ADM. The results also showed the superior corrosion performance for samples with the oxide-hydroxide + ADM surface treatment compared to those with both chromating treatments, either with Cr(III) or with Cr(VI). Cr(III) chromating treatment also provided better corrosion performance than chromating with Cr(VI), suggesting that both surface treatments (oxide-hydroxide + ADM and Cr(III)) are potential candidates for substitution for Cr(VI)-containing processes. However, for effective corrosion protection, the ADM treatment has to be carried out on surfaces previously exposed to treatments that favor oxide growth.

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### 1. Introduction

Aluminum and its alloys tend to develop a thin and adherent oxide layer when exposed to oxygen. This oxide layer acts as a barrier that prevents the continuous attack of the metal substrate exposed to mildly aggressive environments [1,2]. Although this layer exhibits high corrosion resistance in moderately corrosive environments, in severe environments, the thin oxide film does not provide long-term corrosion resistance [2]. Organic coatings are usually used for corrosion resistance. However, organic coatings are not impermeable or free of defects. Therefore, moisture and oxygen can reach the substrate/organic coating interface, creating conditions for corrosion initiation. After corrosion initiation, delamination and adhesion loss

can occur [2,3]. To delay the corrosive attack on the substrate, surface treatments performed before coatings are usually applied.

Several surface treatments for corrosion control are based on the reaction between the metal surface and a specific solution to produce conversion coatings. Chromating and chromium passivation are conversion coating processes that provide good corrosion resistance for aluminum and its alloys [4–6]. However, the intrinsic toxicity associated with the residues generated by the chromating process is demanding new hexavalent chromium-free technologies. New processes are under investigation to overcome the environmental restrictions, such as zinc phosphate for aluminum alloys [7,8], zirconium–titanium-based products [9], cerate and silane products [10–12], and self-assembled molecules [1,13].

Self-assembling molecules are special compounds that according to literature [14,15], spontaneously adsorb on specific substrates to form self-organized layers. Many chemicals are classified as self-assembling molecules, and often, they are specific for certain metals, such as alkanethiol for gold [1], silver [16], and copper [17], alcohol and amines for platinum [18]; and phosphonate compounds for

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aluminum alloys [1,2]. These compounds, when adsorbed, change the surface physico-chemical properties. In recent decades, many researchers have focused on self-assembling molecules and reported the benefits of these molecules in several technological areas, including corrosion protection [18–20]. When metallic substrates are exposed to these molecules, they are initially quickly adsorbed in a non-orientated way. Subsequently, these molecules are slowly organized on the surface, forming a continuous film. Self-assembling molecules can form monolayers or multi-layers depending on whether they present mono- or bi-functionality.

It has been published in the literature [1,19–21] that phosphonate compounds are highly effective for aluminum treatment, showing hydrophobicity over a large pH range. Maegle et al. [1] suggested the application of these molecules for aluminum surface treatments due to their homogeneous adsorption and high-adhesion bonding properties on the substrate as well as the demonstration of a corrosion resistance similar to that provided by chromating conversion layers.

The surface treatment of aluminum alloys with self-assembling molecules prior to painting should improve coating adhesion and form a compact and homogeneous layer with good stability on the metal/coating interface. Additionally, the film should act as inhibitor of the oxygen reduction reaction and have high resistance to the products of this reaction. However, it is known that surface treatment prior to adsorption affects the corrosion resistance performance. Consequently, the surface preparation prior to treatment with this type of molecules is of great importance.

Due to environmental restrictions and the high costs involved in the treatment of residues from processes based on chromium compounds, this kind of surface treatment is becoming economically unviable. The market is increasingly rejecting materials treated by this type of process. The development of new chromium-free technologies should lead to similar or improved corrosion resistance compared to current processes and equivalent process costs to that of chromium-(VI-) based products.

In this study, the effect of surface treatment with alkane diphosphonate molecules (ADM), which are supposed to self-organize on the aluminum surface, on the corrosion resistance of 1050 aluminum was investigated, and the results were compared with those of chromating with Cr(III) and Cr(VI). The effect of surface preparation prior to treatment with ADM was also evaluated. Electrochemical impedance spectroscopy, potentiodynamic polarization curves and salt spray testing were used to evaluate the corrosion resistance of the aluminum after the application of the different tested surface treatments.

## 2. Materials and methods

Samples of 1050 aluminum alloy (whose chemical composition (wt.%) is presented in Table 1) of 20 mm × 20 mm size were used as the substrates. Prior to any coating procedure, all of the samples were blasted to a finishing Sa3, in accordance with standard SIS 055900, and degreased with ethanol for 5 min in a sonifier. Subsequently, the samples were immersed in solutions of low and high alkalinity (SurTec® 133 and 181-B, respectively) and deoxidized by immersion for 3 min in a solution containing SurTec® 495-B at 40 ± 2 °C. Next, the samples were exposed to the surface treatments designated as: (1) Cr(III), (2) Cr(VI), (3) oxide-hydroxide, and (4) oxide-hydroxide + ADM, as specified in Table 2. The surface treatment used in this study consisted of immersion in a solution of 90 ppm alkane diphosphonate (Gardobond® X4661) [22]. This concentration was based on the critical

**Table 1**  
Chemical composition (wt.%) of 1050 aluminum.

Fe	Cu	Mg	Mn	Si	Sn <sup>a</sup>	Zn <sup>a</sup>	Al
0.339	0.009	0.037	0.011	0.177	<0.183	57.58	Balanced

<sup>a</sup> Concentration in ppm.

**Table 2**  
Surface treatments carried out on the 1050 aluminum.

Surface treatment	Description
Cr(III)	Immersion for 3 min in solution of trivalent chromium (SurTec® 650), at 40 °C ± 2 °C, pH = 3.9.
Cr(VI)	Immersion for 3 min in solution of hexavalent chromium (SurTec® 653), at 40 °C ± 2 °C, pH = 3.7.
Oxide-hydroxide	Immersion for 1 h in boiling water.
Oxide-hydroxide + ADM	Immersion for 1 h in boiling water followed by immersion during 3 h, at 40 ± 2 °C, in solution with 90 ppm of alkane diphosphonate (Gardobond® X4661, from Chemetall GmbH).

micellar concentration (CMC) determination by conductivity measurements [23].

Electrochemical tests were carried out in 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> electrolyte at 23 ± 2 °C, naturally aerated, with the pH adjusted to 4 using a solution of potassium hydrogen phthalate (C<sub>8</sub>H<sub>5</sub>O<sub>4</sub>K) as a buffering agent with NaOH for pH 4. This solution was used to simulate an industrial environment and to avoid the localized corrosion effects of chloride ions. After surface preparation, the working electrodes were immersed in the electrolyte and the corrosion resistance of the electrodes was monitored by electrochemical impedance spectroscopy measurements. After three days of immersion, the electrodes were anodically polarized. For the electrochemical measurements, a platinum wire was used as a counter electrode and a mercurous sulfate electrode (MSE) was used as a reference. Electrochemical impedance spectroscopy (EIS) measurements were accomplished with a SI 1260 Solartron frequency response analyzer coupled to a SI 1287A potentiostat. All EIS measurements were performed in the potentiostatic mode at the open circuit potential, OCP. The amplitude of the perturbation signal used was 10 mV (rms), the frequency range studied was from 10<sup>5</sup> to 10<sup>-1</sup> Hz, and the data acquisition rate was 10 points per decade. The potentiodynamic polarization measurements were carried out from OCP up to 2.5 V, with a scan rate of 1 mV s<sup>-1</sup> by means of a SI 1287A potentiostat coupled to a computer. The corrosion resistance of the coated samples was investigated by corrosion-accelerated experiments (Salt Spray), according to Standard Method ASTM B117.

## 3. Results and discussion

The experimental EIS results and fitted data for the 1050 aluminum exposed to the surface treatments corresponding to (1) Cr(III), (2) Cr(VI), (3) oxide-hydroxide, and (4) oxide-hydroxide + ADM, after one day of immersion in naturally aerated 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> solution with the pH adjusted to 4, are shown in Figs. 1 and 2. The EIS results for an untreated AA1050 sample are also shown in Fig. 1 for comparison.

For the Cr(III)-treated AA1050 samples, Nyquist diagrams show higher impedance, especially in comparison with the surface treatment containing Cr(VI) in Fig. 1(a), and the Bode diagrams in Fig. 1(b) indicate two time constants for the Cr(III) treatment. The time constant at the high-frequency (HF) region is related to the chromate film, whereas the medium-frequency (MF) one (10 to 100 Hz) is associated with the charge transfer processes. The large peak at the MF region for AA1050 samples untreated and treated with Cr(VI) may be related to the interaction of two time constants, but this assumption will be discussed later.

In the present work, the beneficial effect of the treatment for oxide-hydroxide growth and oxide-hydroxide + ADM on the corrosion protection is clearly shown in Fig. 2(a) and (b). The Nyquist diagrams in Fig. 2(a) exhibit the higher impedances associated with these treatments comparatively to those associated with the untreated samples. Three times constants are indicated in the Bode diagrams of Fig. 2(b) for the oxide-hydroxide and oxide-hydroxide + ADM surface treatments. Additionally, the HF time constant is displaced to higher

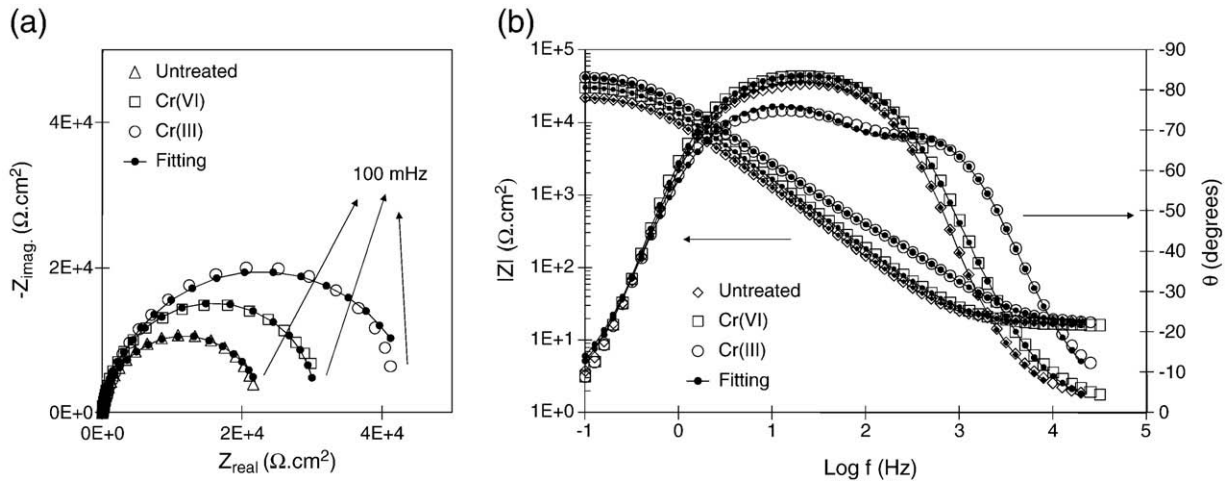


Fig. 1. (a) Nyquist and (b) Bode phase angle diagrams for the 1050 aluminum untreated and treated with Cr(III) or Cr(VI), after one day of immersion in a  $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$  buffered solution, pH 4.

frequencies and the MF one is displaced into lower frequencies due to these two treatments. The time constant at low frequencies (LF) could be related to interfacial processes at the exposed areas of the substrate. The results suggest the slowing down of interfacial processes due to the passivating films associated with the oxide-hydroxide and oxide-hydroxide + ADM treatments. The results also show that the main effect of ADM treatment is on the MF time constant, causing its displacement into lower frequencies and suggesting slower kinetics of charge transfer processes due to ADM adsorption on the surface oxide film. This suggests the slowing down of interfacial processes due to the passivating film formation, leading also to hindered interfacial processes.

The EIS data of the present study suggested that the treatments investigated could be separated into two groups according to the fitted results. Two models were proposed to simulate the EIS experimental data, and these are presented in Fig. 3(a) and (b). The equivalent circuit shown in Fig. 3(a) is similar to that proposed by Mansfeld and Kendig [24] to represent the unsealed oxide layer on anodized aluminum, and the model proposed in Fig. 3(b) has been previously used in the literature [25] to represent sealed alumina. The experimental results of the untreated and Cr(III)- or Cr(VI)-treated samples were adjusted according to the equivalent circuit (EC) shown in Fig. 3(a), whereas those of the AA1050 samples treated with oxide-hydroxide or oxide-hydroxide + ADM were fitted according to the EC

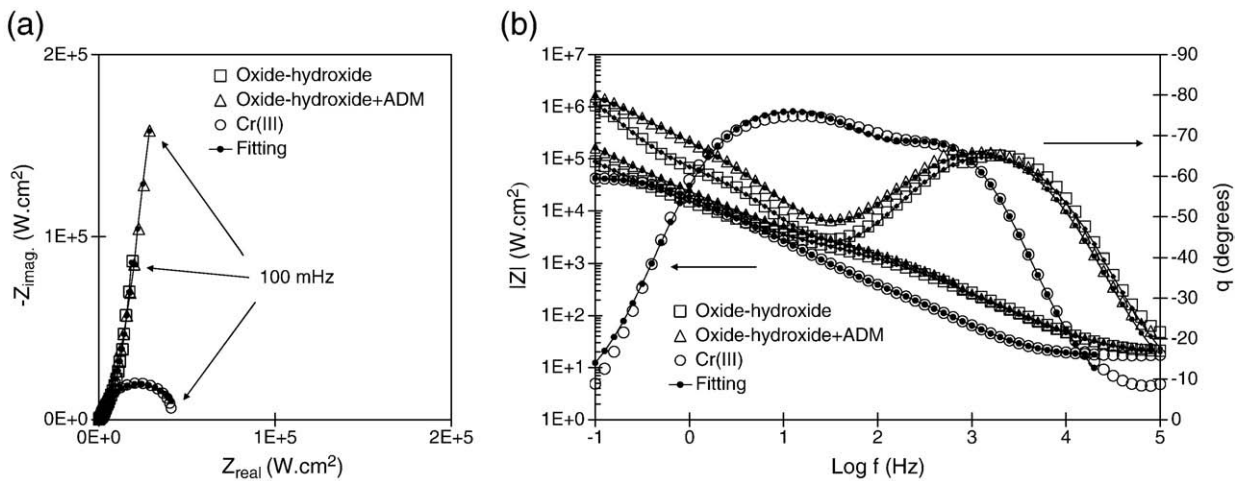


Fig. 2. (a) Nyquist and (b) Bode phase angle diagrams for the 1050 aluminum after surface treatments with Cr(III), oxide-hydroxide or oxide-hydroxide + ADM, corresponding to one day of immersion in a  $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$  buffered solution, pH 4.

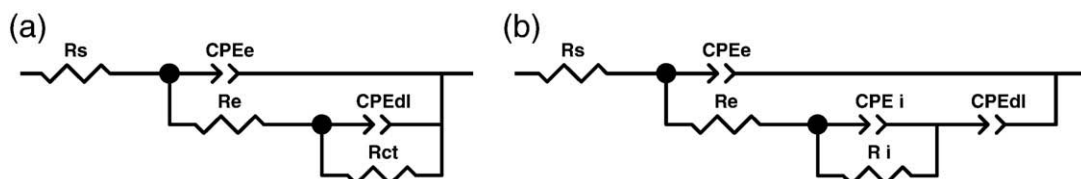


Fig. 3. Equivalent circuit (EC) used for fitting the experimental impedance data corresponding to the following surface treatments: (a) untreated, Cr(III) or Cr(VI); and (b) oxide-hydroxide or oxide-hydroxide + ADM.

**Table 3**

Results from fitting the experimental impedance data to the equivalent circuit of Fig. 3(a), for 1050 aluminum samples untreated and treated with Cr(VI) or Cr(III).

Electric parameter	Surface condition					
	Untreated		Cr(VI)		Cr(III)	
	Value	Error (%)	Value	Error (%)	Value	Error (%)
$R_e$ [ $\Omega$ cm <sup>2</sup> ]	17.49	0.41	16.22	0.54	16.77	0.87
$R_e$ [ $\Omega$ cm <sup>2</sup> ]	43.89	16.99	78.69	16.87	1046.00	6.18
$CPE_e$ [ $\mu$ F cm <sup>-2</sup> s <sup>(<math>\alpha-1</math>)</sup> ]	14.53	1.25	8.71	1.90	6.22	3.05
$\alpha_1$	0.94	<sup>a</sup>	0.97	<sup>a</sup>	0.90	0.37
$R_{ct}$ [ $K\Omega$ cm <sup>2</sup> ]	23.08	0.38	31.69	0.57	44.29	0.87
$CPE_{dl}$ [ $\mu$ F cm <sup>-2</sup> s <sup>(<math>\alpha-1</math>)</sup> ]	1.29	10.41	2.74	6.83	2.73	4.63
$\alpha_2$	1	<sup>a</sup>	0.94	0.51	0.91	<sup>a</sup>
$\chi^2$	3.42E-4		7.94E-4		1.12E-3	

<sup>a</sup> Value was fixed.

shown in Fig. 3(b). To take into account the heterogeneities in the system, constant phase elements (CPEs) were used instead of pure capacitors.

In the EC of Fig. 3(a), the pair [ $R_e/CPE_e$ ] corresponds to the data obtained at HF, which is associated with the external oxide-hydroxide film on the surface. For surface treatments with Cr(III) or Cr(VI), the film is composed mainly of chromates, but it is seemingly thicker for the Cr(III) treatment. The [ $R_{ct}/CPE_{dl}$ ] pair represents charge transfer processes and charging of the double layer through the oxide film. For the oxide-hydroxide or oxide-hydroxide + ADM treatments, the proposed EC is shown in Fig. 3(b). In this EC, the two pairs [ $CPE_e/R_e$ ] and [ $CPE_i/R_i$ ] are related to the characteristics of the oxide-hydroxide film artificially grown during immersion in boiling water. It is proposed that this film has a duplex structure composed of a porous external layer, associated with the pair [ $CPE_e/R_e$ ], and an intermediate and thicker layer composed of oxide-hydroxide hydrated products, related to [ $CPE_i/R_i$ ]. For samples that were exposed to the ADM solution, after immersion in boiling water, the adsorption of ADM molecules on the thicker oxide layer was facilitated, either on the porous external layer or on the inner and hydrated layer. Consequently, the resistances of both layers were affected by ADM. The  $CPE_{dl}$  component is associated to charging of the double layer. The results from fitting the experimental impedance data to both of the proposed ECs (Fig. 3(a) and (b), respectively) are presented in Tables 3 and 4, respectively.

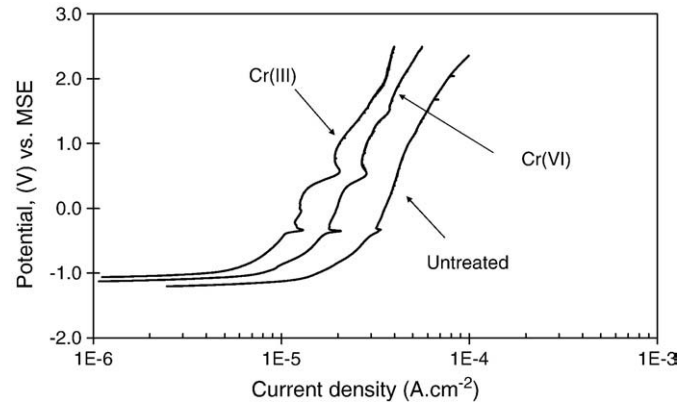
Analysis of the electric parameters of Table 3 shows that the Cr(III) treatment produces a passivating film with higher corrosion resistance compared to the Cr(VI) treatment. The highest  $R_e$  and lowest  $CPE_e$ , besides the highest  $R_{ct}$  in comparison with the untreated or Cr(VI)-treated samples, indicate that this treatment could replace the Cr(VI) treatment with advantageous corrosion protection properties.

**Table 4**

Results from fitting the experimental impedance data to the equivalent circuit of Fig. 3(b), for 1050 aluminum samples treated with oxide-hydroxide or oxide-hydroxide + ADM.

Electric parameter	Surface condition			
	Oxide-hydroxide		Oxide-hydroxide + ADM	
	Value	Error (%)	Value	Error (%)
$R_e$ [ $\Omega$ cm <sup>2</sup> ]	18.38	<sup>a</sup>	18.40	0.89
$R_e$ [ $K\Omega$ cm <sup>2</sup> ]	1.95	3.65	3.04	2.43
$CPE_e$ [ $\mu$ F cm <sup>-2</sup> s <sup>(<math>\alpha-1</math>)</sup> ]	2.39	3.09	2.50	2.41
$\alpha_1$	0.84	0.36	0.82	0.30
$R_i$ [ $K\Omega$ cm <sup>2</sup> ]	27.76	11.08	44.10	10.27
$CPE_i$ [ $\mu$ F cm <sup>-2</sup> s <sup>(<math>\alpha-1</math>)</sup> ]	25.29	5.27	19.21	1.61
$\alpha_2$	0.64	2.42	0.63	(1)
$CPE_{dl}$ [ $\mu$ F cm <sup>-2</sup> s <sup>(<math>\alpha-1</math>)</sup> ]	16.98	2.11	7.66	1.83
$\alpha_3$	1	<sup>a</sup>	1	<sup>a</sup>
$\chi^2$	9.49E-4		6.28E-4	

<sup>a</sup> Value was fixed.



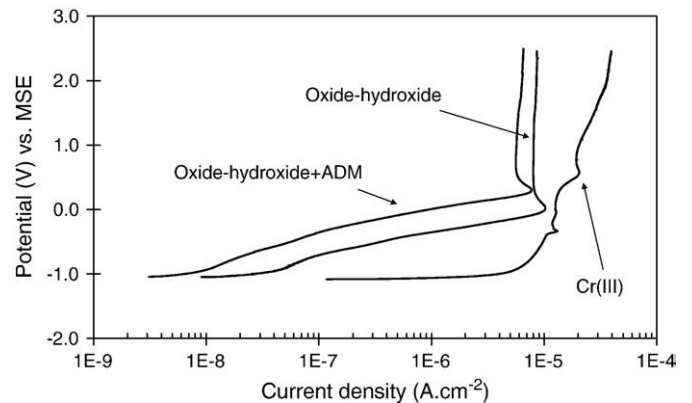
**Fig. 4.** Anodic polarization curves for 1050 aluminum samples untreated and treated with Cr(III) or Cr(VI), after three days of immersion in a 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> buffered solution, pH 4. Scan rate: 1 mV s<sup>-1</sup>.

The results associated to the oxide-hydroxide and oxide-hydroxide + ADM surface treatments reveal that the ADM treatment increases the resistance of both layers that compose the oxide-hydroxide film, and this is attributed to the strong interaction of the alkane diphosphonate molecules with the alumina film.

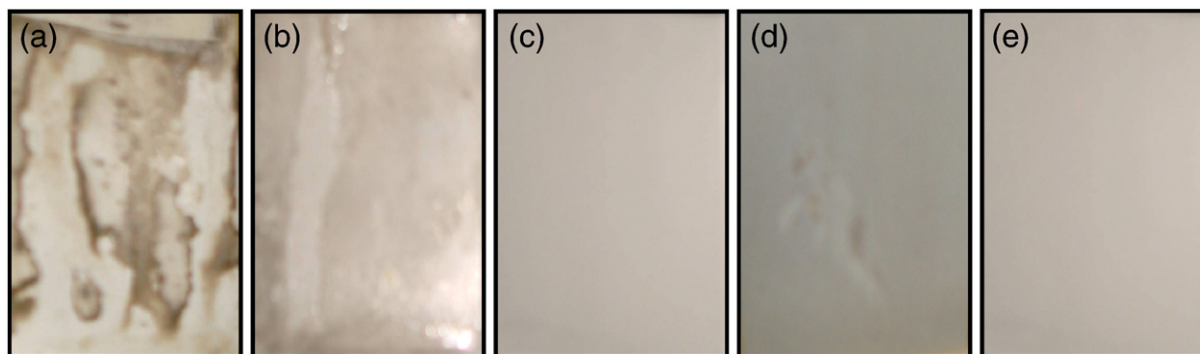
According to the literature [1], the adsorption of self-assembling molecules occurs on Al<sub>2</sub>O<sub>3</sub> by an acid–base reaction, and this leads to a more hydrophobic surface, increasing the corrosion resistance of the substrate. In the present study, however the results suggest that the effect on the corrosion resistance of the tested 1050 aluminum was mainly caused by oxide-hydroxide growth on the surface. The CPE component associated to the external layer ( $\alpha_1$ ) was around 0.8, whereas that related to the intermediate layer ( $\alpha_2$ ) was close to 0.6, indicating the influence of diffusion processes through this last layer.

Figs. 4 and 5 show the anodic polarization curves for the various treatments tested, separated in two groups according to the EC proposed, for a period of immersion corresponding to three days in the same test solution. The anodic polarization results supported the EIS ones. In the first group (Fig. 4), despite the similar features for all tested samples, the noblest potentials and lowest passive current densities are associated with the Cr(III) treatment.

According to Fig. 5, it is observed that much lower current densities were associated with the treatments that involved immersion in boiling water, compared to the Cr(III) treatment, for the whole polarization range in the 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> buffered solution, pH 4. The subsequent ADM treatment led to further decreases in the current densities, corroborating the stronger passivating property of the surface treatment with ADM.



**Fig. 5.** Anodic polarization curves for 1050 aluminum samples treated with Cr(III), oxide-hydroxide or oxide-hydroxide + ADM, after three days of immersion in a 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> buffered solution, pH 4. Scan rate: 1 mV s<sup>-1</sup>.



**Fig. 6.** Macrographs, obtained after 168 h of salt spray testing, for samples in the following conditions: (a) untreated, (b) treated with Cr(VI), (c) treated with Cr(III), (d) treated by immersion in boiling water, and (e) treated by immersion in boiling water followed by SAM adsorption.

Results corresponding to 168 h of salt spray test for all of the investigated surfaces are shown in Fig. 6. The surfaces associated with the best corrosion performances were those obtained either by immersion in boiling water followed by treatment with ADM (oxide-hydroxide + ADM) or by the treatment with Cr(III). These results also support those obtained by electrochemical methods (EIS and anodic polarization). The salt spray results allow the ranking of the various treatments according to their corrosion resistance performance in the following order: oxide-hydroxide + ADM > Cr(III) > oxide-hydroxide > Cr(VI) > untreated.

#### 4. Conclusions

Various surface treatments were tested to evaluate their effect on the corrosion resistance of 1050 aluminum. Surface treatments associated with corrosion protection that was superior to that provided by chromating with Cr(VI) compounds were those corresponding to immersion in boiling water to favor the oxide-hydroxide growth followed by immersion in a solution containing ADM or chromating with Cr(III). These two last treatments (oxide-hydroxide + ADM and Cr(III)) produced higher impedances, lower corrosion currents and better corrosion performances after 168 h of exposure to the salt spray test. The results of this study suggest that both surface treatments, oxide-hydroxide + ADM and Cr(III), are alternatives to replace chromating with Cr(VI) compounds.

#### Acknowledgement

The financial support given by FAPESP (Proc. 2004/12189-1 and 2007/55383-0) is gratefully acknowledged.

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