

# Electrochemical characterisation of gallium–aluminium amalgams

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## Abstract

The electrochemical behaviour of aluminium recovered by a film of liquid gallium and gallium–aluminium amalgams in chloride and acetic acid solutions and in distilled water has been investigated using electrochemical and surface analytical techniques. The development of a very reactive interface is described. It is proposed that, besides gallium losses, the deposition of corrosion products on the electrode surface also contributes to passivation. The influence of electrode configuration and electrolyte composition on the development of the active interface as well as on its posterior deactivation is discussed.

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## 1. Introduction

Pure Al is unsuitable for use as a sacrificial anode material because the presence of a protective oxide film on its surface. Gallium, among other low melting point elements, when added to Al produces alloys with more negative potentials than unalloyed Al [1,2]. Pure Al can also be activated in solutions containing gallium ions [3,4] or in molten Ga[AlCl<sub>4</sub>] [5]. It was considered that activation of Al–Ga alloy is related with an accumulation of a layer of Ga which allows rapid diffusion of Al through the Ga overlayer [1]. It was also proposed that the activation is related with the increased adsorption of chloride ions at more negative potentials [3,4].

In a previous paper it was reported that a very negative potential was measured when metallic gallium was mechanically attached to Al [6]. This effect was explained considering that an amalgam is formed, which detaches the oxide film and avoids repassivation. Depending on whether Ga at the active interface is solid or liquid, two activation mechanisms of Al dissolution are operative: (i) when sufficient amount of Ga at quasi-liquid state is present, an amalgam is responsible for the activation process and (ii) at higher anodic potentials where the presence of solid Ga (saturated amalgam) at the interface facilitates a chloride adsorption process which depolarises the anodic reaction.

Because the proposed mechanism considers the formation of an amalgam, a better knowledge of the effects of Ga on the activation of Al can be obtained by analysing the electrochemical behaviour of Ga–Al amalgams.

It is well known that Al and their alloys may be embrittled by molten Ga over a range of conditions [7–9]. The melting point of pure gallium is 29.7 °C but this is lowered somewhat by the presence of aluminium, so that the phenomenon of liquid metal embrittlement occurs even at room temperature [9]. However, there are few data on the electrochemical behaviour of the interface generated when oxide-free Al surface is brought into contact with liquid gallium.

The aim of the present work is to get a better knowledge of the electrochemical response of Ga–Al amalgams and gallium-wetted aluminium electrodes in distilled water, and in weakly chloride and acetic acid electrolytes.

## 2. Experimental details

Three working electrodes were used in the present work:

- (i) Gallium–aluminium amalgams. The amalgams have been prepared with high purity metals and Al has been added in amounts ranging 0.5–5.0 wt%. Preweighed amounts of Al were dipped in concentrated NaOH solution for about 180 s in order to remove the aluminium oxide and then they were placed in a pool of liquid Ga under vigorous stirring. This was placed into a Teflon holder with an exposed area of 0.50 cm<sup>2</sup> and the electrical contact was made with a platinum wire inserted through the bottom of the holder.

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- (ii) Aluminium disc electrodes covered with gallium. The discs were embedded in a Teflon holder with an exposed area of  $0.07 \text{ cm}^2$ . A drop of liquid Ga (0.15–0.20 g) was placed on top of the disc surface which was previously treated with concentrated NaOH solution.
- (iii) Aluminium sheet electrodes covered with gallium. Aluminium sheets of 1 mm thick with an exposed area of  $1 \text{ cm}^2$  were also treated in concentrated NaOH solution to make the liquid Ga wet the aluminium surface.

It should be pointed out that the Ga–Al amalgams as well as the wetting Ga film are liquid at the working temperature ( $25^\circ\text{C}$ ).

The auxiliary electrode was a large Pt sheet. Potentials were measured against a SCE reference electrode.

Potentiodynamic and open circuit-time experiences were performed with a potentiostat-galvanostat PAR Model 273A. A dual stage ISI DS 130 SEM and an EDAX 9600 quantitative energy dispersive X-ray analyser were used to examine the electrode surface characteristics.

Chloride solution (0.5 M NaCl) was prepared and the pH was adjusted to 2.5 with HCl. Acetic acid (HAc) solutions (0.5 M) were also used. All chemicals were reagent grade and solutions were freshly made in triply-distilled water. Measurements were performed in a purified nitrogen gas saturated atmosphere.

### 3. Results

#### 3.1. Studies in chloride media

##### 3.1.1. Potentiodynamic polarisation measurements

Fig. 1 shows the potentiodynamic anodic polarisation for Ga–Al amalgams containing different amounts of Al at  $0.005 \text{ V s}^{-1}$  in a 0.5 M NaCl, pH 2.5 solution. The responses corresponding to pure gallium (Fig. 1) and gallium-wetted aluminium electrodes (Fig. 2) are also presented. No electrodis-solution process takes place for pure Ga in the potential range analysed. It is seen from Fig. 1 that Ga–Al electrodes exhibit exceptionally active dissolution under anodic polarisation. A linear current increase is observed and much higher currents are measured for increasing Al content. The onset of anodic oxidation occurs at about  $-1.75 \text{ V}$ . For the cases of Ga–Al amalgams and Ga-wetted Al disc electrode, as soon as the scan initiates it was observed corrosion products as a gelatinous material emanating from the electrode towards the solution while the surface of the sample kept its metallic appearance. A different response was obtained when an Al sheet covered by Ga was used. In this case it was observed the formation on the surface of a dark prod-

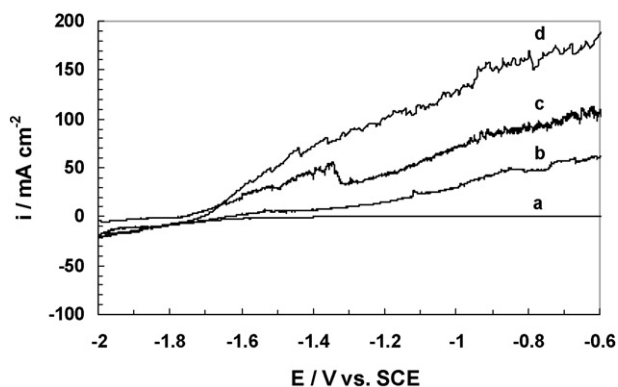


Fig. 1. Potentiodynamic polarisation of Ga–Al amalgams and pure Ga at  $0.005 \text{ V s}^{-1}$  in a 0.5 M NaCl, pH 2.5 solution at  $25^\circ\text{C}$ : (a) pure Ga, (b) Ga-0.5 wt% Al, (c) Ga-1 wt% Al and (d) Ga-5 wt% Al.

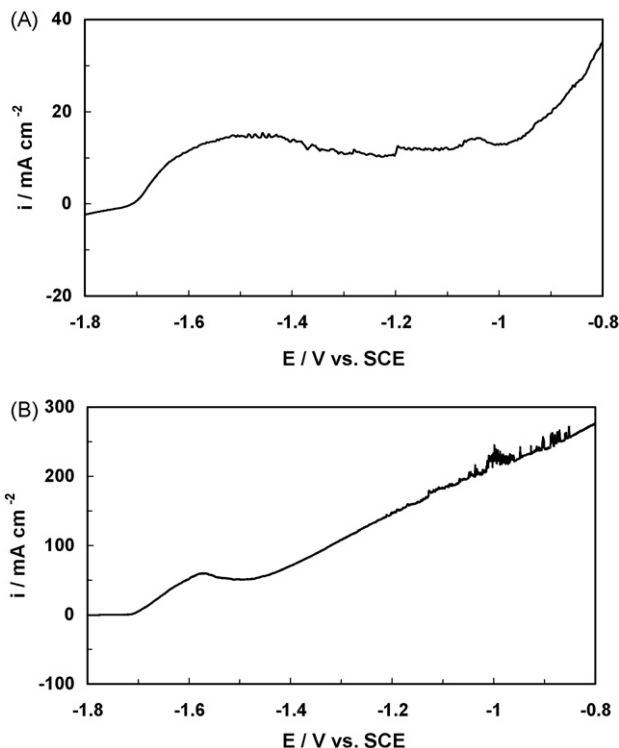


Fig. 2. Potentiodynamic polarisation of Ga-wetted Al electrodes at  $0.005 \text{ V s}^{-1}$  in a 0.5 M NaCl, pH 2.5 solution at  $25^\circ\text{C}$ : (A) Al sheet electrode covered with liquid Ga and (B) Al disc electrode covered with liquid Ga.

uct that initiates at the edges of the sheet and propagates towards the centre of the sample. Then Ga detached from the electrode and fell to the bottom of the cell. When this happens, the current density stops increasing and current fluctuations are recorded (Fig. 2A).

The anodic maximum is more clearly defined for a gallium-wetted aluminium disc electrode (Fig. 2B) and the influence of the scan rate ( $v$ ) on the anodic polarisation was analysed. Fig. 3A shows some representative examples of the curves obtained at different scan rates. A linear relationship was observed between the peak current and the square root of the scan rate in the range of  $0.0025$ – $0.075 \text{ V s}^{-1}$  (Fig. 3B), indicating a diffusion-type control for the oxidation process. The voltammetric response did not change when the solution was magnetically stirred. Moreover, the charge of the peak is practically independent of chloride concentration in the range of 0.1–2 M, and of solution pH in the range of 2.5–6.5. It should be mentioned that activation ceased almost instantaneously when the sample was immersed in a chloride solution with a concentration lower than 0.05 M.

##### 3.1.2. Open circuit potential-time measurements

Further details of the corrosion process can be obtained by examining the open circuit potential (OCP) against time for the different type of electrodes. Fig. 4 shows the OCP vs. time plot obtained for pure Ga (curve a) and Ga-1 wt% Al amalgam (curve b) in chloride solution. As soon as the amalgam electrodes were immersed in the solution very negative potentials were measured. These potentials are closed to those corresponding to the

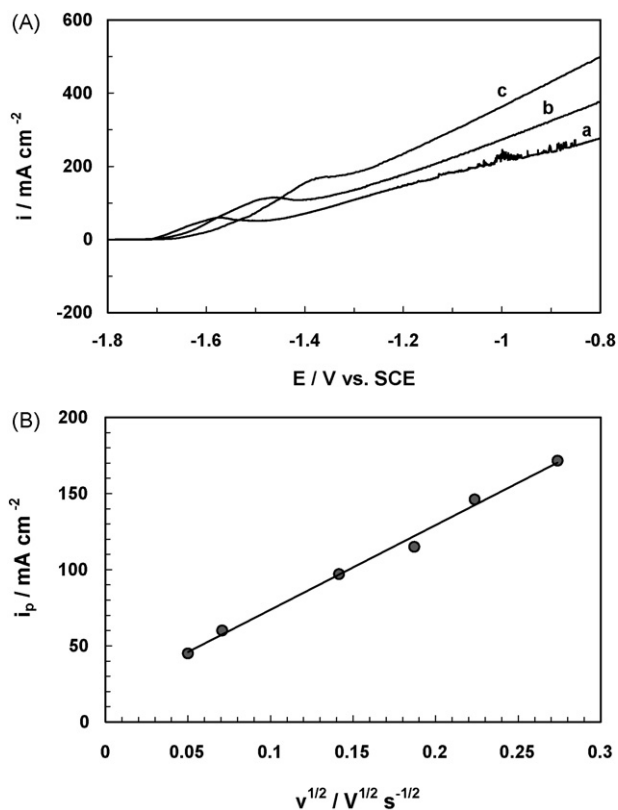


Fig. 3. (A) Potentiodynamic polarisation of Ga-wetted Al disc electrodes at different scan rate in a 0.5 M NaCl, pH 2.5 solution at 25 °C: (a) 0.005 V s<sup>-1</sup>, (b) 0.035 V s<sup>-1</sup> and (c) 0.075 V s<sup>-1</sup>; and (B) relationship between peak current density ( $i_p$ ) and  $v^{1/2}$  derived from voltammetric data.

onset of anodic currents in the  $i/E$  curves presented in Fig. 1. Afterwards the OCP for the Ga–Al amalgam increases in the positive region and the curve tends to become coincident with that of pure Ga. In the case of Ga-wetted Al sheet electrodes, the activation is maintained for much longer periods of time and finally the potential shifted positively to a value close to that corresponding to the Al–Ga alloys [10] (Fig. 5). At this stage, the potential of the disc, although unstable, remained active. After a few seconds of immersion, corrosion products have seen to be emanating from the surfaces of all the samples, together with hydrogen evolution. It was observed that the Ga–Al amalgams

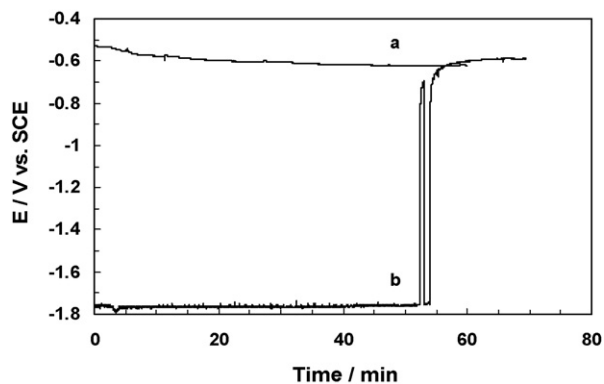


Fig. 4. Open circuit potential vs. time of pure Ga (curve a) and Ga-1% wt Al amalgam (curve b) in a 0.5 M NaCl, pH 2.5 solution at 25 °C.

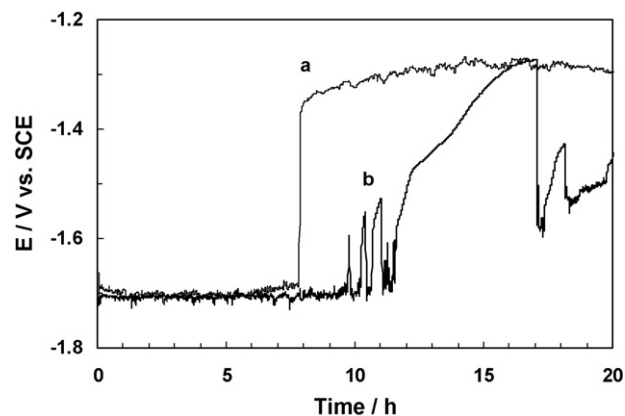


Fig. 5. Open circuit potential vs. time of Ga-wetted Al electrodes in a 0.5 M NaCl, pH 2.5 solution at 25 °C. (a) Al sheet electrode covered with liquid Ga and (b) Al disc electrode covered with liquid Ga.

maintained their metallic brightness when they were extracted from the cell. The Ga-wetted Al electrodes became gradually covered by a film of corrosion products and the solution was turned very cloudy at prolonged immersion times. When the potential of the recovered sheet electrode shifted to more positive values, it was observed the same sequence of events previously described for the electrode undergoing potentiodynamic polarisation. That is, Ga and the corrosion products deposited on it were detached from the sheet.

In order to gain more insight about the dissolution process an analysis of the corrosion products formed on the Ga-wetted Al sheet electrode was performed by SEM/EDX. The electrode was removed from the solution when the reactive interface was developed (–1.7 V) (Fig. 5, curve a). SEM micrograph of the activated sample (Fig. 6A) shows spherical particles of Ga (Fig. 6A, point a) determined by EDX (Fig. 6B) within a thick spongy oxide (Fig. 6A, point b) that covers the electrode surface. EDX analysis performed on the spongy oxide (Fig. 6C) showing different amount of Ga, Al, O and Cl. After removing the corrosion products, the film of Ga wetting the Al sheet could still be seen. A sample was also removed when the activity ceased (–1.3 V) and according to the image shown in Fig. 7, it is observed that the sheet was subjected to exfoliation corrosion.

### 3.1.3. Effects of temperature

The influence of temperature was analysed for the Ga-wetted Al sheet electrode. Polarisation curves and OCP vs. time plots in a 0.5 M NaCl, pH 2.5 solution at 3 °C are shown in Figs. 8 and 9, respectively. The low temperature scan reveals that the current–voltage curve is almost identical than that for the Al–Ga alloy [10]. On the other hand, the OCP measured at 3 °C is more positive than that measured at 25 °C (Fig. 9).

### 3.2. Studies in distilled water and in acetic media

The electrodes were also immersed in distilled water where only a very temporary activation was observed. After a few seconds of immersion, the formation of a dark product was observed accompanied by a violent hydrogen evolution. Immediately after

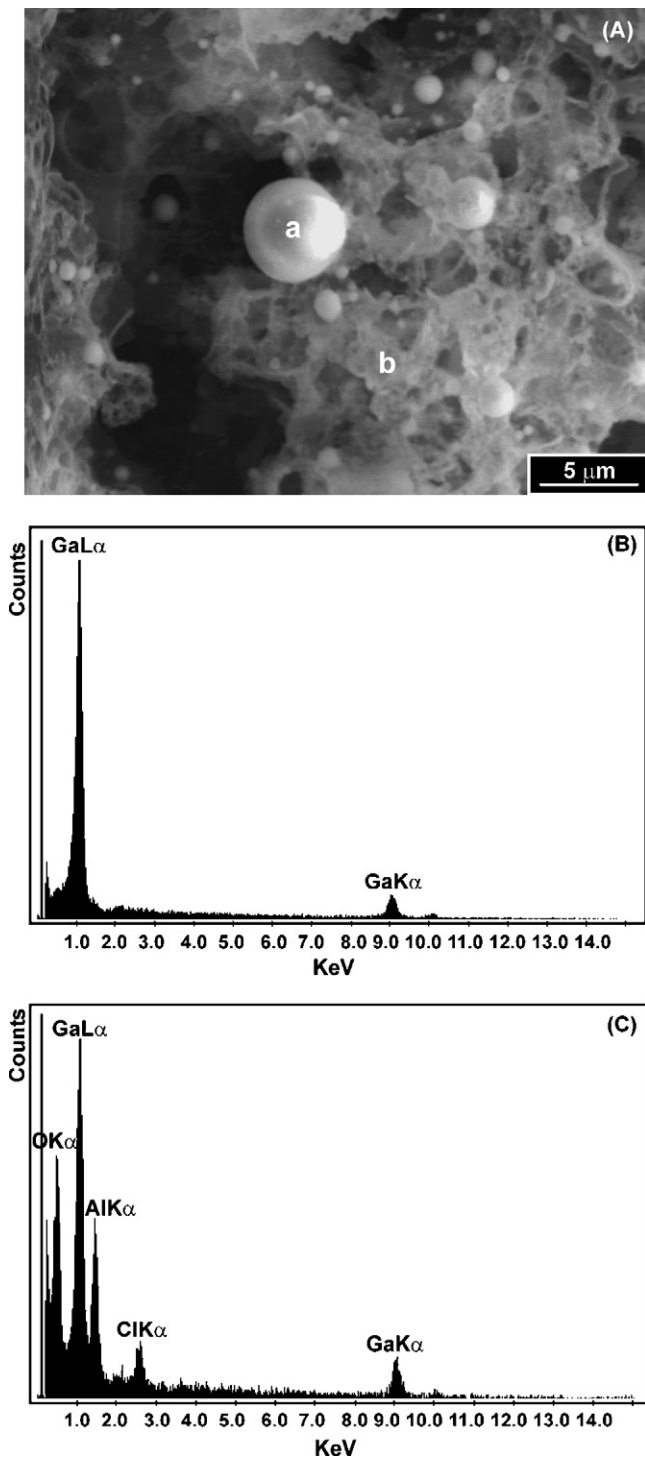


Fig. 6. (A) SEM micrograph showing the electrode surface of an Al sheet covered with liquid Ga. The sample was removed from the 0.5 M NaCl, pH 2.5 solution after 1 h of immersion, (B) EDX spectrum of the spherical particle (point a) and (C) EDX spectrum of the spongy oxide (point b).

these events, all sign of activity disappears and the surface passivates. This was observed for all types of electrodes used in this work. A similar sequence of events was observed in HAc, where the OCP-time dependence for a Ga-wetted Al sheet was measured (Fig. 10). The potential remains around  $-1.65$  V during 60 s and then it tends to  $-1.050$  V, indicating that the time of

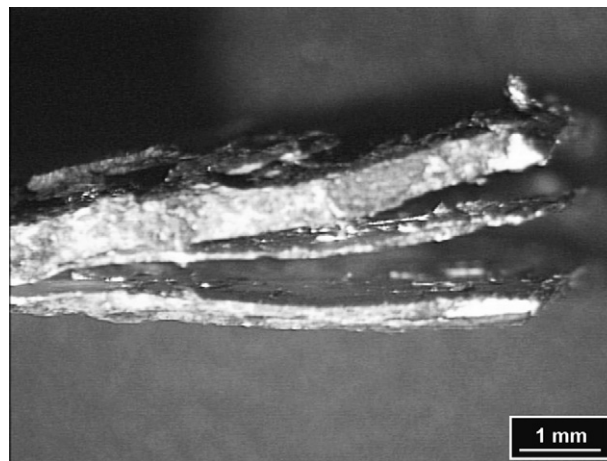


Fig. 7. Macroscopic photograph showing the Al sheet electrode covered with liquid Ga after 20 h of immersion in 0.5 M NaCl, pH 2.5 solution.

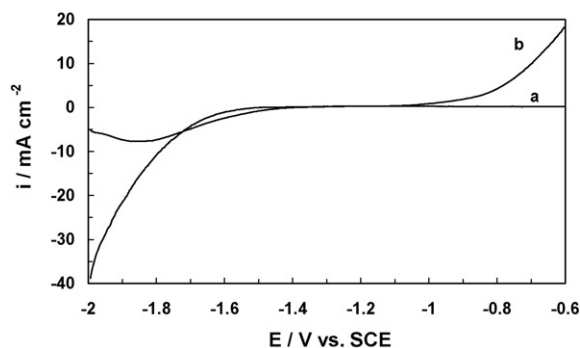


Fig. 8. Potentiodynamic polarisation of pure Ga (curve a) and Ga-wetted Al sheet (curve b) at  $0.005 \text{ V s}^{-1}$  in a 0.5 M NaCl, pH 2.5 solution at  $3^\circ\text{C}$ .

active behaviour in HAc solution was significantly shorter than that in chloride media.

#### 4. Discussion

Aluminium corrosion in chloride medium has been extensively studied. When Al is covered by its oxide, its dissolution is controlled by the interaction between chloride ions and the oxide film originating pitting corrosion [11]. Aluminium diffusion into Hg or Ga brings Al free of its oxide at the amalgam/electrolyte

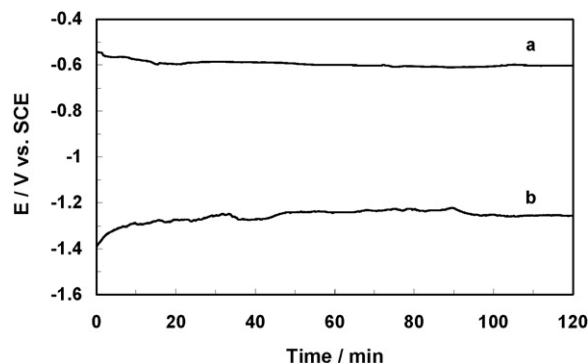


Fig. 9. Open circuit potential vs. time of pure Ga (curve a) and Ga-wetted Al sheet (curve b) in a 0.5 M NaCl, pH 2.5 solution at  $3^\circ\text{C}$ .

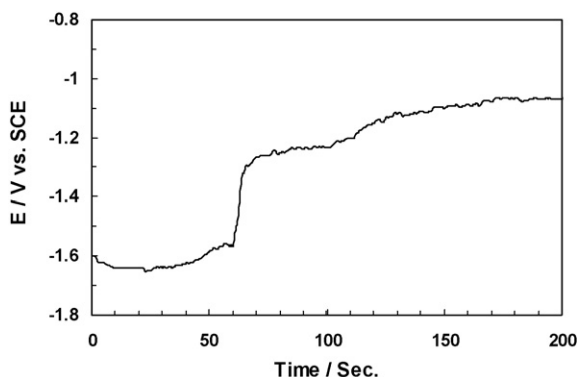


Fig. 10. Open circuit potential vs. time of Ga-wetted Al disc in a 0.5 M HAc, pH 2.5 solution at 25 °C.

interface where it is oxidised and then, very reactive interfaces are created. The length of the active interface will depend on the composition of the electrolyte solution. The polarisation curves presented in Fig. 1 indicate that very high currents associated with Al oxidation are measured in chloride solution in a potential range where Ga remains passive.

Results in Fig. 4, curve b and Fig. 5 demonstrate that as soon as the substrate is immersed in the chloride solution the corrosion reaction takes place. As Al is oxidised, it is replaced by Al coming from the amalgam, the disc or the sheet. The liquid Ga film acts as a medium for rapid transport of Al atom from the solid–liquid interface to liquid–liquid interface where it is oxidised to  $\text{Al}^{3+}$ . As expected, an inactive interface was produced when Ga is in the solid state by lowering the solution temperature (Fig. 8, curve b and Fig. 9, curve b). This electrode behaviour resembles that of the Al–Ga alloy [10]. The very reactive interface is maintained during prolonged times in the case of Ga-wetted Al electrodes which provide a more permanent source of fresh Al. The corrosion products deposited onto the surface of an activated sample consist of aluminum oxide/hydroxide, spherical particles of Ga in between and some amount of chloride entrapped into the film (Fig. 6).

A diffusion-type control for the oxidation process at the lower overpotentials can be inferred from the linear dependence between the peak current and the square root of the scan rate (Fig. 3B). This diffusion control could be given by the Al diffusion through liquid Ga or by the mass transport of  $\text{Al}^{3+}$  towards the bulk of the solution. The independence of the voltammetric response with the hydrodynamic conditions suggests that the process is controlled by the diffusion of Al in the film of Ga. Besides, the fact that the peak charge is practically independent of the chloride concentration and solution pH is also consistent with a diffusion-type process limited by the transport of Al in the liquid film in the potential range analysed. At higher overpotentials the film of corrosion products acts as an ohmic resistance.

It was reported that reactions between Hg-wetted Al in liquid water conducted to the formation of Al oxide [12]. It is likely that the same product is formed when the Al sample is covered with Ga. At this point it should be taken into account a remarkable difference between Al diffusion in Hg and Ga. While the Al solubility in Hg is extremely low at room temperature (0.003 wt%)

[13], Al is soluble in Ga up to about 2 wt% [14]. Another contrast exists between the diffusion coefficient of Al in liquid Ga and Hg, which is  $0.64 \text{ cm}^2 \text{ s}^{-1}$  [1] and  $1.65 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  [15], respectively. It was postulated that because the low solubility of Al in Hg, the dilute solution of Al in Hg is incapable of creating a self-protective oxide film at the amalgam/solution interface, and then an active state is developed [16]. On the contrary, due to the higher solubility of Al in Ga a lot amount of oxide can be formed, blocking of the active surface of the electrode by the corrosion product. When this happens the wetting ceases with subsequent exposure of bare Al surface to water. Then, a violent hydrogen evolution accompanies Al dissolution and finally the surface is passivated by a dark product. This quick loss of activity, which was also observable in the presence of HAc, caused the potential to rise (Fig. 10). The length of activation increases in the presence of chloride since the blocking of active sites is retarded by the competitive formation of Al chloride complexes.

It was previously reported that when a Ga particle was placed in a hole drilled on an Al sheet and this sample was immersed in distilled water, HAc or NaCl solutions a quick activation was observed with a strong  $\text{H}_2$  evolution followed by a rapid passivation given by a grey product [6]. It was suggested that losses of Ga produce a Ga film thinning which facilitates amalgam saturation. Gallium losses originate from lateral surface diffusion, bulk intergranular diffusion, surface turbulence (given by mechanical agitation during strong hydrogen evolution) and convective forces (exothermic hydrolysis reaction of  $\text{Al}^{3+}$ ). It is unlike that these Ga losses take place when the Ga-wetted Al disc electrode was exposed to water. In this case the accumulation of oxide on the electrode surface would be the principal factor in reducing Al dissolution by blocking the activation sites. Moreover, the linear dependence between oxidation currents and potential in Fig. 1 suggests the build-up of an ohmic resistance due to poorly conductive corrosion products on the electrode surface. It is probably that the surface tension of Ga increases as a result of the presence of these products on the amalgam.

It was postulated from vacuum measurements that aluminium solute in gallium–aluminium alloys will be oxidised to form aluminium oxide which is insoluble in the liquid gallium, and so a surface layer of aluminium oxide will be built up even in a very dilute alloy [17]. Thus, the formation of a thin layer of this oxide is probably responsible for the loss of activity in the Ga–Al amalgams (Fig. 4, curve b).

The very reactive interface is maintained during prolonged times in the case of Ga-wetted Al electrodes although the rate of penetration of Ga into Al is significantly higher in the sheet than in the disc. Liquid Ga diffuses predominantly along the grain boundaries in the rolling direction of the aluminium sheet, forming corrosion products that forced metal away from the body of the material, giving rise to a layered appearance (Fig. 7).

When the passive state was reached, the potential measured depends on the amount of Al still remaining at the interface. In the case of the Ga–Al alloys this amount is expected to be very small and the potential corresponds to that of pure Ga (Fig. 4). In the case of Al electrodes covered by Ga, the content of Al is

high enough to allow the formation of an Al–Ga alloy, which has a determinant effect on the electrode potential (Fig. 5).

Contrasting with the behaviour of the electrodes used in this work, when a Ga particle was mechanically attached to Al the activation is maintained for a short period of time even in chloride solution [6]. The particle is an anodic area which is surrounded by a large cathodic area (Al). Comparing with the Ga-wetted Al electrodes it is expected a higher local alkalisation when a particle of Ga is attached to Al because the relative low hydrogen overpotential for Al compared to Ga. This fact would contribute to attain a rapid passivation even in chloride solution.

## 5. Conclusions

The following conclusions may be drawn from the obtained results.

Very negative potentials were measured when Al is brought into contact with liquid Ga in distilled water and in chloride and acetic acid media. The development of this active state is ascribed to the oxidation of oxide-free Al at the amalgam/electrolyte interface. Dissolution of free Al ceases by amalgam saturation due to Ga losses, as was concluded previously [6]. According to the present results, surface covering by a passive oxide film also contributes to deactivation. The interface remains active for longer periods of time in the presence of chloride. Activation is hindered principally by the build-up of an Al oxide on the surface of the Ga–Al amalgams. Comparing with Ga–Al alloys, Ga-wetted Al electrodes are not quickly passivated and for longer times oxidation of Al proceeds continuously. The electrochemical behaviour depends on the metallurgical structure of the material. Unlike the Al disc plated with Ga, high losses of Ga in the case of the covered Al sheet results in exfoliation corrosion. When dissolution ceased, Ga was detached from the Al surface and the electrode potentials shifted to more positive values.

Under anodic polarisation, the activation would be controlled by a diffusion-type process given by the diffusion of Al in the liquid film of Ga. Towards more positive potentials the dissolution is controlled by the rate of ionic migration through the film of reaction products.

## Acknowledgments

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