



Comprehensive model for the activation mechanism of Al–Zn alloys produced by indium

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Received 8 September 2003; accepted 10 May 2004

Available online 19 July 2004

Abstract

Exploratory work on the electrochemical behaviour of the Al–4%Zn alloy in the presence of In^{3+} in weakly acid chloride and acetic media is reported. It was found that in chloride solutions, active dissolution takes place at very negative potentials ($-1.5 \text{ V}_{\text{SCE}}$). This significant enhancement in the electrochemical activity of the alloy is described and discussed. The aim of this paper is to explain the relationship between the operating potential ($-1.1 \text{ V}_{\text{SCE}}$) given by the commercial alloy (basically an Al–Zn–In alloy), its high efficiency, its quasi-uniform attack observed and the enhanced activity found ($-1.5 \text{ V}_{\text{SCE}}$). An unified model that explains this findings and the activation process of pure Al by In^{3+} is proposed. It was found that two activation mechanism are operative on Al: (i) When sufficient amount of In at the interface in quasi-liquid state is present, an In–Al amalgam is responsible for the activation process ($-1.5 \text{ V}_{\text{SCE}}$). This process is favoured by Zn reach zones that favours In enrichment at the interface by displacement reaction. (ii) At higher anodic potentials (near $-1.2 \text{ V}_{\text{SCE}}$), the presence of In at the interface facilitates a chloride adsorption process which depolarised the anodic reaction.

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Keywords: Aluminium alloy; Activation mechanism; Amalgam

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1. Introduction

It is well known that the presence of aluminium oxide films passivates the Al anode preventing its active dissolution. The incorporation of alloying elements such as Hg, In, Ga, Zn or Sn shifts the pitting potential of Al towards more negative values. Some of them (Hg, Ga, In) produce a more uniform dissolution in environments containing aggressive ions. The presence of the activator as a metal ion produces similar potential displacement. Mercury is the most reactive of the activators used. The open circuit potential shifts to $-1.50 V_{SCE}$ in chloride solutions. On the other hand the attack morphology of the specimen activated with Hg is different to the other activators. There is no evidence of localised attack and the activation process is not chloride dependent, suggesting that activation proceeds by the formation of an amalgam [1–4].

From commercially produced Al sacrificial anodes, the Al–Zn–In alloy presents the best performance in seawater with an average potential of $-1.1 V$. Efficiencies over 90% have been reported, related to a quite uniform attack [5]. The activation potential is sustained by the chloride adsorption assured by the presence of In [6–8]. The activation of Al in chloride solutions containing Zn^{2+} and In^{3+} is related to an In accumulation and preferential Zn dissolution [9,10].

A very negative potential of an Al–5%Zn alloy was measured when In^{3+} was introduced to an aerated 3.5% NaCl electrolyte [11]. It was suggested that the incorporation of In^+ or In^{2+} intermediates into the passive film leads to an increase in anionic vacancies and a decrease in the number of electrons, promoting active aluminium dissolution. Also, it has been reported an accelerated activation of an Al–Zn alloy polarised at $-1.14 V$ in the presence of In^{3+} concentration higher than 0.003 M [12]. Taking into account that the hydrolysis of Al^{3+} ions is an exothermic reaction ($\Delta H^0 = -1406.7 K cal mol^{-1}$) [13], increasing temperature at the active interface is expected. This effect will increase as the active interface increases.

In the present paper, the Al–4%Zn alloy in the presence of In^{3+} in weakly acid chloride and acid acetic media is reported. The significative enhancement in the electrochemical activity of the alloy ($-1.5 V_{SCE}$) is described and discussed. It is intended here to find out whether the chloride adsorption is the unique process responsible for the activation potential and the attack morphology or there is another process kinetically present.

2. Experimental

Disc electrodes of $0.636 cm^2$ made from Al–4%Zn, pure Al, commercial Al and a commercial Al–Zn–In alloy, with compositions according to Table 1, were polished with 1000 emery paper, 1 and $0.3 \mu m$ grit alumina suspensions, then cleaned with triply distilled water. The auxiliary electrode was a large Pt sheet. Potentials were measured against a SCE reference electrode. Potentiodynamic, galvanostatic and open circuit-time experiments were performed with a potentiostat–galvanostat (PAR Model 173). A dual stage ISI DS 130 SEM and an EDAX 9600 quantitative energy

Table 1
Material composition

Sample	Zn (wt%)	Si (ppm)	Fe (ppm)	Cu (ppm)	In (wt%)
Pure Al	–	5	4	3	
Commercial Al	0.00203	0.14 wt%	0.18 wt%	7.2	
Al–4%Zn	3.86	152	70	31	
Al–Zn–In	4.3	0.1 wt%	0.12 wt%	70	0.02

dispersive X-ray analyser were used to examine the surface characteristics of gold-metalized electrodes.

Chloride solution and acetic acid solutions (0.5 M) were prepared from analytical grade chemicals and triple-distilled water. The pH was adjusted with HCl, and the working temperature was always kept at 25 °C.

3. Results

3.1. Studies in chloride acid media

The Al–Zn specimen was immersed in 0.5 M Cl^- , pH = 3 solution with and without 0.01 M In^{3+} and its open circuit potential (OCP) vs. time response was followed. Fig. 1, curve a, shows practically a constant OCP when no In^{3+} ions are present, while curve b, shows that the electrode potential is shifted to -1.56 V in the presence of In^{3+} . After reaching this active state, a potentiodynamic run initiating at -1.70 V was applied. A current plateau is obtained preceding a sharp current increase (Fig. 2, curve b). This current increase is due to the Al pitting process sustained by the chloride adsorption that the presence of In produces at that potential [8]. Considering the current plateau zone, the oxidation current increases from

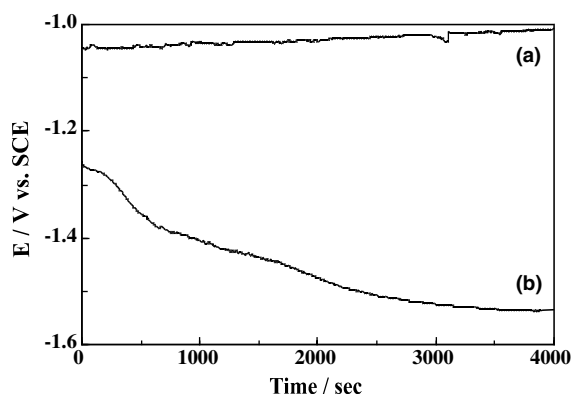


Fig. 1. Open circuit potential (OCP) vs. time plot of Al–4%Zn in 0.5 M NaCl, pH = 3. (a) $[\text{In}^{3+}] = 0$ and (b) $[\text{In}^{3+}] = 0.01$ M.

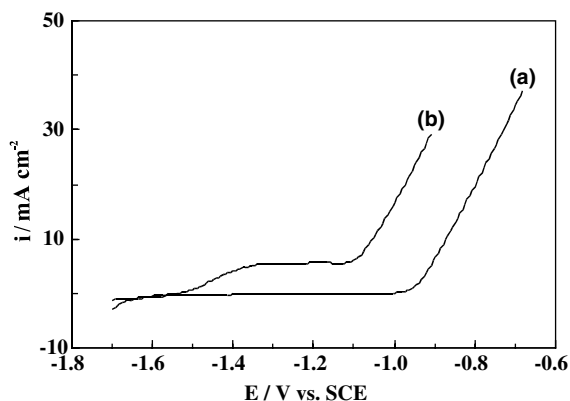


Fig. 2. Potentiodynamic polarisation at $v = 0.050 \text{ V s}^{-1}$ of Al-4%Zn in 0.5 M NaCl, pH=3 after establishing the conditions of curves a and b in Fig. 1.

microamperes (μA) to milliamperes (mA) when the systems without and with In^{3+} ions are compared (Fig. 2 curves a and b).

Similar result was obtained when the same experimental conditions were applied to a commercially produced Al sacrificial anode (Al-Zn-In alloy). On the contrary, the open circuit potential vs. time response did not show further activation to approximately -1.5 V when pure Al or commercial Al were immersed in a 0.5 M chloride solution containing 0.01 M In^{3+} .

The same activation effect can be observed when the Al-Zn alloy is anodically polarised under a galvanostatic mode in the presence of 0.01 M In^{3+} (Fig. 3). The E/t response obtained at $10 \mu\text{A cm}^{-2}$ demonstrates that a very active behaviour is attained, whereas the potential displayed oscillations at 1 mA cm^{-2} . In contrast, at higher current densities (10 mA cm^{-2}), this system is polarised to an operating

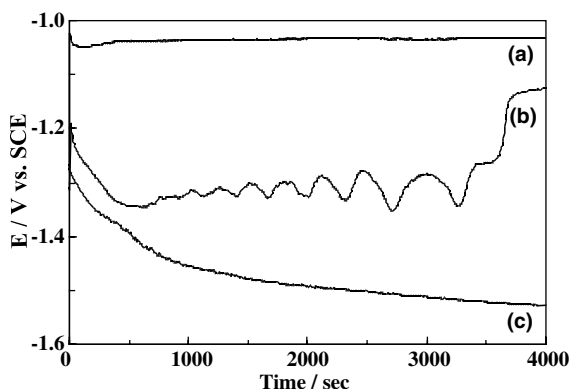


Fig. 3. Influence of current density on the activation process of Al-4%Zn in 0.5 M NaCl, pH=3 with $[\text{In}^{3+}] = 0.01 \text{ M}$: (a) 10 mA cm^{-2} ; (b) 1 mA cm^{-2} and (c) $10 \mu\text{A cm}^{-2}$.

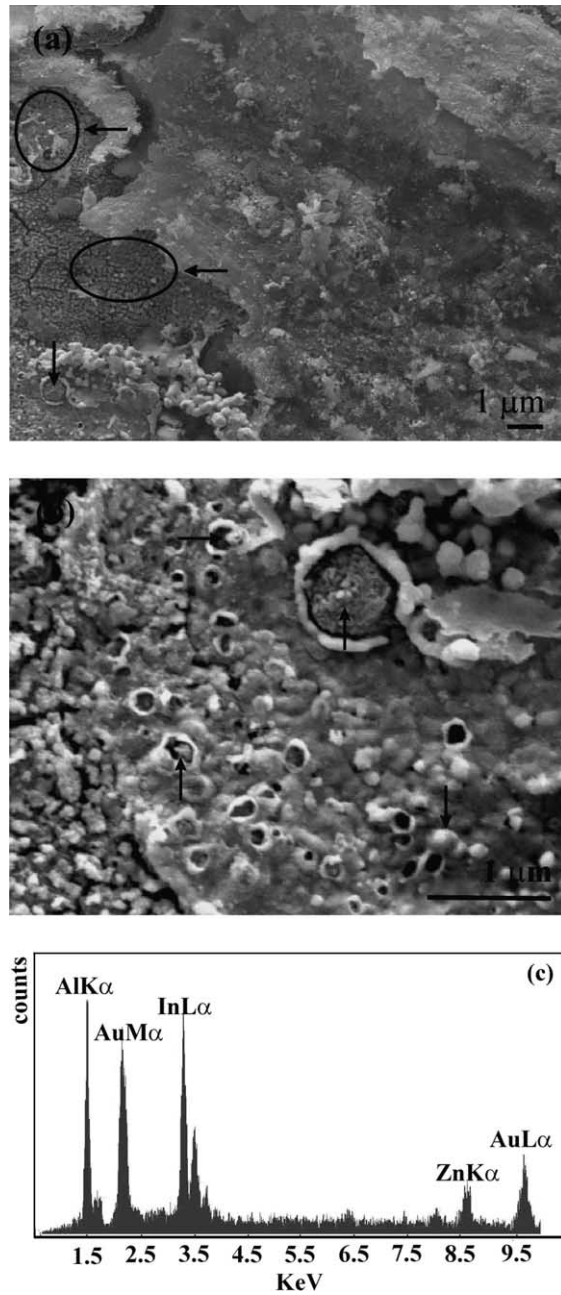


Fig. 4. SEM/EDX examination of the electrode surface after polarisation at $10 \mu\text{A cm}^{-2}$ in 0.5 M NaCl, pH = 3: (a) image showing high amount of spherical particles; (b) image showing wide circular cavities and (c) EDX analysis at the middle of the cavity (on feathers like corrosion products). Arrows on (a) and (b) show the presence of In particles.

potential where a sufficient depolarised process takes place (> -1.1 V—pitting). After reaching the very active state under the galvanostatic mode, it was changed to a potentiostatic one and the electrode was polarised potentiodynamically in the positive potential direction from -1.7 V. The i/E curve is the same than that obtained after open circuit activation conditions.

Fig. 4a shows a SEM/EDX examination of the electrode surface after polarisation at $10 \mu\text{A cm}^{-2}$. High amount of spherical In particles identified by X-ray mapping were found in between the corrosion products. These corrosion products do not seem to be forming any film. On the contrary, they appear as a result of an active, depolarised interface. Special features can be seen, already observed under the Al activation produced by Hg (amalgamation process) [2]. Wide circular cavities showing a mud structure with incipient feathers in their middle can be seen (Fig. 4b). EDX analysis performed at this point (on the feathers) shows increasing amount of In and Zn, compared to the rest of the mud structure (Fig. 4c).

Decreasing In^{3+} cation concentration has not the same activating effect on the Al–Zn alloy potential. The galvanostatic curves performed at $10 \mu\text{A cm}^{-2}$ (Fig. 5) show that as the In^{3+} concentration is decreased the potential becomes less active, till below 0.001 M no activation is obtained.

3.2. Studies in acetic acid media

An activation process is also observed when the Al–Zn electrode was placed in 0.5 M acetic acid containing 0.01 M In^{3+} , under OCP condition (Fig. 6). In this case a lower active potential is reached (approximately -1.3 V).

The formation of a resistive film is corroborated when a linear polarisation is applied after the OCP experiment (Fig. 7). An ohmic control appears within the hole range of polarisation. This film was observed by SEM/EDX (Fig. 8a) where few

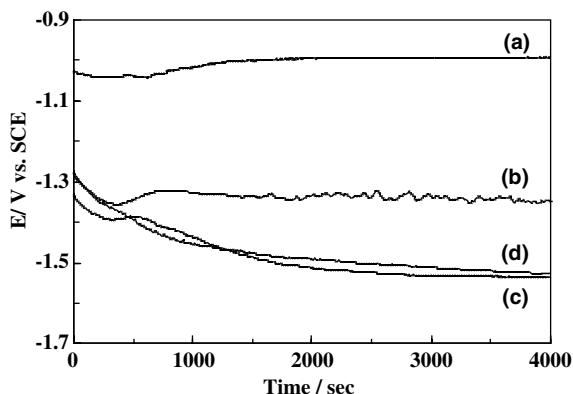


Fig. 5. Influence of In^{3+} concentration on the activation of Al–4%Zn in 0.5 M NaCl, pH=3; a galvanostatic study at $i = 10 \mu\text{A cm}^{-2}$: (a) $[\text{In}^{3+}] = 0$; (b) $[\text{In}^{3+}] = 0.001$ M; (c) $[\text{In}^{3+}] = 0.005$ M and (d) $[\text{In}^{3+}] = 0.01$ M.

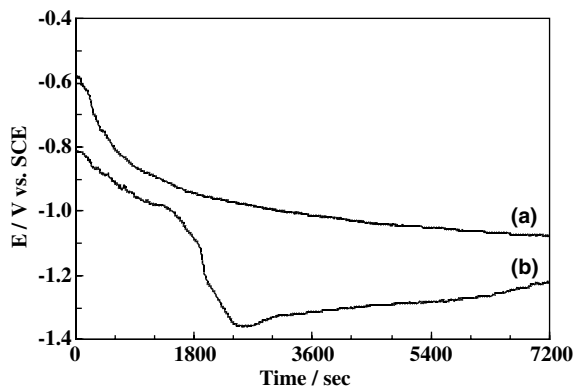


Fig. 6. OCP vs. time plot of Al-4%Zn in 0.5 M acetic acid: (a) $[\text{In}^{3+}] = 0$ and (b) $[\text{In}^{3+}] = 0.01$ M.

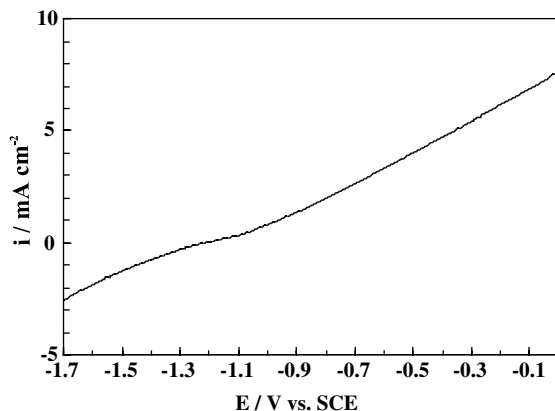


Fig. 7. Potentiodynamic response of Al-4%Zn in 0.5 M acetic acid after the OCP activation with $[\text{In}^{3+}] = 0.01$ M, $v = 0.050$ V s⁻¹.

spherical particles were seen in between the disrupted film. EDX analysis on the film and particles show the presence of In (Figs. 8b and c). Comparison of XRD analysis produced before and after the In deposition on Al-4%Zn in acetic acid shows that Zn signal disappeared. This result supports the idea that In deposition is mainly sustained by Zn oxidation coming from the Al-4%Zn alloy.

4. Discussion

The very active state obtained when the Al-Zn alloy is in contact with a Cl⁻ solution containing In³⁺ was not observed using pure Al or commercial Al. This result indicates that the presence of Zn is determinant in the development of the

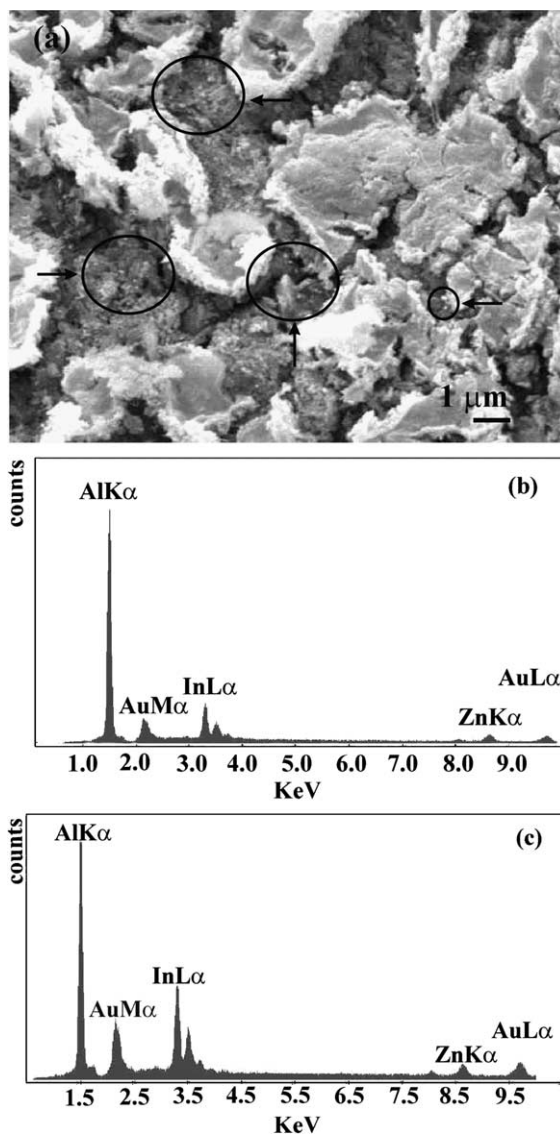


Fig. 8. SEM/EDX analysis of surface products obtained under conditions in Fig. 7: (a) SEM image of the film formed (arrows show the presence of In particles); (b) EDX analysis on film; (c) EDX analysis on particles.

active surface. On the other hand, the Al–Zn activation appears to be related to the reduction of In^{3+} onto the alloy surface. This process is the consequence of a direct In^{3+} reduction and/or the displacement of In^{3+} from the solution by the galvanic action produced by the electrooxidation of Al and principally of Zn. It has been demonstrated that in the presence of Zn the accumulation of In is favoured [9,10].

Possibly, the oxide film on Al–Zn or Al–Zn–In alloys is less resistive and/or presents higher amount of oxide flaws [14]. In this way In^{3+} reduction is kinetically favoured by the Al–Zn system. In chloride media, increased amount of deposited In and no film formation is observed with respect to acetic media. These results justified the more active state attained and the polarisation behaviour observed (Fig. 2 vs. Fig. 7). The activation degree attained depends on the amount of In^{3+} present at the interface (Fig. 5). As the In^{3+} concentration is decreased, lower activation potential is observed.

The above experimental findings can be interpreted on the basis of the alloy surface dissolution through an amalgam formation, as was postulated for the Al activation by Hg [1–4]. The amalgam-activation process is autocatalytic. It needs a minimum amount of In deposited on Al in true metallic contact to produce oxide detachment and Al oxidation in order to reach sufficient Al^{3+} ion concentration at the active interface. Thus, the high rate of the alloy dissolution and the exothermic hydrolysis reaction of Al^{3+} ions provide a temperature high enough to promote the presence of quasi-liquid In. This high temperature facilitates In surface diffusion, then more oxide is detached, increasing the active area. Also, the Al atom diffusion into the amalgam is in this way facilitated. On the contrary, if the amount of In deposited is not high enough, the amalgam-activation process will not occur and repassivation will prevail. The system evolves towards this case when the In^{3+} ion concentration is reduced and lower activation potentials are attained (more positive potentials) (Fig. 5). The amount of deposited In at the active interface can be also diminished by (a) $\text{In}(\text{OH})_3$ precipitation due to the local alkalisation produced by hydrogen evolution which take place at the same potentials considered, (b) deposition of In on cathodic impurities present in the Al matrix (Fe, Cu, etc.) which does not produce Al activation, and (c) the presence of an effective barrier oxide film which does not present sufficient flaws or crack-healing events (case of pure and commercial Al). Once the amalgam is formed, an anodic limiting current is obtained (Fig. 2, curve b).

Previous results have shown that In oxidation, even in a strong alkaline solution (1 M NaOH), is initiated at -1.24 V, which is also the corrosion potential [15]. Thus, it seems that pure In oxidation is not associated with this anodic limiting current.

The presence of the amalgam shifts the potential towards the most active direction. The current plateau (Fig. 2, curve b) is probably related to the Al diffusion through the amalgam. The sustainable current density is low compared to that observed when the mechanism of activation is related to Cl^- adsorption. When a high anodic current is required, the high current cannot be sustained by the dissolution of Al through the amalgam, therefore the potential is shifted to -1.1 V, where the depolarised pitting chloride assisted mechanisms is able to support this current. This fact explains the results found in Fig. 3, where according to the current imposed the operating potential is very active ($i < 1 \text{ mA cm}^{-2}$), fluctuates between the amalgam-activation mechanism and the chloride assisted activation mechanism ($i = 1 \text{ mA cm}^{-2}$) or is mainly sustained by this later mechanism ($i > 1 \text{ mA cm}^{-2}$).

The presence of In at the Al active interface is evidenced by (i) the presence of tiny spheres, in between the corrosion products, identified as In particles, in acid and

acetic media (Figs. 4a and 8a); (ii) the presence of wide circular cavities with a mud structure and feathers like corrosion products in their middle (Fig. 4a–c) in chloride acid media. These feathers coming from the middle of the circular areas are $\text{Al}(\text{OH})_3$ produced by the oxidation of Al present in the In–Al amalgam formed. Although an ohmic control is present in acetic media, the amount of current passed when a linear polarisation is applied (Fig. 7) is demonstrative that an active behaviour is given by the only presence of an In–Al amalgam. These facts and the limiting current found on the curve b in Fig. 2 constitute the main evidences attained within this paper, to assess the In amalgamation process as responsible for the Al activation to that very negative potential found (-1.56 V). Thus, depending on whether the In present at the active interface is solid or quasi-liquid and the anodic current density required, two activation mechanisms for Al dissolution are operative. They can operate in parallel or in series according to the interface temperature:

- (a) *Via In–Al amalgam.* When sufficient amount of In at the interface in quasi-liquid state is present. The Zn reach zones in the alloy favour In enrichment at the interface by displacement reaction. Al oxidation at the amalgam/solution interface gives an active potential about -1.5 V. This process attains an anodic limiting current.
- (b) *Via pitting of Al.* When low In concentration at the interface is present, in solid state. It facilitates chloride adsorption at a potential near -1.2 V, which establishes the pitting potential. This process is a depolarised one.

5. Conclusions

From the results obtained, the following conclusions can be drawn:

- (1) It is possible to activate Al–Zn based alloys by In deposition. An In–Al amalgam is formed which detaches the oxide film and avoids repassivation.
- (2) Amalgam Al saturation assesses the anodic limiting current for Al dissolution. Al incorporation and diffusion within the amalgam depends on its aggregate state. In turn, it depends upon the interface temperature which is given by the Al^{3+} hydrolysis reaction. Therefore, the Al^{3+} concentration at the interface will determine the interface temperature and the i_{lim} attained.
- (3) In aggressive media, besides the amalgam-activation mechanism, a chloride pitting activation process is added. This process will be effective once the chloride adsorption potential on In is overcome.
- (4) Thus, depending on whether the In present at the active interface is solid or quasi-liquid and the anodic current density required, two activation mechanisms for Al dissolution are operative. They can operate in parallel or in series according to the interface temperature: (a) via In–Al amalgam; (b) via pitting of Al.
- (5) Depending on the anodic current density required and the interface temperature, the operating potential will be below or over the pitting potential (-1.1 V).

Acknowledgements

The Secretaría de Ciencia y Técnica (UNS) and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) are gratefully acknowledged for the financial support.

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