

CORROSION BEHAVIOUR IN NaCl SOLUTIONS OF AMCS: MATERIALS AND PARAMETER TEST INFLUENCE

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ABSTRACT

The following contribution describes results from corrosion tests on a series of AMCs that were obtained by following a powder metallurgy route combined with a secondary consolidation process.

Cyclic polarization (CP) studies were performed with the aim of determinate the corrosion potential (E_{corr}), pitting potential (E_p) and protection potential (E_{pp}). In order to corroborate the obtained previous results, another set of specimens was used and potentiostatic polarization tests were also performed.

The composite fabrication conditions were modified to observe its influence on corrosion parameters. There were employed two consolidation processes (hot extrusion *vs.* centrifugal casting), matrixes on different precipitation state (composite as obtained *vs.* composite with an optimum artificial aging), different type of reinforcement particles (ceramic & intermetallic) and various amounts of them (5, 10 and 15% *vl.*). An example of found differences is shown in figure 1.

Some test parameters were also modified: aeration or deaeration of solution test, sample area exposed to the solution and polishing grade of the sample.

The pit morphology of the localized attack on the MMCs samples after corrosion was assessed by scanning electron microscopy (SEM). Specimens were examined after exposure to the corrosive observing the type and amount of corrosion.

1. INTRODUCTION

Many engineering alloys, such as stainless steels or aluminium alloys, are useful because of passive films (in nm scale) formed naturally as an oxide layer on the metal surface. Such layers are often susceptible to localized breakdown resulting in accelerated dissolution of the underlying metal. If this attack initiates on an open surface is called pitting corrosion. This type of corrosion has been studied for several decades by many researchers and considerable understanding of the pitting phenomenon has been generated [1-3], but in-depth description of many steps and the influence of many parameters, is still lacking. Fundamental studies typically have focused on: characteristics of the passive film, the earliest stages of passive films breakdown, the growth of metastable pits and the growth of larger, stable pits. However, phenomenology of pitting also has special interest. It includes test parameters as environment, surface properties and sample specifications as alloying, precipitation state of the alloy or reinforcing with discontinues particles. The role of both the environmental and material parameters on the pitting behaviour can be explained by their effects on pit growth stability for passive metals of technology importance such aluminium alloys and their composites.

Corrosion behaviour of particle reinforced aluminium alloys (AMCs) are of special interest on the study of these type of materials because they often are used or have been proposed for applications in contact with aggressive environments (for instance, in automotive components such as suspensions) [4-7]. There are some important scientific investigations of the corrosion sensibility of AMCs but there are still numerous open questions due to the extreme sensibility of the corrosion behaviour. So finally as viewed before, the corrosion behaviour of a particular AMC material is very complex property determined by a wide range of factors.

The following paper presents results concerning electrochemical analysis on different aluminium alloys and their composites. The influence of test parameters and metallurgical variables of the material on the analysis is also investigated.

2. EXPERIMENTAL PROCEDURE

Materials

Tests were carried out on different materials. Two aluminium alloys AA3003 (G-69 and G-100 ASTM aluminium alloy standard) and AA6061 were employed and aluminium matrix composites of AA6061 with TiB_2 ceramic particles were fabricated.

AA3003 was supplied by Alcoa España, as a sheet of 3 mm thickness. This matrix was employed for the electrochemical tests as received.

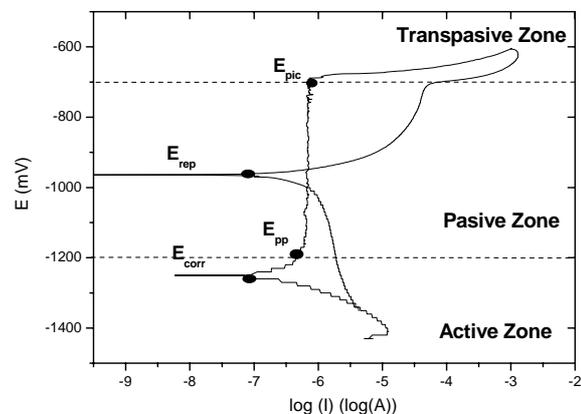
AA6061 was supplied by The Aluminium Powder Co. Ltd as metallic powders obtained by atomisation of the molten metal by argon and TiB_2 particles were supplied by Advanced Refractory Technologies, INC as powders with an average size of 9.4 μm . The unreinforced alloy and the composites were produced by a powder metallurgy route: after mechanically blending of matrix and reinforcement powders during 2 hours and 90 rpm (1.5 s^{-1}), the mixture was uniaxially cold compacted up to a pressure of 250 MPa. Cylindrical samples obtained had 25 mm of diameter and 34 mm of thickness, with a density of 86%. A secondary process of hot extrusion was carried out at 530°C and 25:1 extrusion ratio and bars of 5 mm diameter were obtained.

Corrosion testing

Experiments were carried out at a EG&G flat cell, and the potential was controlled by an EG&G 263A potentiostat; 3.5 wt% NaCl was employed as aerated and deaerated solutions; AgCl/Ag was selected as reference electrode and Pt as counter-electrode; as work electrodes sheet samples had exposed area of 0.2 and 1 cm^2 and extruded samples 0.2 cm^2 . All samples were mounted in an epoxy resin and with the aim of assuring their good electrical conductivity, there were fixed cooper bars to their basis. Specimen surfaces were ground successively from 500 to 1000 SiC grit. A couple of each material was also polished with alumina paste.

Potentiodynamic Polarization Tests consist on measuring free corrosion potential after 90 minutes (5400 s) of exposing the sample to the test solution. With this time the system equilibrium was assured. Then, cyclic potentiodynamic polarization with a 10 mV/min (0.16 mV/s) anodic scan rate was applied, starting from a value 150 mV more negative from the corrosion potential. When the current density exceeded 5 mA/cm^2 , the scanning was reverse in the cathodic direction. The experiment finished when it was reached the initial potential value. With cyclic polarization curves obtained, it was possible to measure different potentials, figure 1: corrosion potential (E_{corr}), primary passivation potential (E_{pp}) and pitting potential (E_{p}), as well as it was estimated the amplitude of the passive zone as ($E_{\text{pp}} - E_{\text{p}}$) in order to evaluate the effectively of this layer. After exposure to the solution, samples were washed in an ultrasonic bath to clean the corrosion products.

Potentiostatic polarization tests were carried out in order to have further information on studied materials behaviour. Another set of specimens was tested at a fixed potential, following the current of the sample regarding time. Samples were polarized anodically at a potential value situated in the passive zone of the sample for 60 min (3600 s). After polarization, samples were cleaned as shown above.



“Figure 1. Cyclic Polarization: Potential Values.”

A duplicate set of samples was anodically polarized at a potential 50 mV more positive to E_b , for 120 min (7200 s) to promote pitting.

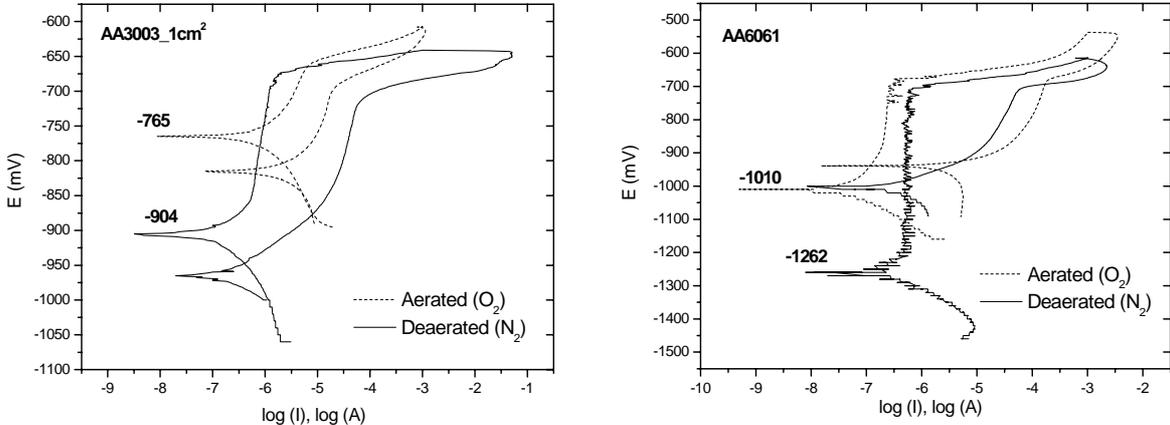
Specimen examination

The cleaned sample surfaces were examined by scanning electron microscopy (JEOL 6300) to characterize the morphology (size and shape) and spatial distribution of corrosion pits at the surface. The cross-sectioned samples were studied to measure depth of the developed pits.

3. RESULTS & DISCUSSION

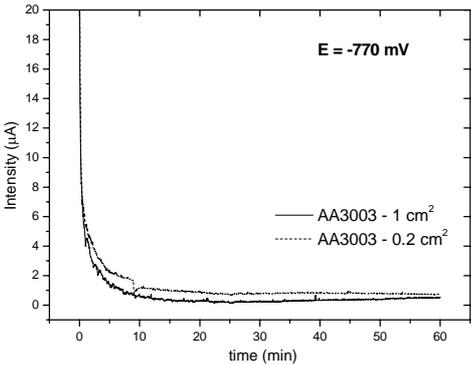
Polarization curves showed typical behaviour of aluminium in NaCl solutions. All results showed typical pitting behaviour on the forward scan and repassivation on the reverse scan. Variations on potentiodynamic and potentiostatic curves were observed when modifying environment and sample parameters.

Test parameters

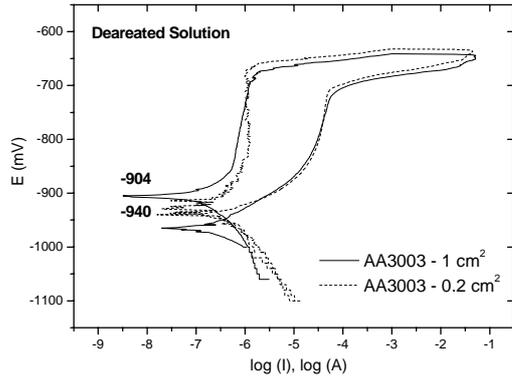


“Figure 2. Influence of dissolved O₂.”

The influence of dissolved O₂ in the test solution can be observed in figure 2. The cyclic polarization curves exhibit apparent spontaneous passivation. The deaeration of the solution shifts the E_{corr} to more cathodic values that indicates a decreased on the corrosion resistance of the alloy. The corrosion density (i_{corr}) decrease with the substitution of O₂ by the N₂ that indicates a better protectiveness of the passive layers and also a reduction on the corrosion rate.

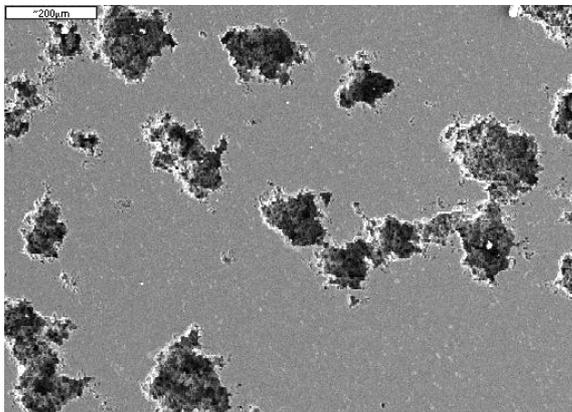


“Figure 3. Influence of sample area”

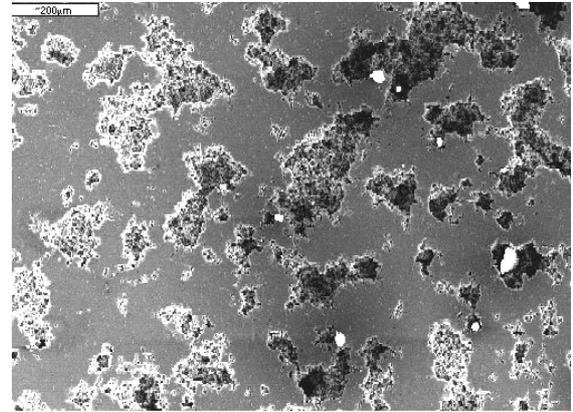


There is no appreciable variation on the corrosion behaviour when the surface area is modified as shown in figure 3. Similar values for all the potentials are observed in both the cyclic polarization curves and in potentiostatic curves. Despite, slight increase on E_{pit} and an decrease on pitting intensity, i_{pit} (which was the maximum current density obtained in the passive region in the forward scan prior to pitting occurrence), is achieved when the surface area is smaller. It indicates that less pits appear on surfaces as shown in the micrographs of the surfaces, figure 5.

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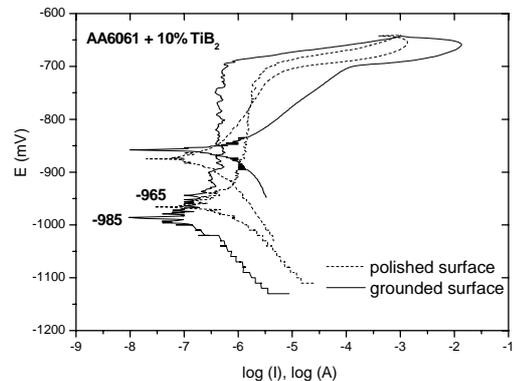
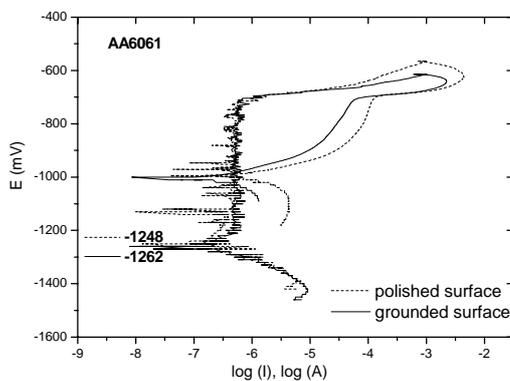
(a) AA3003 – 0.2cm²



(b) AA3003 – 1cm²

“Fig 5. SEM micrographs of corroded surfaces”

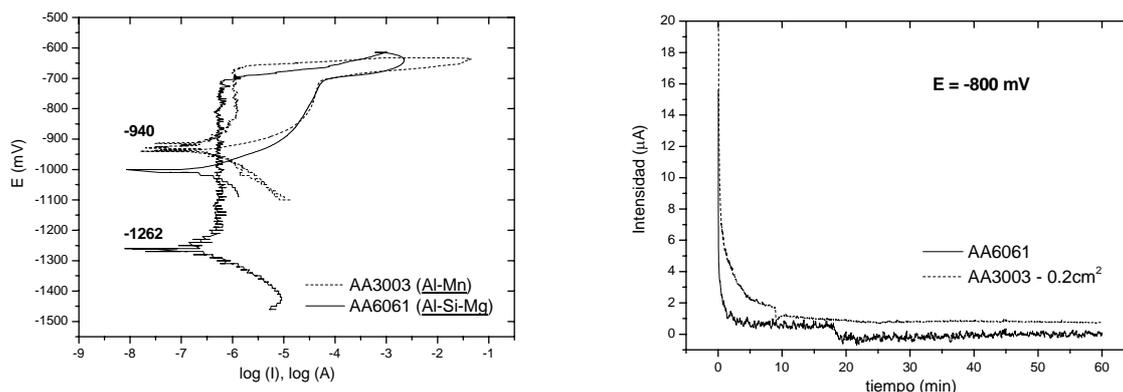
Figure 6 shows the influence of the surface preparation on corrosion behaviour on unreinforced AA6061 and in a composite with a 10% of volume fraction of TiB_2 particles. It can be observed no significant differences on potential values as a function of surface preparation although more unstable passive film is achieved on polished surfaces.



“Figure 6. Influence of surface preparation.”

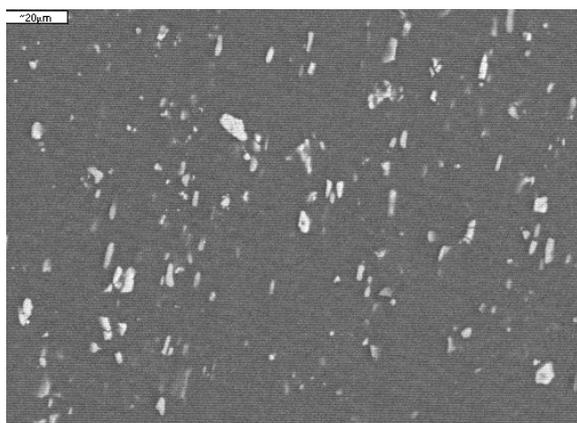
As a brief resume of test parameters influence, it can be establish that the presence of dissolved O_2 on test solution is the only factor that really influence the electrochemical analysis. Sample factors such exposed area or surface preparation have less importance for this type of experiments. So, much more attention has to be paid on solution conditions than on surface preparation.

Metallurgical variables



“Figure 7. Influence of alloying elements.”

The corrosion potential of an aluminium alloy is primarily determined by the composition of the aluminium-rich solid solution. Most commercial aluminium alloys contain additions of more than one of the principal alloying elements. In this cases, the effect on corrosion potential is additive. If an alloying element is over complete solid solution, it forms in aluminium second-phase particles of microscopic size. These second phases not affect significantly the corrosion potential of the alloy.



“Figure 8. AA3003 microstructure.”

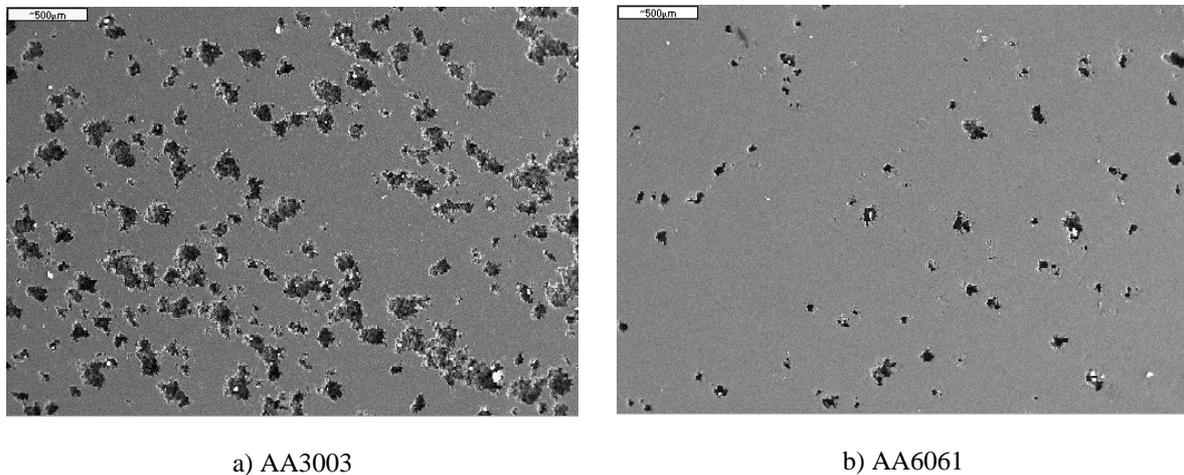
Two aluminium alloys with different main alloying elements were analysed:

AA3003 (Al-Mn) has a very high resistance to corrosion. The manganese is present in the aluminium solid solution, in submicroscopic particles of precipitate and in larger particles of second phases that could be observed by SEM, figure 8. The composition of these particles was established by EDX analysis, corresponding to $Al_{15}(Mn,Fe)_3Si_2$ phase.

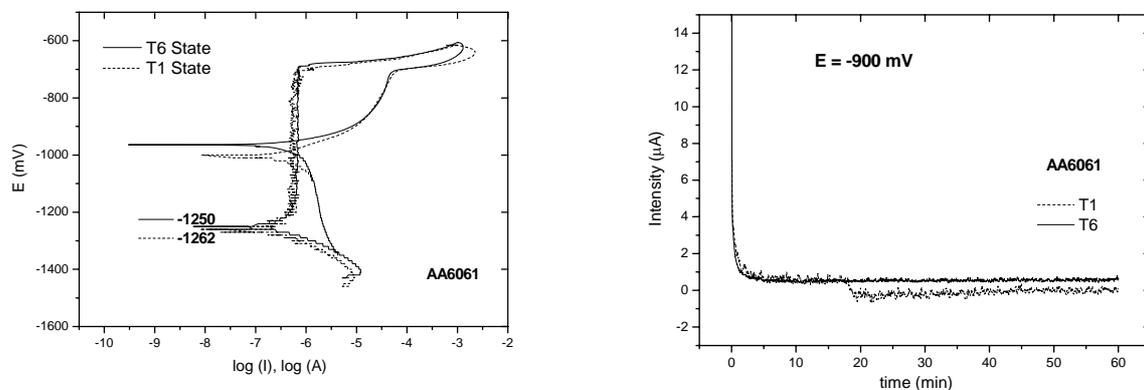
AA6061 (Al-Mg-Si) has a good resistance to corrosion. The AA6061 employed at this work was stoichiometric balanced of Mg and Si so under heat treatments, only Mg_2Si phase is formed. In the extrude condition, no precipitates were observed by SEM.

As observed in figure 7, corrosion potential is more anodic for the AA3003 that indicates a more resistance to corrosion of this alloy. The

pitting potential is also higher for these alloy due to a more purity of these alloy comparing with the AA6061. Figure 9 shows corroded surfaces of both aluminium alloys. Despite the better pitting potential found for AA3003, larger and more quantity of pits were found for these alloy. It can be associated with a highest rate of pit propagation under chloride environments .



“Figure 9. SEM micrographs of corroded surfaces.”

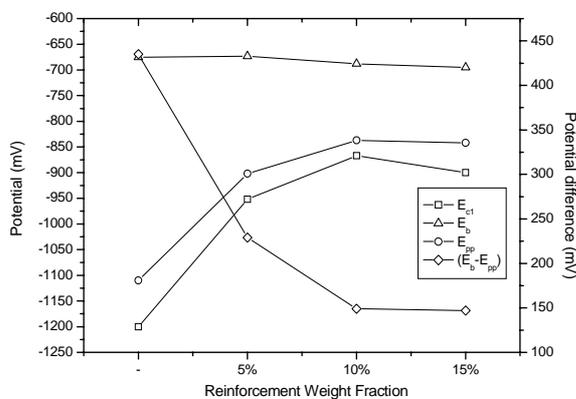


“Figure 10. Influence of the precipitation state of the matrix .”

As said before, AA6061 contains balanced Mg and Si elements that lead to the formation of Mg_2Si phase under heat treatments. Intermetallic precipitates were observed by SEM studies and it was also confirmed their presence by tensile testing. Mechanical resistance of the aluminium matrix was improved in a 60% after the artificial aging treatment as a consequence of the presence of small intermetallic precipitates. Coherent precipitates increase the material flow strength trough the well-known mechanism of dislocation-precipitate interaction. Mg_2Si is an ionic compound and has a potential value that differs from that of the solid-solution matrix. Localized galvanic cells formed between second-phase particles and the matrix can modify corrosion behaviour but in this study, negligible effect on corrosion and pitting

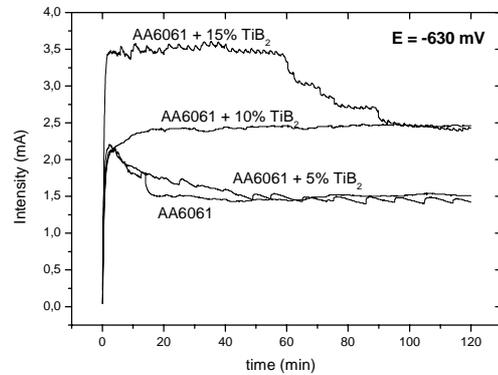
potential were observed, figure 10. The same corroded surfaces were observed for both states after the corrosion studies.

The presence of reinforced particles on the aluminium matrix can also modify its corrosion behaviour. Composites, by the nature, combine materials having considerably different corrosion properties. The galvanic couple formed between matrix and reinforcement can be an important source of corrosion in composites. The corrosion behaviour on a composite is a complex issue and depends on particular matrix-reinforcement system, the anodic film produced on surface and the interfacial characteristics between matrix and reinforcement.



a) Potentiodynamic results: potential values

results, figure 11 (a), show remarkable shift on the anodic direction of the corrosion potential. It implies better resistance to corrosion of composites compared with unreinforced matrix under anodic polarization. The primary passivation potential (the potential where passive layer appears) is also moved to a more anodic value in composites and as a result, less passive zone was observed for them. The mean values of pitting potential were found to have small differences for matrix and composites as shown in figure 11 (a). However, effect of TiB_2 weight fraction on the pitting potential for composites, is significant. Pitting potential slightly decreases as the weight fraction increases.

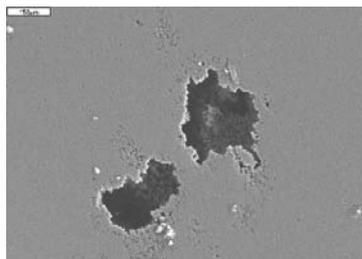


b) Potentiostatic results

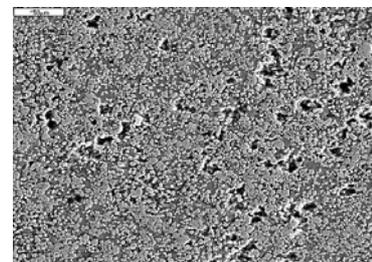
“Figure 11. Influence of the presence of ceramic particles.”

In this work, as describe before, powder composites of AA6061/ TiB_2 were fabricated to study their corrosion behaviour. Figure 11 shows the results obtained for the different studied composites. The potentiodynamic

“Figure 12. SEM micrographs of corroded surfaces.”



a) AA6061



a) AA6061 + 5% TiB_2

Even more, in cyclic polarization curves, a perfect passive zone in the aluminium matrix is observed. The addition and the increase of the weight fraction of TiB_2 particles, implies the formation of an imperfect layer by means of increasing current density when increasing potential. It can be establish that the increase of the

reinforcing phase develops on more imperfect passive zones due the greater difficult to form the oxide passive layer. In potentiostatic tests, figure 11 (b), the time where the first pit is

formed is calculated. For matrix as well as matrix reinforced with 5% TiB_2 , the main peak in the current is associated to ≈ 12 min, whereas for reinforcement contents of 10 and 15%, this time is situated at ≈ 2.3 min. These results are in concordance to those ones founded in cyclic polarization tests, where it is established smaller resistance to the pitting corrosion for composites with high reinforcement contents. It is believed that the presence of TiB_2 particles has disrupted the continuity of the passive film, thus causing a gradually increased in corrosion current over the passive region.

SEM studies, figure 12, exhibit typical features of pitting corrosion in NaCl solution as showed in all the others micrographs. Dissolution of matrix took place at localise points. The reinforcement addition shows to change morphology of pitting corrosion. TiB_2 particles do not constitute preferred sites for pit initiation, however pit initiation was localised near particulate aggregates and developed pits were found to have higher size.

As a brief resume of metallurgical variables influence, it can be establish that they have importance on the corrosion behaviour of aluminium alloys. Regarding the presence of second phases on the aluminium matrix, results show that only those that are not in solid solution with the matrix affect the corrosion behaviour.

4. CONCLUSIONS

Test parameters show to influence the electrochemical behaviour of aluminium alloys:

- Deaeration of the solution decreases the corrosion resistance of the alloy but produces better protectiveness of the passive layer.
- Sample factors such exposed area or surface preparation have few importance for this type of experiments. The area of the exposed surface or surface preparation do not give important changes on corrosion behaviour of the alloy.

Metallurgical variables considerably affect the electrochemical behaviour of aluminium alloys:

- Alloying elements are crucial on corrosion behaviour. AA3003 shows better corrosion potential and pitting potential rather than AA6061. So, the more purity of the considered alloy, implies more corrosion resistance. Despite the better pitting potential found for AA3003, larger and more quantity of pits were found for these alloy.
- Coherent particles that precipitate in aluminium alloy after heat treatments, do not affect the corrosion of the AA6061.
- TiB_2 particles produce an acceleration of anodic solution of the metallic matrix under anodic polarization.
- While pitting potential was rather unaffected by the presence of TiB_2 particles, continuity of passive region was disrupted for 10 and 15% reinforcement contents. This fact was related to the existence of less homogeneity and more particulate aggregates for high weight fractions of TiB_2 composites.
- In composites appear fewer pits after potentiodynamic tests, but they have a bigger size comparing with the unreinforced matrix. Pit initiation was localized near particulate aggregates. For the AA6061, pits present shallow shape meanwhile for composites they have a narrow shape.

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References

1. **Bond, A.P., Bolling, G.F. and Domain, H.A.**, *J. Electrochem. Soc.*, **113** (1966), 773.
2. **Wood, G.C., Sutton, W.H., Richardson, J.A., Riley, T.N.K. and Malherbe, A.G.**, “ Proceedings of the U.R. Evans Conference on Localized Corrosion”, *National Association of Corrosion Engineers, Houston* (1971), 526.
3. **Nisancioglu, K.**, “ Proceedings of the 3rd International Conference on Aluminium Alloys: Their Physical and Mechanical Properties”, *Norwegian University of Science and Technology, Trondheim*, **3** (1992), 239.
4. **Trzaskoma, P.P., McCafferty, E. and Crowe, J.**, *J. Electrochem. Soc.*, **130** (1989), 804.
5. **Trzaskoma, P.P.**, *Corrosion.*, **46** (1990), 402-409.
6. **Nunnes, P.C., and Ramanathan, L.V.**, *Corrosion.*, **51** (1995), 610-617.
7. **Mamsfeld, F., Lin, S., Kim, S. and Shid, H.**, *J. Electrochem. Soc.*, **137** (1990), 78-82.