



EIS testing of new aluminium sacrificial anodes[☆]

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Abstract

Aluminium alloys In/Hg free, suitable as sacrificial anodes for cathodic protection, have been developed. Short-term electrochemical tests were performed on these new alloys to obtain their electrochemical efficiency and to reveal any tendencies to passivation. Samples were galvanostatically held at different current densities, which changed every 24 h according to DNV RP 401. Electrochemical impedance spectroscopy (EIS), polarization curves and electrode potential against time measurements were employed to study the main features of the processes taking place at the alloy–solution interface.

1. Introduction

The most frequently used sacrificial metals for cathodic protection systems are alloys of magnesium, zinc and aluminium. Although aluminium is relatively new as an anode material, its undeniable economic advantages over magnesium and zinc have pushed these alloys into an offshore leadership role. Performance characteristics of the Al anodes are related to alloy chemistry and the application environment. Unfortunately, many alloys of Al, having been promoted as anode materials, have failed upon continued application. Of the 30–35 Al anodes that have appeared on the market from 1960 up to the present more than half have disappeared from commercial use for technical reasons.

Aluminium has considerable merit as the basis for a galvanic anode principally because of its low density, large electrochemical equivalent (high current capacity), availability and reasonable cost. Its electrochemical equivalent is 1.6 and 1.35 times that of zinc and magnesium, respectively. The low electrode potentials of such anodes are readily adapted to a variety of saline environments such as seawater, marine muds and brackish waters, though their interesting properties are often hindered by the presence of a passive oxide film, which causes several difficulties regarding their use as sacrificial anodes.

Unalloyed Al adopts a relatively noble solution potential in saline media as a result of its protective oxide film. The oxide is the cause of rapid polarization when Al is placed under corrosion load in a cathodic protection circuit. Numerous alloying combinations have been made with Al to reduce anodic polarization traits. With few exceptions, the alloying approaches which are used to eliminate passivation, thus promoting surface activation, have been largely empirical, with the result that several acceptable commercial alloys are now available. Unfortunately, it is not always clear why these activating materials are successful or how they work. Nonetheless, the success of the Al anode is dependant upon the alloying of certain metals whose surface role is ultimately to prevent the formation of a continuous, adherent and protective oxide film on the alloy, thus permitting continued galvanic activity of the Al.

Aluminium alloys suitable for cathodic protection have been developed in recent years, and the influence of alloying elements such as Zn, titanium (Ti), mercury (Hg), and indium (In) has been studied by several researchers [1, 2]. Much of the work done refers to the addition of Hg, gallium (Ga), tin (Sn), and In to aluminium alloys. Each of these elements has been demonstrated to improve aluminium activation in neutral chloride media; however, the good results obtained in this field clash with the increased sensitivity to environmental protection. The use of Hg in particular, which may be dangerous during the manufacture of the anodes, together with In, pollutes marine life, thus giving rise to environmental concern. In a 500 kg Al-anode, 50–100 g correspond to In and 175–200 g

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corresponds to Hg [3, 4]. Research towards the substitution of dangerous elements such as In and Hg involves scientific knowledge of solidification processes, the kinetics of precipitation of primary binary/ternary intermetallics, the distribution of intermetallics and/or precipitates in α -Al solid solution after heat treatment, and the corrosion mechanisms involved during the dissolution of this kind of anode.

Technical knowledge involves the melting/casting of aluminium alloys with ternary additions of elements belonging to the groups IA, IIA and IIB of the periodic table, and the implementation of suitable electrochemical techniques for the evaluation of anode current efficiency.

The resulting Al-anode must have the properties, in terms of current efficiency, of commercial Al–Zn–In and/or Hg, must be easy to produce, and must not contain In and/or Hg.

It has been reported [5] that in the Al–IIB–IIA system, the α -Al solid solution and the τ -phase with a composition close to $\text{Al}_2\text{IIB}_3\text{IIA}_3$ are present [6]. In the as-cast condition the main microstructure is formed by the α -Al solid solution and the second phase τ [6]. The eutectic formed by a fine dispersion of the $\alpha + \tau$ is segregated at grain boundaries and, to some extent, the τ -phase is partially dispersed in the core of the aluminium grains. To promote further fine dispersion of the τ -phase in the matrix, thermal treatment can be carried out on the resulting ingots by taking advantage of the fast kinetic reactions occurring in the solid state. The addition of a combination of IIA and IIB elements in Al is practised with the aim of assuring that the aluminium oxide does not develop protective properties against dissolution. The amount and distribution of intermetallic compounds is relevant on the electrochemical and corrosion behavior of the alloy.

With reference to the Al–IIB–IIA ternary phase diagram [7], in the isotherm at 400 °C (720 °F), the α -Al solid solution is present plus eutectics of IIA_2Al_3 and $\text{Al}_2\text{IIB}_3\text{IIA}_3$, which ensure, via ageing treatments, a fine dispersion of these eutectics which help the non-passivation of the anode. To make the Al–Zn–Mg ternary system more efficient with respect to the superficial activation of the anode (preventing the formation of superficial aluminium oxide films) additions of IA are appropriate [8] with the aim of precipitating Al_3IA (δ') at grain boundaries and the matrix, by taking advantage of the fact that Zn lowers the solid solubility of IA in the α -Al phase and also that Zn can be incorporated in to the δ' phase.

This research has as its main objective, the substitution of Al–Zn–In and Al–Zn–Hg alloys used as aluminium sacrificial anodes for alloys of the Al–IIB–IIA–IA type in order to avoid pollution of the marine environment by elements such as Hg and In, without at the same time decreasing the current efficiency of the resulting anodes. The choice of the alloy system, has as its basis the precipitation and distribution of fine intermetallic phases belonging to the ternary Al–IIB–

IIA system, in the α -Al matrix, with the aim of achieving two ends: (i) a good surface activation of the anode and (ii) corrosion products similar to those found in the salts of the sea water, thus preventing the pollution of sea life.

2. Experimental details

An Al–Zn (5 at %)-Mg (5 at %)-Li (0.1 at %) alloy was prepared with commercially available Al, Zn and Mg with purities of 99.98%. Li was used as a wire of 3.2 mm in diameter and 99.9% of purity with 4.5 mg cm^{-3} of sodium (Na). From previous experiments, and to prevent losses of Mg, Zn and Li during the melting process of these alloys, the elements were placed in Al capsules. Initially, the Al was placed in an alumina/graphite-coated crucible and melted in a resistance furnace under an argon atmosphere. Once the Al was melted, the liquid bath was overheated 150 °C and the Al capsules containing Zn and Mg were added. The bath was stirred with argon for 10 min to obtain a uniform distribution of Zn and Mg. Immediately after this operation, the Al capsule containing Li was added to the liquid bath, which was stirred with a flux of argon for another 5 min, after which time the liquid alloy was poured into a copper mould of dimensions $8 \times 8 \times 50 \text{ cm}$. The top and bottom of the ingot were cut off for chemical analysis, thus obtaining a nominal composition of Al–Zn (4.8 at %)-Mg (5.1 at %) and Li (0.09 at %).

A representative microstructure observed in the as-cast ingot, as shown in Figure 1, consisted of α -Al dendrites with sizes between 130 to 150 μm . In the interdendritic regions, the presence of eutectic and black spherical particles was observed. The eutectic showed a white colour with a maximum width of 10 μm , always following the contour of the dendritic arms. This eutectic, instead of presenting a platelet morphology such as has been reported [5], showed the presence of rows formed by grey spherical particles.

A short-term electrochemical test [9] was performed on the Al–Zn–Mg–Li alloy anode, corresponding approximately to Al–5Zn–5Mg–0.1Li. Cubic anodes were machined from the ingot, thus eliminating the structure formed by direct contact with the mould wall. The samples were put in a specially designed electrochemical cell, leaving only the cross section area of 1 cm^2 exposed and connected anodically to a d.c. current source, the cathode of which was a sheet of carbon steel. All the specimens were polished with 1200 emery paper, then degreased in acetone, washed thoroughly in double distilled water and kept in a dessicator.

An accelerated electrochemical test was carried out to determine anode efficiency and working potential [9]. All potentials were measured relative to a saturated calomel reference electrode (SCE). Samples were held galvanostatically at different current densities, Figure 2. Each level was applied for a 24 h period. The total, duration of the test was 96 hours. During the test, the anode

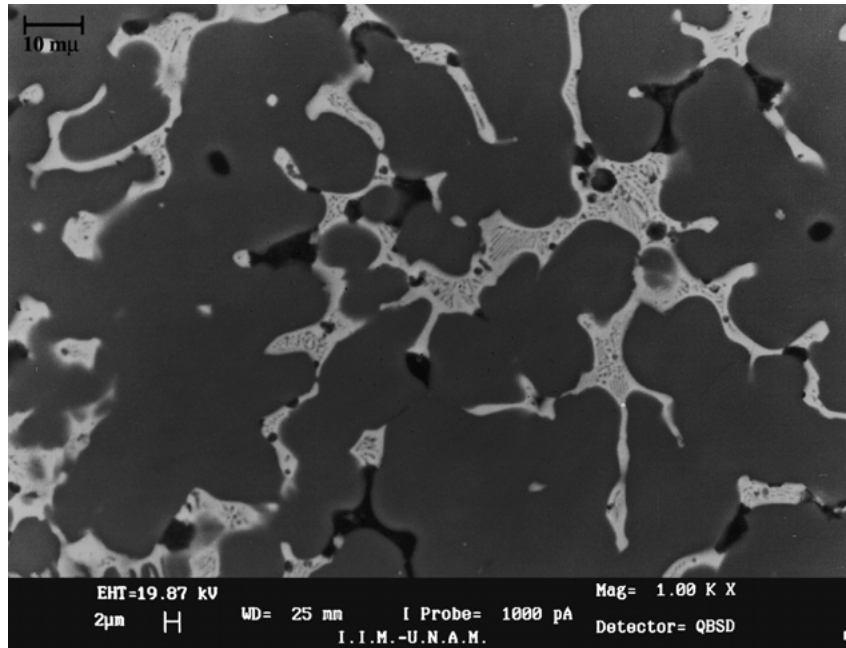


Fig. 1. Microstructure of the Al-Zn-Mg-Li anode in the as-cast condition.

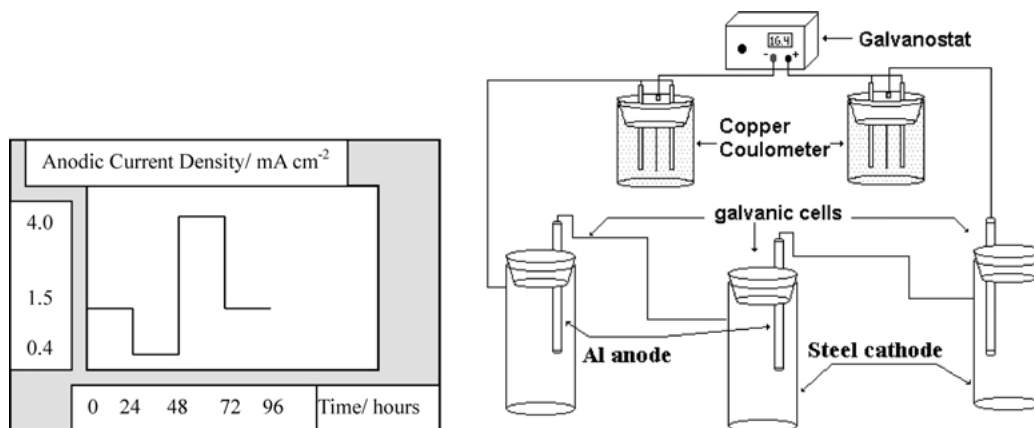


Fig. 2. Experimental set-up short-term electrochemical test (after DNV RP B401) [9].

potential was determined and electrochemical impedance spectroscopy (EIS) measurements were made at the beginning and end of each current density level period (every 24 h). This revealed any tendencies to passivation. The test solution was aerated substitute ocean water with an initial pH of 8.3 according to ASTM D1141 [10]. Electrochemical impedance was conducted by using a Gamry CMS300 Instrument over a frequency range of 10 kHz to 100 mHz (10 points per decade) superimposing a 10 mV a.c. signal and interpreted in terms of equivalent circuit with frequency dependent components. The equipment was controlled with a PC running EIS software, also from Gamry. EIS measurements were used to monitor the corrosion process on the aluminium anode daily for the 96 test hours.

At the end of the test, the samples were removed, cleaned and weighed to obtain the weight loss. The anode efficiency was obtained by calculating the total charge passed through the system, the weight loss of the

anode specimen and the corresponding electrochemical equivalent.

3. Results and discussion

The trend of the anode potential (open-circuit potential) against time when the experimental alloys are immersed in a 3% NaCl is reported in Figure 3. The alloy needs time to reach a steady potential. This potential, (~ 1020 mV vs SCE) is very close to the electrode potential reported by Barbucci et al. [5] and Foley and Trzaskoma [11], who used an aluminium alloy very similar to that used in this study in a chloride containing solution.

The calculated electrochemical efficiency [9], ϵ , for the as-cast Al anode samples was 61.43%, corresponding to 1832 Ah kg^{-1} . The closed-circuit potentials measured were in the range -1.05 V vs SCE at 0 mA cm^{-2} to

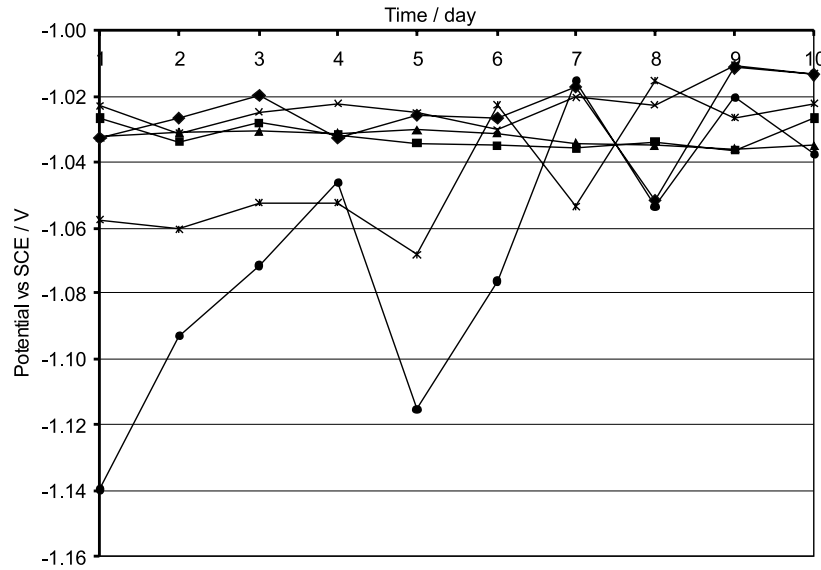


Fig. 3. Anode potential of Al-Zn-Mg-Li alloy versus time of different samples tested. Key: (◆) sample A, (■) sample B, (▲) sample C, (×) sample D, (*) sample E and (●) sample F.

−0.86 V vs SCE at 4.0 mA cm^{−2}. An active closed-circuit potential is desirable because a relatively noble potential could indicate the presence of passivation. Anodes must also possess high faradaic efficiency to prevent frequent anode replacement. The NACE [12] and DNV [9] tests specify that an Al anode should have a closed-circuit potential active to −1.0 V vs SCE and a ϵ between 2300 and 2700 Ah kg^{−1}. Then the anode analysed met the potential criterion, but appeared to exhibit only moderate efficiency. Theoretically, uniform anode dissolution will give maximum efficiency. Either secondary cathodic reaction on the same interface and/or mechanical grain loss due to local macro or micro-corrosion cells will reduce the anode efficiency [13]. In Al-Zn alloys, Zn tends to be rejected to interdendritic zones or grain boundaries. This effect is favoured by the cooling rate and the alloying element characteristics

(lower melting point than aluminium). Under polarization, this local composition variation will favour the initiation and propagation of macro- and microlocal events (galvanic corrosion and pitting for example). These events are responsible for lowering anode efficiency by electrochemical or mechanical mass loss [13]. The low efficiencies shown by the studied anodes are similar to those obtained by Salinas et al. [13] for Al-5%Zn alloy. A possible explanation is that the main efficiency loss can be ascribed to the secondary reactions, since they are produced by the relatively high content of impurities, particularly Fe and Cu, that cause local cell action.

Another possible reason for the low efficiency of the anode alloys tested is the effect of the formation of corrosion products on the self-corrosion rate of the anode. The formation of these corrosion products on

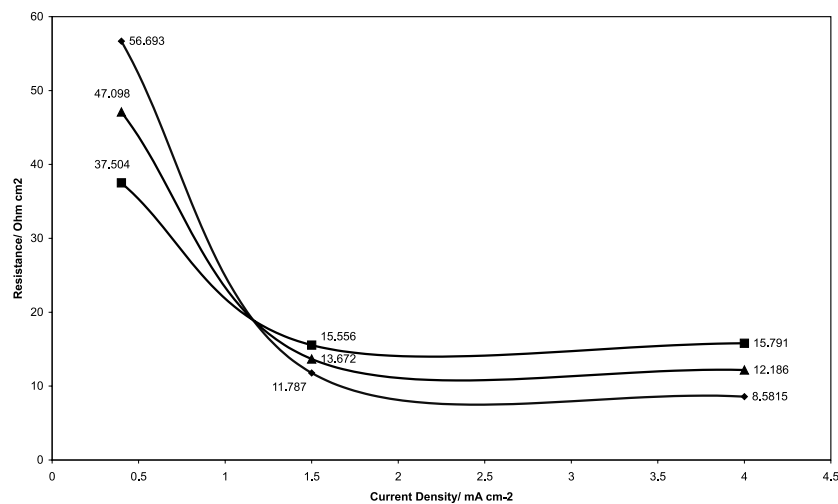


Fig. 4. Corrosion products resistance as a function of current density. Estimated values from corresponding EIS diagrams, at the beginning of applied current density (◆), after 24 h (■) and average (▲).

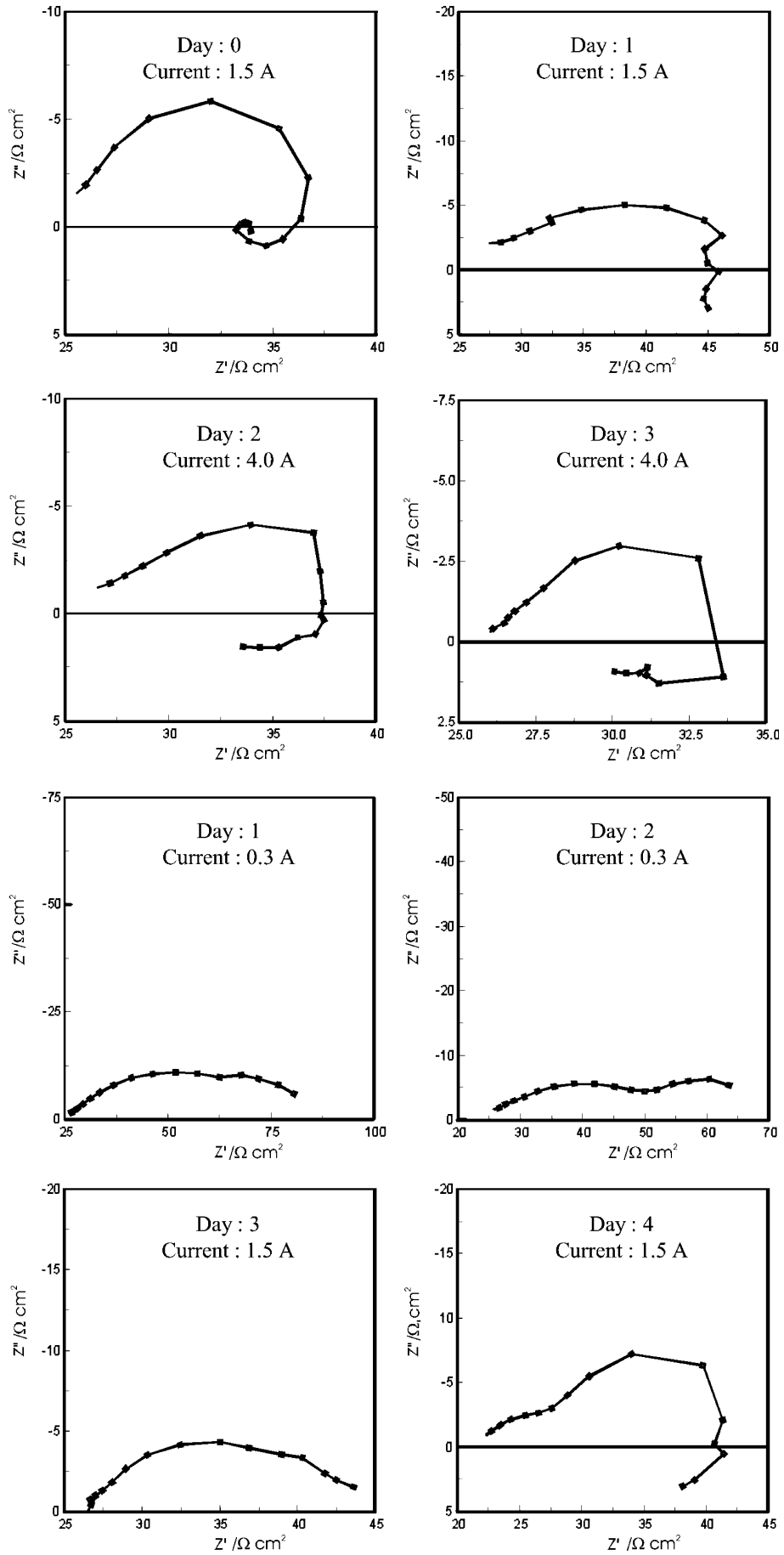


Fig. 5. Typical Nyquist diagrams of Al-Zn-Mg-Li alloy obtained at the different current densities applied.

the anode surface significantly affects the electrochemical efficiency of the material, as pointed out by the results shown in Figure 4, in which it can be observed that the electrochemical behaviour (performance) of the Al anode alloy is strongly dependent on the formation of surface corrosion products. Figure 4 summarizes the resistance of the corrosion product film as a function of applied current density. It is clear that the increase in current density produces a decrease in the resistance value of the corrosion products, R_{cp} , formed on Al anode. This is probably due to the fact that a heavier and denser corrosion product forms at a higher current density, thus promoting the self-corrosion activity [14]. This seems to prove the effect of the formation of corrosion products on the self-corrosion rate of the anode. Several authors [15, 16] have shown a relation between the electrochemical efficiency of anode materials and the anodic current densities. The anodic current density is therefore a test parameter that should be given due consideration. On specimens without a well-developed corrosion product, the self-corrosion rate will account for a relatively higher portion of the total mass loss at lower anodic current densities. On partly consumed anodes, where corrosion products have settled, the maintenance and development of the corrosion products will be more efficient at higher current densities than at lower current densities. Consequently, the self-corrosion rate due to a more corrosive environment beneath the corrosion product will be correspondingly higher at high anodic current density [14].

EIS measurements were performed during the DNV test, Figure 5. The shapes of the diagrams show significant differences. At high and medium frequencies two depressed capacitive loops are evident, probably due to the oxide and to the aluminium faradaic dissolution. At low frequencies an inductive loop is detected. These results are in agreement with those obtained by Barbucci et al. [17] and other authors [18–20], although in their research unalloyed aluminium was studied. The capacitive behavior at high and medium frequencies might be due to the oxide passive film and the metal–oxide interface (the charge transfer processes, Al dissolution through the film oxide), whereas for the inductive behaviour, an oxide–solution interface (oxygen ion ingress in the oxide film) could be ascribed to the faradaic processes.

It is evident from the electrochemical impedance data, Figure 5, that the current density condition plays a critical role on the resistive property of the corrosion products, suggesting a significant change on the corrosion product property formed on the Al anode. Dark grey corrosion products were formed. The surface dissolution morphology exhibited a rough, pitted surface. The EIS diagrams showed evidence of both passivation and pitting. The lower electrochemical activity exhibited by the Al anode samples strongly suggests that secondary reactions may be the fundamental cause of this behavior. In our experiments, the EIS diagrams obtained at higher current densities show

an inductive semicircle, Figure 5, which may be attributed to pitting corrosion. The preferred dissolution morphology is general attack rather than pitting, since pitting attack has been correlated to less than optimal performance.

Galvanostatic polarization was applied to the anode after the test. Under these conditions, the actual active electrode area had already reached a steady state value. The polarization test was performed at the end of the short-term electrochemical test to determine the anode behaviour type. The anodic polarization behaviour showed that the anode efficiency obtained at low current densities would be the same as that obtained at high current densities. These results consolidate the accelerated dissolution test performed.

Formerly an argument against using the short-term electrochemical test stated that in the two-week [9] or four-day [12] test, only the outer 260 μm is consumed, whereas in the one-year test at least 0.5 cm penetration is achieved. Murray et al. [21] have obtained successful results by showing that the evaluation of both the as-cast material simultaneously with the cut surfaces (which are representative of the bulk material) makes the short-term test appear representative of the cast anode long-term performance.

4. Conclusions

- (i) The presence of a secondary phase strongly affects the electrochemical behaviour of the Al–Zn–Mg–Li alloys studied.
- (ii) A secondary reaction led to significant loss in current efficiency and was dependent on the microstructure of the Al anodes.
- (iii) EIS is a useful tool to study the dissolution behaviour of Al-alloy sacrificial anodes when subjected to cathodic protection.

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