JOURNAL OF APPLIED ELECTROCHEMISTRY **29**: 245–251, 1999.

Electrodeposition of indium and zinc on aluminium

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Received 5 December 1997; revised 6 June 1998

Zinc and indium were deposited from sulphate and chloride electrolytes onto aluminium electrodes under potentiostatic conditions. The role of the anion, pH, cation concentration, cathodic potential and agitation were investigated. The deposit morphology and composition were studied by SEM and EDX. Potentiodynamic and galvanostatic techniques were also applied for product characterization. Once a critical amount of Zn was deposited preferred In deposition began without agitation. But under rotation or at low cathodic potentials Zn^{2+} discharge became the prevalent reaction. The results support the earlier hypothesis of the preferential adsorption of Zn ions [1].

Keywords: *aluminium*, *electrodeposition*, *indium*, *zinc*

1. Introduction

The presence of zinc and indium on bare aluminium produces surface activation in chloride media at a convenient potential which allows it to be used as anode material in Al-batteries as well as sacrificial anode in cathodic protection systems. Thus, the electrochemical behaviour of the Al–Zn–In alloy, among others, is of interest because of these applications. The deposition of zinc and indium on aluminium should present a similar situation to that given by the active interface of an Al–Zn–In alloy. The study of this system offers possibilities in understanding the role of zinc and indium in the corrosion of aluminium, and also in understanding the cathodic behaviour of aluminium. On the other hand, considerable research has been focussed on zinc alloy deposition due, principally, to technical requirements for zinc coatings. Thus, the understanding of the anomalous codeposition of zinc alloys, in which the less noble zinc deposits preferentially to the more noble metal, has been also of interest.

In a previous paper [1] the cathodic and active behaviour of aluminium in acid chloride solutions containing zinc and indium ions were studied. On the one hand, preferential adsorption of Zn occurred and as soon as conditions on the electrode surface allowed a critical content of deposited Zn, preferred In deposition on freshly nucleated Zn was initiated. On the other hand, the active behaviour was explained considering displacement reactions that produced In accumulation and preferential Zn dissolution. The presence of accumulated In at the Al interface favoured chloride adsorption thus avoiding repassivation.

In this paper we extend this work to the effects of agitation, pH, ratio of ion concentrations and anions on the electrodeposition, in order to gain a better understanding of the process. To address these issues the morphology and composition of the deposits were observed. Potentiostatic and galvanostatic techniques and potentiodynamic stripping methods were used.

2. Experimental details

The experimental set-up has been described previously [2]. Pure aluminium (99,999%, Aldrich Chemical Company) rod samples in the form of discs axially mounted in PTFE holders, were used as working electrodes. The electrodes were polished successively with 400, 600 and 1200 emery papers and $1\,\mu$m and $0.3\,\mu$m grit alumina suspensions and then thoroughly rinsed with triply distilled water. The auxiliary electrode was a large Pt sheet. Potentials were measured against a SCE reference electrode properly shielded and connected through a Luggin–Haber capillary tip.

Runs were made in $0.5\,\mathrm{M}$ NaCl or $0.5\,\mathrm{M}$ Na_2SO_4 solutions containing $x\,\mathrm{M}\,In^{3+} + y\,\mathrm{M}\,Zn^{2+}$ $(0.001 \leqslant x, y \leqslant 0.1)$ in a purified nitrogen gas saturated atmosphere at 25 °C. The pH of the solutions $(2 \leqslant \mathrm{pH} \leqslant 4)$ was adjusted by addition of HCl or H_2SO_4. The solutions were prepared from analytical grade chemicals with triply distilled water.

Constant potential steps with potential holding at E_τ, for different times (τ), constant current steps and conventional sweeps at different potential sweep rates (v) were applied to electrodes either still ($\omega = 0$) or under rotation ($\omega = 2000$ rpm). Electrochemical measurements were complemented with SEM and EDX.

Unless otherwise stated, all Al cathodic polarization and electrodeposition were performed at -1.50 V in a $0.5\,\mathrm{M}\,SO_4^{2-}$ solution, at pH 3, for 10 min. At this potential hydrogen evolution occurred and local alkalization produced aluminium oxide removal and/or hydration [3]. This condition facilitated Zn and In deposition onto Al and defined a reproducible initial surface. Afterwards, and unless otherwise stated, all potentiodynamic anodic runs were performed in sulphate electrolyte at 0.1 V s^{-1} under no agitation. When sweep rates lower than 0.01 V s^{-1} were used, local alkalization vanished with increasing potential, repassivation took place and no Zn or In anodic peak was found. The stripping voltammetry was only performed in sulphate solution due to pitting of Al at −1.10 V in chloride solutions containing In^{3+}.

3. Results

3.1. *Indium deposition*

The current density–time plot obtained during the cathodic polarization of Al under potentiostatic control at −1.50 V in a 0.5 M SO_4^{2-} is shown as an insert in Fig. 1. The shape of the curve is the same as that in chloride solution [4] and is independent of stirring conditions. A similar curve was obtained in the presence of 0.01 M In^{3+} in sulphate or chloride media.

It has been suggested that electrochemical hydrogen evolution at the active Al surface is the major cathodic process for $E_\tau = -1.50$ V and the deposit of In occurs principally by the displacement reaction [4]:

$$Al + In^{3+} \rightarrow Al^{3+} + In$$

or

$$Al + InO_2^- + 4\ H^+ \rightarrow Al^{3+} + In + 2\ H_2O$$

After cathodic polarization in a solution containing 0.01 M In^{3+}, a potentiodynamic run in the anodic direction exhibited a very small oxidation peak, initiated at the In/In^{3+} reversible electrode potential (−0.65 V) (Fig. 1).

3.2. *Zinc deposition*

The current density–time (*i*/*t*) profile recorded for the cathodic polarisation of Al in a solution containing 0.01 M Zn^{2+} without agitation shows that the current increased to reach a maximum and finally decreased slowly to approach a steady value (Fig. 2, curve (a)). A potentiodynamic run in the anodic direction at 0.100 V s^{-1} shows an anodic peak initiated at −1.10 V, which corresponds to the oxidation of pure electrodeposited Zn (Fig. 3, curve (a)).

A monotonic current increase in the (*i*/*t*) transient associated with Zn deposition was obtained in sulphate solution under agitation ($\omega = 2000$ rpm) (Fig. 2, curve (b)). Zn was also displaced from solution by the galvanic action produced by the electro-oxidation of bare Al transiently exposed at cracks in the oxide film. The subsequent anodic scan showed a relatively wide band of anodic current (Fig. 3, curve (b)).

3.3. *Indium + zinc deposition*

3.3.1. Deposition without agitation. The *i*/*t* response of cathodically polarized Al in a solution containing 0.01 M In^{3+} + 0.01 M Zn^{2+} shows that the current due to the electrodeposition begins to increase after a time delay (Fig. 2, curve (c)). The deposit morphology shows rounded grains (Fig. 4(a)). SEM–EDX analysis revealed the presence of 83 and 17% of In and Zn on average, respectively. Some hexagonal Zn platelets were also observed (Table 1). Figure 4(b) shows one of these, where deposited In, identified by X-ray mapping, was found above it. According to previous results [1], this morphological study suggests that In deposition was initiated onto initially deposited Zn.

The anodic stripping at 0.100 V s^{-1} showed only two anodic peaks, which corresponded to the oxidation of pure Zn and pure In (Fig. 5, curve (a)). Thus, under the present conditions, the formation of alloys or intermetallic compounds of Zn and In was not detected.

After potentiodynamic polarization, a SEM–EDX examination of an Al electrode removed at −0.40 V

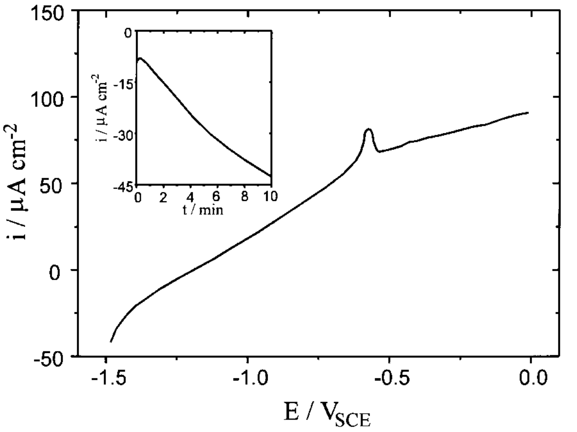

Fig. 1. Potentiodynamic polarization curve for Al at 0.100 V s^{-1} recorded in a 0.5 M SO_4^{2-}, pH 3 solution containing 0.01 M In^{3+}. The electrode was previously cathodically polarized at −1.50 V for 10 min and the corresponding current density–time profile is also included.

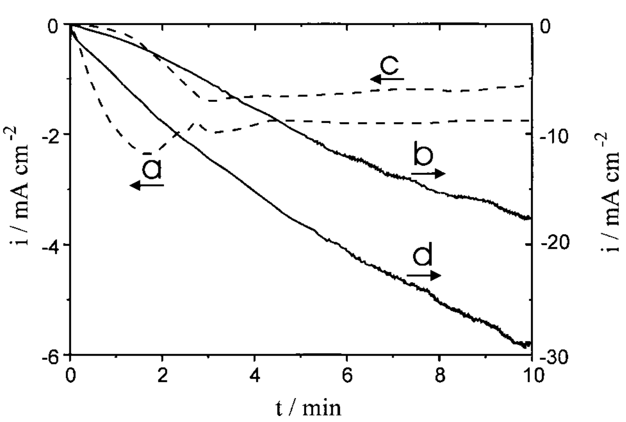

Fig. 2. Current density-time response for Al at $E_\tau = -1.50$ V in 0.5 M SO_4^{2-}, pH 3 solution containing: (a) 0.01 M Zn^{2+}, without rotation; (b) 0.01 M Zn^{2+}, $\omega = 2000$ rpm; (c) 0.01 M In^{3+} + 0.01 M Zn^{2+}, without rotation and (d) 0.01 M In^{3+} + 0.01 M Zn^{2+}, $\omega = 2000$ rpm.

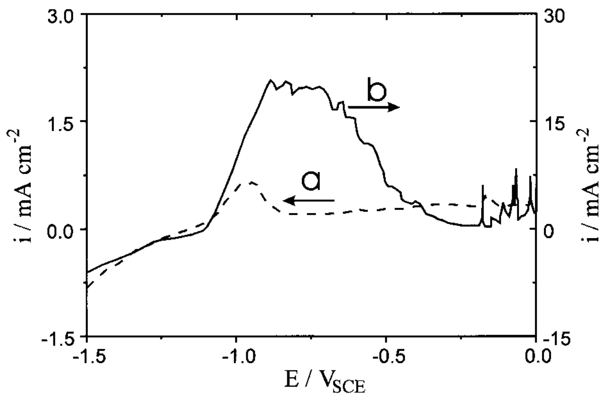

Fig. 3. Potentiodynamic polarization curves for Al at 0.100 V s^{-1} under stagnant conditions in 0.5 M SO_4^{2-}, pH 3 solution containing 0.01 M Zn^{2+}. The electrode was previously cathodically polarized at −1.50 V for 10 min: (a) without rotation; (b) $\omega = 2000$ rpm.

still showed the presence of a large amount of deposit with composition and structure similar to those obtained after 10 min of cathodic polarization. Accordingly, it was noted that current efficiency, taken as the ratio between the total anodic charge obtained by integration and the cathodic charge passed during deposition, is very low (0.2%). This may be due to the simultaneous hydrogen evolution, but can principally be explained considering that Al oxide forms an insulating film between the deposit and the base metal during the anodic polarization, thus avoiding further Zn or In oxidation.

3.3.2. Deposition with agitation. The *i*/*t* curve at −1.50 V in sulphate or chloride solution was significantly changed by agitation. The *i*/*t* response in a solution containing 0.01 M In^{3+} and 0.01 M Zn^{2+} at $\omega =$ 2000 rpm is shown in Fig. 2 (curve (d)). The transients were very similar to that obtained in solution containing only Zn^{2+}, but higher current densities were measured in the presence of both ions. Besides, the *i*/*t* curves in chloride solutions (not shown in the Figure) gave current densities twice that in sulphate.

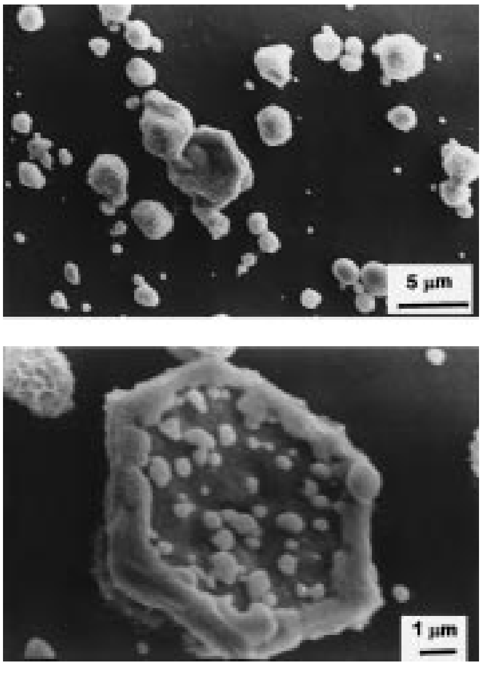

Fig. 4. SEM micrographs of Al surface after potentiostatic polarization at $E_\tau = -1.50$ V without rotation for 10 min, in 0.5 M SO_4^{2-}, pH 3 solution containing 0.01 M In^{3+} + 0.01 M Zn^{2+}. (a) and (b) are different magnifications.

Deposits obtained with agitation were entirely different: grains normal to the Al substrate grew as dendrites in both chloride (Fig. 6) and sulphate solutions, indicating that the deposit growth was limited by diffusion. In some of them, the characteristic hexagonal shape was still observed. The Zn content in the deposit was now about 80% (Table 1). Thus, anomalous codeposition was obtained under rotation.

The anodic stripping was not very reproducible, particularly the ratio between the amount of In dissolved to that of Zn dissolved, reflected by the anodic charge densities under the corresponding peaks. As an example, the curves (b) and (c) in Fig. 5 show the results obtained under the same experimental conditions. Therefore anodic stripping can be discussed only qualitatively.

Two anodic peaks associated with In and Zn oxidation were found (Fig. 5, curves (b) and (c)). Both peaks were shifted towards more positive potentials especially that of In. This effect may be assigned to the barrier generated by the oxidation products [5].

A large amount of deposit on the electrode surface was still observed by SEM–EDX analysis when the Al electrode was removed at 0.0 V after potentiodynamic stripping. This was reflected in the very low current efficiency (3%).

3.3.3. Effect of pH. The effect of pH ($2 \leqslant \text{pH} \leqslant 4$) on the *i*/*t* curve at −1.50 V in a solution containing 0.01 M In^{3+} and 0.01 M Zn^{2+} is shown in Fig. 7. At pH 4, In oxide precipitation can be detected. As a result, the pH increase produced, not only a decrease in hydrogen evolution, but also a decrease in the electrodeposition current. In the pH range between 2 and 4, the Al oxide dissolution rate increased with pH decrease. By contrast, the formation of a Zn^{2+} ion pair with SO_4^{2-} is favoured at higher pH [6], thus inhibiting Zn discharge. These considerations may explain the decrease in the electrodeposition current as the pH increases. The same tendency was attained under rotation.

3.3.4. Effect of E_τ. The *i*/*t* transients at different potentials without rotation were recorded in a solution containing 0.01 M In^{3+} and 0.01 M Zn^{2+} (Fig. 8). After a time delay, a current increase to a maximum was observed. At longer times the current decayed following a linear relationship with $t^{-1/2}$, indicating a diffusion-controlled process. The initial time delay was probably related to Al oxide removal and nucleation of In on freshly deposited Zn. Both processes were retarded as the potential became more positive.

The deposit obtained at −1.40 V in chloride solution showed smaller and fewer dendrites compared to those obtained at −1.50 V. The surface analysis

Table 1. Morphology and composition of the deposits obtained after potentiostatic polarization at −1.50 V for 10 min in a pH 3 solution containing 0.01 M *In^{3+} + 0.01* M *Zn^{2+}*

Electrolyte	ω = 0 rpm		ω = 2000 rpm	
	Morphology	*Composition*	*Morphology*	*Composition*
0.5 M Cl^-	Large number of dendrites	84 wt % In 16 wt % Zn	Non uniform and dense dendritic deposit	19.5 wt % In 80.5 wt % Zn
0.5 M SO_4^{2-}	Rounded grains and some hexagonal Zn platelets with In above it.	83 wt % In 17 wt % Zn	Non uniform dendritic deposit	16 wt % In 84 wt % Zn

showed an increase in Zn content (58%). This indicated that in chloride solution the proportion of Zn in the deposit increased at lower cathodic potentials. To obtain further details of the process, stripping analysis was performed in sulphate solutions. After deposition at E_τ = −1.35 V for τ = 1 h, In peak dissolution cannot be detected (Fig. 9, curve (a)). However, this peak appeared after deposition at −1.45 V for 10 min (Fig. 9, curve (b)). Considering the detection limits of stripping voltammetry in the present conditions, it cannot be concluded that no In is present in the deposit. However, the results allow us to conclude that at low cathodic potentials preferential Zn deposition occurs in sulphate solution.

3.3.5. Effect of τ. The deposition of In and Zn in 0.5 M Cl^-, pH 3 solution on Al electrodes at E_τ = −1.50 V for 10 min showed a large number of dendrites. SEM–EDX analysis of the deposits revealed the presence of 84 and 16 wt % of In and Zn on average, respectively [1]. A similar composition was obtained in chloride solution when the Al electrode was removed after 30 s of cathodic polarization. The morphology and composition of the deposits in the early stages of cathodic polarization in sulphate solution were not the same as those obtained after 10 min. After 1.5 min at −1.50 V in pH 3, 0.5 M SO_4^{2-} solution a SEM–EDX examination of the Al surface showed a small number of deposits with 16 and 84 wt % of In and Zn on average, respectively (Fig. 10).

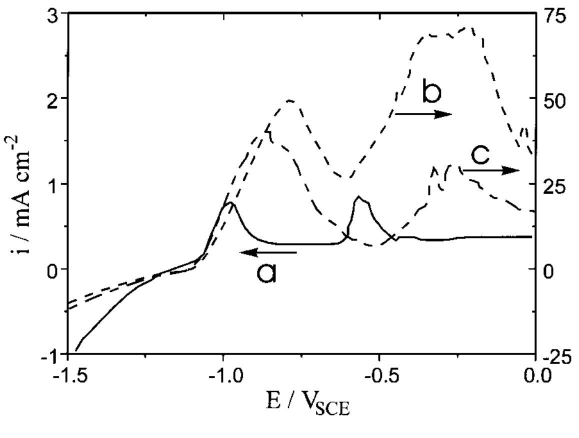

Fig. 5. Potentiodynamic polarization curve for Al at 0.100 V s^{-1} recorded in a 0.5 M SO_4^{2-}, pH 3 solution containing 0.01 M In^{3+} + 0.01 M Zn^{2+} under stagnant conditions. The electrode was previously polarized at −1.50 V for 10 min: (a) without rotation; (b) and (c) ω = 2000 rpm.

The effect of τ was also studied by potentiodynamic anodic stripping in sulphate solution. After cathodic polarization at −1.50 V at times lower than 1.50 min, anodic runs at 0.100 V s^{-1} were carried out. The curve presented a small oxidation peak associated with Zn dissolution, but the In anodic peak was not detected. This suggests that in sulphate solution In deposition is not favoured in the initial stages of cathodic polarization. However, further research using nanometric techniques is required.

3.3.6. Effect of In^{3+} and Zn^{2+} concentrations. To obtain more information about the interaction between In^{3+} and Zn^{2+} during deposition, the polarization behaviour in 0.5 M SO_4^{2-}, pH 3 solution was studied in the presence of constant Zn^{2+} concentration and varying In^{3+} concentration, and vice versa.

The *i*/*t* response without rotation and the corresponding potentiodynamic stripping obtained with 0.001 M In^{3+} + 0.01 M Zn^{2+} was similar to that obtained with no In addition. The potentiostatic transient at −1.50 V without agitation in the presence of 0.1 M In^{3+} (Fig. 11, curve (a)) was similar to that for 0.01 M In^{3+} + 0.01 M Zn^{2+}, but higher currents were obtained and the time elapsed to attain the steady state was longer. It must be noted that cathodic currents were significantly higher than that obtained for 0.1 M In^{3+} in chloride solution [4]. On the other hand, the transients obtained under rotation were practically independent of In^{3+} concentration (0.001, 0.01 or 0.1 M) in the presence of 0.01 M Zn^{2+} (Fig. 11, curve (b)).

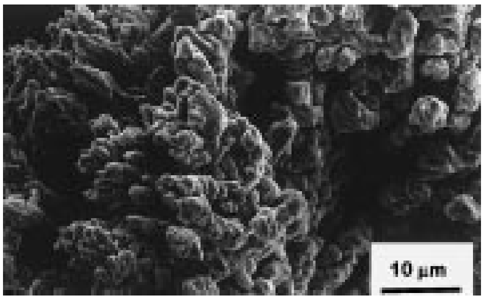

Fig. 6. SEM micrograph of Al surface after potentiostatic polarization at E_τ = −1.50 V for 10 min in 0.5 M Cl^-, pH 3 solution containing 0.01 M In^{3+} + 0.01 M Zn^{2+}. ω = 2000 rpm.

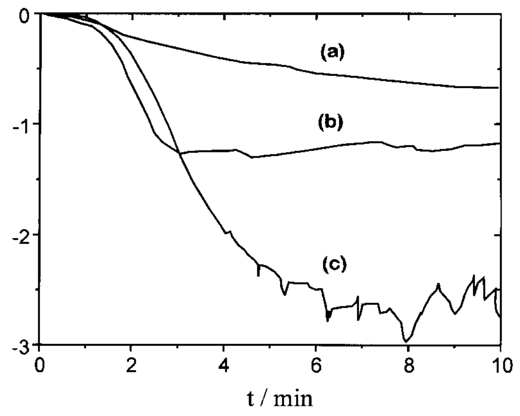

Fig. 7. Influence of pH on current density–time profiles for Al at $E_\tau = -1.50$ V in 0.5 M SO_4^{2-} solution containing 0.01 M In^{3+} + 0.01 M Zn^{2+}. pH: (a) 4; (b) 3 and (c) 2.

No significant changes were detected in the potentiostatic transient when 0.001 M Zn^{2+} was added to a solution containing 0.01 M In^{3+} without rotation (Fig. 11, curve (c)), indicating that the Zn^{2+} concentration is not sufficiently high to promote In deposition. However, in the stirred solution, the shape of the curve is similar to that obtained for a solution containing only 0.01 M In^{3+}, but higher currents were measured (Fig. 11, curve (d)).

The electrochemical response of 0.1 M Zn^{2+} + 0.01 M In^{3+} remained almost the same as found with 0.1 M Zn^{2+} [1].

3.3.7. Galvanostatic stripping. Further details of the process can be obtained by analysing the *E*/*t* transient. After the cathodic polarisation of Al at $\omega = 2000$ rpm in a solution containing 0.01 M Zn^{2+} + 0.01 M In^{3+}, a current step of 0.70 mA cm^{-2} was immediately applied. The chronopotentiogram without electrode rotation showed that the electrode potential was initially shifted to the Zn/Zn^{2+} potential (Fig. 12). Then, a current plateau due to the In dissolution was observed. Its partial coulombic charge was 70 mC cm^{-2}, which is very close to that obtained by potentiodynamic stripping (Fig. 5, curve (b)). The increase in *E* with time indicates simultaneous growth of Al oxide.

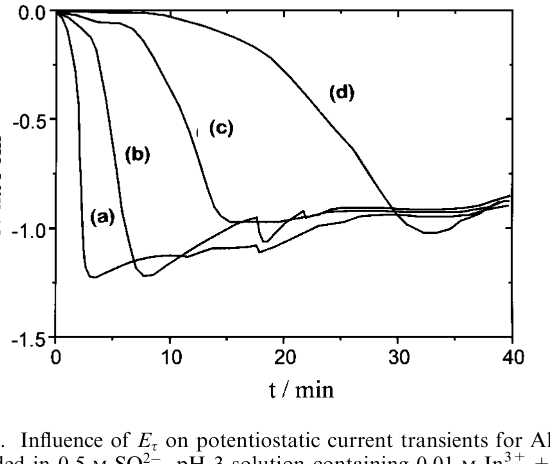

Fig. 8. Influence of E_τ on potentiostatic current transients for Al recorded in 0.5 M SO_4^{2-}, pH 3 solution containing 0.01 M In^{3+} + 0.01 M Zn^{2+}. E_τ: (a) −1.50; (b) −1.45; (c) −1.40 and (d) −1.35 V.

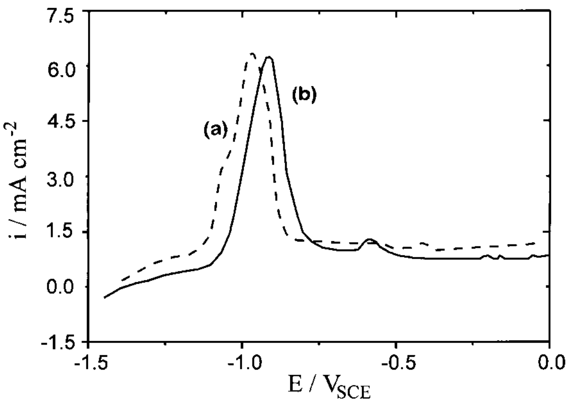

Fig. 9. Potentiodynamic polarization curve for Al at 0.100 V s^{-1} in a 0.5 M SO_4^{2-}, pH 3 solution containing 0.01 M In^{3+} + 0.01 M Zn^{2+} under stagnant conditions. The electrode was previously polarized (a) at $E_\tau = -1.40$ V for 1 h; (b) at $E_\tau = -1.45$ V for 10 min.

4. Discussion

The results of this study have shown that In was deposited on Al electrodes without alloying with Zn. The same results were obtained on vitreous carbon electrodes [7].

The experiments at −1.50 V in Cl^- solutions with no agitation showed that, for all times studied, In was preferentially deposited. In the early stages of cathodic polarization Zn-rich deposits were obtained in sulphate electrolyte, but the In content increased with time. However, Zn was preferentially deposited under agitation, independently of In^{3+} concentration. To explain the anomalous deposition, where less noble Zn deposits preferentially to the more noble metal, the hydroxide suppression mechanism seems to be the most accepted [8–10]. In this mechanism, the formation and adsorption of Zn hydroxide film inhibits the more noble deposition and favours Zn reduction.

The solubility of Zn oxide was reported as $10^{6.26}$ g atom dm^{-3} at pH 3, while at the same pH the solubility of In oxide is $10^{-0.35}$ g atom dm^{-3} [11]. Thus, in the presence of Zn and In ions the pH rise at the electrode surface due to the simultaneous evolution of hydrogen was expected to favour In hydroxide precipitation rather than Zn hydroxide. It is difficult to explain why In was preferentially deposited with-

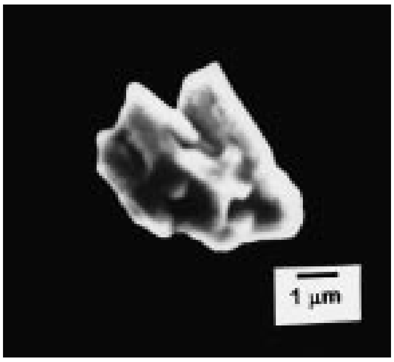

Fig. 10. SEM micrograph of Al surface after potentiostatic polarization at $E_\tau = -1.50$ V for 1.5 min in 0.5 M SO_4^{2-}, pH 3 solution containing 0.01 M In^{3+} + 0.01 M Zn^{2+}.

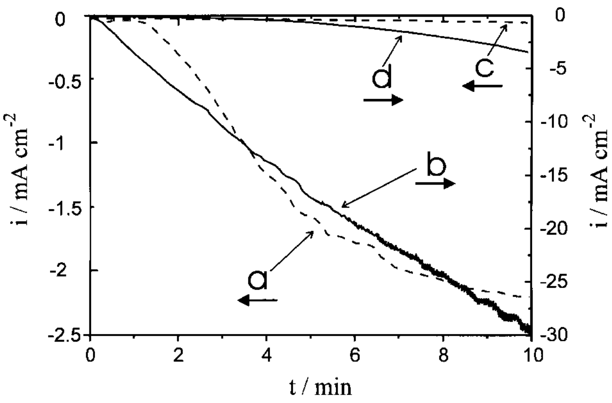

Fig. 11. Current density–time response for Al at $E_\tau = -1.50$ V in 0.5 M SO_4^{2-}, pH 3 solution containing: (a) 0.1 M In^{3+} + 0.01 M Zn^{2+}; without rotation; (b) 0.1 M In^{3+} + 0.01 M Zn^{2+}; ω = 2000 rpm; (c) 0.01 M In^{3+} + 0.001 M Zn^{2+}, without rotation and (d) 0.01 M In^{3+} + 0.001 M Zn^{2+}, ω = 2000 rpm.

out electrode rotation considering the Zn hydroxide formation and the reduction of Zn from this hydroxide. Also, no evidence of significant changes in deposit composition was obtained when varying solution pH. Under rotation, the possibility of a local pH rise was minimized. At low cathodic potentials the pH rise was expected to be lower. However, the deposit was rich in Zn. Therefore, all this experimental evidence denied the hydroxide suppression mechanism for this system.

The possibility that In^{3+} reduction occurred from In hydroxide may also be taken into account. The pH rise due to hydrogen evolution may be higher for a solution that contains In alone, because adsorption of Zn^{2+} on the Al surface may occur and this surface blockage reduces the hydrogen current [12]. Conversely, In deposition was very difficult for Zn-free solution. We conclude that the reduction of In from In hydroxide was not possible.

In the early stages of cathodic polarization, adsorption of Zn^{2+} mainly occurred compared to that of H^+ and In^{3+}[1, 12]. Then, the deposition of In on freshly nucleated Zn was favoured under no agitation. Thus, Zn has a catalytic effect on In deposition. However, when Zn^{2+} is present in high concentration near the electrode, as occurs under rotation, its discharge becomes the prevalent reaction. In other words, the deposition rate of Zn, controlled by mass transfer, produced a Zn-rich deposit.

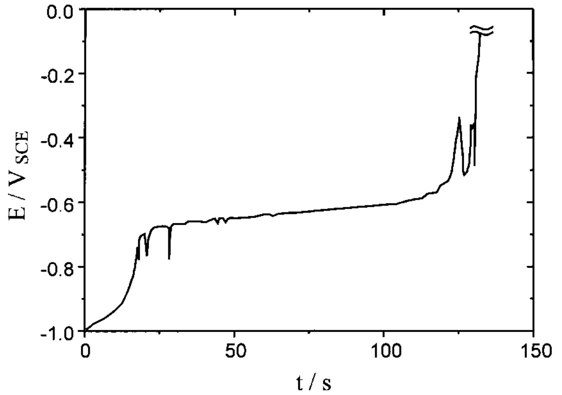

Fig. 12. E against t plot obtained for Al without rotation in 0.5 M SO_4^{2-}, pH 3 solution containing 0.01 M In^{3+} + 0.01 M Zn^{2+} after applying a current step of 0.70 mA cm^{-2}. The electrode was previously polarised at $E_\tau = -1.50$ V for 10 min at 2000 rpm.

The induction period for In nucleation on electrodeposited Zn in sulphate solution was higher compared to that obtained in Cl^- solution. This can be explained taking into account that In deposition is greatly improved in the presence of chloride ions [13]. Different deposit morphologies were observed, although the composition after 10 min of cathodic polarisation was anion independent.

The stripping efficiency was very low due to the insulating properties of Al oxide generated between the base metal and the deposit.

The anomalous codeposition was directly related to Zn ion transport. Probably, as was suggested by Gómez and Vallés [14], anomalous codeposition occurs when the depletion of Zn^{2+} near the electrode is avoided, as occurred under rotation. Electrodeposit characteristics attained during cathodic polarization determine the electrochemical response during activation of the Al electrode in chloride media at more positive potentials. Further work on this issue is being carried out.

5. Conclusions

This study of Zn and In electrodeposition on Al leads to the following conclusions:

(i) In the initial stages of cathodic polarisation Zn is preferentially deposited since its adsorption and nucleation on Al is favoured compared to that of H^+ and In^{3+}.

(ii) Deposition of In on freshly nucleated Zn is favoured at high cathodic potentials under no agitation, denoting the Zn catalytic effect. The process is accelerated in the presence of Cl^-. Deposits obtained in chloride or sulphate solutions result in similar compositions but different morphologies.

(iii) The fast transport of Zn^{2+} deposition under rotation hinders its depletion near the electrode and Zn rich deposits are obtained independently of In^{3+} concentration. Thus, large amounts of deposit with different composition and morphology are obtained under agitation.

(iv) The formation of alloy or intermetallic compounds between Zn and In was not detected.

Acknowledgements

This research was financially supported by the Universidad Nacional del Sur (PGIC–UNS) and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, PIA 7293/97)

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