



# Anodic activation of aluminium containing small amounts of gallium and tin



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## ABSTRACT

Anodic activation due to surface enrichment of Sn and Ga on AlGaSn model alloys, containing 50–1000 ppm Sn and 1000 ppm Ga in pure aluminium, as a result of heat treatment was investigated. Sn was enriched because of annealing at 300 °C, while Ga was stable in solid solution because of its high solubility in Al. Anodic polarization in 5% NaCl solution resulted in highly active surfaces in relation to the binary alloys AlGa and AlSn. Presence of segregated Sn at the surface catalysed dealloying, such that Ga was enriched on the corroding surface giving increased activation.

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## 1. Introduction

Small additions of IIIA–VA Group elements are known to activate aluminium in chloride and alkaline environments with significance for the development of sacrificial anodes for cathodic protection and active anodes for the Al/air battery [1–3]. However, the effect of these elements on the surface properties, if they are present as trace elements in commercial Al alloys, is not well-known. The subject is of increasing significance because of increasing types and amounts of various trace elements in recycled aluminium. The role of these elements, in particular Pb, In, Sn, Bi and Ga, in anodically activating the surface as a result of heat treatment, chemical processing and corrosion in chloride media and its relation to causing filiform corrosion of coated commercial sheet, have been demonstrated, based on extensive work during the past decade on model and commercial alloys in this laboratory, as reviewed in Ref. [4].

Anodic activation of commercial alloys AA8006 [4–6] and AA3102 [7] in chloride solution, after annealing at 600 °C, has been shown to result from the segregation of the trace element Pb to the surface. TEM studies on model binary AlPb alloys, containing 50 ppm showed that a Pb-rich nano-film, which was formed during annealing at the metal–oxide interface [8,9], was the cause of activation as the corrosion propagation followed the film, thereby

undermining the passivating oxide [10]. However, segregation of Pb alone could not explain the finding that maximum activation of commercial alloys AA3005 and AA8006 occur as a result of annealing at 350 °C [11–13].

Work with model binary AlSn alloys [14–16] showed that Sn, present at concentrations in the range 20–1000 ppm, segregated to the surface and activated aluminium by annealing at 300 °C. This was attributed to the low melting point and limited solubility of Sn at this temperature. The solubility of Sn in Al solid solution is negligible at 300 °C, and it increases to a maximum of 0.12 wt% at 600 °C [17]. The added presence of the trace element Sn was subsequently shown to cause activation by heat treatment at temperatures as low as 350 °C on alloy 8006, as a result of segregation together with Pb to form an interfacial nanofilm of Pb and Sn [4].

Gallium has a low melting point at 29.8 °C, and it is highly soluble in aluminium, up to 20 wt% (9 at.%) at 26.6 °C [18]. Presence of 50–1000 ppm Ga in homogenised AlGa model binary alloys did not cause anodic activation, since Ga remained stable in solid solution [19,20]. Alkaline etching caused significant enrichment of Ga by dealloying of the Al component, and anodic activation occurred by subsequent exposure to chloride solution. Segregated Ga dissolved back into aluminium by annealing for 1 h at 600 °C after etching, eliminating anodic activation. Activation is caused by formation of a liquid GaAl surface alloy, which destroyed the passivating oxide film. With reference to the classical mechanism of activation of Al by Hg [21], the liquid GaAl alloy wets the bare Al surface and prevents the direct contact of the surface with oxygen. Al dissolves into Ga which enables the transport of Al to the GaAl

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alloy surface in contact with an aqueous environment, where Al oxidizes [22].

Solubility and diffusivity of Al in the liquid GaAl alloy are important properties for amalgam formation and corrosion of aluminium by transport through the amalgam film. Solubility of Al in Ga is about 0.8 wt% at the eutectic temperature [18], in comparison to only  $\sim 1.35 \times 10^{-5}$  wt% in Hg [23]. Aggressive ions were not necessary for activation in aqueous environment if liquid phase GaAl alloy was formed at the surface [24,25]. These data suggest that Ga must be at least as effective as Hg in activating Al by the amalgamation mechanism.

Activation of aluminium containing 0.4 wt% Mg, 700 ppm Sn and 500 ppm Ga occurred in 2 M NaCl solution by lowering the corrosion potential down to  $-1.5 V_{SCE}$  and increasing the corrosion rate of the aluminium alloy with hydrogen evolution around Sn inclusions, which acted as cathodic sites for hydrogen evolution [26–28]. The role of gallium on increased activation was not explained even though its contribution was evident from the electrochemical results [26].

Gallium is commonly present as a trace element up to 100 ppm depending on the source of the primary aluminium production [29], while tin is incorporated as a result of recycling at concentrations smaller than 100 ppm, if present at all. The aim of this study is to clarify the combined role of trace elements Ga and Sn on the passivity breakdown of aluminium and the mechanism of anodic activation. Single and combined effects of Ga and Sn were investigated by using binary and ternary model alloys.

## 2. Experimental

### 2.1. Materials

Model ternary AlGaSn alloys were prepared from pure components by first casting two master alloys containing 2 wt% Ga and 2 wt% Sn. The alloys containing 100 ppm Sn and two different concentrations of Ga (50 and 1000 ppm) were then prepared by remelting and diluting the master alloy. The alloys were cast in chilled copper moulds. These alloys were designated as AlGa50Sn100 and AlGa1000Sn100, respectively. The binary model alloys AlGa50, AlGa1000 [19,20] and AlSn100 [15,16], which were prepared for previous studies, were also used for comparison. After homogenisation for 20 h at 600 °C, the cast alloys were scalped and cold rolled from 20 mm to a final thickness of about 2 mm. Samples were ground with SiC paper and polished metallographically through 1  $\mu$ m diamond paste finish. The alloying element concentrations were measured by glow discharge mass spectroscopy (GDMS) analysis of the rolled samples, verifying the intended concentrations of Ga and Sn within 5–15% error. The polished samples were heat treated in an air circulating furnace for 1 h at temperatures varying in the range 300–600 °C, followed by cooling in water or air.

### 2.2. Electrochemistry and corrosion

Electrochemical characterization was performed in 5 wt% NaCl and 5 wt% Na<sub>2</sub>SO<sub>4</sub> solutions at 25 °C. The solutions were exposed to ambient air. Reference electrode used in NaCl solutions was saturated calomel electrode (SCE), while saturated Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode was used in Na<sub>2</sub>SO<sub>4</sub> solutions. The reported potentials were converted to SCE. Anodic polarisation curves were obtained potentiodynamically at a sweep rate of 0.1 mV/s in the positive potential direction, starting from 50 mV below the initial corrosion potential. Potentiostatic polarisation was performed for 3 h at selected potentials in the range  $-0.8 V_{SCE}$  to  $-1.4 V_{SCE}$ . The cell geometry, solution volume and the stirring rate in the solution

were identical in all electrochemical runs. The sample area exposed to the solution was 0.64 cm<sup>2</sup>.

Electrochemical polarisation data for aluminium alloys in aqueous solution in the presence of chloride are known to be difficult to reproduce because of the dynamic nature of the surface during measurement. This is caused by changing oxide properties and surface chemistry and structure due to various factors, the most important being dealloying. The measured current density during a potential controlled run below the breakdown potential could vary by as much as an order of magnitude among replicate runs in the present work, especially below the breakdown potential. One reason for the data scatter in the passive region was extremely low current densities (nearly zero) observed on the heat-treated specimens, in relation to that expected for mechanically-polished specimens. The results reported below are based on typical curves selected among at least three replicate runs, which show a clear trend related to the selected set of parameters.

### 2.3. Surface characterisation

Characterisation before and after the electrochemical polarisation test was performed using a Zeiss Ultra 55 field emission gun scanning electron microscope (FE-SEM), equipped with Inca (Oxford Instruments) X-ray electron diffraction spectrometer (EDS) capability.

Glow discharge optical emission spectrometer (GD-OES) was performed by an Horiba Jobin Yvon instrument in radio frequency (RF) mode to measure elemental depth profiles. A 4-mm-anode was used for Ar sputtering in GD-OES measurements. The data were recorded once every 5 ms. Because of instability of the instrument at the start of an experiment, the data obtained was reliable after 0.1 s of sputtering. The sputtering rate during the analysis was roughly 70 nm/s in the metal and 40 nm/s in the oxide. Concentration data are reported qualitatively as intensity in arbitrary units (a.u.) versus sputtering time (s).

Secondary Ion Mass Spectroscopy (SIMS) analysis was also performed for better lateral resolution than GD-OES for elemental mapping of corroded surfaces using a Cameca IMS 7f dynamic SIMS with elemental mapping capability and sub-micron lateral resolution. O<sub>2</sub><sup>+</sup> ions were used as the incoming beam for sputtering, giving a few atomic layers of depth resolution. The SIMS maps were obtained from an area of 500  $\mu$ m  $\times$  500  $\mu$ m and 100  $\mu$ m  $\times$  100  $\mu$ m with image lateral resolution of about 10  $\mu$ m.

## 3. Results

### 3.1. Surface characterisation

#### 3.1.1. SEM

Fig. 1 shows the surface morphology of sample AlGa1000Sn100 after annealing at 300 °C and quenching in water. Fig. 1a–d show clusters of oxide mounds formed on the sample with increasing magnification. The mounds were nearly circular in shape, up to 10  $\mu$ m in diameter, either discrete (Fig. 1b) or merged with other mounds in a cluster (Fig. 1c). The thick oxide was cracked (Fig. 1d) while the mound was being formed, probably during water quenching. Fig. 1e shows a magnified back-scattered electron image of the crack in the oxide mound marked by a white arrow in Fig. 1d. The bright contrast indicated Sn enrichment in the crack. At a higher magnification, nanosized Sn segregations were observed on top of the oxide mound, as shown in Fig. 1f. These results for alloy AlGa1000Sn100 were representative also for alloy AlGa50Sn100 and similar to those reported earlier for AlSn model alloys, containing 30 and 100 ppm Sn, after similar heat treatment [15].

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