



Aluminium activation produced by gallium

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Abstract

The electrochemical behaviour of pure aluminium in the presence of gallium ions or in direct contact with gallium, in chloride, acetic acid solutions or distilled water is reported. The enhance activity of aluminium is described and discussed. Two active regions were observed, one at approximately -1.5 V and the second at near -1.1 V.

Two activation mechanisms are proposed. One where a critical surface concentration of liquid gallium is achieved, a Ga–Al amalgam is responsible for the activation process (-1.5 V) and a uniform attack morphology is observed. This process is favoured by the exothermic Al ion hydrolysis reaction and hindered by Ga losses at the active interface. And a second at higher anodic potentials (near -1.1 V), and in chloride containing media, where the presence of solid Ga (saturated amalgam) at the interface facilitates a chloride adsorption process which depolarised the anodic reaction, and produced localised attack.

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1. Introduction

It is well known that Ga, among others activator elements, when added to Al produces surface activation in chloride media, shifting the operating potential to more

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negative values [1,2]. It has also been demonstrated that pure Al can be activated in solutions containing gallium ions [3,4] or in molten Ga[AlCl₄] [5]. However, some controversy exists about the mechanism of activation. Bai and Conway have described a temporary activation effect of Ga in an Al–Ga alloy in an anhydrous solution of AlCl₃ in CH₃CN [6]. This effect appeared after the alloy had been kept at the open-circuit potential and was attributed to a process of slow diffusion of Ga leading to its accumulation on the electrode surface.

Tuck et al. have proposed that activation of Al–Ga alloys in chloride media takes place at localised surface sites which are associated with Ga particles at the metal/oxide interface [1]. These particles caused local thinning of the passivating film and then Al from the alloy diffuses rapidly through the Ga prior to its oxidation. The dissolution of the alloy occurred via the formation of a surface Ga–Al alloy. Gallium must be in the liquid state to be effective in its activation procedure.

It was possible to deposit Ga onto the Al surface by a cathodic polarization at -2.0 V in chloride solutions containing Ga³⁺ [3]. This was achieved by an alkalization process which favoured the formation of hydrolysed gallium species of the form HGaO₃²⁻ and GaO₂⁻ which subsequently led to the formation of metallic gallium at the surface. But the deposition of Ga achieved by this process is not sufficient to provide complete activation. The authors suggested that the role of Ga is to bias the surface charge in the direction of activation. This biased condition facilitates the adsorption of halide anions at more electronegative potentials than those observed with unalloyed Al. El Shayeb et al. have also considered that the activating effect of Ga was related with the increased adsorption of Cl⁻ ions at more negative potentials [4].

Liquid metal embrittlement (LME) of Al by liquid Ga is a well-known phenomenon [7–9]. The precursor process is the penetration of Ga into the grain boundaries of polycrystalline Al. This process occurs when liquid Ga wets the surface of Al.

In a previous paper, the activation of Al–Zn alloy by In deposition was studied [10]. The very active potential measured, about -1.5 V, was explained by an amalgam-activation mechanism. The presence of zinc-rich zones in the alloy favours In enrichment at the interface by a displacement reaction. Because of the low melting point of Ga, the study of the Al activation by Ga offers new possibilities to understand this type of mechanism. On the other hand, the cathodic deposition of Ga onto Al does not produce the active electrode potentials attained with Al–Ga alloys [2,3]. The understanding of this discrepancy is also of interest.

The aim of the present paper was to obtain additional information concerning the actual surface state that produces the Al activation process. The study of the electrochemical behaviour of Al was investigated in the presence of Ga³⁺ and also with metallic Ga on the Al surface in distilled water, and in weakly chloride and acetic acid electrolytes at different temperatures.

2. Experimental

Disc electrodes of 0.07 cm² were made from pure Al (99.999%, Aldrich Chemical Company), or 1 mm thick Al sheet (99.99%, with 5 ppm of Si, 4 ppm of Fe and

3 ppm of Cu). The discs were polished with 1000 emery paper followed by 1 and 0.3 μm grit alumina suspensions and then cleaned with triply distilled water. Another set of experiments were performed using an Al sheet (1 cm^2 to 1 mm thick) with a Ga particle (30–50 mg) mechanically attached. Afterwards the sheet was heated and the surface underneath the liquid gallium was scratched with a glass tip in order to break the aluminium oxide film, and reached a true metallic contact.

The auxiliary electrode was a large Pt sheet. Potentials were measured against a SCE reference electrode connected through a Luggin–Haber capillary tip.

Chloride solution (0.5 M NaCl) and acetic acid (0.1 M HAc) solution were prepared from analytical grade chemicals and triple-distilled water.

The pH was adjusted with HCl to 2.5.

Potentiodynamic and open-circuit time experiments were performed with a potentiostat–galvanostat PAR Model 273A.

A dual stage ISI DS 130 SEM and an EDAX 9600 energy dispersive X-ray analyser were used to examine the electrode surface characteristics.

3. Results

3.1. Gallium ions in acidified chloride solution

Pitting of aluminium is a localised process controlled by the adsorption potential of Cl^- ions [11]. The possible influence of Ga in this process was analysed. Fig. 1 shows the potentiodynamic anodic polarisation at 0.001 V s^{-1} for an Al electrode after cathodic polarisation at -2.0 V in 0.5 M Cl^- , pH 2.5 solution with and without

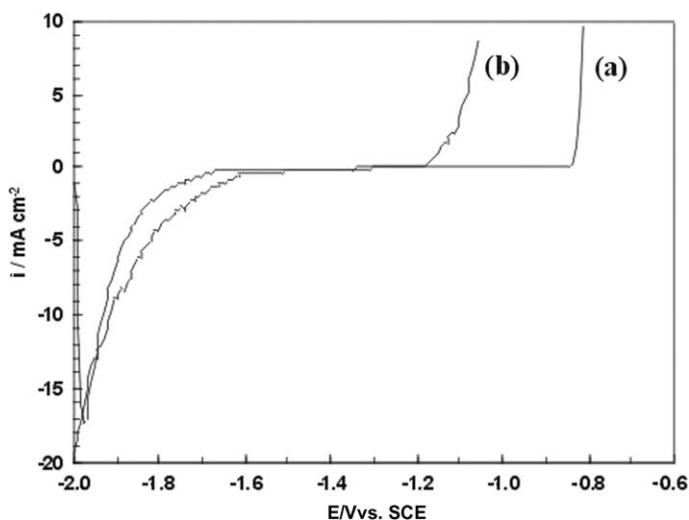


Fig. 1. Potentiodynamic polarisation of Al at $v = 0.001 \text{ V s}^{-1}$ in 0.5 M NaCl, pH 2.5 without Ga^{3+} (curve a) and with 0.01 M Ga^{3+} (curve b). The electrode was previously cathodised at -2.0 V during 30 min.

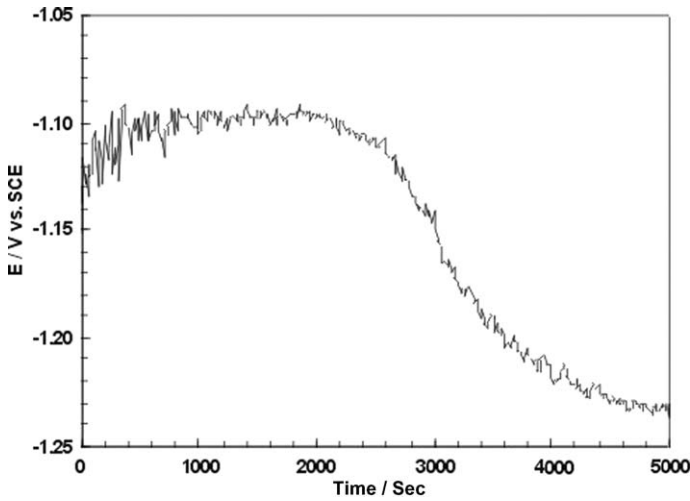


Fig. 2. Open-circuit potential (OCP) vs. time plot of Al in 0.5 M NaCl, pH 2.5 containing 0.01 M Ga^{3+} . The electrode was previously cathodised at -2.0 V during 30 min. After elapse of 2000 s, the temperature of the electrolyte was increased from 22 to 50 °C.

0.01 M Ga^{3+} . In the absence of Ga^{3+} after the polarisation at -2.0 V, the pitting potential is observed at -0.83 V (Fig. 1, curve a). If the Al electrode was not held at -2.0 V prior to the potentiodynamic sweep, the pitting process initiates at -0.77 V. This result is explained by the oxide hydration/elimination by local alkalinisation resulting from H_2 evolution [12]. In the presence of Ga deposited from the solution after the polarisation at -2.0 V, the breakdown potential is -1.2 V (Fig. 1, curve b). The presence of Ga has changed the chloride adsorption potential on the Ga–Al interface.

Further details of the activation process can be obtained by analysing in chloride media the open-circuit potential (OCP) against time. Fig. 2 shows the OCP against time profile obtained after cathodic polarisation at -2.0 V in the presence of Ga^{3+} . The initial OCP is not very reproducible but was always lower than -1.12 V, denoting that some activation in the pitting process of the Al electrode took place. Then the potential moves positively indicating that activation is not maintained. After about 30 min, the temperature of the electrolyte was increased to 50 °C. After this, the electrode potential shifts to -1.24 V. In the case of Al without deposited Ga from the solution, the increase of temperature results in a potential shift of only 10 mV.

3.2. Gallium ions in acetic acid solution

In order to analyse the influence of a non aggressive anion and temperature on the activation process, the OCP of an Al electrode was measured in a solution of 0.1 M HAc with 0.01 M Ga^{3+} . The electrode was first polarised at -2.0 V in a solution with Ga^{3+} at 22 °C and after this its OCP was measured. In this case the OCP was shifted to -0.3 V, denoting passivation. When the same experiment was performed at 50 °C,

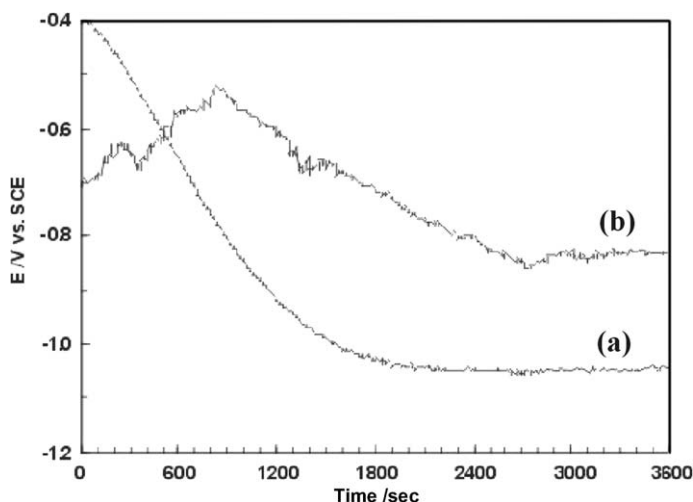


Fig. 3. Open-circuit potential (OCP) vs. time plot of Al in 0.1 M HAc, pH 2.5 with 0.01 M Ga^{3+} (curve a) and without Ga^{3+} (curve b) at 50 °C. The electrode was previously cathodised at -2.0 V during 30 min.

(Fig. 3, curve a) the OCP shifts slowly in the negative direction achieving a value of -1.050 V. An OCP value of -0.820 V was measured when the Al electrode was previously polarised at -2.0 V in a solution without Ga^{3+} at the same temperature (Fig. 3, curve b). Thus, the results show that activation was produced in presence of Ga and at 50 °C, although the degree of activation attained is lower than that in chloride media.

3.3. Metallic gallium experiments

3.3.1. In distilled water

Information about the Al activation exerted by Ga was also obtained when metallic gallium was mechanically attached to Al. First, in order to obtain a metallic contact between the Al sheet and the Ga particle, a hole on the Al sheet was drilled (Fig. 4a) and a Ga particle was placed on top (Fig. 4b). Afterwards, the Al sheet was heated until Ga was liquid. In this condition, several drops of distilled water were placed on top. Immediately a strong reaction took place, producing a huge amount of H_2 bubbles (Fig. 4c) and heat due to the exothermic Al^{3+} hydrolysis reaction, which tends to dry the reactive surface (Fig. 4d). It is observed an oxide coming from the zone where the Ga particle was placed (Fig. 4e and f), till complete dryness was reached (Fig. 4g and h). Here, tiny metallic droplets within the corrosion products can be seen (Fig. 4h). The corrosion products were analysed by SEM/EDX. Fig. 5a shows points where EDX analysis was performed: point 1, on the nearest surrounding area of the particle; point 2, on the following surrounding area and point 3 on the oxide-feathers like. EDX results are presented in Fig. 5b–d, respectively, showing different amount of Ga and Al. A close view of the surrounding area of

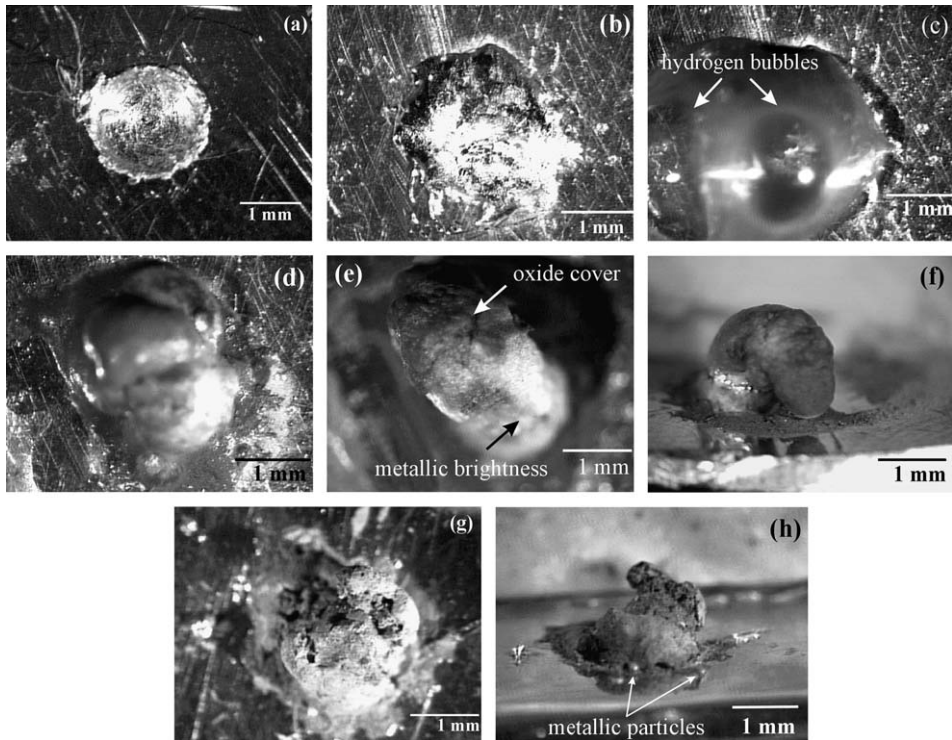


Fig. 4. Chronological sequence of macroscopic photographs of pure Al in metallic contact with Ga after placing a drop of distilled water on top: (a) hole drilled on the Al sheet; (b) gallium placed on the hole; (c) and (d) formation of big hydrogen bubbles after placing a drop of distilled water on top; (e) and (f) plant and lateral views, respectively, of corrosion products coming from the zone where gallium was placed; (g) and (h) plant and lateral views, respectively, after complete dryness.

the particle shows a mud-cracked structure of passive product and tiny Ga particles in between (Fig. 6). After cleaning the surface with distilled water a better insight of the concentric surface diffusion of Ga from the particle can be seen (Fig. 7—zone 1, 2 and 3—marked with a dotted line). It produced a smooth-wide cavities attack morphology. If the same procedure is repeated and afterwards the Ga solid particle is cleaned in distilled water (Fig. 8) and separately analysed, the presence of Al can be clearly observed (Fig. 9), denoting the formation of an amalgam.

3.3.2. In different media and temperature

Another set of experiments also shows important features related to the amount of Ga needed to reach full activation of Al and the corresponding working temperature. In these cases, experimental conditions were more controlled in order to measure the OCP. After mechanically placing Ga on an Al sheet, it was immersed in HAc solution and the $E-t$ response was registered (Fig. 10). Increasing temperature was applied. Only when the temperature of solution reached 30 °C, a quick activa-

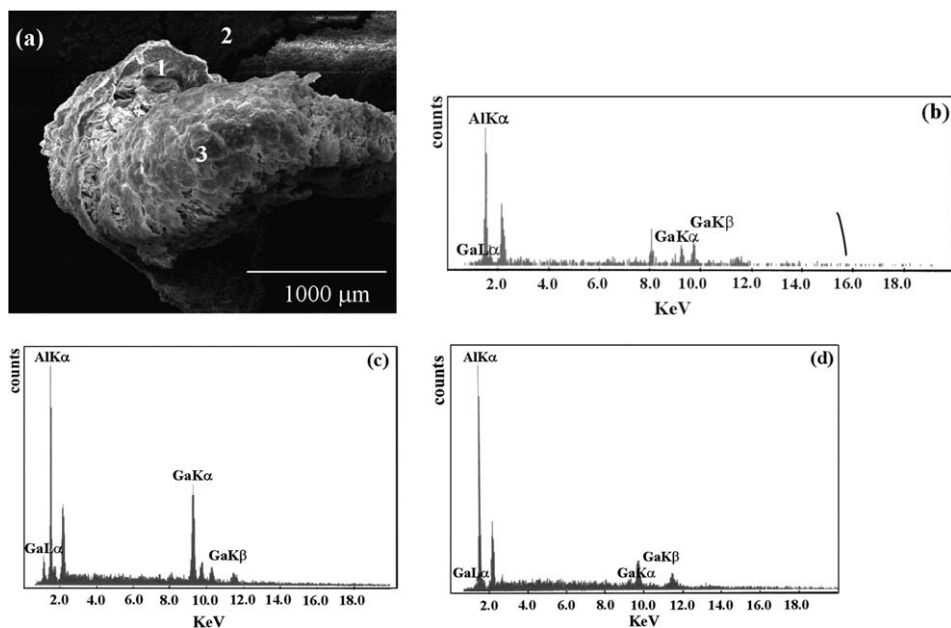


Fig. 5. (a) SEM micrograph of an Al sheet modified with metallic Ga mechanically attached, after reaction with distilled water; (b) EDX spectrum at point 1; (c) EDX spectrum at point 2 and (d) EDX spectrum at point 3.

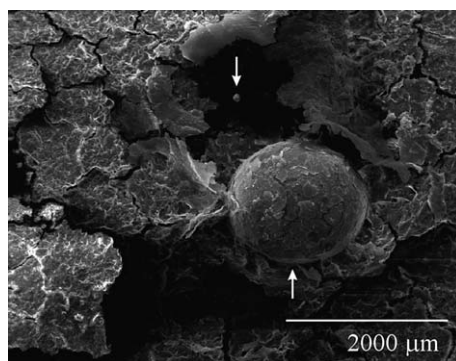


Fig. 6. SEM micrograph of the surrounding area of the Ga particle observed in Fig. 5 (a)—zone 2. Arrows indicate spherical particles of Ga.

tion occurred with a strong H_2 evolution followed by a rapid passivation given by a grey product. The same result was obtained in HCl solution. It is interesting to note that while the Ga particle remains solid; the OCP in Cl^- media is around -1.1 V.

If the same procedure is followed but the Ga–Al electrode is directly placed in the HAc solution at $50^\circ C$, the OCP measured indicates that full activation was reached

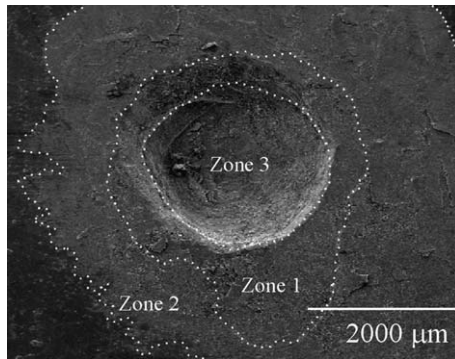


Fig. 7. After reaction, the surface observed in Fig. 5a was cleaned with distilled water. The micrograph shows the attack morphology produced by the amalgam surface diffusion (zones 1–3).

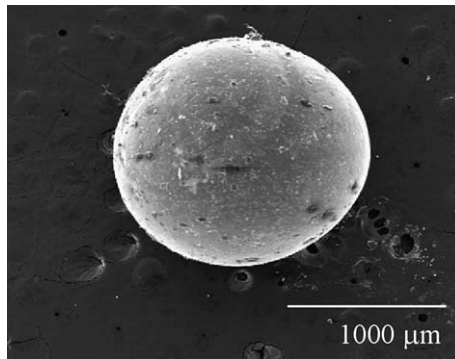


Fig. 8. SEM micrograph of the Ga particle mechanically attached to Al in contact with distilled water. After reaction, the particle was separated, cleaned and placed on a carbon cloth.

immediately (Fig. 11), with vigorous hydrogen evolution. This activation lasted about 15 min, but cannot be maintained and after approximately 20 min the OCP tends to -1.050 V. At this point a dark film obscured the surface. Spherical particles of Ga fell to the bottom of the cell, and hydrogen evolution coming from them, was still observed for a while. After reaching -1.050 V, a potentiodynamic polarisation at 0.001 V s $^{-1}$ indicates an ohmic control (Fig. 12).

4. Discussion

Full activation of Al was reached in HAc solution when metallic gallium is mechanically attached to the Al surface (Fig. 11) at temperature higher than 30 °C. It is a very interesting result because it demonstrates that Al activation can be attained not only in chloride but also in acetic solution. The single presence of

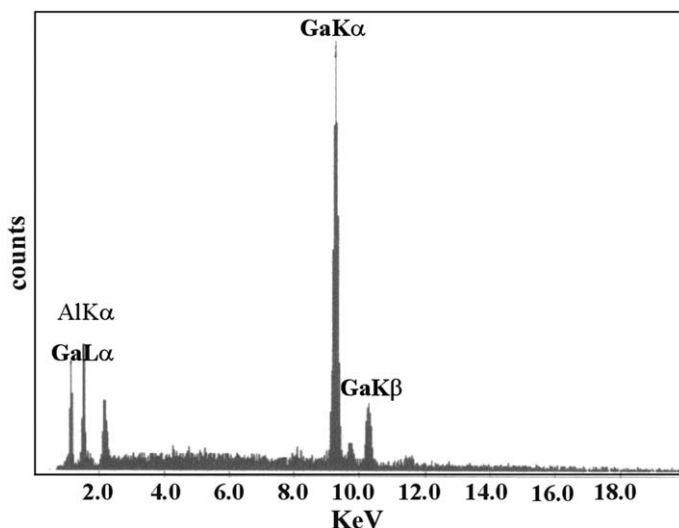


Fig. 9. EDX spectrum of the particle shown in Fig. 8.

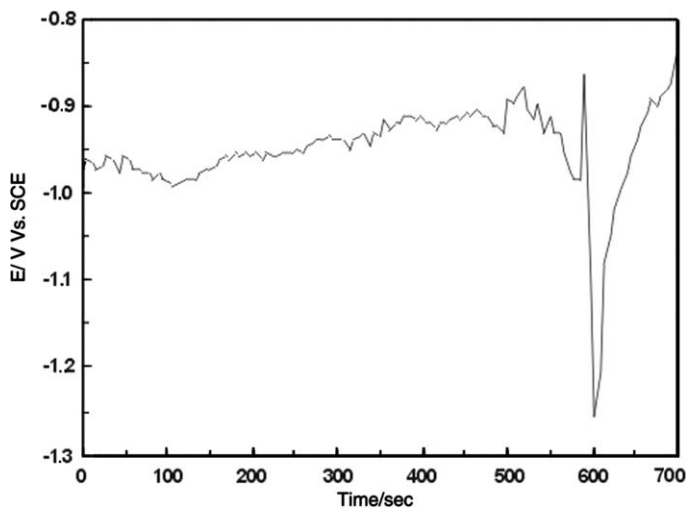


Fig. 10. Open-circuit potential (OCP) vs. time plot of Al with metallic Ga mechanically attached in 0.1 M HAc. The temperature was increased from 22 °C and after 570 s reached 30 °C.

pure water is also enough to promote a strong reaction at the metal/solution interface (Fig. 4). Regardless of the presence of an aggressive ion such as Cl^- , the presence of metallic contact between Ga and Al and cathodic species like protons and dissolved oxygen results in a very active surface. In this state, the Al^{3+} hydrolysis exothermic reaction ($\Delta H^0 = -1406.7 \text{ kcal mol}^{-1}$) [13], help to produce a surface temperature high enough to promote liquid gallium formation, facilitating its

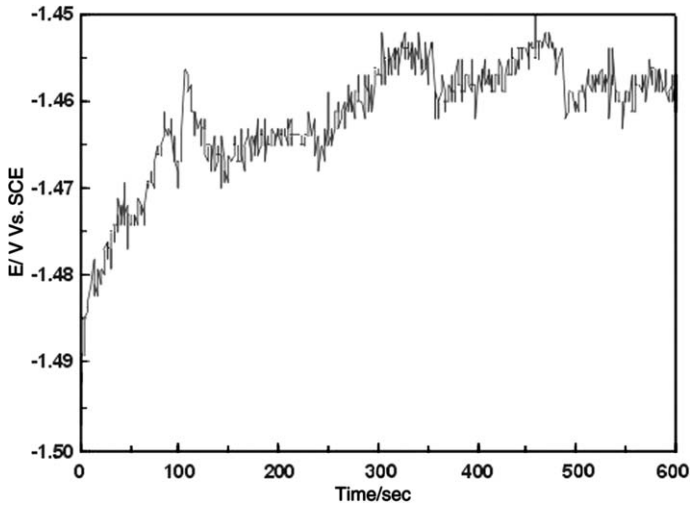


Fig. 11. Open-circuit potential (OCP) vs. time plot of Al with metallic Ga mechanically attached in 0.1 M HAc at 50 °C.

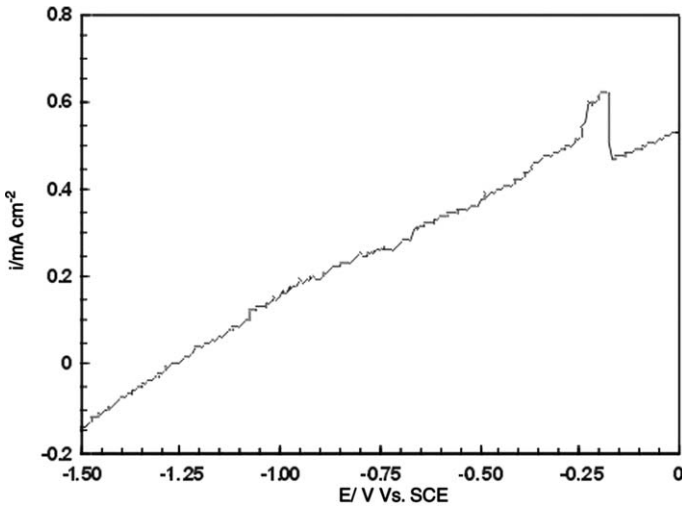


Fig. 12. Potentiodynamic polarisation of Al with metallic Ga mechanically attached in 0.1 M HAc, at $v = 0.001 \text{ V s}^{-1}$, after reaching -1.050 V in the OCP measurement shown in Fig. 10.

wetting action and surface diffusion. The presence of spherical particles of Ga in the corrosion products (Figs. 4h and 6) and at the bottom of the cell, supports the liquid Ga formation.

The present results resemble those obtained when aluminium is in contact with mercury. It is known that Al in contact with a solution of a mercury salt forms

metallic mercury, which then amalgamates the aluminium [14,15]. The amalgamation occurs immediately when the Al oxide film is broken by mechanical or chemical action. Aluminium amalgam reacts with moisture to form a metal oxide film (feathers like) plus free mercury, which then can continue the corrosion process. It has been found that Hg surface diffusion undermined and detached the Al oxide [15–17]. As a consequence, the amalgam formed is exposed, attaining a potential similar to that of bare aluminium. The formation of a surface Ga–Al alloy was postulated by Tuck to explain the activation of Al–Ga alloys in chloride media. A rapid diffusion of Al through the agglomerated Ga prior to its oxidation and direct chemical reduction of water by aluminium atoms have been suggested.

Bearing in mind the above discussion, it seems reasonable to assume that the mechanism of Hg-activation can be applied successfully to interpret the activation behaviour by Ga. Considering the corrosion products coming from the particle (Fig. 5a), the presence of Al in the Ga particle (Fig. 9) and the hydrogen evolution observed in particles that had fallen to the bottom of the cell, the formation of an amalgam in the case of Ga can be proposed.

Several experiences show different degree of activation followed by a quasi-passivation process characterized by a potential of approximately -1.050 V. In the presence of Ga mechanically attached to the Al surface a very active OCP was measured in HAc at 50 °C (Fig. 11) and then the electrode surface slowly passivates till the potential reaches -1.050 V. If the HAc solution was heated from room temperature, a quick activation occurred when 30 °C was attained (Fig. 10). Afterwards repassivation was observed, reaching again the potential a value of -1.050 V. When Ga is deposited in the cracks of the oxide film from an acetic solution and the temperature is high enough to maintain Ga liquid (Fig. 3), an activation was observed but the potential only reached -1.050 V. Coming either from a passive state (Fig. 3) or a very active one (Fig. 11) a gradual return to a defined potential was always observed (-1.050 V). At this potential, it is likely that the amalgam becomes saturated due to the rapid diffusion of Al through it. To explain this process, losses of Ga and Ga film thinning have to be considered. All these results suggest that the degree of activation depends on the amount of Ga accumulated on the Al surface and its liquid or solid state. Under the experimental conditions used, the activation state ranged from -1.500 to -1.050 V. The most active potential is obtained when sufficient amount of liquid Ga allows a quick Al diffusion from the metal matrix. If this amount is small, the rapid atomic diffusion of Al will become inactive in the amalgam by saturation. The following facts contribute to Ga losses: (i) lateral surface diffusion (Fig. 7), which is favoured when Ga is liquid; (ii) bulk intergranular diffusion [7–9]; (iii) surface turbulence, given by mechanical agitation (strong hydrogen evolution) and convective forces (exothermic hydrolysis reaction of Al^{3+}), evidenced by tiny spherical Ga particles observed in between the corrosion product (Figs. 4h and 6) and also at the bottom of the cell. Thus, when Ga actually wets Al these losses produce a Ga film thinning which facilitates amalgam saturation. At this stage, a quasi-solid state is attained, and as a consequence the atomic Al diffusion and the Al oxidation rate at the amalgam/media interface diminish. The interface temperature produced by the exothermic Al^{3+} hydrolysis reaction lowers, and

the amalgam finally solidifies. Through this process, the evolution of hydrogen diminishes, decreasing the local pH. All these conditions favour passivation and the OCP evolves to more noble values (-1.050 V). This explains why, although a huge amount of Ga (particle) is placed on Al in acetic media, after a long period of time, amalgam solidification occurred and the corrosion potential is shifted from approximately -1.500 to -1.050 V. The ohmic control observed (Fig. 12) is probably exerted by the slow atomic Al diffusion through the quasi-solid Ga–Al amalgam and/or the Al^{3+} transport across the oxide formed at the amalgam/solution interface.

It is interesting to note here, that when Ga is in chloride solution and in true contact with Al but in solid state, the active potential reached tends to -1.1 V (Figs. 1 and 2). According to Frumkin et al. [18] the potential of zero charge, E_{pzc} , measured for Ga in a 1.0 M KCl solution was -1.10 V. This means the possibility of a dual activation mechanism produced by Ga on Al: (i) when a liquid Ga–Al amalgam is formed, a very active dissolution of Al is possible, whose corrosion potential is about -1.5 V, and a smooth-wide cavities attack is expected (Fig. 7); (ii) when this amalgam is inactive, either due to saturation and/or solidification, Ga presence facilitates the Cl^- adsorption when the pzc is overcome, that is activation occurred through a pitting process. In other words, two active potential region are expected, a very negative one given by a physical corrosion (amalgamation) followed by an electrochemical corrosion at the amalgam/media interface, which produces a smooth attack, and a second region (for $E > E_{\text{pzc}} = -1.10$ V) where a depolarised pitting process is developed.

It is possible to obtain more and better accumulation of Ga at the bare Al interface. This will enhance the amalgam formation. Further work on this issue and on the electrochemical characterization of the Ga–Al amalgam is now on its way.

5. Conclusions

The activation effect exerted by Ga on Al is likely given by two mechanisms:

- (i) Once a critical surface concentration of Ga in the liquid state on Al is achieved, wetting of Al facilitates the formation of a Ga–Al amalgam. Its surface diffusion is responsible for detachment of the Al oxide film and a very active state (-1.5 V). A quasi-uniform attack evident as smooth-wide cavities is observed. This process is favoured by the exothermic Al ion hydrolysis reaction and hindered by Ga losses at the active interface.
- (ii) Ga losses at the active interface and/or its surface diffusion produce film thinning and facilitate amalgam saturation and solidification. In this case passivation is maintained till another activation process is effective. In aggressive media, a chloride pitting activation process is added. This process will be effective once the chloride adsorption potential on Ga is overcome (near -1.1 V). Thus, it is possible that both processes operate, either in parallel or in series, according to the interface temperature and the amount of Ga agglomerated.

Acknowledgements

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