

# EIS investigation on Al 5052 alloy surface preparation for self-assembling monolayer

F.M. Reis<sup>a,c</sup>, H.G. de Melo<sup>b</sup>, I. Costa<sup>c,\*</sup>

<sup>a</sup> *Chemetall do Brasil Ltda, São Paulo, Brazil*

<sup>b</sup> *Chemical Engineering Department of the Polytechnic School of the University of São Paulo, São Paulo, Brazil*

<sup>c</sup> *Energy and Nuclear Research Institute, IPEN/CNEN-SP, CCTM, São Paulo, Brazil*

Received 23 June 2004; received in revised form 2 December 2004; accepted 8 February 2005

Available online 8 September 2005

## Abstract

Environmental restrictions are leading to the research for environmentally friendly Cr-free treatments to substitute chromating. Recently, promising results have been reported for the corrosion protection offered by self-assembly monolayer (SAM) on different metals. In the present work, the influence of surface preparation on the electrochemical behaviour of SAM-treated Al 5052 alloy in naturally aerated 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution (pH 4) has been investigated using EIS. The effects of three different surface treatments were compared: (A) alkaline cleaning; (B) alkaline cleaning followed by SAM treatment; (C) alkaline cleaning followed by acid etching and then SAM treatment. The results indicate that the acid-etching step, carried out after cleaning had a favourable effect on the corrosion behaviour of the Al 5052 alloy when it is subsequently treated with SAM process.

© 2005 Elsevier Ltd. All rights reserved.

**Keywords:** Self-assembling monolayer; Aluminium alloy; Electrochemical impedance spectroscopy; Surface treatment; Chromating

## 1. Introduction

Aluminium and its alloys show good corrosion resistance in mildly aggressive environments. However, to assure long-term protection, organic coatings are frequently employed. Nowadays, chromate conversion coating is one of the most used adhesion promoters for aluminium and its alloys due to its characteristics such as easy application and effectiveness [1–5]. Moreover, this pre-treatment increases the corrosion and wear resistances of the substrate.

Recently, environmental requirements are prompting many surface suppliers to develop new technologies based on environmental friendly processes [6]. Chromating is one of the surface treatments being banned due to environmental restrictions and self-assembling molecules (SAM) are being investigated as a potential substitute for it.

SAM are low-solubility compounds that adsorb spontaneously on specific substrates forming an organized monolayer [7–9] and changing the physical–chemical properties of the surface. The possibility to tailor molecules with two different functional groups makes SAM real candidates as adhesion promoters and potential substitutes to usual surface treatment processes prior to painting [10,11]. SAM are composed of three parts: (i) the head, responsible for chemisorption; (ii) the spacer; (iii) the functional group that is accountable for its designed properties. One head of the molecule is hydrophilic and the other is lipophilic, explaining the low solubility of fatty acid in aqueous solutions. During adsorption, firstly the hydrated oxide layer is fixed by acid bonding and subsequently, stable resonance is established [12].

SAM as surface pre-treatment for painting must improve coating adhesion and form a compact and homogeneous layer. For this purpose, they must have good stability on the metal/coating interface, act as oxygen reduction reaction

\* Corresponding author. Tel.: +55 11 3816 9456; fax: +55 11 3816 9370.  
E-mail address: [icosta@ipen.br](mailto:icosta@ipen.br) (I. Costa).

inhibitor and have high resistance to the products of this last reaction.

Most of the published papers on self-assembled monolayer are related to pure metals [8–11,14] and only some refer to commercial alloys [11,13]. Besides, few papers refer to the use of electrochemical impedance spectroscopy to characterize SAM-treated metals or alloys [10,11,14]. One of the main drawbacks in using commercial alloys for SAM treatment is related to the lack of knowledge about the effects of impurities and/or precipitates and their interaction with the SAM layer. Only recently, research on the influence of surface treatment on the electrochemical behaviour of SAM-treated pure Al and Al alloy has been carried out [11,14]. The results of these studies have indicated that surface preparation prior to SAM adsorption affects its corrosion resistance [11] and also pointed out to the need of further investigation.

The aim of the present work is to investigate the influence of surface preparation on the corrosion resistance of Al 5052 alloy treated with SAM. This was carried out in a naturally aerated 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution, acidified to pH 4.

## 2. Experimental

A commercial Al 5052–H32 alloy produced by Alcan BRAZIL (composition given in Table 1) was used in this investigation.

The effects of four surface treatments on the electrochemical behaviour of the Al alloy were compared. The surface treatments used were: (A) alkaline cleaning in 50 g L<sup>-1</sup> Oakite Aluminium Cleaner NST at 50 °C for 5 min, followed by rinsing in deionized (DI) water, (B) same as in (A) followed by SAM treatment, (C) same as in (A) followed by acid etching in nitric acid (320 g L<sup>-1</sup>) and hydrofluoric acid (20 g L<sup>-1</sup>) solution for 2 min at room temperature, rinsing in DI water and SAM treatment and (D) same as in B replacing SAM treatment for chromatizing. Chromatizing was carried out according to industrial procedures using ALSURF 1200 with concentration of 8 g L<sup>-1</sup>, as the chromatizing solution. This solution was at room temperature and the dipping time was 3 min. The stages used in the chromatizing process were alkaline cleaning, rinsing, dipping and drying. The SAM treatment was accomplished by immersion in a solution 300 mg L<sup>-1</sup> alkane diphosphonate (Gardobond X4661)

at 50 °C for 5 min. The alkaline cleaning is of mild aggressiveness. The process parameters and surface treatments stages used in this investigation were based on recommendations provided by the chemical supplier.

For the sake of comparison, the same treatments, A–C, were carried out to high purity aluminium (99.99%), however, before the treatments, the surfaces of the working electrodes were polished with 600 grit emery paper and rinsed with deionized water. The EIS responses of these electrodes were assessed after 1 day of immersion in the electrolyte.

The effect of surface treatment on the electrochemical behaviour of the Al 5052–H32 alloy was evaluated by open circuit potential (OCP) measurements and electrochemical impedance spectroscopy (EIS) at increasing times. Potentiodynamic polarization measurements in 0.5 M sodium sulphate solution were also performed. The pH of the test solution was adjusted to 4.0 with sulphuric acid. The test solution used was quiescent, naturally aerated and at a temperature of 20 ± 1 °C. A solution of similar composition has been previously used to investigate the degradation behaviour of chromate layers [1,2] or self-assembling monolayer [11].

A three-electrode cell arrangement was used for the EIS and polarization measurements, 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 analyser coupled to a 1287 Solartron potentiostat connected to a computer. The exposed area to the electrolyte was 1.13 cm<sup>2</sup>. All EIS measurements were performed in the potentiostatic mode at the OCP. The amplitude of the perturbation signal was 10 mV (rms) and the frequency range studied from 10<sup>5</sup> to 2 × 10<sup>-3</sup> Hz, with an acquisition rate of 10 points per decade. The EIS measurements were carried out from 1 to 6 days. To evaluate reproducibility each test was performed four times.

Scanning electron microscopy (SEM) was used to observe the Al alloy surface, both, before and after surface treatment. Energy dispersive spectroscopy (EDS) of the matrix and precipitates in the Al 5052–H32 alloy was also carried out.

## 3. Results and discussion

Fig. 1 shows a SEM micrograph of the Al 5052 alloy surface prior to surface treatment and the corresponding EDS spectra of regions 1 (Al alloy matrix) and 2 (white particles). A large number of intermetallics (white regions) are clearly seen on the surface, which EDS spectra (2) revealed to be Fe-rich. Defects that appear as grooves on the micrograph, produced by the alloy fabrication process (rolling), are also evident.

SEM micrographies of the Al alloy after alkaline cleaning with Oakite Aluminium Cleaner NST and with alkaline cleaning plus acid etching in a solution of nitric acid (320 g L<sup>-1</sup>) and hydrofluoric acid (20 g L<sup>-1</sup>) solution are shown in Fig. 2a and b, respectively. The alkaline cleaning treatment caused the preferential attack of the Al alloy matrix

Table 1  
Chemical composition of Al 5052 H32 alloy

Element	% Mass
Cu	0.02
Mn	0.03
Mg	2.48
Si	0.09
Cr	0.23
Fe	0.3
Ti	0.02
Al	Balance

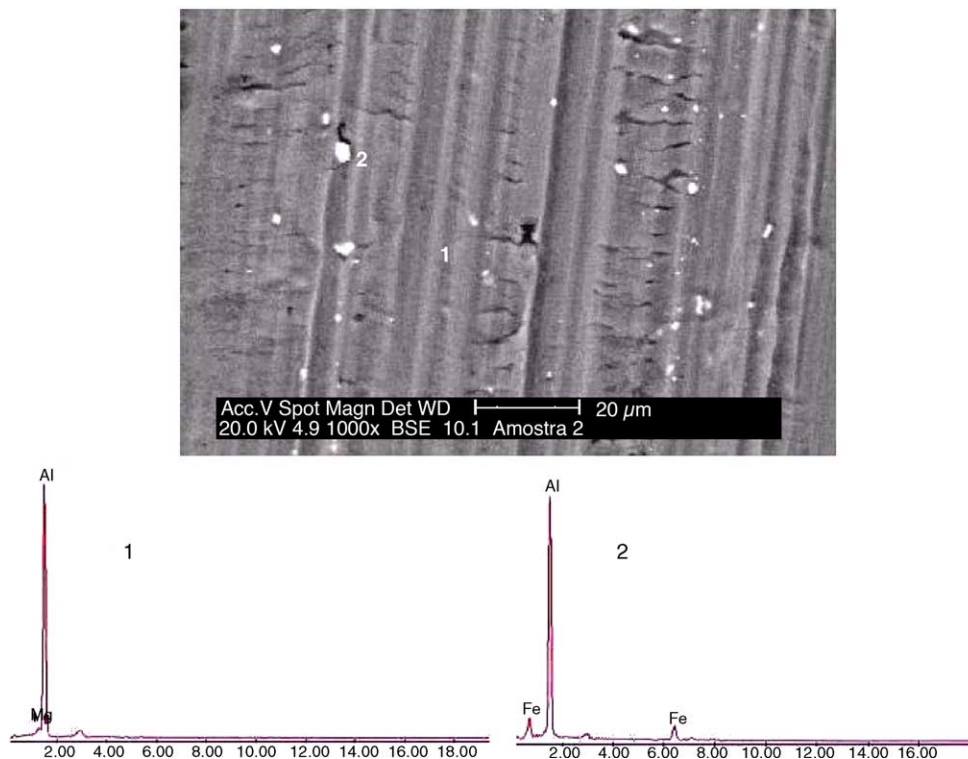


Fig. 1. SEM micrograph of Al 5052–H32 alloy without surface treatment (as-received) and corresponding EDS spectra of regions 1 (matrix) and 2 (white precipitates).

near the Fe-rich precipitates producing shallow and round cavities, clearly indicated in Fig. 2a by intermetallic particles that remain on the surface. As already suggested in other works [15], due to hardness differences, regions around precipitates are severely deformed during fabrication processes, like rolling. Consequently, these regions are more prone to be dissolved during chemical treatments that attack the metal matrix. The acid etching treatment, on the other hand, caused the dissolution of the Fe-rich intermetallics and produced a larger number of pits (Fig. 2b) comparative to the alkaline treatment (Fig. 2a). This latter feature indicates that localized attack occurs during this treatment, which can be explained by the opposite actions of HF, extremely harmful to the Al passive layer and  $\text{HNO}_3$ , which tends to repassivate it. However,

both, alkaline cleaning and acid etching resulted in cleaner and smoother surfaces compared to the as-received condition.

The OCP variation with time for Al alloy samples submitted to surface treatments A–C and immersed in naturally aerated 0.5 M  $\text{Na}_2\text{SO}_4$  solution (pH 4) for a time span of up to 6 days, is shown in Fig. 3, together with micrographs obtained prior and after the experiments. As it can be seen in the insert of this figure, high surface activity followed by fast potential stabilization is indicated for the sample after treatment A for the first 4 h of immersion and this can probably be explained by the detachment of intermetallic particles loosely adhered to the surface after this treatment, as shown in Fig. 2a. From 22 h to 6 days of immersion, the OCP slightly increased. More noble potentials were recorded for samples

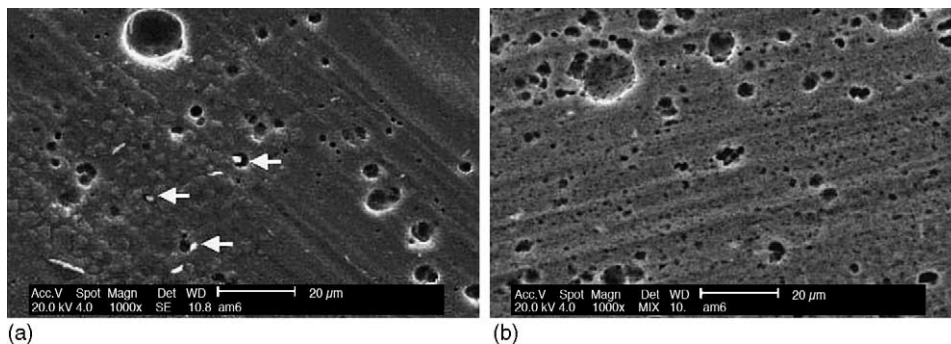


Fig. 2. SEM micrographs of Al 5052 alloy surface after: (a) alkaline cleaning and (b) alkaline cleaning plus acid etching in nitric acid ( $320 \text{ g L}^{-1}$ ) and fluoridric acid ( $20 \text{ g L}^{-1}$ ) solution.

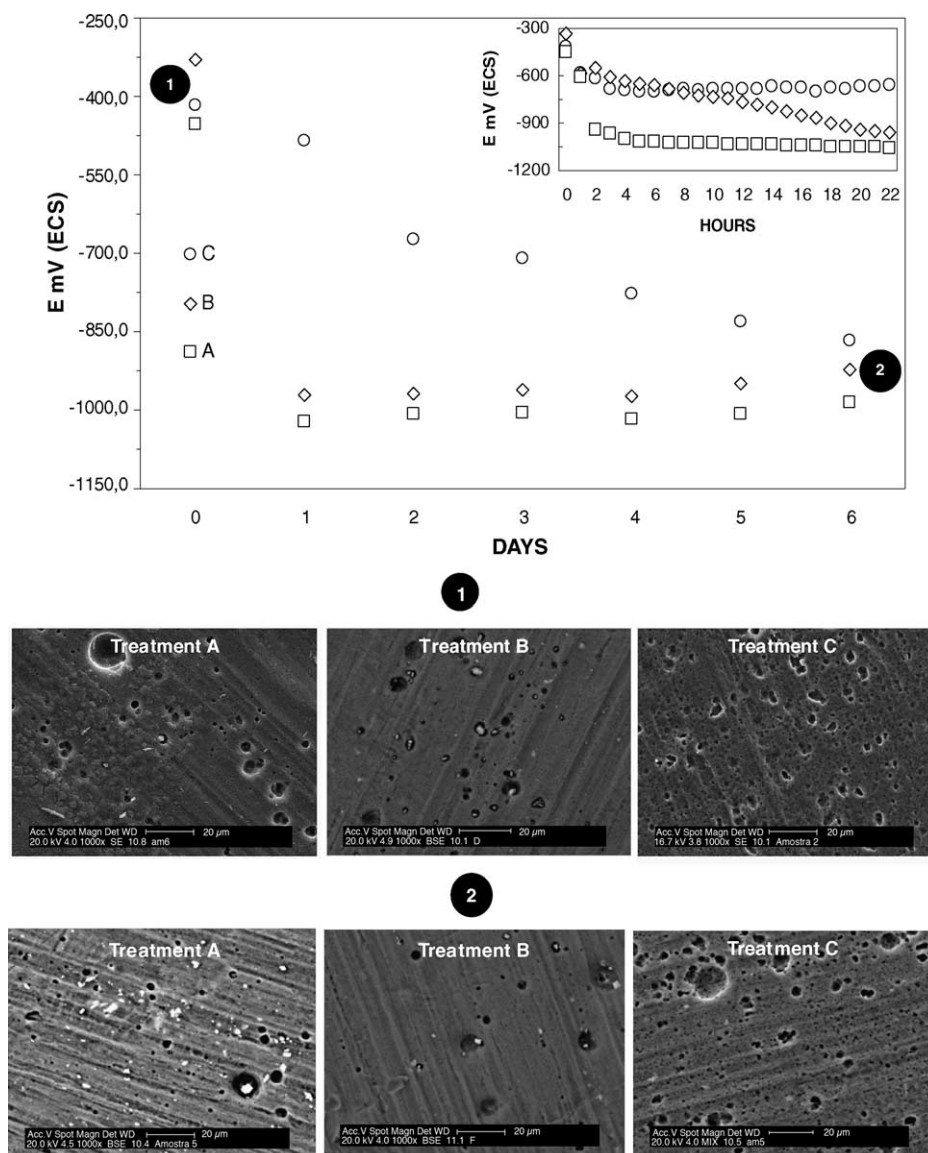


Fig. 3. OCP vs. time curves for Al 5052–H32 alloy in naturally aerated 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution (pH 4) at 20 °C, after surface treatments A–C.

submitted to treatments B and C for the whole test period. However, the potential of the former sample decreased continuously with time, approaching the potential exhibited by sample submitted to treatment A after 22 h of exposition to the test electrolyte, remaining near it up to 6 immersion days, suggesting similar corrosion behaviour for both samples, from this point on.

The OCP variation with time for the sample submitted to treatment C has shown more noble values and faster stabilization than for samples prepared with treatments A and B, indicating a favourable role of the acid etching treatment on the SAM layer adsorption process. The beneficial role is likely due to the removal of precipitates and to the formation of an oxide layer with better characteristics due to the action of the nitric acid, producing a more homogeneous surface that favours SAM adsorption, since it is known that phosphonates present strong interaction with oxide covered

metals [10]. However, the OCP of the sample submitted to treatment C becomes similar to that of the uncoated one after few days of immersion, indicating deterioration of the SAM layer.

Fig. 3 also presents micrographies of the samples surface prior and after the 6 days test period. For the sample submitted to treatment A, an intense attack of the matrix surface can be observed, with the emergence of many new intermetallics from the attacked matrix. Moreover, only few loosely adhered intermetallics are present at the surface, supporting our previous hypothesis that they must be detached during the first hours of immersion. These results indicate that even though sulphates can act as corrosion inhibitor for Al alloys [16–18], they are not so effective in such an acidic pH, the emergence of these intermetallics may be responsible for the slow positive drift of the OCP, which could be due to depolarization of the cathodic reactions. For B- and C-treated samples, hardly

any change in the surface condition can be observed prior and after the exposure period, indicating the effective protection afforded by the SAM treatment. For the sample treated with sequence B, it is worth noting that few loosely adhered intermetallics, likely produced during the alkaline cleaning step, are still present on the sample surface, confirming the low surface activity for this sample.

EIS results at increasing immersion times in the naturally aerated 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution, with pH 4, for Al 5052–H32 alloy samples after treatments A–C, are shown in Fig. 4. As a first remark, it must be said that the general shape of the diagrams is very similar for all the samples and that this is maintained throughout the whole test period, indicating that almost no change in the corrosion mechanism occurred either due to the different surface treatments or to the immersion time. Moreover, no impedance diagram was obtained for the sample submitted to treatment B after 4 h of immersion in the test solution due to OCP drift. For this particular sample, the stability needed to perform impedance measurements was not attained after this time span.

For the sample not treated with SAM (Fig. 4a), the augmentation of the impedance response with immersion time, from 4 h to 3 days of test, is likely due to the dissolution of the more active areas of the sample surface, as already reported by other authors for different Al alloys [14,19]. It must be pointed out that the dissolution of the active regions (produced during rolling and not completely removed during the mild alkaline etching treatment) must be very slow, due to the low aggressiveness of the electrolyte. Indeed, the impedance exhibited by the A-treated sample, after the accomplishment of the test period, remains in the order of tenths of kilo ohms, even though no further protection has been provided to it. Conversely, during the first immersion hours, it is possible that the presence of a great number of loosely adhered intermetallics on the sample surface would be accountable for the intense surface activity, leading to the scattering of the low-frequency data and to the increase in impedance. In addition, some concurrent inhibitory effect from the sulphate ions must also be expected during the first hours of immersion, contributing to the verified behaviour. The decrease in impedance between 3 and 6 days could have been caused by the natural attack of the Al passive layer by the acidic test solution, leading to a gradual deterioration of its corrosion resistance and this can be likely ascribed to the formation of galvanic couples between the matrix and the emergent intermetallics from the underlying matrix. This hypothesis is supported by the micrographies of Fig. 3 and also by the slow increase in the OCP, likely due to cathodic depolarization. Bode phase angle diagrams for this sample are constituted by a broad capacitive phase angle in the high frequency (HF) region, an inductive behaviour in the low-frequency (LF) region and an incipient capacitive loop in the lowest frequency range. This is in accordance with the findings of other authors for Al in different acidic media and is ascribed to the dissolution of the metal in the presence of a passive layer and to adsorption processes taking place at the metal surface [20,21].

For 1 day of test, the HF capacitive loop for the sample submitted to treatment B (Fig. 4b) exhibited a diameter only slightly superior to that presented in Fig. 4a, for the same test period, indicating that this treatment is not very effective in promoting SAM adsorption. However, a continuous increase with immersion time of the diameter of the HF capacitive loop was observed, attaining values 1.5 times superior to that exhibited by the A-treated sample at the end of the experiment, pointing towards an augmentation of the corrosion resistance of this sample. This response can be possibly explained by the organization of the SAM molecules adsorbed to the electrode surface. Indeed, a closer observation of the Bode phase angle diagrams for this sample shows a slight broadening of the HF capacitive phase angle for longer immersion times, supporting this hypothesis. Felhösi et al. [22], using iron electrodes, have reported that SAM adsorption to the electrode surface was a relatively fast phenomenon, whereas its organization was a very slow process. It is likely that during the first day of immersion, where a high potential drift was observed for this particular sample, loosely adhered SAM molecules are detached from the electrode surface and after this period, the remaining well-adhered molecules would interact increasing their organization and enhancing the impedance response.

Fig. 4c shows the impedance response with increasing immersion time in the electrolyte for a sample treated with procedure C. For 4 h of immersion the impedance exhibited by this sample is considerably higher than the previous ones. Moreover, there are instabilities in the LF range, likely due to very small interfacial currents, since the OCP was stable (Fig. 3). For this particular experiment, the Bode phase angle diagram is characterized by a HF capacitive response, close to  $-90^\circ$ , suggesting the existence of a compact adsorbed layer, moreover, a second time constant is evident in this frequency range. After 1 day of immersion, this sample presents a significant decrease of impedance, however, it is still considerably higher than those presented by the samples submitted to treatments A and B. Using the typical interpretation adopted for impedance response of coated metals, it can be supposed that the capacitive phase angle at higher frequencies is due to the presence of the SAM adsorbed layer, the response of the metal/solution interface lying below  $10^3$  Hz. In this manner, it can be supposed that the difference in response verified during this time period (smaller than 1 day) can be mainly ascribed to a rapid deterioration of the SAM adsorbed layer, since a huge difference was found in the highest frequency region of the Bode phase angle diagram. Upon increasing the experiment time from 1 to 3 days, an important decrease in the HF capacitive loop diameter was still observed and this was accompanied by the disappearance of the higher frequency capacitive feature in the Bode phase angle diagram and the merge of the two HF capacitive time constants in lower frequencies values, suggesting an even stronger deterioration of the SAM adsorbed layer. For longer test periods, only a slight evolution of the impedance response was verified, characterized by a diminution of the HF capacitive loop

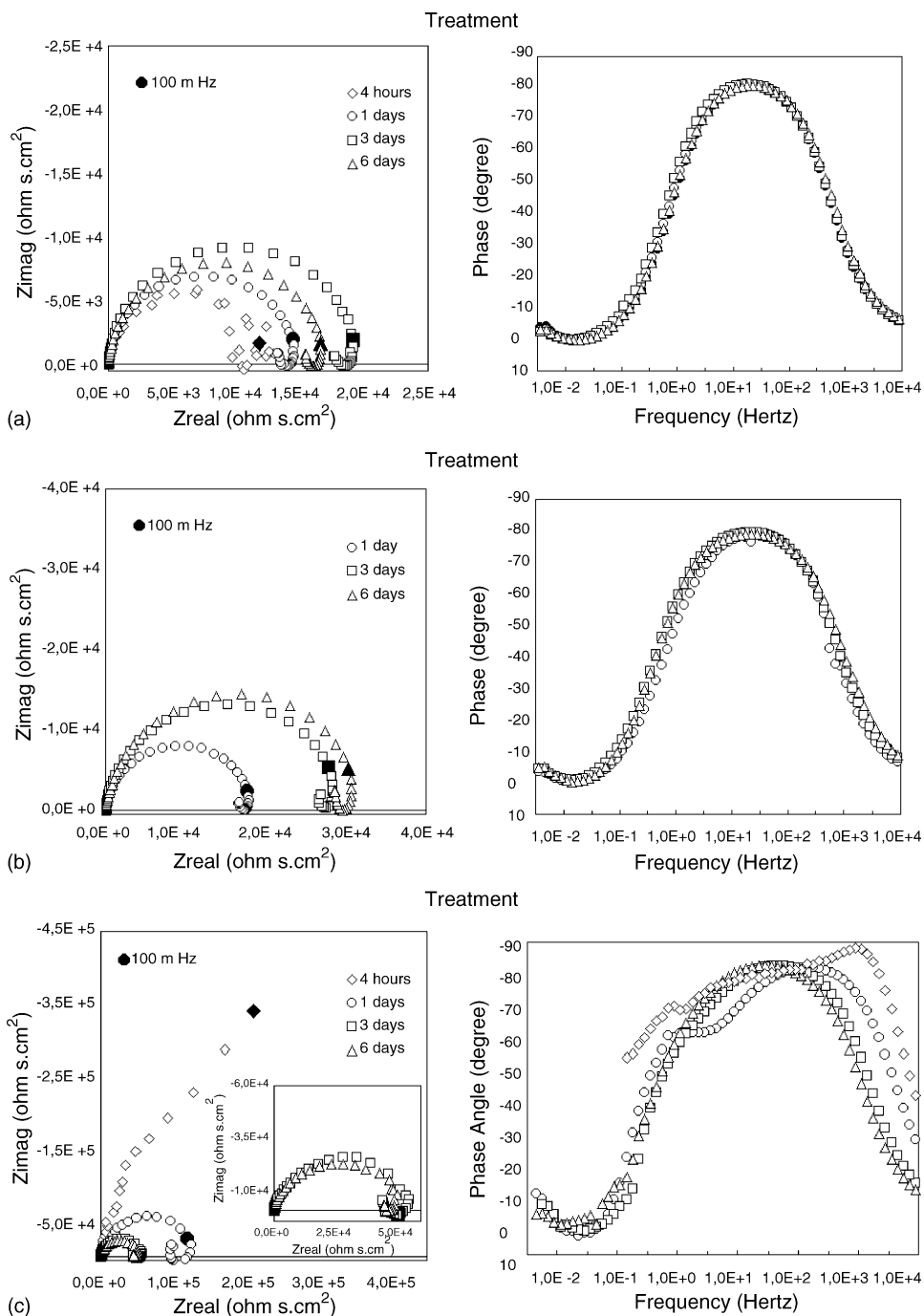


Fig. 4. Nyquist and Bode diagrams of Al 5052–H32 alloy at increasing times in naturally aerated 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution (pH 4). Sample after: (a) treatment A; (b) treatment B; (c) treatment C.

diameter and by a slight displacement to lower frequencies of the capacitive feature of the Bode phase angle diagram. Nevertheless, at the end of the 6 days exposure period, this sample still exhibited impedance values approximately 1.5 higher than those presented by the one submitted to treatment B, indicating better corrosion performance. Indeed, impedance results, not presented here, obtained with samples submitted to treatment C and not immersed in the SAM solution have shown impedance values very similar to those presented with

treatment B after the same time span, indicating that some molecules still remains protecting the surface of samples submitted to treatment C.

As proposed earlier, the acid-etching step promotes surface homogenization assisting SAM adsorption; this would lead to the higher impedance values observed in the first days of test for the sample treated with procedure C. However, the major decrease in impedance of Al 5052–H32 alloy observed during the first 3 days of experiment, suggests weak

SAM–substrate surface interactions. This response could be likely ascribed to the effects of hydrofluoric and nitric acids on the stability of the Al passive layer and on the sample surface morphology. The presence of a cleaner and smoother surface after the acid etching procedure must favour the SAM adsorption process, as phosphonates, the SAM's hydrophilic group used in this study, have high affinity for oxide layers [10]. However, as evidenced in Fig. 2b, the acid etching pre-treatment step also provokes the formation of small pits on the sample surface. The trapping of the etching solution inside these microstructural features may play a role in the impedance response of this sample, contributing to the detachment of the SAM from the electrode surface, due to the corrosion of the subjacent alloy matrix. Pit enlargement and the diffusion of aggressive specimens, mainly fluoride ions, out of the cavities would likely explain the stabilization of the corrosion behaviour for longer immersion periods. Indeed, impedance experiments, not presented here, performed with C-treated samples which were ultrasonically cleaned in DI water prior to their immersion in the SAM solution have shown more stable impedance responses.

To better clarify the effect of surface preparation on the electrochemical behaviour of Al 5052–H32 alloy, samples were prepared using procedures B and C (with and without SAM stage) and their anodic potentiodynamic polarization behaviour investigated in the test solution with the addition of 30 ppm of chloride ions. The results of these experiments are presented in Fig. 5. Three main features are evident from the observation of this figure. The first one is the confirmation of the beneficial effect of acid etching for SAM adsorption, already evidenced in the EIS results, since the passive current presented for the sample submitted to treatment C is two orders of magnitude smaller than that exhibited by the one treated with procedure B. Secondly, it is evident that the surface quality after both treatments are equivalent, since both

samples exhibit similar current values in the current plateau. Finally, this figure shows that acid etched samples exhibits lower pitting potential, irrespectively if they have been treated with SAM or not. This latter feature shows that, even though the acid etching procedure removes most of the intermetallics present at the sample surface, it also increases its susceptibility to localized corrosion, which could be likely due to trapping of the etching solution inside the etching pits, as already suggested. These results confirm that acid etching in HF containing solutions, favours the adsorption of SAM, but might also have harmful effects on the surface preparation prior to SAM treatment.

Fig. 6 presents EIS diagrams obtained for pure (99.99%) Al electrodes submitted to treatments A–C after immersion in the  $\text{Na}_2\text{SO}_4$  test electrolyte for 1 day. As expected, the A-treated sample presents a higher impedance than that exhibited by the Al 5052–H32 alloy treated in the same way, since intermetallics are not present at the pure Al surface. The sample submitted to the C procedure displays impedance of the same order of magnitude of the alloy, confirming that the acid-etching step is highly effective in removing intermetallics from the electrode surface, however, the two HF time constants are better separated for the pure Al sample, indicating that, somehow, SAM adsorption is favoured on pure Al.

The only unexpected result was the one obtained with pure Al electrode submitted to treatment B, once this particular sample presented the lowest impedance value among all. One hypothesis that can explain this behaviour is the difference in the surface condition prior to the samples being submitted to any of the three treatments. While the alloy was used in the as-received condition, i.e. after rolling to mimic industrial application, the surface of the pure Al electrodes was previously abraded in order to re-use them for other experiments. It is widely known the susceptibility of Al alloys to alkaline and acidic attacks. It is possible that during the B treatment,

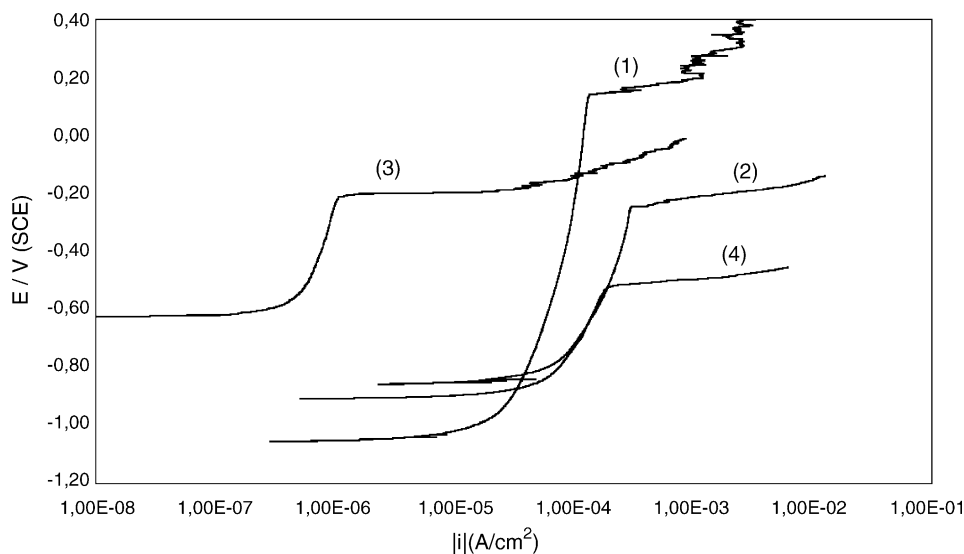


Fig. 5. Potentiodynamic polarization curves of Al 5052–H32 alloy in naturally aerated 0.5 M  $\text{Na}_2\text{SO}_4$  solution (pH 4) with the addition of 30 ppm of chloride ions. Samples submitted to: (1) treatment B; (2) treatment A; (3) treatment C; (4) as treatment C without SAM stage.

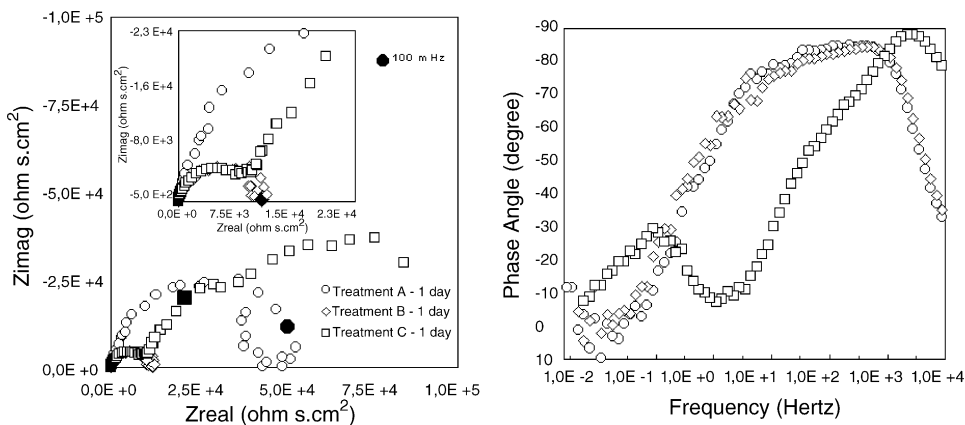


Fig. 6. Nyquist and Bode diagrams of Al (99.999%) after 1 day of immersion in naturally aerated 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution (pH 4). Samples submitted to treatments: A (□); B (◇); C (△).

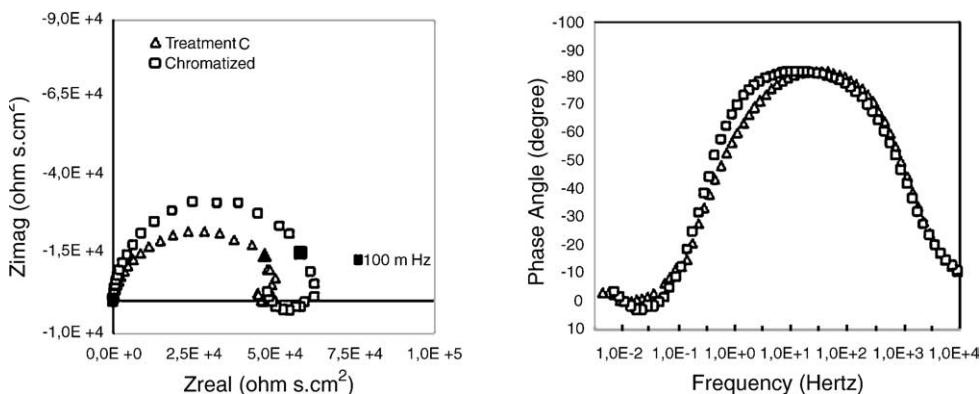


Fig. 7. Comparison of EIS results for Al 5052–H32 alloy samples (□) acid etched and SAM-treated (treatment C) or (△) chromatized. Results were obtained after 6 days of immersion in naturally aerated 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution (pH 4) at 20 °C.

which only takes 5 min and is accomplished in an industrial solution of complex composition and mild aggressiveness, the oxide formed during the rolling step is not completely removed. In this way, when the alloy sample is exposed to the SAM solution, which pH is approximately 3, it is still partially protected against the acidic attack by the oxide layer, allowing SAM adsorption to take place. On the other hand, the freshly formed oxide layer on the pure Al sample after grinding would be completely dissolved during the alkaline etching step, rendering the electrode very susceptible to the acidic attack during immersion in the SAM solution. However, this hypothesis needs further investigation. Two possible ways would be to increase the immersion time in the alkaline cleaning solution, so the oxide layer formed during the rolling stage would be completely removed or, either, to perform this stage in concentrated NaOH solutions, however, this is not representative of industrial conditions and, consequently, it is beyond the aim of the present work.

It must be emphasized that even though the acid etching solution attacks the oxide layer, it also rebuilds it due to the beneficial effect of nitric acid on the formation of the Al oxide layer [23]. In this way, the pure Al sample submitted to C treatment would not be liable to be attacked in the SAM

solution, which has an acidic pH, allowing the formation of the SAM adsorbed layer.

The electrochemical behaviour of the Al 5052–H32 alloy after C treatment has also been compared to the one exhibited by a chromatized sample, treatment D, which impedance response in the same electrolyte had already been investigated by our group [11]. The general results indicate that the chromate layer presents more stable behaviour than the SAM-treated one, showing higher impedance values and slower degradation kinetics. However, impedances of both chromatized and SAM-treated samples decrease with experiment time, indicating that these layers do not impede the access of the electrolyte to the metallic interface. Nevertheless, for longer test periods (6 days) the impedances of the samples prepared in both ways are of the same order, as shown in Fig. 7.

#### 4. Conclusions

The results obtained in this study indicated that adsorption and SAM layer is strongly affected by surface preparation procedures and also by the surface morphology. The cleaner



surfaces produced by the acid-etching step with hydrofluoric and nitric acids, favours the SAM adsorption process. However, the presence of etching pits seems to hinder the interaction between the adsorbed molecules and the sample surface, leading to a fast reduction of the impedance values, apparently due to trapping of the etching solution inside them.

From the experimental point of view, EIS proved to be very sensitive to the SAM adsorption process, mainly due to analysis of the variation in the high frequency part of the Bode phase angle diagrams.

The results also indicated the viability of SAM treatment for substituting yellow chromating on Al 5052–H32 aluminium alloy. However, it seems that better surface conditions than those produced in this work are necessary in order to guarantee stronger SAM–substrate surface interactions and this will be carried out in forthcoming works.

### Acknowledgment

The authors are grateful to Chemetall for providing the chemical products and ALCAN for the Al alloy used in this study.

### References

- [1] P. Campestri, E.P.M. van Westing, J.H.W. de Wit, *Electrochim. Acta* 46 (2001) 2553.
- [2] P. Campestri, E.P.M. van Westing, J.H.W. de Wit, *Electrochim. Acta* 46 (2001) 2631.
- [3] A.O. Ita, *Metal. Finish.* 98 (2000) 74.
- [4] M. Kending, S. Jeanjaquet, R. Addison, J. Waldrop, *Surf. Coat. Technol.* 140 (2001) 58.
- [5] J.H. Osborne, *Prog. Org. Coat.* 41 (2001) 280.
- [6] M. Schneider, M.M. Lohrengel, C. Rosenkranz, A. Schreiber, E. Kock, M. Beneke, *Proceedings of the Third International Symposium on Aluminium Surface Science and Technology*, vol. 43, Benelux Métallurgie, Bonn, Germany, 2003, p. 247.
- [7] A. Ulman, *J. Mater. Ed.* 11 (1989) 207.
- [8] A. Ulman, *An Introduction to Ultrathin Organic Films: From Langmuir–Blodgett to Self-Assembly*, Academic Press, Boston, 1991.
- [9] A. Ulman, *Chem. Rev.* 96 (1996) 1533.
- [10] I. Maeghe, E. Jaehne, A. Henke, H.-J.P. Adler, C. Bram, C. Jung, M. Stratmann, *Prog. Org. Coat.* 34 (1998) 1.
- [11] F.M. Reis, H.G. de Melo, I. Costa, *Proceedings of the Fifth NACE Latin-American Region Corrosion Congress and Eighth Ibero-American Congress of Corrosion and Protection*, Santiago de Chile, Chile, 2003, p. 121.
- [12] M. Stratmann, M. Rohwerder, *Mater. Res. Soc. Bull.* 27 (7) (1999) 43.
- [13] E. Kálman, *Electrochim. Acta* 46 (2001) 3607.
- [14] L.V. Aoki, F.M. Reis, I.V. Aoki, I. Costa, H.G. de Melo, *Proceedings of the Third International Symposium on Aluminium Surface Science and Technology*, vol. 43, Bonn, Germany, Benelux Métallurgie, 2003, p. 364.
- [15] A. Tahara, C. Filipini, H.G. de Melo, I. Aoki, *Proceedings of the Eighth Encontro Brasileiro de Tratamento de Superfície*, São Paulo, Brasil, 1994, p. 149.
- [16] A. Kolics, A.E. Thomas, A. Wieckowski, *Langmuir* 11 (1995) 4605.
- [17] C. Blanc, B. Lavelle, G. Mankowski, *Mater. Sci. Forum* 217 (1996) 1559.
- [18] C. Blanc, B. Lavelle, G. Mankowski, *Corros. Sci.* 39 (1997) 495.
- [19] L.E.M. Palomino, J.F. de Castro, I.V. Aoki, H.G. de Melo, *J. Braz. Chem. Soc.* 14 (2003) 651.
- [20] I.V. Aoki, M.C. Bernard, S.I.C. de Torresi, C. Deslouis, H.G. de Melo, S. Joiret, B. Tribollet, *Electrochim. Acta* 46 (2001) 1871.
- [21] H.J.W. Lenderink, M.V.D. Linden, J.H.W. De Wit, *Electrochim. Acta* 38 (1989) 1993.
- [22] I. Felhősi, J. Telegdi, G. Pálkás, E. Kálman, *Electrochim. Acta* 47 (2002) 2335.
- [23] C. Blanc, S. Gastaud, G. Mankowski, *J. Electrochem. Soc.* 150 (8) (2003) B396.