Latin American Applied Research 33:275-280 (2003)

CORROSION MECHANISM OF AL-ZN-IN ALLOYS IN CHLORIDE SOLUTIONS

A. G. MUÑOZ, S. B. SAIDMAN and J. B. BESSONE

Instituto de Ingeniería Electróquimica y Corrosión (INIEC)
Dpto. de Ing. Quimica – Universidad Nacional del Sur
Av. Alem 1253 – 8000 Bahía Blanca – Argentina
jbessone@criba.edu.ar

Abstract- **The electrochemical behavior of Al-Zn-In alloys was investigated in chloride media by means of potentiodynamic techniques, complemented by Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDX) and Transmission Electron Microscopy (TEM). The influence of local alkalization produced by previous cathodization was analyzed at potentials more negative than the rest potential. The electrochemical response of alloys is given by the sum of those corresponding to the different present phases. Thus, the electrochemical behavior of each metal and bimetallic alloy (Al-In, In-Al and Zn-In) was analyzed in the same solution conditions at a potential region near the corrosion potential of the ternary alloy. The low solubility of In in Al favors its segregation at grain boundaries, where the formation of Zn-In alloys was detected. The initiation of the attack in the Al-Zn-In alloy is mainly localized in these zones. This is a consequence of the enhanced adsorption and surface accumulation of Cl^- promoted by In at potentials more positive than - 1.1 V_{SCE}. Close similarities of the anodic behaviors of the Al-In and ternary alloys lead us to propose a mechanism where the In distribution plays the major role. The In dissolution from homogeneous solid solution phases allows an enrichment of this element at the Al and Zn rich phases by displacement reactions.**

$$(Al,Zn)In + Cl^- \rightarrow InCl^{2+} + 3e^-$$

$$2\,InCl^{2+} + 3\,Zn \rightarrow 2\,In^0 + 3\,Zn^{2+} + 2\,Cl^-$$

This, in turn, assures an accumulation of adsorbed Cl^-, which maintains an active state of the Al matrix. Thus, the rapid Zn dissolution reaction ensures a better redistribution of In, so bringing the system towards potentials near those for Cl^- adsorption on In. The attack morphology was also analyzed in order to explain the smooth wide cavities embracing many grains.

Keywords- **Aluminium, Al-Zn-In alloy, corrosion of Aluminium, Chloride adsorption.**

.

I. INTRODUCTION

Regarding commercially produced Al sacrificial anodes, there is little doubt today that Al-Zn-In base anodes present the best performance in seawater (Wolfson, 1994). The average operating potential of these anodes in this media is - 1.1 V vs. SCE. The activating elements (Zn, In) ensure its uniform dissolution and avoid polarization. Then, it seems reasonable that one way to obtain a fundamental understanding of this behavior lays in a better knowledge of the electrochemistry of the different phases constituting the ternary Al-Zn-In alloy. Previous studies have suggested that the initial step in the dissolution mechanism of the Al-In alloy can be interpreted in terms of a chloride adsorption process (Saidman *et al*., 1995). Thus, the more negative potential of zero charge (pzc) of In, compared with that of Al, allows the adsorption of Cl^- and the destabilization of the aluminium oxide film to occur at more negative values. The present contribution gives a better knowledge of the electrochemical response of the Al-Zn-In alloy. A commercial Al-Zn-In-Si anode and a ternary alloy, prepared in our laboratory, were used as working electrodes. The anodic behavior of pure metals (Zn e In) and the binary alloys Al-5%Zn, Zn-5%In, and Al-5%In are compared with that of the ternary Al-5%Zn-0.02%In in 0.5 M NaCl solution of pH 5. In order to obtain more information about mechanistic aspects of surface activation, the analysis of the synergistic effect produced by the deposition of Zn and In on Al, when their cations are present in solution, was also considered.

II. EXPERIMENTAL

The ternary alloy Al-5%Zn-0.02%In was obtained using pure Al, Zn and In (Aldrich Chemical Co., with impurities according to Table I). They were first etched in a 2% HNO_3 ethanol solution and then introduced in a quartz furnace with Ar atmosphere. It was heated at approximately 20 °C higher than the highest element melting point, shacked and then quenched in cold water. Due to the very low solubility of In and Zn in Al at room temperature (Baker and Okamoto, 1992) and the nominal composition used, the presence of rich In and Zn phases is expected. Higher solubilities, however, are possible as a consequence of quenching. A commercial Al-Zn-In-Si alloy, whose composition and impurities are also shown in Table I, was used for the sake of comparison. Cylindrical rods were mounted in a PTFE holder configuring a disk electrode with a diameter of 7 mm. Electrodes were polished with 1000 emery paper, 0.3 μm grit alumina suspension and finally rinsed with abundant triple distilled water.

Table 1 Composition analysis of the Al-Zn-In and the commercial Al-Zn-In-Si alloys.

Elements	Al-Zn-In	Al-Zn-In-Si
Zn	4.970	4.106
In	0.021	0.015
Si	0.015	0.093
Fe	0.077	0.120
Cu	0.022	0.034
Cd	0.003	0.012
Pb	0.025	0.042
Al	Remainder	Remainder

Chloride solutions were prepared from analytical grade chemicals and thrice distilled water. The pH was adjusted with HCl. A large Pt sheet was used as a counter electrode. As a reference, a SCE connected through a Luggin-Haber capillary tip was used and potential in the text are referred to this.

The experiments were carried out in a purified N_2 saturated atmosphere at 25 °C. Runs were made using a potentiostat-galvanostat PAR Model 173, after 20 min of stabilization at the rest potential. Potentiodynamic polarizations were performed at 0.001V s^{-1}, initially towards cathodic potentials and then in the anodic sense. Results were corrected for ohmic drop using the solution resistance obtained from impedance measurements. From results of at least three runs, a fairly good reproducibility with variations below ± 5% was attained. A rate of 2600 rpm was used with rotating disk experiments. A dual stage ISI DS 130 SEM and an EDAX 9600 quantitative energy dispersive analyzer were used to examine the electrode attack.

III. RESULTS

A. Pitting of Al

In order to obtain a better insight into the fundamental aspects of pitting of Al, it was analyzed in non-aqueous chloride solutions. Thus, the possibility of a local acidification, as the main cause for pit initiation, may be ignored. Pitting initiates at a potential near – 0.76 V, in a similar manner as it occurs in aqueous chloride solutions (Fig.1). Only a slight influence of electrode rotation on the hysteresis cycle is detected, indicating a surface controlled process.

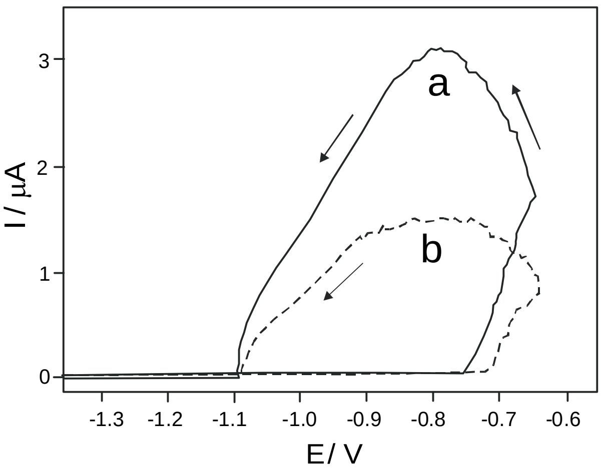

Fig. 1: Cyclic voltammetries of Al with and without electrode rotation in 0.5 M LiCl (Dimethylformamide). (a) $\omega = 0$ rpm; (b) 1800 rpm. V = 0.001 V s^{-1}.
$E_{s,a} = -0.63$ V, $E_{s,c} = -1.36$ V.

B. Electrochemical studies

The polarizations of the ternary Al-Zn-In and commercial alloys, obtained in deareated 0.5 M NaCl solution, are shown in Fig.2. A corrosion potential (E_{corr}) of - 1.3 V is found for the ternary alloy. This potential differs from - 1.1 V obtained in the case of the commercial alloy. This is a consequence of an enhanced hydrogen evolution given by the presence of impurities. The shape of the anodic curve is, however, similar to that for the ternary alloy, but displaced about 100 mV towards more positive potentials.

Dissolution was preferentially started at the grain boundary regions, where segregated Zn and Si were detected. Indium could not be detected by X-ray analysis due to its low level in the commercial alloy.

For the sake of comparison, polarizations on Zn, In (Fig.2a) and the binary alloys Al-5%In and Zn-5%In (Fig.2b) were carried out under the same conditions. It is interesting to note, that the presence of In shifts the rest potential of both Zn and Al alloys to a value of approximately - 1.16 V. This fact may be related to a necessary threshold potential for Cl^- adsorption. Indium on the other hand, remains cathodic at this potential region.

To assess the effects of chloride adsorption caused by the presence of In, the polarization of the In-5%Al alloy was also studied at different chloride concentrations (Fig.3). The curves exhibit an anodic peak followed by a current plateau. At more positive potentials a breakdown process takes place. The presence of an anodic peak, more evident at the most concentrated solutions, can be observed at a potential very close to the corrosion potentials for Al-In alloys.

Additional and interesting conclusions about the behavior of the ternary alloy could be found with the polarization initiated at - 1.8 V with and without electrode rotation (Fig.4).

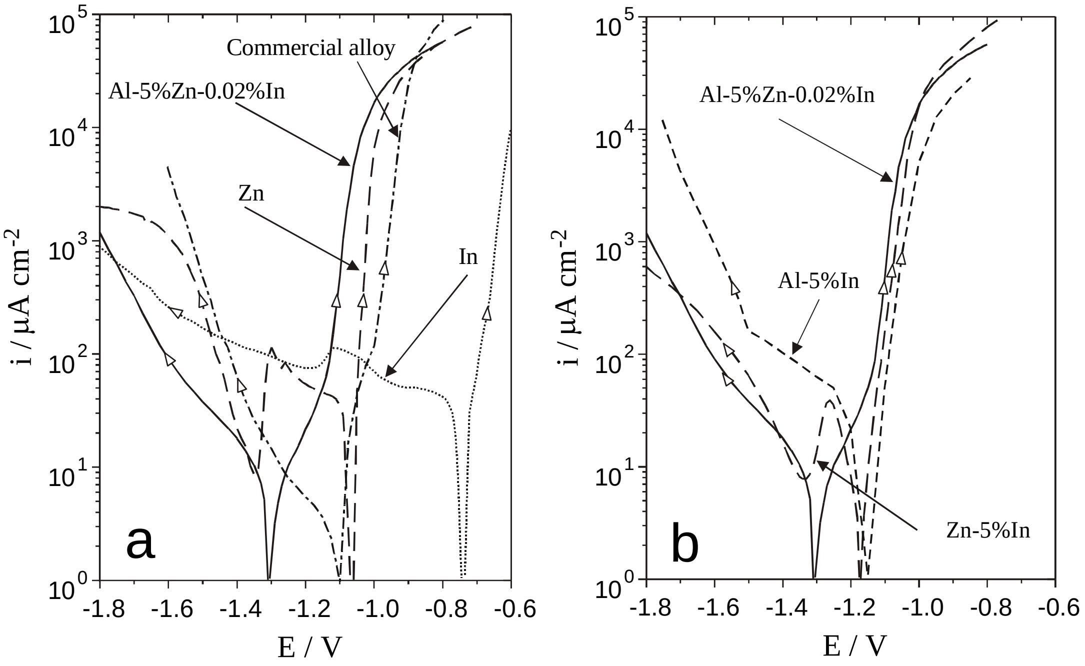

Fig. 2: Comparison of the potentiodynamic polarizations of Al-Zn-In with other alloys in areated 0.5 M NaCl solution, pH = 5. (a) Al-Zn-In alloy, commercial Al-Zn-In-Si alloy, Zn and In; (b) binary alloys Zn-5%In and Al-5%In. v = 0.001 V s^{-1} .E_i = E_{corr}.

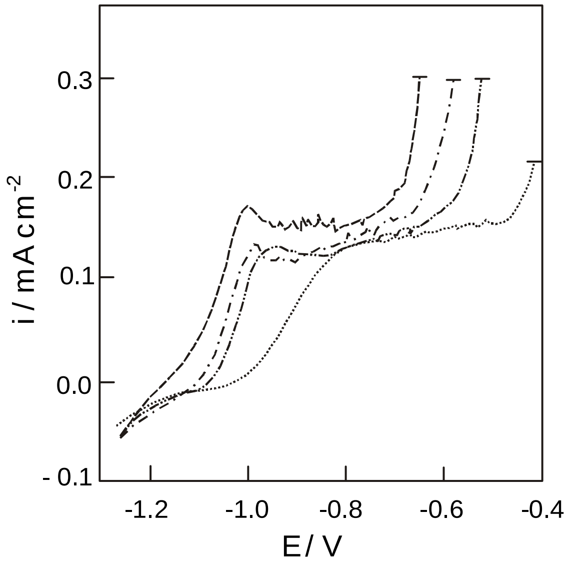

Fig. 3: Influence of Cl^- concentration on the polarization of the In-5%Al alloy. v = 0.001 V s^{-1}. $E_{s,c}$ = - 1.25 V. NaCl concentration: (….) 0.01 M; (–..–) 0.1 M; (– . –) 0.5 M; (–––) 1.0 M.

It is known that the hydration and/or dissolution of Al oxide take place by local alkalization, when Al and Al alloys are polarized at relatively high cathodic potentials. Thus, a polarization for a determined period of time at -1.8 V, previous to the potentiodynamic run in the positive sense, would ensure a quasi-bare Al surface. The profile recorded without rotation shows that the current density changed its sign at - 1.54 V and tends to a constant value ca. 30 µA cm^{-2} (Fig.4). This behaviour may be mainly attributed to Al dissolution through the quasi-dissolved oxide generated by local alkalization (Yan *et al.*, 1996). Under rotation, the possibility of a local pH rise was minimized and a similar curve to that shown in Fig.2 is obtained. The electrochemical behavior obtained at potentials more positive than - 1.1 V is very similar to that obtained without previous cathodization (Fig.2).

C. Attack morphology studies

A preferential attack at the grain boundary extending to the grain body was found after the ternary alloy was polarized from the rest potential towards anodic values and removed at - 0.95 V (Fig.5a). At higher magnification, corrosion products at the grain boundary can be observed (Fig.5b). X-ray maps indicate an enrichment of In and Zn. Initiation and propagation of the attack is associated with the microstructure and composition of the alloy (Fig.5c).

Dissolution was preferentially started at interdendritic zones present at the grain boundary regions. The presence of corrosion products, indicating the initiation of attack, can be also observed distributed along the cell

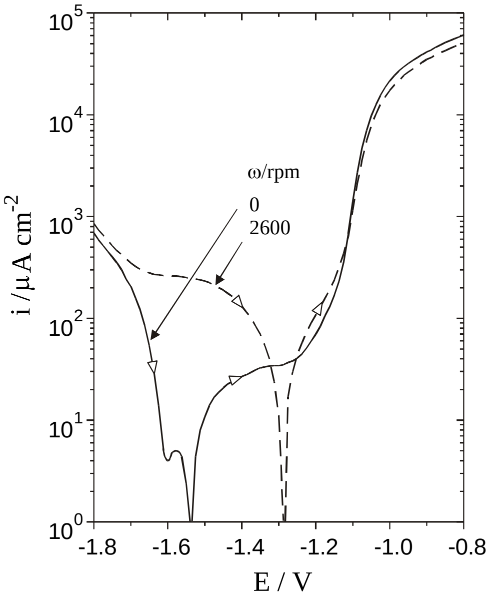

Fig. 4: Potentiodynamic polarization of the Al-Zn-In alloy in deareated 0.5 M NaCl solution, pH = 5 with and without electrode rotation. v = 0.001 V s^{-1}. E$_i$ = -1.8 V. ω= 2600 rpm.

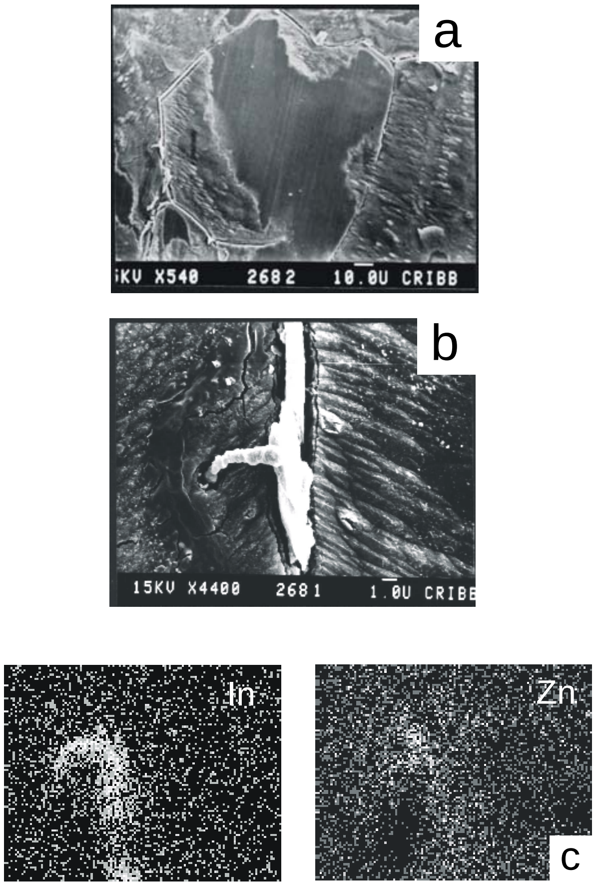

Fig. 5: (a) SEM micrograph of the Al-Zn-In alloy after being anodically polarized from E$_{corr}$ and removed at – 0.95 V in deareated 0.5 M NaCl solution, pH = 5. v = 0.001 V s^{-1}. (b) Higher magnification of the corrosion products at the grain boundary. (c) X-ray map of the corrosion products corresponding to (b) (Zn-Lα and In-Lα signals).

boundaries formed during the retrograde solidification process (k < 1, where k: partition coefficient). The same type of attack was observed when the polarization was begun from potentials more negative than the rest one. Thus, this fact suggests an independence of the properties of the active surface from previous alkalization.

The Al-Zn-In base anodes show a uniform dissolution under operating conditions, giving rise to the well-known higher efficiency. Fig.6a shows a section perpendicular to the corroded surface of an Al-Zn-In alloy after operating 206 days in seawater. As can be observed, smooth hemispherical cavities were developed at the anode surface. Etching with Keller's reagent indicates that these cavities are not associated with a preferential attack along particular regions, i.e., grain boundary zones (Fig.6b).

IV. DISCUSSION

The activation of Al may be interpreted in terms of a penetration of Cl$^-$ through the defective sites of the oxide and its adsorption on the Al surface. This process is only possible when the pzc of Al is anodically exceeded (Muñoz and Bessone, 1999b). The polarizations performed in non-aqueous solutions demonstrate that the formation and stability of pits will be given by the presence of adsorbed Cl$^-$ at the Al/oxide interface (Fig.1).

Then, the appearance of a wide hysteresis cycle gives evidence for the formation of a salt film, which makes difficult the repassivation process. At potentials more negative than the adsorption one, the pit growth stops and further dissolution is ohmic controlled. Thus, due to the absence of water, the stability of pits in terms of a local acidification may be rejected. The effects of incorporating alloying elements on the activation of Al will be, thus, analyzed in terms of the adsorbability of Cl$^-$ on the different alloy phases. The operation potential of based Al-Zn-In alloys has been widely reported to be around - 1.1 V in different chloride media. Then, due to its high anodic dissolution rate, this potential practically does not change in the range embraced from 10^2 to 10^4 µA/cm^{-2}. The more negative rest potential found in the case of the ternary Al-Zn-In alloy (E$_{corr}$ = - 1.3 V) may be attributed to the absence of cathodic impurities.

They enhance the hydrogen evolution, which in turn polarize the system and shift the surface potential to more negative values. The activation generated by the presence of In and Zn on Al is indicated by a displacement of the rest potential towards more negative values. This fact may be analyzed in terms of a higher interaction of Cl$^-$ with the metal surface brought about by the presence of In. In the case of the electrochemical behavior of Zn, adsorption of Cl$^-$ ions has been postulated as a step on the Zn oxidation mechanism (Banás *et al.*,1986). Then, a value of - 0.96 V was reported as the

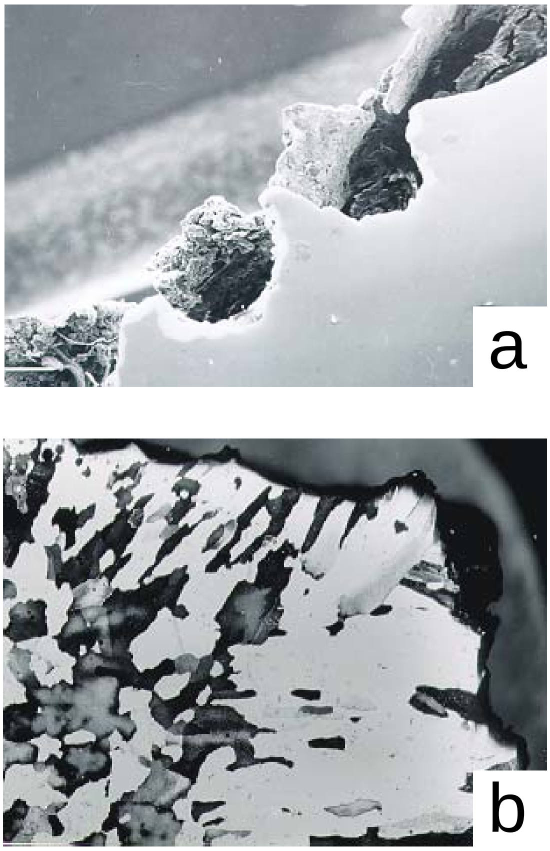

Fig. 6: SEM micrograph of an Al-5%Zn-0.02%In alloy after 206 days in sea water: (a) 17X; (b) surface etched with Keller's reagent, 4X.

pzc in this media (Baugh and Lee, 1973). Also, the very rapid anodic dissolution (Fig.2a) is controlled by the diffusion of $ZnCl_n^{2-n}$ species from the surface to the bulk solution (Asakura and Nobe, 1984). According to our adsorption model, the presence of Zn would make possible the adsorption of Cl^- to be sustained at potentials more positive than the pzc of Zn in Al-Zn alloys. This is just the pitting potential found for the Al-5%Zn alloy, where Zn is mainly present in the form of α phase (Salinas *et al.*,1999).

Taking into account the electrochemical behavior reported for In in chloride (Muñoz *et al.*, 1999a) and alkaline media, a strong adsorption of Cl^- and/or OH^- may be expected once - 1.1 V is anodically exceeded. This promotes the formation of a thin salt film before massive metal dissolution begins at more positive potentials. It means that In brings about a strong increase of Cl^- concentration at the metal surface once - 1.1 V is overcome. The influence of In on the anodic dissolution of Zn has been also recently analyzed by kinetic studies and electrochemical impedance spectroscopy (EIS) performed on Zn and the binary alloy Zn-5%In in Cl^- solutions (Muñoz *et al.*, 2002). The presence of In, as a segregated phase at grain boundaries or as rich In phases in the interdendritic zones of the grain, promotes a higher Zn dissolution rate as well as a higher overtension for the hydrogen evolution. Both facts shift the corrosion potential of the alloy and its active potential towards more negative values.

On the other hand, when the activation effect of In is considered on Al, the strong Cl^- adsorption exerted by rich In phases promotes the activation at more electronegative potential ($E < - 1.1$V) than that corresponding to pure Al (Saidman *et al.*, 1995). The active dissolution region and the corrosion potential of both the Zn-In and Al-In alloys are practically coincident with those showed by the ternary alloy (Fig.2b). According to the anodic behavior showed by the In-5%Al alloy (Fig.3), the dissolution mechanism seems to be associated with the Cl^- adsorption on the different phases present. Then, the anodic peak observed around - 1.1 V corresponds to the dissolution of Al present as In or Al rich solid solution phases. At more anodic potentials, the activation of pure Al is evident.

Which is the role played by Zn? The electrochemical behavior given by the ternary and commercial alloys in Fig.2 can be explained considering the synergistic effect of In and Zn on Al. It has been demonstrated that Al activates when it is placed in neutral solutions containing In^{3+} and Zn^{2+} (Saidman *et al.*, 1999). Deposition of Zn and In on bare Al occurs by displacement reactions giving rise to similar surface features as those found at the active surface of Al-Zn-In alloys used as anode material. The presence of Zn^{2+} seems to favor an accumulation of In by dissolution of previous deposited Zn. The presence of different adsorption states of Zn would also make easier the steps for In^{3+} reduction mechanism. The presence of accumulated In at the active Al surface favors chloride adsorption, so avoiding repassivation. Furthermore, the hydrolysis of Al^{3+} is a strong exothermic reaction. Thus, the surface temperatures generated within the pits are high enough to promote the formation of In-Al phases and enhance surface diffusion. The much lower mobility of Zn, compared to that of In, and its tendency to dissolve from the surface would also explain the decreasing surface concentration of Zn (Saidman and Bessone, 1997). In this way, the presence of Zn at the active surface causes In enrichment. This, in turn, assures the adsorption of Cl^- and the increase of its surface concentration at potentials more positive than - 1.1 V, considered as the pzc for In. Thus, this surface condition promotes and maintains the activation of Al.

As expected, the attack initiates at grain boundaries, where phases enriched in In and Zn would be present. Then, it propagates into the bulk of the grain through interdendritic zones, where the hardly soluble In and Zn were rejected during the solidification process. The corrosion products observed in Fig.4b and analyzed by EDX clearly demonstrate the presence of these rich In and Zn phases. Thus, the initial alloy dissolution promoted by these enriched In-Zn zones explains the coincidence between the anodic response of the ternary alloy with the binary Al-In and Zn-In alloys.

The high galvanic efficiencies observed with the ternary alloy in seawater (Bessone *et al*., 1981) is directly associated with the type of attack. The presence of In ensures the development of smooth wide cavities (Fig.5). This fact can be explained by a continuous redistribution of In at the surface. The In dissolved from solid solution phases is re-deposited at the nearest zones. This dissolution-deposition process of In, which would be assisted by Zn dissolution, allows the active state propagating to the region poor in In. Also, the strong exothermic hydrolysis of Al^{3+} will facilitate the surface diffusion of In. This enhances the capacity for Cl^- adsorption which extents to many grains. A salt film is formed and an ohmic control, leading to a smooth wide cavities attack, is established.

On comparing the ternary with the commercial alloy (Fig.2), practically the same anodic behaviour is observed, although difference appears in the E_{corr} values. The higher amounts of cathodic impurities present in the commercial alloy (Table 1), induce a higher polarization of the anodic areas, which now are able to reach the chloride adsorption potential on In-Zn rich zones. Thus, the E_{corr} of the commercial alloy attains and maintains - 1.1 V. In the ternary alloy, however, the polarization produced by the cathodic impurities is not enough to polarize the anodic areas to this value, and practically no chloride-assisted attack is obtained at its E_{corr}.

V. CONCLUSIONS

According to the electrochemical and morphology studies, the following conclusion can be addressed:

i. The attack initiation of the Al-Zn-In alloy is related to rich In-Zn zones, segregated to grain or cell boundaries.

ii. The presence of In in electric contact with Al and Zn promotes Cl^- adsorption at potentials more positive than - 1.1 V, considered as the pzc of In in such conditions.

iii. The presence of Zn facilitates a surface In enrichment by a displacement reaction. This, in turn, assures an accumulation of adsorbed Cl^-, which maintains the active state of the Al matrix.

Acknowledgements

The Secretaría de Ciencia y Técnica UNS (UNS-CSU-170/99) and The Consejo Nacional de Ciencia y Tecnologia (CONICET) are gratefully acknowledged for the financial support.

REFERENCES

Asakura S and K.Nobe, *Corrosion*, **40**, 227-231 (1984).

Baker H. and H. Okamoto (Eds.). *ASM Handbook*, Vol.3, ASM International, Materials Park, Ohio, (1992).

Banás J, K.G.Schütze and E. Heitz, *J.Electrochem. Soc*., **133**, 253-256 (1986).

Baugh L.M. and J.A.Lee, J.Electroanal. Chem., **48**, 55-61 (1973).

Bessone, J.B., Suarez Baldo R.A., De Micheli S.M. de, *Corrosion*, **37**, 533-540 (1981).

Muñoz, A.G., S.B.Saidman and J.B.Bessone, *J. Electrochem. Soc.*,**146**, 2123-2130 (1999).

Muñoz A.G. and J.B.Bessone, *Corros. Sci*., **41**, 1447-1463 (1999).

Muñoz, A.G., S.B. Saidman and J.B.Bessone, *Corros.Sci*., **44**, 2171-2182 (2002).

Saidman, S.B., S.G.García and J.B.Bessone, **25**, 252-258 (1995).

Saidman S.B. and J.B. Bessone, *J. Appl. Electrochem*., **27**, 731-737 (1997).

Saidman S.B., A.G.Muñoz and J.B.Bessone. J.Appl. Electrochem., 29, 245-251 (1999).

Wolfson S.L., Mat. Performance, **33**, 22-28 (1994).

Yan H., J. Downes, P.J. Boden and S.J. Harris, J.Electrochem. Soc., **143**, 1577-1583 (1996).

Received: September 16, 2001.
Accepted for publication: February 12, 2003.
Recommended by Guest Editors: J. Cerdá, S. Diaz and A. Bandoni.