EVALUATION OF SELF-ASSEMBLED MONOLAYER COMPARED TO CHROMATIZING OF ALUMINUM ALLOY BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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ABSTRACT

In this study, the electrochemical behaviour of 5052 H32 aluminium alloy surfaces after a metal free and environmental friendly process based on diphosphonildecane (Self Assembly Molecules) was investigated in a mildly aggressive solution. The results were compared to those obtained for the same alloy treated by the currently used process, chromatizing, for surface preparation prior to coating. The effect of the surface condition on the corrosion performance of this alloy treated by SAM was also evaluated. Experimentally, the study was carried out by electrochemical impedance spectroscopy. The results obtained indicated the viability of a SAM treatment substituting yellow chromatizing for the 5052 H32 aluminium alloy.

INTRODUCTION

The naturally air formed oxide film on aluminium and its alloys presents high corrosion resistance at mild atmospheres, however, for industrial uses, this film does not assure a long term corrosion resistance performance and coating is usually used. Even though organic coatings are applied for corrosion resistance, their permeability and defects allow that moisture and oxygen reach the substrate/coating interface creating conditions for corrosion initiation. Once corrosion has developed on the surface, delamination and loss of paint adhesion might occur.[1-3]

To improve the interaction between substrate and coating, several methods, such as conversion coatings, are used. Conversion coatings are based on the reaction between the metallic substrate and a specific solution producing a conversion layer on the metallic surface. Conversion coatings can act as adhesion promoters or as barrier layers and their homogeneity is strongly dependent on the surface characteristics. Highly homogeneous coatings are associated to surfaces free of oil, oxides, fatty acids, grease and other dirties.[4-7] Chromatizing is a conversion coating process where a layer of chromium trioxide is produced by reaction of aluminium or its alloys in a solution of consisting of chromic acid and additives. The main purpose of the chromate layer is to improve corrosion performance, acting as a barrier layer and as adhesion promoter for paints. [4,8,9]

Self Assembly Molecules (SAM) are molecules that form an organized monolayer on a particular substrate by a chemisorption process.[10-12] Although SAMs are often classified as corrosion inhibitors their mechanism is different from that related to corrosion inhibitors. For instance, the adsorption mechanism of corrosion inhibitors involves electrostatic attraction, that is, physisorption, where the exchange of electrons is fast and highly reversible. On the other hand, during SAM adsorption, exchanging electrons are incorporated into the empty sublevel, resulting in adsorbates of higher stability on the substrate. Thus, SAM adsorption occurs by chemisorption and the layer formation is slow and highly irreversible. Figure 1 illustrates the adsorption of phosphonates on aluminium oxide. The monolayer formed by SAM treatment must be resistant to the oxygen reduction reaction and to the product of this reaction, acting as adhesion promoter for paints.

In this study the corrosion resistance of 5052 H32 aluminium alloy after chromatizing and after a treatment with Self Assembly Molecules (SAM) has been investigated in 0.5 M sodium sulphate solution by Electrochemical Impedance Spectroscopy (EIS). This solution has been used to investigate the degradation behaviour of chromate layers. [4,8]

2. MATERIALS AND METHODS

The chemical composition of the 5052 H32 aluminium alloy used in this investigation is shown in Table 1.

Table 1 – Chemical composition of the 5052 H 32 aluminium alloy.

Element	Al	Cu	Mn	Mg	Si	Cr	Fe	Ti	Pb	V	Zn	Zr
% w/w	96.82	0.02	0.03	2.48	0.09	0.23	0.3	0.02	0.001	0.01	0.001	0.001

The corrosion behaviour of SAM (GARDOBOND X4661) treated specimens was compared with that of the same alloy after chromatizing, by EIS measurements. To evaluate the effect of the surface condition on the corrosion performance of the 5052 H32 aluminium alloy treated by SAM, an intermediate stage of acid etching was also used before SAM treatment and the electrochemical behaviour of SAM treated specimens, with and without previous acid etching, was compared. The process parameters and stages of the surface treatments used in this investigation were based on recommendations provided by the chemical supplier and are shown in Tables 2 and 3, respectively.

2.1 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

A three-electrode cell arrangement was used for the EIS measurements, as illustrated in Figure 2, with a platinum wire and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. EIS measurements were accomplished with a 1260 Solartron frequency response analyzer coupled to a 1287 Solartron Potentiostat connected to a computer. Before performing EIS experiments, the aluminium alloy was pretreated as indicated in Table 3. The exposed area to the electrolyte was 1.13 cm^2. The electrolyte used for evaluation of corrosion resistance by EIS measurements was naturally aerated Na_2SO_4 0.5 M solution with pH adjusted to 4. All measurements were performed in the potentiostatic mode at the corrosion potential. The amplitude of the perturbation signal was 10 mV, and the frequency range studied from 10^5 to $2x10^{-3}$ Hz. The solutions were all quiescent, naturally aerated and at a temperature of (20 ± 1)°C. The EIS measurements were carried out daily from 1 to 5 days. To evaluate reproducibility each test was performed four times.

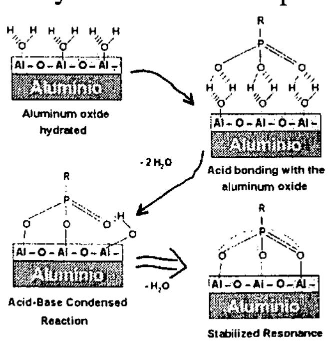


Figure 1 – Adsorption of phosphonate

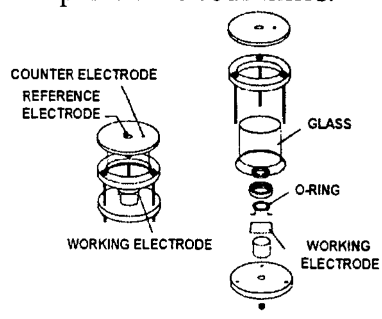


Figure 2 – Electrochemical cell set-up used

compounds on aluminium oxide for EIS measurements.

Table 2 – Work parameters for each process stage.

Stage	Product Name	Concentration	Dip Time	Temperature
Cleaner	OAKITE ALUMINUM CLEANER NST	50 g L^{-1}	5 minutes	$(55 \pm 5)^{o}$ C
Rinsing	DI Water			
Acid Etch	NHO_3 : HF	32.5% m/v : 1.0% m/v	2 minutes	RT
Rinsing	DI Water			
SAM	GARDOBOND X 4661	250 mg L^{-1}	5 minutes	$(50 \pm 5)^{o}$ C
Chromate	ALSURF 1200	7.5 g L^{-1}	3 minutes	RT
Rinsing	DI Water			
Dryer	Hot air blowing			

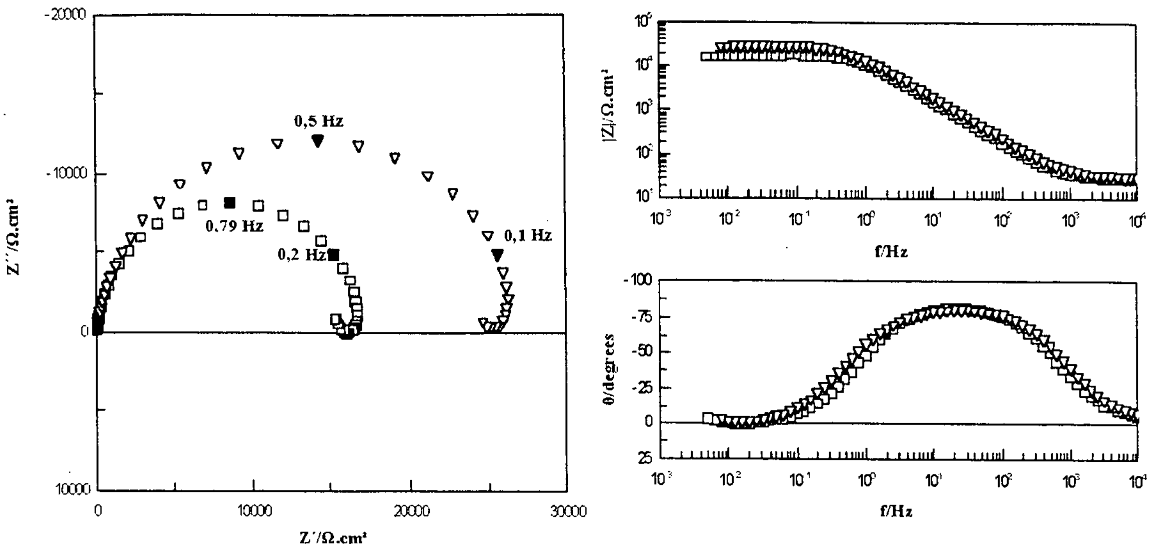
Table 3 – Surface treatments used and their stages.

Treatment	Cleaner	DI Water Rinse	Acid Etching	DI Water Rinse	Chromatizing	SAM	DI Water Rinse	Drying
A	X	X						X
B	X	X	X	X		X	X	X
C	X	X				X	X	X
D	X	X		X	X		X	X

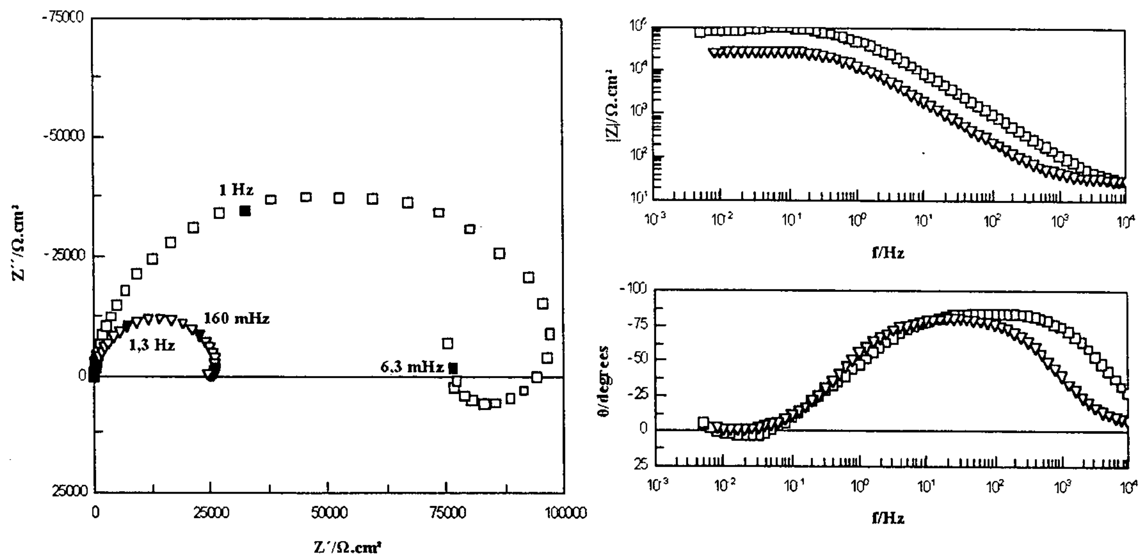
3. RESULTS

Eis measurements

EIS results for specimens after treatments A and C and immersed in 0.5 M Na_2SO_4 for 2 days are shown in Figure 3 (a). The results at high frequencies indicate similar phase angles for these two treatments (A and C) after 2 days of immersion. This could be due to partial SAM degradation or incomplete monolayer assembling. Similar results to that presented in Figure 3 (a) were also obtained for specimens exposed to treatment B after 5 days in the acid solution. Figure 3 (b) shows Nyquist and Bode plots for specimens after B and C treatments and immersed in acid solution for 2 days. The results in this last figure indicates a beneficial effect of acid etching on the performance of SAM treated specimens. Higher phase angles at high frequencies were obtained for the acid etched specimens previous to SAM treatment. The chemical attack of the surface in nitric-fluoridric acid solution, carried out after degreasing and before SAM treatment, therefore had a favourable effect on the corrosion behaviour of the 5052 H32 aluminium alloy. These results indicate that adsorption and monolayer formation is strongly affected by surface preparation. The monolayer formed on a homogeneous and stable oxide layer associated to the chemically etched surface was related to better corrosion resistance. The SAM treatment without previous acid etching produced surfaces of lower corrosion resistance in the 0.5 M Na_2SO_4 solution.



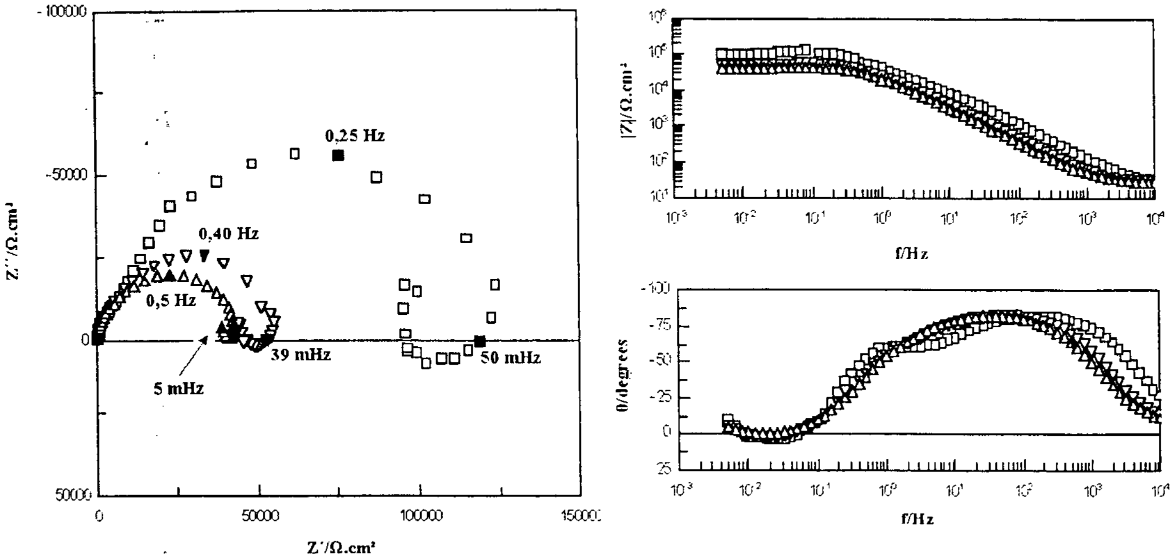
(a)



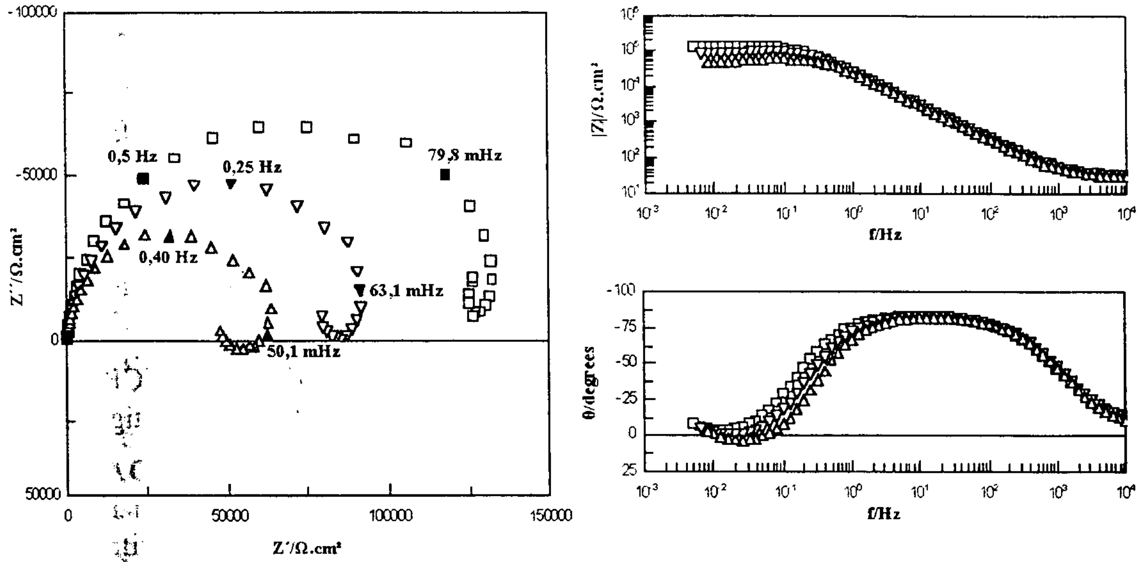
(b)

Figure 3 – EIS of specimens exposed to treatments (a) A and C (A, ∇ C); (b) B and C (B, ∇ C), after 2 days in naturally aerated 0.5M Na_2SO_4 solution (pH = 4).

Figures 4 (a) and (b) show the effect of increasing time in naturally aerated 0.5M Na_2SO_4 solution on the EIS response of specimens after treatments B (SAM after acid etching) and D (chromatizing), respectively. Figure 4 (a) shows two time constants associated to the SAM treated specimen after 1 day of immersion. The phase angles at high frequencies slightly decreased with time and moved into lower frequencies between one and three days of immersion, indicating a small degradation of the monolayer on the specimens exposed to treatment B. The chromate layer however is more stable and no significant changes are seen from one to five days of immersion for this specimen at the high frequency range. Nevertheless, both layers, SAM or chromate layer, do not impede the access of the electrolyte to the metallic interface and the impedance at low frequencies decreases with time.



(a)



(b)

Figure 4 – EIS of specimens exposed to (a) treatment B and (b) treatment D, at increasing times in naturally aerated 0.5M Na_2SO_4 solution (pH = 4).
(1 day of immersion, ∇ 3 days of immersion, Δ 5 days of immersion)

Figure 5 compares the EIS results of specimens exposed to treatment B and to treatment D after 5 days in 0.5 M Na_2SO_4 electrolyte. The EIS results show similar high frequency features for both treatments (B and D) after 5 days of test. However, from mid to low frequencies the impedances associated to the chromatized specimens were slightly higher. Figures 3 to 5 show similar mid and low frequency features for all surface treatments used. These results suggest that the different layers do not change the corrosion mechanism of the substrate. However, this hypothesis must be further investigated by surface and corrosion products analysis.

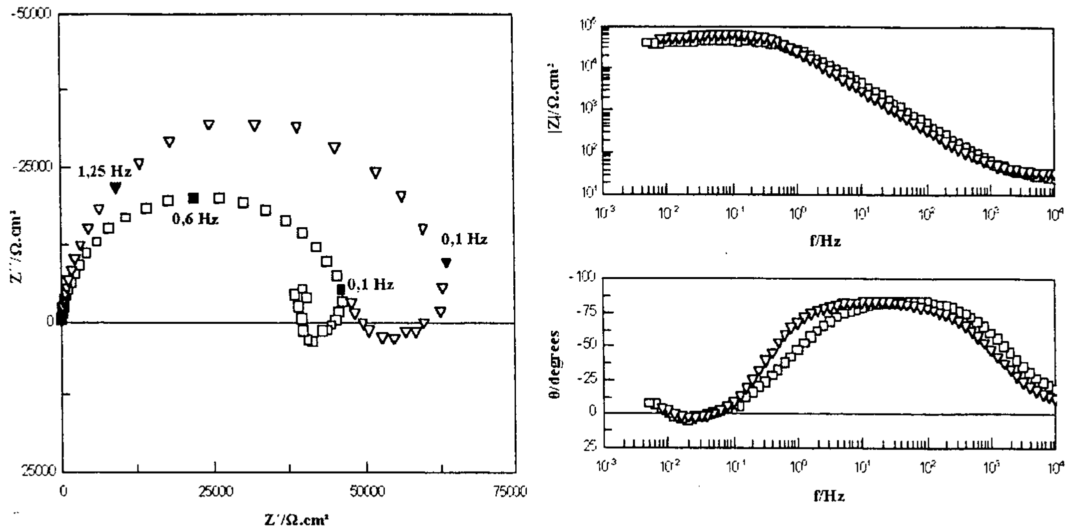


Figure 5 – EIS results of specimens exposed to treatment B ( ) and treatment D (∇), after 5 days of immersion in naturally aerated 0.5 M Na_2SO_4 solution (pH = 4).

4. CONCLUSIONS

The EIS results in the naturally aerated 0.5 M Na_2SO_4 solution indicated the viability of a SAM treatment substituting yellow chromatizing for 5052 H32 aluminium alloy. The results also indicated that adsorption and monolayer formation is strongly affected by surface preparation. The monolayer formed on a homogeneous and stable oxide layer resulting from chemical etching was related to better corrosion resistance.

5. ACKNOWLEDGEMENTS

The authors are grateful to ALCAN ALUMÍNIO DO BRASIL and particularly to Alexandre Sartori for supplying the 5052 H32 aluminium alloy. They are also thankful to CHEMETALL GmbH for providing the chemical products used in the surface treatments investigated.

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First Announcement

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