Preface

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Firstly, I would like to thank my supervisor, Professor Kemal Nisancioglu, for his constructive advices and inspiring supervising during these three years.

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Special thanks go to all my friends and colleagues at the department for making this period enjoyable, particularly Kjell Røkke and Martha Bjerknes, for their great help with technical and administrative issues, as well as learning Norwegian.

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Esma Senel
Summary

Gallium is used as an alloying element to destabilise passive aluminium oxide and consequently activate aluminium in applications as sacrificial anodes in seawater and active anodes in Al/air batteries using chloride and alkaline electrolytes. The amount of Ga needed in the alloy is at least 0.1 wt% for these applications. Ga is also a common trace element in commercial Al alloys, which contain Ga in the range of 50-200 ppm depending on the quality of the bauxite ore.

While the conditions under which the other elements, such as Pb, In, Sn and Bi in Group IIIA-VA, segregate to the surface and thereby activate Al anodically are relatively well documented, the effect of Ga as a trace element on the surface properties of Al alloys is not known. The effect of Ga cannot be predicted by comparing it with the other activating trace elements because Ga has a much lower melting point (29°C) and a higher solid solubility (20 wt% at 26.6°C) in Al than those of Pb, In, Sn and Bi. Ga also causes liquid metal embrittlement of aluminium when it is brought into contact with aluminium. However, it is not known whether Ga present as a trace element can cause a similar effect by somehow becoming enriched at the surface of commercial alloys, e.g., as a result of alkaline etching, a common step in chemical processing of Al alloys. Whether trace element gallium is an important factor in causing embrittlement and contributing to surface activation as a result of thermal and chemical processing has to be addressed. The main objectives of this thesis are therefore to clarify the role of Ga, alone and together with other common trace elements Pb and Sn, on the surface properties, electrochemical behaviour and liquid metal embrittlement of Al subjected to annealing and alkaline etching. The work is mostly based on model alloys; however a comparative study with a selected commercial alloy (AA6060) with increased Ga content is also included.

Various model binary and ternary alloys of type AlGa, AlGaSn, AlGaPb and AlGaMg alloys with various compositions of the activating elements Ga, Sn and Pb were cast from pure components, followed by homogenisation and cold rolling. These were designated according to composition of the alloying elements in ppm, e.g., AlGa1000Sn50 stands for the AlGaSn ternary alloy containing 1000 ppm Ga and 50 ppm Sn. Commercial AA6060 alloy was received as a DC cast billet. Test samples of the alloy were prepared by cold rolling of pieces cut from the billet. Pieces were also remelted and recast after increasing the Ga concentration from about 130 ppm to 500 (designated as AA6060Ga500) ppm. Specimens were ground, metallographically polished and then heated treated for 1 h in the temperature range 300-600°C followed by water quenching.

Potentiodynamic polarisation was performed in stirred solutions of 5 wt% NaCl at 25°C, exposed to ambient air. Corrosion potential measurements were performed in synthetic sea water solution according to ASTM D1141. The corrosion morphologies were investigated by FEG-SEM and EDS. Etched samples were prepared from specimens which were heat-treated at 600°C, at which all alloying elements were
homogenised in the model alloys. Etching was performed for 2 min in 12 wt% NaOH solution maintained at 45°C. Etching temperature was chosen to be above melting point of Ga. Corrosion potential was also measured during alkaline etching. The specimens were desmutted in concentrated HNO₃ and rinsed in distilled water subsequent to the alkaline etching. Elemental depth profiles after heat treatment and alkaline etching were performed by use of glow discharge optical emission spectrometry (GD-OES). Surface morphology and chemistry of as annealed, alkaline etched and corroded surfaces and fractured grain boundaries were investigated and compared in detail by a field emission gun scanning electron microscope (FE-SEM), Auger electron spectroscopy (AES)- X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) techniques. Changes in the mechanical properties of the samples resulting from Ga embrittlement and recovery from embrittlement were characterised by three point bending test.

Study with the model AlGa alloys showed that gallium was highly stable as a trace element in solid solution with aluminium. It did not segregate as a result of heat treatment for 1 h at temperatures in the range of 300-600°C. Potentiodynamic polarisation in 5% NaCl solution did not indicate any anodic activation caused by annealing. Passivity breakdown potential was lowered slightly (about 50 mV) even at the highest level of Ga, while the current density output was increased significantly when Ga concentration was 1000 ppm. Effect of annealing temperature on activation was of no importance. The reason for increased current density was Ga enrichment at the surface by selective dissolution of aluminium, i.e. dealloying. Ga enrichment gave circular etch morphology instead of crystallographic pitting. Alkaline etching caused significant enrichment of Ga at the surface, which activated AlGa alloys containing at least 50 ppm Ga. Corrosion potential during alkaline etching was lowered by Ga enrichment. Enriched Ga diffused into the grain boundaries and caused embrittlement of AlGa alloys containing at least 250 ppm Ga. Annealing the etched alloys for 1 h at 600°C eliminated anodic activation and grain boundary embrittlement. A critical level of Ga enrichment was required for stable activation which was determined by the amount of gallium in the alloy and the corrosion rate of aluminium.

Ternary alloys AlGa50Sn100 and AlGa1000Sn100 exhibited higher anodic activation than binary alloys of the constituents of the ternary alloys. Sn segregated during annealing due to low solubility of Sn in Al at 300°C. Segregation of Sn was localised, as indicated by nearly hemispherical oxide mounds of diameter 1-10 μm formed at the segregation sites by oxidation during quenching after heat treatment. Ga was homogenised similar to binary AlGa alloys. However, the ternary alloys annealed at 300°C became anodically activated in chloride solution, as a result of synergistic interaction of Ga and Sn giving a more significant depression of the passivity breakdown potential and a much higher anodic current density in relation to the binary alloys with comparable Ga and Sn contents. Surfaces of alloys AlSn100 and AlGa50Sn100 passivated after the active layer corroded away, whereas the higher Ga concentration in alloy AlGa1000Sn100 prevented passivation during polarisation at the same conditions as the former two alloys. Alloy AlGa1000Sn100 annealed at 300°C became activated to the same extent in chloride-free solution as in chloride solutions, whereas alloys AlGa50Sn100, AlGa1000 and AlSn100 did not activate in the absence
of chloride. Characterisation of the corroded surfaces showed Ga became enriched by dealloying, while the amount of segregated Sn decreased in relation to the uncorroded condition. Corrosion morphology was in the form of circular attack, propagating radially from the oxide mounds by Ga segregation at the periphery of attack, forming a liquid phase GaSn(Al) alloy, which caused activation of aluminium.

Annealing of the AlGaSn alloys at 600°C caused homogenisation of both Ga and Sn in the Al substrate. The passivity breakdown potential became more positive than the alloys annealed at 300°C. Ga enrichment at the corroded sites caused high corrosion rates than that of pure aluminium above the breakdown potential. Ga enrichment was not high enough to cause grain boundary embrittlement.

Pb segregation on AlGaPb alloys due to annealing at 600°C was the dominant factor in causing activation, causing superficial etching, which followed the nanofilm Pb segregation along the oxide-metal interface at potentials (~ -0.95 V_{SCE}) significantly more active than the pitting potential of pure Al, similar to the known behaviour of AlPb model alloys in chloride solution. Ga did not segregate during annealing and did not influence the segregation behaviour of Pb. The effect of Ga on anodic activation was significant only for the alloy containing 1000 ppm Ga. It caused an increase in the anodic current density above the breakdown potential, whereas its effect on the passivity breakdown potential was negligible. Current increase was caused by Ga enrichment by dealloying. It caused deep pits locally well below the pitting potential of pure Al (~0.915 V_{SCE}).

After annealing at the lower temperatures 300°C and 450°C, alloy AlGa1000Pb50 exhibited higher anodic activation than the binary alloys AlPb and AlGa annealed at the same temperatures. This was attributed to enrichment of Ga by dealloying during corrosion initiated by segregated Pb particles at the surface. Such corrosion could not be sustained by the Pb particles in the absence of Ga in the alloy.

Alkaline etching of AlGaPb alloys (annealed at 600°C) under the specified conditions (2 min in 12 wt% NaOH at 45°C) caused activation by enrichment of Ga. However, grain boundary embrittlement was delayed, probably due to Pb, until alkaline etching removed most of Pb segregated at the surface. Re-annealing after etching caused diffusion of segregated Ga into the bulk alloy, while Pb was segregated to the surface again and restored the activation effect of segregated Pb. Annealed AlGaPb alloys had a more negative corrosion potential and a reduced amount of corrosion rate during alkaline etching compared to AlGa alloys. As the etching rate was lower due to Pb segregation, Ga enrichment that occurred was not sufficient to cause embrittlement. As a result of prolonged etching for about 10 min, corrosion potential increased as the Pb-enriched layer was etched away, and grain boundaries were embrittled as the necessary amount of Ga was produced by dealloying at the surface.

Alkaline etching caused Ga enrichment also at the surface of commercial alloys with normal (130 ppm Ga) and increased amount (500 ppm Ga) of Ga in the bulk. Ga enrichment caused by etching however did not have any remarkable effect on activation and mechanical properties of commercial alloys. Only Pb segregation activated after
Summary

annealing at 600°C, while etching caused passivation even for the alloy with increased amount of Ga. Corrosion potentials obtained during alkaline etching of the commercial alloys were nobler than pure Al, while the corrosion potentials of AlGaMg and AlGa model alloys were more negative than pure Al. Annealed and etched AlGaMg alloys were significantly activated in chloride solution and fractured at the grain boundaries similar to AlGa alloys. Increased resistance to anodic activation of commercial alloys was attributed to ennobling effect of alloying elements such Si, Fe, Mn dissolved in the bulk during annealing and their enrichment and segregation at the surface during alkaline etching. Segregations of these elements at the surface and grain boundaries are believed to reduce or block diffusion of segregated Ga from the surface into the grain boundaries and, thereby, prevent or delay grain boundary embrittlement.

To sum up, annealing caused homogenisation of trace element Ga (50-1000 ppm) in solid solution for AlGa, AlGaPb, AlGaSn, AlGaMg and commercial alloys due to high solid solubility limit of Ga in Al. Passivity breakdown potential was lowered and activation was initiated by segregating elements Pb and Sn during annealing, while the effect of Ga, as long as it remained dissolved in the bulk was negligible. Thermally segregated Pb and Sn alone caused a temporary activation that was removed after the active surface corroded away. However, Ga enriched at the surface over a critical level as a result of dealloying caused by sustained corrosion by, e.g., alkaline etching, caused activation in chloride or alkaline solution (also chloride free solution for alloy AlGaSn). Once this occurred, activation also became sustained because Ga was replenished from the bulk by continuing corrosion and dealloying. This was attributed to a stable amalgamation enabled by low melting point of Ga and higher solubility of Al in Ga than those in Pb and Sn.

This work showed that Ga, at levels normally present in commercial Al alloys, is not a threat to commercial Al alloys in causing anodic activation or grain boundary embrittlement in connection with normal thermomechanical processing. In the presence of transition elements (Fe, Cu, Mn, etc.) and Si in commercial alloy AA6060, Ga enrichment did not cause anodic activation or grain boundary embrittlement.
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1 Introduction

1.1 Background

Gallium is present as a trace element in most commercial Al alloys within the range 50-200 ppm [1]. Its actual amount depends on the quality of the raw materials used in aluminium production [2]. The main concern for the presence of Ga as a trace element in Al alloys is related to the possibility of its causing liquid metal embrittlement by segregation to the grain boundaries, despite the fact that it is highly stable in solid solution in Al (20 wt% at 26.6°C [3]). Moreover, embrittlement of Al by Ga has been reported to occur in almost all cases when liquid Ga and Al were brought into physical contact [4-7]. Only in one case, an AlGa alloy containing 18 at% Ga, which is above its solubility limit in Al at room temperature, was reported to cause embrittlement [8]. Anodic activation of aluminium by means of segregation during thermomechanical processing has not been reported. No altered surface properties was caused by Ga as a result of heat treatment for AlGa alloys containing 1300 ppm Ga to be exploited for electrolytic capacitor applications [9]. Segregation of Ga to the grain boundaries was reported not to occur by annealing when Ga in Al alloy was below 5.2 at% [8]. There is a strong need in the scientific and industrial community for a more definitive clarification of the possibility of liquid metal embrittlement by trace element Ga in Al, the amount of Ga required for this to occur, its mechanism and the effect of other alloying, impurity and trace elements commonly found in commercial alloys.

Differing from the foregoing situations, significant segregation of Ga can occur as a result of chemical processing, such as caustic etching [9-11] and anodising [9, 12]. Selective dissolution (dealloying) of aluminium caused surface enrichment of Ga in these cases. Embrittlement of the alloy as a result of Ga enrichment of the surface by dealloying has not been reported. However, surface enrichment of alloyed Ga is known to activate aluminium anodically in chloride and alkaline solutions in relation to development of Al/air battery and sacrificial anodes for cathodic protection [13-16]. Anodic activation is characterised by a significant negative shift in the passivity breakdown potential relative to that for pure aluminium and a significant anodic current density output at potentials at which pure aluminium is expected to be passive [17]. Nevertheless, the amount of Ga needed in the bulk alloy to cause appreciable activation in this manner is at least 0.1 wt% [14].

Activation is caused by enrichment of Ga in the form of a liquid phase GaAl alloy [18, 19], as in the case of the classical activation mechanism of the Al surface in metallic contact with an Hg drop [20, 21]. Presence of an aqueous environment enhances the process. The presence of otherwise aggressive chloride ions is not required. The results available in the literature about surface enrichment of trace element Ga by dealloying and activation of the enriched surface in aqueous environment are in almost all cases reported for pure Al or model Al alloys. Such phenomena have not been reported for commercial alloys. Nevertheless a more concrete scientific evidence of the effect of other elements present in the commercial alloys is not available in the open literature.
1. Introduction

In contrast to the behaviour of trace element Ga, anodic activation of aluminium by other low melting point trace elements close to Ga in Group IIIA-VA, specifically Pb [22-26], In [27], Sn [28, 29] and Bi [17, 30] was reported to require segregation of the activator elements to the surface during annealing at temperatures above the melting points of these elements, at which the elements also have virtually no solubility in Al. Alloy compositions of these elements, much smaller (of order 100 ppm and lower) than that required for Ga, are sufficient to cause activation. The trace elements Pb and Sn, documented now to be present together in certain recycled commercial alloys [31], readily segregate to the surface by thermomechanical processing, in particular hot rolling, and cause filiform corrosion as a negative consequence of anodic activation.

It is not known whether trace element Ga can segregate to the surface together with other trace elements, such as Sn and Pb, during thermal and chemical processing. Model alloys of type Al-Ga 0.05-Sn 0.1-Mg 0.5 [32, 33], Al-Zn 5.6-Ga 3.0 [34] and Al-Ga 0.4-In 0.2 [35] were reported to exhibit active behaviour in chloride solution. However, these papers did not report interaction of these elements and the role of Ga in increasing active behaviour, if any, in relation to the binary alloys AlGa, AlIn and AlSn with similar content of the activating element. Alloying Al with high amounts of Ga, In and Sn has been exploited for hydrogen evolution by destabilizing the passive oxide and enabling the reaction of aluminium with water [36, 37].

1.2 Objectives

In view of the background and unknown issues discussed above, this work focuses on the effect of trace element Ga on anodic activation of Al. The main objectives are to investigate

- segregation of Ga in AlGa binary model alloys as a result of heat treatment and alkaline etching and its effect on liquid metal embrittlement,
- effect of segregated Ga on anodic activation of Al in chloride solution,
- Ga segregation in combination with the trace elements Sn and Pb as a result of heat treatment and alkaline etching and its effect on embrittlement and anodic activation of Al in chloride solution and,
- effect of Ga segregation by similar processes in commercial alloy AA6060 in comparison to the results for model alloys.

1.3 Structure of the thesis

The thesis consists of a literature review (Chapter 2), followed by more or less self-standing technical chapters (Chapter 3 to Chapter 7), a summarising discussion of the overall results (Chapter 8) and overall conclusions (Chapter 9). Chapter 2 gives a comprehensive review over the effect of Ga on anodic activation and liquid metal embrittlement of aluminium. Thermal and anodic segregation of trace elements Ga, Pb and Sn, their effect on the activation mechanisms are discussed. In Chapter 3, the effect of Ga on the activation and liquid embrittlement of AlGa binary model alloys is reported as a function of annealing conditions and alkaline etching. Chapter 4 and
Chapter 5 discusses the effect of combined presence of Ga with Pb and Sn on the electrochemical behaviour, respectively, of the model ternary alloys AlGaSn and AlGaPb in chloride solution. In Chapter 6, alkaline etching behaviour and the effect of etching on the anodic polarisation of AlGaPb and AlGa model alloys are compared. Chapter 7 investigates the effect of alkaline etching on the segregation of trace elements Ga and Pb on commercial 6060 alloy and their effect on anodic behaviour, in comparison to the behaviour of model alloys discussed in Chapter 3 and 6.

References

1. Introduction

2 Literature Review

This chapter gives a comprehensive background relevant to the results presented in the thesis. The effect of gallium as a trace element with high solid solubility in aluminium on anodic activation of aluminium in chloride and alkaline solutions is reviewed. Since the thesis is also concerned about the added presence of the trace elements Pb [1] and Sn [2, 3] in Group IIIA-VA, the mechanisms of electrochemical activation of aluminium by these elements are also reviewed based on previous theses completed in this group and other available work about the combined effect of the elements. Liquid metal embrittlement of aluminium by Ga is discussed. The phenomena such as thermal and anodic segregation, melting point depression and formation of liquid phase surface films resulting as a result of these phenomena are also defined and discussed in evaluating the possible activation mechanisms.

2.1 Solid solubility of activating elements in aluminium

Reding and Newport [4] reported earlier that small additions of mercury, gallium, indium, tin and bismuth activated aluminium anodically by shifting the corrosion potential in the negative direction and increasing the anodic current output significantly compared to pure aluminium in chloride solution. The activation mechanism is closely associated with the solid solubility of these elements in aluminium and their segregation to the aluminium metal-oxide interface by heat treatment and dealloying or anodic segregation [5-7]. Therefore, the stability of Ga and the other selected elements in aluminium metal alone and in combination with one another is of prime interest. The nature of these segregations, in terms of phase, composition and microstructure, are also of interest.

The properties common to these activating elements in Group IIIA-VA are low melting point and low solid solubility in aluminium, except for Ga. These elements do not form intermetallic compounds with aluminium. They segregate as pure metal or in the form of a solid-solution alloy with aluminium [8]. Large differences exist in crystal structure, electronegativity and atomic diameter between Al and the other elements, as shown in Table 2.1. The exception Ga nevertheless exhibits high solubility in Al. Solubility of Al in Ga is however small.

Among the elements belonging to Group IIIA-VA, Ga differs with its high solubility (20 wt%) in aluminium at the eutectic temperature of 26.5°C, as shown in Fig 2.1 [9].

At the eutectic point, the liquid phase contains about 0.8 wt% Al. The solubility of Ga in Al decreases as the temperature increases, as shown in Table 2.2.
2. Literature Review

Table 2.1. Physical properties of the activating elements of interest in aluminium.

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>Ga</th>
<th>Hg</th>
<th>Pb</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C) [10]</td>
<td>660.3</td>
<td>29.8</td>
<td>-38.8</td>
<td>327.5</td>
<td>231.9</td>
</tr>
<tr>
<td>Crystal structure [10]</td>
<td>Face-centred cubic</td>
<td>Orthorhombic</td>
<td>Rhombohedral</td>
<td>Face-centred cubic</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Electronegativity (Pauling scale) [10]</td>
<td>1.61</td>
<td>1.81</td>
<td>2.00</td>
<td>2.33</td>
<td>1.96</td>
</tr>
<tr>
<td>Atomic radius (Å) [11]</td>
<td>1.43</td>
<td>1.53</td>
<td>1.5</td>
<td>1.75</td>
<td>1.58</td>
</tr>
<tr>
<td>Max. solid solubility of Al (wt% (at T°C))</td>
<td>-</td>
<td>0.75 (26.5) [9]</td>
<td>nil [12]</td>
<td>nil [13]</td>
<td>0.12 (228) [14]</td>
</tr>
</tbody>
</table>

Figure 2.1. Al-Ga binary phase diagram [9].
Table 2.2. Solid solubility of Ga in Al with increasing temperature [9].

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt% Ga</td>
<td>19.8</td>
<td>18.7</td>
<td>16</td>
<td>13</td>
<td>8.8</td>
<td>3.5</td>
</tr>
</tbody>
</table>

According to the binary phase diagram of Al-Pb in Fig. 2.2, composition of Pb in the liquid phase (L) at the monotectic point (at 660°C) is 1.4 wt% (0.19 at%) Pb and at the eutectic point (at 327°C) is 99.7 wt (99.9 at%), while no solid solubility of Pb in (Al) phase was reported [13]. Increased annealing time of AlPb alloy containing only 20 ppm Pb increased the segregation of Pb instead of homogenisation [15].

Figure 2.2. Al-Pb binary phase diagram [13].

Sn has a small retrograde solubility in the phase diagram around 625°C, as shown in Fig. 2.3., where the maximum solubility is given as 0.11 wt%. Solubility of Sn in Al at 600°C is 0.12 wt%. At the intersection of Sn-rich liquids line and (Al)+L line, the metastable solubility of Al in Sn was determined to be about 0.07 wt% Al (0.26 at%) [14].

According to the binary Ga-Pb bulk binary phase diagram, shown in Fig. 2.4., there is a monotectic transformation point at about 313°C at the composition of 86.47 at% (95 wt%) Pb and an immiscibility gap from the melting point of Pb (327°C) up to about 600°C [16].
2. Literature Review

Figure 2.3. Al-Sn binary phase diagram [14].

Figure 2.4. Ga-Pb binary phase diagram [16].

The Ga-Sn binary system shown in Fig. 2.5 has a eutectic transformation at 20.05°C (L ⇔ (orthorhombic Ga (αGa) + (tetragonal Sn (βSn)) with Sn compositions of about 11.5 wt% (7.7 at%) Sn in liquid phase (L), 0.03 wt% (0.02 at%) Sn in (αGa) phase and 95.8 wt% (93.6 at%) Sn in (βSn) phase [17]. Maximum solubility was experimentally found to be ~0.05 wt% Sn at eutectic temperature, while the solubility of Ga in tetragonal Sn phase (βSn) was measured as about 4.7 wt% Ga (7.1 at%). In the
metastable diagram of monoclinic Ga ($\gamma$Ga) and Sn, a eutectic temperature of -23.36°C at composition of about 5 wt% Sn (3.2 at%) was found [17].

Figure 2.5. Ga-Sn binary phase diagram [17].

2.2 Surface segregation of activating elements

2.2.1 Segregation of gallium

According to the phase diagram for the AlGa system (Fig. 2.3) a significant amount of Ga (20 wt%) is stable in solid solution with Al at 26.6°C, the amount decreasing with increasing temperature. However, the stability of appreciable Ga in Al at quite high temperatures is evident. No Ga segregation was reported to occur after heat treatment of AlGa alloys containing 120 and 1300 ppm gallium for 5.5 h at 550°C [18]. Schmidt et al. [19] investigated thermal segregation of Ga from AlGa alloys containing Ga at concentrations close to its solubility limit in the range 0.4-7.8 at% (~1-18 wt%) at temperatures in the range 110-380°C, respectively. No significant concentration difference between the grain boundaries and bulk of alloy Al-0.4 at% Ga was observed after heat treatment. However Ga segregation was detected at the grain boundaries of 2 at% (~5 wt%) Ga containing alloy by scanning transmission electron microscopy (STEM) after heat treatment for 30 h at 300°C.

Gallium as an alloying element became segregated and enriched at surface during etching and anodizing [18, 20] (anodic segregation), as shown by secondary ion mass spectroscopy (SIMS) [21] and Rutherford back-scattering spectroscopy (RBS) [18, 20, 22]. Ga enrichment increased as a function of time during etching of alloy at 45°C of Al 99.9-Mg 0.5 with a Ga content of 85 ppm in 12% NaOH. 2-8 at% of Ga became enriched after 2 min of etching. Gallium was enriched as a thin metallic film at the metal-oxide interface, as shown by X-ray photoelectron spectroscopy (XPS) [21].
Etching of alloy Al-1300 ppm Ga for 60 s in 0.25 M NaOH at 75°C resulted in enrichment of $3.6 \times 10^{15}$ Ga atoms/cm$^2$ at the surface. Enrichment on alloy Al-120 ppm Ga was one order of magnitude smaller under identical conditions. Amount of Ga enrichment at the surface corresponded to the amount of Ga in the metal layer removed by etching. Ga was enriched in the metallic state as a result of selective oxidation of the more active Al.

2.2.2 Segregation of lead and tin

As discussed above, Pb has no measurable solubility in Al (Fig. 2.2). Pb inclusions were shown by in situ TEM investigation to coarsen and increase in particle size at the grain boundaries and triple junctions during heating at 400°C [23].

Annealing of Al-100 ppm Pb alloy, in vacuum resulted in significant segregation of Pb to the surface, increasing in concentration with increasing annealing temperature. Segregated Pb concentration as a result of annealing at 548°C in vacuum was 55% [24]. Pb enriched after annealing Al-Pb foils containing 100-10000 ppm Pb at 873°C in vacuum was shown to be located in a 500 nm thick region including the oxide and the near-surface of the metal [25]. Electropolishing reduced the concentration of Pb segregated at the surface, while alkaline etching had a negligible effect. Annealing an Al-Pb model alloy, containing 5-50 ppm Pb, at 600°C in air, followed by water quenching, resulted in the segregation of Pb in the oxide, in super-saturated solid solution near the metal-oxide interface and at the grain boundaries near the metal-oxide interface [15]. Recent FE-STEM work showed that Pb segregated in the form of a semi-continuous nano-film between the $\gamma$-Al$_2$O$_3$ oxide crystals and the metal surface, as shown in Fig. 2.6 [26]. The film was formed due to entrapment of the Pb, migrating toward the metal-oxide interface, between the $\gamma$-Al$_2$O$_3$ crystals growing inwards and the metal surface. Annealing in oxygen-free atmosphere prevented formation of crystalline oxide, and the film segregation did not form. Pb segregation to the surface then occurred only in the form of discrete particles [1].

![Figure 2.6](image)

Figure 2.6. a) Cross-sectional STEM bright-field image of the thermal oxide-metal interface together with EDS maps of b) oxygen and c) Pb. d) Colour map resulting from
2. Literature Review

statistical analysis of the EDS data, showing the most probable locations of pure oxide (orange), pure Pb (green) and an area where both Pb and oxide are present [26].

The rate of Sn segregation to Al surface increases with decreasing temperature as its solubility decreases from maximum 0.11 wt% at 625°C (Fig. 2.3). A maximum rate was attained for AlSn alloys with Sn content in the range 30 to 1000 ppm Sn during annealing at 300°C [27]. The rate was reduced by a further decrease of the annealing temperature as the mobility of Sn decreased. Thickness of the oxide formed as a result of annealing the samples at temperatures between 300 and 600°C, followed by water quenching, increased with the Sn concentration in the alloy, reaching of order 1 μm for alloys containing 1000 ppm Sn. Segregation of a nanosize Sn film was detected at the metal-oxide interface by STEM analysis. Particulate segregations were detected at the metal-oxide interface [3]. AlSn alloy containing 100 ppm Sn exhibited an (hydrated-) oxide morphology showing laminated circular forms, as shown in Fig. 2.7a. About 500 nm thick dense oxide was formed at the surface of alloy containing 1000 ppm Sn, as shown in Fig. 2.7b. Formation of the thick oxide was attributed to activation of the surface by liquid Sn segregated during annealing and water quenching. Increasing the annealing temperature toward 600°C resulted in dissolution of most Sn in solid solution with Al. However, some Sn remained segregated along the grain boundaries after 1 h heat treatment. Despite most of Sn was in solid solution also for the alloy containing 1000 ppm, a thick oxide was still formed, probably by Sn enrichment in liquid phase at the metal-oxide interface by dealloying during water quenching, which activated the alloy surface anodically.

Figure 2.7 SEM images of AlSn alloys after annealing at 300°C and quenching in water, showing oxide scale formed during water quenching, a) AlSn100 and b) AlSn1000 [3].

2.3 Anodic activation by gallium

Anodic activation is a significant negative shift in the passivity breakdown potential and a significant increase in anodic current density at potentials at which aluminium is expected to be stably passive. The decrease in the corrosion potential in anodic activation results from an increase in the anodic activation kinetics (anodic activation) as sketched in Fig. 2.8a. However, a similar negative shift in the corrosion potential can occur also by a decrease in the reduction reaction rate, as shown in Fig. 2.8b [28].
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Figure 2.8. An illustration of mechanisms causing a negative shift of the corrosion potential as a result of a shift in the polarisation curves from position 1 to position 2 on the graphs. a) Anodic activation caused by the increase of the anodic reaction rate. b) Cathodic control of the corrosion potential caused by inhibition of the cathodic reaction rate [28].

2.3.1 In chloride solution
Despic et al. showed that addition of Ga in the range 250-1200 ppm in aluminium caused decrease in the corrosion potential and increased corrosion rate during anodic polarisation as Ga content increased in 1 M NaCl de-aerated solution at 25°C [29]. Significant activation behaviour was observed for Ga content higher than 500 ppm, as shown in Figure 2.9.

Figure 2.9. Effect of Ga content on the polarisation curves of Al-Ga alloys in 1 M NaCl solution [29].

Tuck et al. reported that 2.6 wt% Ga was required to give sufficient activation of aluminium in 2M NaCl at 20°C [30] for Al/air battery application. Cooling the alloy to 10°C removed activation. Similar polarisation behaviour was obtained for a Ga-0.1% Al alloy and pure Al if the samples were brought into contact with liquid Ga in chloride or
alkaline solution, and the surface scratched through Ga to obtain metallic contact between Ga and Al as in the classical Hg-drop experiment [31].

Alkaline conditions generated at the surface by pre-polarisation at -2.0 V SCE in chloride solution has been claimed to activate AlGa alloys containing less than 0.1 wt% Ga in the alloy [30, 32]. Pure Al treated similarly in neutral and acidified chloride solutions, containing Ga³⁺ ions, was also activated [33-35]. Addition of Ga³⁺ in sodium chloride solution did not cause any activation of Al in NaCl solution without pre-polarisation at -2.0 V SCE. In 0.5 M perchlorate solutions, the pitting potential decreased only 5 mV for Al-0.026 Ga, 50 mV for Al-0.1 Ga and 605 mV for Al-2.6 Ga alloys compared to pure Al [35]. After pre-polarizing the AlGa alloys at -2.0 V SCE for 5 min in halide and perchlorate solutions at pH 7, metallic Ga deposits were found on the corroded areas [36]. Deposited Ga caused anodic activation by increasing the corrosion attack at the grain boundaries. Increasing time of pre-polarization increased activation. Therefore, enrichment of Ga was suggested to play a role. Enrichment of Ga was claimed to occur, however, due to formation of unstable [HGaO₃]₂⁻ ions during hydrolysis (reaction 2.1), and then deposition back to alloy surface as metallic Ga (reaction 2.2) according to the reactions (2.1) and (2.2) [35].

\[
\text{Ga} + 3\text{OH}^- \rightarrow (\text{HGaO}_3)^2^- + \text{H}_2 \quad \text{(2.1)}
\]

\[
[\text{HGaO}_3]^2^- + 5\text{H}^+ + 3\text{e}^- \rightarrow \text{Ga} + 3\text{H}_2\text{O} \quad \text{(2.2)}
\]

This was based on electrochemical measurements and assumptions without surface characterisation. Increased stability of the aluminium surface against cathodic corrosion [37] at high negative potentials was attributed to enrichment of Ga on the surface according to the reactions above. This requires increased stability of the oxide, which is not likely with increasing pH at the surface, or inhibition of the water reduction reaction by Ga, which delays the alkalinisation of the surface to more negative potentials (see Section 2.7).

Flamini et al. [38] measured the open circuit potential of pure Al, which was wetted by a Ga droplet, and Ga-Al alloys which were brought in physical contact with pure Al in acidified chloride solution (0.5 M NaCl, pH 2.5) at 25°C. As long as Ga was in contact physical with Al, the potential was about -1.6 V SCE. Corrosion potentials of Al - Ga and Al - AlGa0.1wt% alloy couples were similar.

2.3.2 In strong alkaline solution

The potential of Al is expected to approach the theoretical reversible potential values due to the instability of oxide at high pH. Minimum open circuit potential obtained in the pH range of 11.5 - 13.5 was in the range -1.7 - -1.9 V Ag/AgCl, which is close to the thermodynamic corrosion potential of aluminium [39]. The corrosion potential increases in the positive direction with increasing dissolution rate because of increasing polarisation of the anodic and cathodic reactions [40] or precipitation of metallic impurities [41].
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Alkaline etching (at 45°C in 12 wt% NaOH) of Al alloying containing 85 ppm Ga at natural impurity level for varying etching times caused depression of the open circuit potential in 1M NaCl [21]. Accordingly, the open circuit potential of the alloy was -780, -1050 and -1100 mV SCE for the non-etched surface, and after etching for 5 min and 30 min, respectively.

Critical level of Ga in Al-Ga alloys for sufficient activation of Al-air batteries was reported to be less in alkaline solutions (above 500 ppm) than that in neutral chloride solution (2.6 at%). The current density on AlGa anodes, containing Ga at concentrations smaller than 2.6 at%, in an Al-air alkaline battery increased rapidly to values as high as that for the 2.6% Ga alloy, as shown in Fig. 2.10. Ga was detected at the pit bottoms and at metal-oxide interface of the Al-Ga 200 ppm alloy. Enriched Ga was proposed to diffuse back to the bulk alloy by surface and grain boundary diffusion, while some of Ga deposited on the oxide during the experiment. At least 1000 ppm Ga was required in the alloy to obtain a stable activation at the surface in 4M NaOH solution at 60°C.

![Figure 2.10. Current density vs. time for Al-Ga alloys in an Al-air battery with 4M NaOH solution at 60°C [30].](image)

2.4 Anodic activation by other Group IIIA-VA elements

Anodic activation of commercial 8006 alloys in chloride solutions was related to Pb segregation at the surface for the first time by Keuong et al. [42]. This behaviour was demonstrated also by polarisation of AlPb model binary alloys in chloride solution, after heat treatment at 600°C. Surface segregation of Pb by heat treatment of binary [15, 26, 43, 44] and ternary [45-47] model alloys has extensively been investigated, along with its role on anodic activation of the alloy in chloride media [28, 48]. The presence of Pb at ppm level was sufficient to cause enrichment of the element at the surface by heat treatment at 600°C, giving anodic activation due to its limited solubility in Al, as discussed above. Anodic activation of model and commercial Al alloys by Pb occurred by 1 h of heat treatment at 600°C, which is well above the melting point of Pb [15].
Commercial alloys such as 8006 [42] and 3005 [49] became activated also by annealing at temperatures as low as 350°C, while the model AlPb alloys did not. Considering the possible effect of other low melting point elements, model binary aluminium alloys containing Bi, Sn or In were investigated by Gundersen et al [43]. AlSn and AlIn alloys, each containing 1000 ppm of the solute, exhibited high activation, as shown in Fig. 2.11. Graver et al. later showed that maximum activation of Al binary alloys containing 1000 ppm In [6] and Sn [27] containing model binary alloys, annealed in the range 200-600°C, was obtained at 300°C. Activation was caused by segregated In and Sn particles along grain boundaries and at the surface. These results were attributed to a combination of low solubility and sufficiently high mobility of the trace elements in Al at the annealing temperature to give optimal segregation.

![Figure 2.11. Anodic polarisation data for heat-treated model binary alloys Al-20ppm Pb, Al-0.2% Bi, Al-0.1% In and Al-0.1% Sn in 5% NaCl solution [43].](image)

Recent investigations on AlPb alloys showed that a continuous Pb nano-film segregated to the surface by its entrapment at the interface of aluminium metal – thermally formed γ-Al₂O₃ film, which grew into the metal from the surface during heat treatment [26]. Pb segregation in the form of particles during annealing at lower temperatures than 600°C did not wet Al metal surface sufficiently to cause significant activation. Effect of segregated Pb in chloride solution was characterized by polarisation measurements in chloride solution. The anodic polarisation curve showed two oxidation peaks at about -0.91 V<sub>SCE</sub> and -0.88 V<sub>SCE</sub> [15, 26, 42-44, 47]. Each peak was related to stages of superficial etching of the surface, causing multilayered attack [44]. The first layer of corrosion was attributed to the undermining of the thermally formed oxide film along the Pb nano-film [26, 44]. The second layer was a result of crevice corrosion in the gap formed between the undermined oxide and metal surface with acidified anolyte still present. Adding Mg to AlPb model alloys increased activation after annealing at 450°C [45].
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2.5 Activation by gallium together with other elements

Even though some patents are available, there is no application of Ga addition in Al sacrificial anodes, probably due to increased anode consumption despite the advantage of uniform dissolution by Ga addition [50] and a constant anode potential [51]. Reported work is mostly for developing anodes for Al/air batteries as follows. Ga has been reported to activate Al more effectively when it is present in the alloy together with other activator alloying elements such as Sn and In [52]. When amount of Ga and Sn was limited to 0.072 wt% and 0.15 wt%, respectively, hydrogen evolution rate was claimed to decrease to acceptable level and give increased anodic current density in alkaline solution [53, 54]. The advantage of adding Ga was claimed to be increased solid solubility of Sn in Al and higher anodic current density than Al-Sn anodes in 3.5% NaCl solution [54]. Study of alloys of type Al-Sn(max 0.07%)-Ga(0.013-1%)-Mg(0.6-0.7%) in alkaline solutions [55] showed, however, that Ga addition decreased the efficiency of the anode due to high hydrogen evolution resulting in parasitic corrosion.

An Al alloy containing small amounts of Ga, Sn and Mg (0.6 wt % Mg, 0.1 wt % Sn, 0.05 wt % Ga) exhibited high anodic activation in 2 M NaCl solution after applying anodic current of 50 mA/cm$^2$ for 600 s. This resulted in tin segregation at the surface. The role of gallium in the activation process was not reported [56-58]. Corrosion was claimed to initiate around tin inclusions. Pit propagation occurred superficially by forming rounded pits. Ga was suggested to play an important role in activation together with the segregated tin in the formation of pits and further corrosion by preventing repassivation of the oxide film. The open-circuit potential oscillated between -1.5 V$_{SCE}$ and -1.1 V$_{SCE}$, as shown in Figure 2.12, with intensive hydrogen evolution at -1.5 V$_{SCE}$.

![Figure 2.12. Potential of aluminium alloy containing 0.4 wt% Mg, 0.07 wt% Sn and 0.05 wt% Ga during galvanostatic polarisation in 2M NaCl at a current density of 1 mA cm$^{-2}$ [57].](image-url)
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Liquid alloys of Ga with other low melting point activator elements, such as In, Sn, Zn are reported to generate H$_2$ in galvanic contact with aluminium in aqueous solution [59, 60]. The role of Ga was claimed to lower the melting point of the liquid alloy relative to those of the pure components. Penetration of the alloy into the grain boundaries of aluminium increased the contact area between the alloy and aluminium [60].

2.6 Melting point depression

Amalgamation mechanism has been suggested earlier also to explain anodic activation of Al by In [6], Sn [61] and Bi [62]. However the bulk melting points of these elements are significantly higher than that of Ga and Hg. These elements segregated in the form of nano-particles and nano-film locally at the Al surface due to their limited solubility in Al during annealing. It was claimed that the nano-segregations of these elements remained in the liquid state at temperatures much lower than their bulk melting points [63]. The melting point of Pb decreased by 200°K when the particle size was decreased from 10 to 3 nm [64]. Ga and Pb particles of size 30 and 8 nm, respectively, were obtained by high vacuum deposition of from a Ga-15%Pb alloy [65]. The melting point of Ga particles was depressed to -34°C and that of Pb particles to the temperature range 226-261°C.

Nano-particles embedded in a foreign bulk material may show increased or decreased melting points relative to their bulk values, depending on whether their surface atoms are coordinated with the bulk matrix atoms or not, respectively [66]. This is related to melting of particles with coordinated surface atoms from the centre towards the surface, while free nanoparticles melt from the surface towards the centre. Melting point depression of indium particles, which were embedded and homogenously distributed in Al, depended on the epitaxy between the nanoparticles and the matrix. Nano-particles of In, Sn, Pb and Bi embedded in Al, forming incoherent interfaces with Al, showed lower melting points than their respective bulk values, inversely proportional to their size.

2.7 Inhibition of hydrogen evolution

Alloying Al with 100 ppm Hg resulted in an increase in the hydrogen evolution overpotential by 0.9 V (in the negative direction) in NaCl solution relative to that for pure Al [4]. Hydrogen evolution overpotential for Sn [67], Ga [68] and Bi [69] are also known to be high, causing inhibition of hydrogen evolution when alloyed with Al [4, 70]. It was suggested, therefore, that the increase in the hydrogen overpotential by presence of alloyed or trace elements Hg, In, Sn, Bi, and Ga was a cause of depression of the corrosion potential of the Al alloy relative to pure Al. However, Sn in Al was also suggested to act as a catalyst for hydrogen evolution [57]. pH increase due to hydrogen evolution on Sn inclusions was claimed to destabilise the oxide on Al adjacent to the inclusions, causing anodic activation [58]. In contrast to the Group IIIA-VA elements, overpotential for hydrogen evolution is low on transition metals, such as copper, giving increase in the corrosion potential when alloyed with Al [71].
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2.8 Ennobling effect of alloying elements in aluminium

In addition to reduction in the hydrogen overpotential discussed above, common alloying elements such as Cu, Mn, Fe and Si, which are more noble than Al, ennoble Al by shifting the pitting potential in the positive direction in chloride solution if they are in solid solution [72]. In ternary AlPb alloys containing one of these elements, the activation effect of Pb was significantly reduced, in particular by Cu, after annealing at 600°C [1]. Reduced activation occurred by significant reduction of the corrosion rate above the breakdown potential rather than a significant shift in the breakdown potential in the positive direction. GD-OES depth profiling of the alloy containing 20 ppm Pb and 0.5% Cu showed Pb enrichment of the surface similar to the binary AlPb alloy, while the Cu concentration was homogeneous at the bulk value. Cu enrichment occurred by dealloying as a result of corrosion in chloride solution. However, no evidence of any specific interaction between Pb and Cu could be demonstrated by electron spectroscopy, STEM and SIMS [46]. The ennobling effect was therefore attributed to Cu present in solid solution and its enrichment at the corroding sites by dealloying, thereby counteracting the activating effect of Pb [73].

2.9 Liquid metal embrittlement by gallium

Liquid metal embrittlement of aluminium is caused by contact of a liquid metal, often Hg and Ga, causing intergranular failure [74]. When in contact with aluminium, melting point of pure gallium (30°C) is lowered to the eutectic temperature (25°C) [9]. Thus, liquid gallium can penetrate rapidly along the grain boundaries of aluminium even at room temperature and cause fracture without any applied stress [75]. Ga penetrates along the grain boundaries at rates in the range 0.01-12.7 μm/s, and it forms a layer of thickness in the range 0.6-6 mono-layers. 10 ppm gallium implanted on aluminium bicrystal was sufficient to cause embrittlement [76].

According to Stumpf and Feibelman [77], Ga atoms bind stronger to Al atoms than to each other. The first monolayer of Ga covered Al entirely by Ga-Al pair, while the next layers bound poorly to the first layer of Ga as Ga-Ga pairs. This resulted in reduced strength at the grain boundaries. Hugo and Hoagland [78] also found two immobile monolayers of Ga on each Al surface at the grain boundary and one mobile layer by in-situ TEM study. The immobile Ga layers were assumed to bind with Al atoms causing weakening of Al-Al bonds and initiate opening at the grain boundaries while the mobile layer penetrated between the two immobile layers along the opened grain boundary. Ga penetration of the mobile layer caused separation of two grains. Intergranular penetration of Ga in Al was predominant in the temperature range 30°C to 125°C in relation to volume diffusion [79]. Above this temperature volume diffusion of Ga was important. The grain size obtained after different rolling reductions determined the quantity of absorbed gallium and the mechanical behaviour.

The results reviewed above on embrittlement of Al by liquid Ga were obtained by bringing liquid gallium in contact with aluminium surface externally. Embrittlement by Ga as an alloying element in Al was studied only by Schmidt et al. [19]. These authors did not observe embrittlement at Ga concentrations below 7.8 at%, which is close to
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Solubility limit of Ga in Al at about 26.6°C. AlGa alloy containing 0.4 and 5 at% Ga exhibited Ga segregation at the grain boundaries as a result of annealing for 30 h at 300°C, though embrittlement did not occur.

2.10 Possible activation mechanisms

Effect of Ga on activation of aluminium was shown by an experiment [33] identical to the classical Hg drop experiment[31]. Pure Al was brought in metallic contact with Ga by drilling a hole on an Al sheet through a Ga droplet placed on the plate. Wetting Ga with a drop of distilled water caused initiation of hydrogen evolution becoming visible in the form of bubbles. Al(OH)$_3$ forming at the outer Ga surface (Ga-air interface) by oxidation of Al dissolved in Ga at the Al-Ga metallic interface deposited around the Ga particle until the surface was dry. Thus, Al metal dissolved in the Ga droplet forming a liquid phase GaAl alloy (amalgam). Re-passivation of the Al surface at the Al-Ga interface is prevented by amalgam wetting the Al metal. Al diffuses through the amalgam and oxidises at the outer surface of the amalgam, where it comes in contact with ambient oxygen. Solubility of Al in liquid Ga is 0.75 wt% at the eutectic temperature of 26.6°C [9]. Diffusion coefficient of Al in liquid Ga is four orders of magnitude higher [30] than in liquid Hg [80]. These factors are considered more than sufficient to cause high corrosion rates observed on Al surface activated in the manner described. In the presence of water, corrosion is enhanced by hydrogen evolution as the reduction process.

Activation of a solid state Al-Ga alloy, where Ga is originally in solid solution with Al, is suggested to occur as follows (Fig. 2.13) [30]:

- Oxidation of Al and enrichment of the more noble Ga at the surface.
- Formation of GaAl phase.
- Oxidation of Al at the GaAl solution interface to form Al(OH)$_3$.
- Increase in corrosion rate as the amount of Ga enrichment of the surface increases.

![Figure 2.13. Schematic representation of the possible activation mechanisms suggested for Al-Ga alloys [30].](image-url)
Theories based on Ga dissolution and redeposition to explain the enrichment of Ga metal on Al surface cannot be applicable in view of the negative potentials at which this enrichment occurs. These potentials are more negative than the thermodynamic oxidation potential of metallic Ga [39].

Activation by amalgamation was also claimed to occur by segregated Sn during annealing at 300°C and subsequent water quenching [3]. Segregation of Sn at the surface of Al caused simultaneous voluminous oxidation of the surface forming an oxide of about 1 μm thick covering the entire surface [2]. Similar phenomenon was not observed by annealing at 600°C and cooling in air. High oxidation rate was attributed to formation of super-heated steam during water quenching combined with segregation of liquid Sn phase which activated the Al surface by the amalgamation mechanism discussed above. The reaction proceeded until the sample cooled down and the liquid Sn solidified. The similar mechanism was reported by Bi after annealing at 600°C followed by water quenching [81].

Designing eutectic alloys with Ga and other low melting point elements for hydrogen evolution in fuel cell applications, is also based on the activation of Al by amalgamation. A stable liquid phase which can destabilise the passive oxide film at aluminium surface enables the reaction of Al with water at low temperatures. The melting point of Ga-In-Sn-Zn alloy (60:25:10:5) is only 7.6°C [60].

2.11 Discussion

Earlier studies on the activation of aluminium by alloyed gallium in chloride and alkaline solutions are related to development of anodes for Al/air battery and sacrificial anodes for cathodic protection. These require higher amounts of alloyed Ga than the amount of Ga normally present as trace element in commercial Al alloys, to be able to obtain the required activation of the aluminium surface. Anodic activation of Al requires enrichment or segregation of the activating element at the Al surface. If the available thermodynamic data are correct, segregation of Ga by heat treatment is not deemed possible because of the high solubility of Ga in Al relative to the trace element level even at temperatures as high as 600°C. However, the possibility of Ga segregation during heat treatment in the presence of other trace and alloying elements has not been investigated. It is also not clear how segregated Ga in the presence of other segregated elements would affect the electrochemical behaviour of Al. Such segregation can occur also by dealloying during aqueous corrosion or etching of the surface. The synergy reported between Sn and Ga in activating Al in chloride solution [56-58] is discussed in the foregoing review. However, the underlying mechanisms of segregation and activation are not clarified.

Extensive work performed in this laboratory on the activation of Al by the trace elements Pb, In, Bi and Sn, also reviewed above, does not appear to be of direct utility in predicting the behaviour of Ga in Al because of significant differences in the physical properties, especially the melting points of the elements and their solubilities in Al, which appear to be important factors in explaining segregation of the element and its destabilising the passive oxide on Al in causing activation. The closest element to Ga in
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the group is Hg in terms of low melting point, and the mechanism by which Ga is known to activate Al is accepted to be similar to that of Hg (amalgamation), assuming that Ga in contact with the Al surface is in the liquid phase. Hg is not a common trace element in Al. It has nearly zero solubility in Al, in contrast to common presence of Ga and its appreciable solubility in Al. These facts should help explain the concern about segregation of the common trace element Ga and its possible consequences.

Segregation of Ga as a result of deep caustic etching as pretreatment of commercial Al alloys prior to further chemical processing is of particular concern in terms of anodic activation and also in terms of liquid metal embrittlement. As reviewed above, most of earlier work on embrittlement of Al alloys by Ga is based on the condition where metallic Al and liquid Ga are brought into physical contact. It is not known whether segregation of trace element Ga may cause embrittlement of Al. However, no such cases have been reported in the available literature. The present thesis work is therefore undertaken to clarify these issues of uncertainty.

References

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3 Effect of Gallium on Anodic Activation and Embrittlement of Aluminium

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Abstract

This work investigates the effect of small amounts of gallium on the electrochemical and corrosion properties of model binary AlGa alloys after heat treatment. Effect of alkaline etching is also investigated. Alloys containing 50-1000 ppm Ga were cast from pure components, followed by homogenising, cold rolling and heat treatment in the temperature range 300-600°C. Characterisation by electron-optical methods and glow discharge optical emission spectroscopy did not show any Ga segregation by annealing in this temperature range because of high solid solution solubility of Ga in aluminium. Electrochemical characterisation in 5% NaCl solution did not indicate anodic activation, which could be attributed to thermal Ga segregation to the surface. Activation that was observed on the alloy with 1000 ppm Ga was a result of Ga enrichment by dealloying of the Al component. Alkaline etching caused significant enrichment of Ga at the surface by dealloying, which in turn lead to anodic activation in chloride solution. Diffusion of Ga enriched by alkaline etching into the grain boundaries also caused significant liquid metal embrittlement of AlGa alloys containing at least 250 ppm Ga. Segregated Ga dissolved back into aluminium by annealing for 1 h at 600°C after etching, eliminating the grain boundary embrittlement and anodic activation.

3.1 Introduction

Alloying aluminium with gallium at concentrations larger than 0.1% has been exploited in the development of active anodes for sacrificial anodes [1-3] and anodes for the aluminium-air battery [4-7]. However, its effect as a trace element on the electrochemical and corrosion properties of aluminium alloys, in particular as a function of thermomechanical and chemical processing parameters, has not been much investigated.

Concentration of Ga as a trace element in commercial alloys is normally in the range 100-200 ppm depending on the primary source [8]. Other elements In, Sn, Pb and Bi
from Group IIIA-VA have been shown [9-13] to segregate to the aluminium surface by heat treatment at temperatures above their respective melting points. As a result, small amounts, such as 20 ppm of Pb [10, 11] and 30 ppm of Sn [13] and In [14], caused significant anodic activation of aluminium in chloride solution. Anodic activation manifests itself by a significant lowering of the pitting potential with respect to that of pure aluminium and higher current outputs at potentials where pure aluminium is expected to show passive behaviour [11, 15].

Differing from the elements above, 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 [16]. Thus, it is stable in solid solution with aluminium, and it does not segregate to the surface or grain boundaries by heat treatment [17]. Larger amount of gallium than the other elements in Group IIIA-VA is required in aluminium to cause significant activation. The critical amount needed was 0.26 wt% for anodes in Al/air battery application [5] and 500 ppm for sacrificial anodes, both in chloride environment [4]. Smaller gallium contents activated only after extended pre-polarisation at potentials as negative as -2 V_{SCE} [18-20] or after etching in NaOH solution [5], resulting segregation by dealloying. It is well known that gallium becomes enriched by chemical processing in general, such as alkaline etching [17, 21, 22] and anodizing [17, 23], as a result of dealloying of the active aluminium component. However, the effect of such enrichment on the electrochemical properties of aluminium has not been much investigated.

Liquid Ga in contact with Al surface is known to cause liquid metal embrittlement [24, 25], even in the absence of applied stress [26, 27], as a result of penetrating into the grain boundaries. Most studies of embrittlement of aluminium by gallium are based on bringing liquid Ga metal from an external source in physical contact with the aluminium surface [28-31]. Schmidt et al. [31] studied gallium as an alloying element at concentrations of 1, 5 and 18 wt% in aluminium. Embrittlement was caused only by the presence of 18 wt% Ga.

The purpose of this work is to clarify the conditions under which small amounts of Ga alloyed in pure aluminium can become segregated to the surface by heat treatment or alkaline etching and to what extent the segregated Ga can activate the surface and embrittle the grain boundaries.

### 3.2 Experimental

**Materials.** Model binary AlGa alloys, containing 50, 100, 250, 500 and 1000 ppm Ga, were prepared from pure components and cast in chilled copper moulds. These alloys were designated as AlGa50, AlGa100, AlGa250, AlGa500 and AlGa1000, respectively. After homogenisation for 20 h at 600°C, the cast alloys were scalped and cold rolled from 20 mm to a final thickness of 2 mm. Weighed in concentrations of Ga during casting were verified within 5-15% by glow discharge mass spectrometry analysis of the rolled samples.
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Samples were ground with SiC paper and polished metallographically to 1 μm diamond paste finish. They were then heat treated for 1 h in the temperature range 300-600°C in an air-circulating furnace, followed by quenching in water.

Etched samples were prepared from specimens that were heat-treated at 600°C. Etching was performed for 2 min in 12 wt% NaOH solution maintained at 45°C. The specimens were thereafter desmutted in concentrated HNO₃ and rinsed in distilled water and ethanol.

**Electrochemistry and corrosion.** Potentiodynamic polarisation was performed in stirred 5 wt% NaCl solution at 25°C, which was exposed to ambient air. The sample area exposed to the solution was 0.64 cm². Anodic polarisation curves were measured with respect to a saturated calomel electrode (SCE) at a sweep rate of 0.1 mV/s in the positive potential direction, starting at 50 mV below the corrosion potential. The cell geometry, solution volume and the stirring rate in the solution were identical in all runs.

Corrosion potential measurements were performed as a function of time for a period of 48 h in ASTM D1141 synthetic seawater whose pH was adjusted to 3 by adding glacial acetic acid. This corresponds to the solution composition used in the acidified synthetic seawater (fog) test, ASTM G85-98, A3. This choice of solution was made to obtain slow etching of the sample surface during exposure, such that the variation in the corrosion potential could be recorded, as the surface was gradually removed or modified by dealloying.

Corrosion potential was measured also during alkaline etching for 10 min. The surface area exposed to the NaOH solution was 1.33 cm². Hg/HgO reference electrode (-129 mV with respect to saturated calomel electrode) was used in order to avoid chloride contamination.

Selected samples were polarized potentiostatically at pre-determined potentials. The corrosion morphologies resulting from 4 h polarisation were investigated by FEG-SEM and EDS.

**Surface characterisation.** Elemental depth profiles after heat treatment were measured qualitatively by using glow discharge optical emission spectrometry (GD-OES). The measurements were quantified for Al and O by using the standards available. Calibration data for small Ga concentrations in Al were not available. The data reported for Ga were calculated by assuming a linear relationship between the known amount of gallium in the bulk of the samples and the measured intensity (V). Since the measured Ga concentration at the alloy surface could exceed the maximum bulk concentration (1000 ppm) of the test samples by an order of magnitude, the reported values, based on extrapolation of the linear relationship, were semi-quantitative at best. However, the reported data for Ga were deemed comparable for different samples, as long as the instrument settings used for the measurements were identical. The GD-OES data were measured at 5 ms, intervals of Ar-beam sputtering. The sputtering rate was about 70 nm/s in the metal and 40 nm/s in the oxide. Sample surfaces were characterised after
3. Effect of Gallium on Anodic Activation and Embrittlement of Aluminium

heat treatment and etching also by using a field emission gun scanning electron microscope (FE-SEM).

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) techniques were used for chemical analysis of the fractured grain boundaries due to liquid metal embrittlement.

XPS analysis of the etched samples were performed on a Kratos Axis Ultra\textsuperscript{DLD} instrument using monochromatic Al K\textalpha\ radiation ($\nu = 1486.6$ eV) at 15 kV and 10 mA. The vacuum chamber was cooled to -200°C in order to prevent the diffusion of gallium from the surface into the bulk of the sample during measurement. Angle resolved X-ray electron spectroscopy (AR-XPS) was performed to obtain non-destructive depth profiles by changing the emission angle from 0° (bulk sensitive) to 64° (surface sensitive) to the surface normal. XPS depth profiling was performed also by using Ar ion beam sputtering at 2 kV. The surface was sputtered first for 5 s cycles. The XPS spectra was measured for the energy windows selected for Al, O and Ga peaks at the end of each sputtering cycle. However, the Al-O, O and Ga signals were found to be strong at the end of the 4 such cycles, and therefore, the sputtering time was increased to 10 s for the next cycle, then to 20 s for the following 8 cycles until the oxygen intensity became weakened. Sputtering rate was about 0.2 nm/s calibrated by measuring the sputtered depth for pure Al.

In investigating the fractured grain boundaries by XPS, the brittle specimen was bent in a glove box, which was flushed with high purity Ar gas. The grains were then directly transferred into the analysis chamber in order to avoid contact with air as much as possible.

AES was used for higher lateral resolution analysis of individual grains. A JEOL 9500F Auger Microprobe instrument, equipped with a hemispherical electron spectrometer, was used. The spectra were obtained at 10 keV accelerating voltage and a primary electron beam current of 20.4 nA at energy resolution of 0.35% with a lateral resolution of 8 nm. For the depth profiling, the beam diameter was increased, and an area of approximately 1.4 mm\textsuperscript{2} was sputtered with a sputtering rate of 6.3 nm/min (calibrated for Si) for 15 s per cycle. The depth profile data were quantified by calculating the peak-to-peak intensities of the differentiated peaks and using JEOL database for the relative sensitivity factors (RSFs) of the elements. Reference spectra for Ga metal and Ga\textsubscript{2}O\textsubscript{3} powder were measured in the laboratory by using high purity materials (Fig. 3.1), indicating 7 eV kinetic energy shift between metallic and oxidized Ga (Ga\textsubscript{2}O\textsubscript{3}). For quantification of Al-oxide and metallic Al, the first and the last cycles of the depth profile were used as reference, respectively. The observed chemical shift between metallic and oxidised Al was in agreement with the published data [21].

**Mechanical testing.** Changes in the mechanical properties of the samples resulting from Ga embrittlement and recovery from embrittlement were characterised by three point bending test using a 0.2 kN load cell. Load was applied at a constant rate of 0.05 mm/s for 18 mm. The sample size was 55 x 30 x 2 mm.
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3.3 Results

3.4 Surface characterisation

As heat-treated surface

The size of grains containing Ga did not differ significantly from the grain size of pure Al after heat treatment for 1 h in the range 300 - 600°C. The grain size was in the range of 30 – 100 µm after heat treatment at 300°C. Heat treatment above 300°C resulted in significant grain growth up to 2-3 mm at 600°C.

GD-OES elemental depth profiles showed that Ga concentration in alloys AlGa50, AlGa500 and AlGa1000, annealed in the range 300-600°C was uniform, as shown for alloy AlGa1000 in Fig. 3.2a and 3.2b for 300 and 600°C, respectively. Ga intensity decreased from the metal-oxide interface to the oxide surface.

The oxide thickness did not change with the Ga content of the metal. It was about 5-10 nm for samples heat treated at 300°C and about 50 nm for samples heat treated at 600°C, i.e., identical with the oxide thickness on pure aluminium heat treated under identical conditions [10].
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Figure 3.2. GD-OES depth profiles of alloy AlGa1000, heat-treated for 1 h at a) 300°C and b) 600°C for 1 hour.

*As etched surface*

Fig. 3.3 shows the surface morphologies of pure Al and AlGa alloys after alkaline etching. The etch morphologies of alloys AlGa50 and AlGa250 ppm, shown in Fig. 3.3b and 3.3c, respectively, were identical to the etched surface of pure Al with well-known scalloped morphology (Fig. 3.3a) [22, 32, 33]. Etch morphology of alloy AlGa1000, shown in Fig. 3.3d, showed a coarser cellular structure in comparison to pure Al and AlGa alloys with lower Ga content. EDS mapping of etched surface of alloy AlGa1000, shown in Fig. 3.4, indicated Ga enrichment of the surface, especially along the ridged cell boundaries.
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Figure 3.3. FE-SEM plane view micrographs after 1 h heat treatment at 600°C, followed by etching, for a) pure Al, b) AlGa50, c) AlGa250 and d) AlGa1000.

Figure 3.4. EDS maps of heat treated (1 h at 600°C) and alkaline-etched surface of alloy AlGa1000. a) Surface morphology, b) Al, c) Ga and d) O.
GD-OES depth profiling of etched alloys AlGa50 and AlGa1000 showed that surface enrichment of Ga was significant, and it occurred at the metal-oxide interface, as shown in Fig. 3.5a and 3.5b, respectively. The peak concentration of gallium at the metal-oxide interface of alloy AlGa50 was about 0.1 wt%. The Ga peak on alloy AlGa1000 was very high and not possible to quantify. Thus, enrichment of Ga by etching increased with the bulk concentration of Ga. It also increased with increasing time of etching (not shown). The O and Al profiles intersected at about 5 nm depth from the oxide surface, and this value is probably representative of the oxide thickness. The Ga concentration was at a maximum at the sputtering depth of 17 nm. Peak broadening due to surface roughness did not allow determination of the thickness of Ga-enriched layer. However, the sputtering time required, for Ga concentration to attain the bulk level from the high levels near the surface, increased with etching time (not shown), probably because of Ga diffusion into the grain boundaries.

Repeating the heat treatment (1 h at 600°C) on the samples analysed in Fig. 3.5 caused the segregated Ga to dissolve back into solid solution with aluminium, as shown in Fig. 3.6a and 3.6b for alloys AlGa50 and AlGa1000, respectively.
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Figure 3.6. GD-OES depth profiles of alloys in Fig. 3.4 after repeating the heat treatment (600°C for 1 h). a) AlGa50 and b) AlGa1000.

XPS depth profile, measured by Ar sputtering, for the etched surface of alloy AlGa1000 (heat treated at 600°C) is shown in Fig. 3.7. These results confirmed the GD-OES data (Fig. 3.5b) insofar as the oxide thickness (about 17 nm) and Ga enrichment, for which the peak appears to exist in the metal slightly below the oxide-metal interface, at a depth of about 20 nm from the oxide surface. Only metallic Ga was detected at 1116.6 eV binding energy corresponding to the Ga 2p peak [34]. However, non-destructive angle resolved analysis gave the oxide thickness to be about 4 nm. Surface roughness probably was a factor in significant broadening of the Ga peak along with the enrichment of the grain boundaries with Ga near the surface.
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3.4.1 Characterisation of embrittled grain boundaries

Caustic etching at 25°C, which is below the melting point of Ga, did not cause embrittlement. Etching for 2 min at 45°C resulted in significant embrittlement and intergranular fracture of alloy AlGa1000, as shown in Fig. 3.8a. Fracture occurred by slight bending of the etched samples. Entire sample thickness of 2 mm was affected. While the surface grains and grain boundaries at the surface showed the etching morphology due to alkaline etching (Fig. 3.8b), the fractured grain boundaries were smooth (Fig. 3.8c). Certain grains showed striated fracture surfaces and pits, as shown in Fig. 3.8d, indicating stepwise development of fracture, as Ga segregating at the surface penetrated into the grain boundary. Some fracture surfaces exhibited dimples of about 1 μm in size, as shown in Fig. 3.8d. Ga was detected in the dimples by EDS spot analysis. Ga film on the grain boundary surfaces, as indicated by the bright-contrast area in the backscattered image in Fig.3.8e, was probably formed by diffusion of Ga segregated at the surface during etching in to the grain boundary. Ga coverage of the grain boundary surface was expected to be more extensive. This was probably not detectable by EDS (insufficiently sensitive) or some of the Ga diffused back into Al between alkaline etching and SEM analysis. Dimples probably formed during fracture due to deformation, while some areas exhibited striations, as in Fig. 3.8f.

Auger line scan along a 0.5 μm long track, shown in Fig. 3.9a along an embrittled grain boundary surface, indicated (Fig. 3.9b) that the surface was uniformly coated with metallic Ga, in support of the argument above. The line of analysis crossed a grain boundary without significant change in the Ga concentration between the neighbouring grains. Results from Auger depth profiling of a similar grain boundary surface (with the
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sputtered area and its elemental profile shown in Fig. 3.10a and Fig. 3.10b, respectively) indicated that the metallic Ga film was not thicker than 10 nm. XPS analysis of such area showed that the outermost surface of the Ga film was oxidised, probably by exposure to air after etching (Fig. 3.11). Repeating the analysis of the same sample after 12 days of exposure to air caused significant reduction in the metallic Ga in relation to the peak for oxidised Ga. This was attributed to diffusion of Ga back into the grain during storage at room temperature.

Figure 3.8. Embrittled grain boundaries on alloy AlGa1000, heat treated at 600°C, after alkaline etching for 2 min at 45°C. a) Plan view showing separated grain boundaries. b) Etch morphology on grains and grain boundaries. c) Smooth grain-boundary surfaces appearing after removal of fractured grains. d) Separated grain boundary surface with dimples. e) Back-scattered electron image of the black frame in (d) showing Ga film (light grey contrast) and spot EDS analysis at the pit marked with arrow. f) Striation on the fractured grain boundary.
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Figure 3.9. a) Track along the embrittled grain boundary surface of alloy AlGa1000 for Auger line scan. b) Auger elemental concentration profiles along the line.
Figure 3.10. a) Area on an embrittled grain boundary surface of alloy AlGa1000 subjected to Auger depth profile analysis and b) Auger elemental concentration profile along the sputtered thickness.
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3.4.2 Bending test

Etching of the 600°C-annealed AlGa specimens in NaOH solution for 2 min at 45°C resulted in significant reduction in the strength of alloys containing more than 100 ppm Ga, as shown in Fig. 3.12. The specimens etched for 1 min did not show brittle behaviour. Etching of alloys AlGa50 and AlGa100 for 30 min did not cause embrittlement either.

Bending test results for heat-treated (HT) and heat-treated and etched (HT+E) samples of alloy AlGa1000 are compared with samples which were heat treated, etched and re-annealed (HT+E+HT) in Fig. 3.13. Re-annealing of the etched sample (HT+E+HT) caused recovery, and possibly even improvement, of the strength of the sample, as shown in Fig. 3.13a. This result can also be visually discerned by comparison of the appearance of the samples tested in the HT, HT+E and HT+E+HT conditions, shown in Fig. 3.13b-d, respectively. The SEM micrograph of the HT+E+HT surface in Fig. 3.14 shows the etched morphology of the surface and fused grain boundaries.

Figure 3.11. Ga XPS spectra on an embrittled grain of alloy AlGa1000 soon after etching (red) and after 12 day exposure to air (green).
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Figure 3.12. Bending test results for AlGa alloys, annealed at 600°C after alkaline etching for 2 min at 45°C in 12 wt% NaOH solution.

Figure 3.13. a) Bending test results for alloy AlGa1000 in heat-treated (HT), heat treated and etched (HT+E) and heat treated, etched and reheat-treated (HT+E+HT) conditions. Appearance of b) HT, c) HT+E and d) HT+E+HT conditions after the test.
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3.4.3 Electrochemical characterisation

As heat-treated samples in chloride solution

Fig. 3.15a and 3.15b show the potentiodynamic polarisation curves for AlGa alloys heat-treated for 1 h at 300°C and 600°C, respectively, in 5% NaCl solution. Alloys AlGa50 and AlGa100 did not show significant change in the pitting potential ($E_p$) in relation to pure Al treated in the same manner. As the Ga concentration increased, $E_p$ decreased. However, the difference of $E_p$ from pure Al, even for 1000 ppm Ga content, was only about 55 mV for heat treatment at 300°C and 35 mV at 600°C. The corrosion potential ($E_c$) obtained from the potentiodynamic polarisation data was not reproducible. $E_c$ measured separately under open circuit conditions as a function of time in acidified synthetic seawater for alloys AlGa50 and AlGa1000, annealed for 1 h at 600°C was close to the corresponding $E_p$, as shown in Fig. 3.16. The difference in $E_c$ between alloys AlGa50 (-0.75 V$_{SCE}$) and AlGa1000 (-0.83 V$_{SCE}$) was 70 mV after 24 h exposure. $E_c$ decreased slightly with time for AlGa1000, while it did not vary much for alloy AlGa50. After 48 h, the $E_c$ of alloy AlGa1000 was about -0.9 V$_{SCE}$. $E_c$ and $E_p$ of alloy AlGa1000 did not change significantly with annealing temperature.
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Figure 3.15. Potentiodynamic polarisation curves for pure Al and AlGa alloys after heat treatment for 1 h at a) 300°C, b) 600°C. Test solution: 5% NaCl solution at 25°C.
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Figure 3.16. Corrosion potential variation with time measured in acidified synthetic seawater at 25°C.

Alloy AlGa1000, the only alloy that showed appreciable activation among the AlGa alloys in foregoing experiments, was investigated further by potentiostatic polarisation in 5% NaCl solution. Current-time data for various applied potentials are shown in Fig. 3.17a. Starting from a small value for the passive surface, the current density at -0.8 V\text{SCE} increased to a pseudo steady-state plateau of about 1-3 mA/cm² within 1 h, independent of the heat treatment temperature. After about 2.5 h, a new current increase was observed to a new steady state of about 25 mA/cm². At -0.85 V\text{SCE}, the current density increased to about 1 mA/cm². The second step of increase was not observed. However, the surface remained passive at -0.9 V\text{SCE}. At the end of 1 h polarisation, the current density was nearly zero.

The long-time current-time data for the AlGa alloys, heat-treated at 600°C, are shown in Fig. 3.17b at an applied potential of -0.8 V\text{SCE}. Increase of current density with time was significant for alloy AlGa500, increasing by several orders of magnitude to about 18 mA/cm² after 24 h. The magnitude of the initial current density for alloy AlGa250 was similar to that of alloy AlGa500. However the increase of current with time was not as significant on alloy AlGa250, still of order 1 μA/cm² after 16 h of exposure. The base current level of AlGa250 was lower by two orders of magnitude than AlGa500. The current density of alloy AlGa100 remained nearly zero during the test period of 16 h.
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Figure 3.17. Potentiostatic polarisation results in 5% NaCl solution at 25°C for a) alloy AlGa1000 heat treated at 300°C and 600°C at selected potentials. b) Long time data (up to 24 h) for other AlGa alloys, heat treated at 600°C, at an applied potential of -0.8 V\textsubscript{SCE}.

**Corrosion potential during alkaline etching**

Alloys AlGa500 and AlGa1000, which were heat treated for 1 h at 600°C, were etched for 1 min in alkaline solution, instead of the usual 2 min, in order to avoid
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Embrittlement. The samples containing lower Ga concentration and pure Al were etched for 2 min to obtain an observable change in anodic behaviour.

$E_c$ of alloys AlGa50 and AlGa100, measured during etching in 12 wt% NaOH solution, was similar to that of pure Al during the first 2 minutes, giving first a maximum or a plateau at about -1.95 V\textsubscript{SCE}, and then increasing again to a new maximum of about -1.85 V\textsubscript{SCE}, period depending on the Ga content, as shown in Fig. 3.18. A cyclic time variation was then observed, frequency depending on the Ga content (9 min for alloy AlGa50 and one min for alloy AlGa100) giving negative potential surges from the base potential of about -1.85 -- -1.9 V\textsubscript{SCE} to about -2.1 V\textsubscript{SCE}. Intensive gas evolution was observed visually at each negative surge. $E_c$ of alloy AlGa250 decreased significantly to about -2.13 V\textsubscript{SCE} after 2 min and then stabilised at about -2.05 V\textsubscript{SCE}. $E_c$ of alloy AlGa500 and AlGa1000 decreased from the start and stabilised after 1.5 min and 45 s, respectively, at about -2.05 V\textsubscript{SCE}.

The average etching rate measured by weight loss after 30 min of immersion in the alkaline solution was 0.0005 g/cm\textsuperscript{2}/min for pure Al and for alloys AlGa50 and AlGa100, while it was 0.002, 0.004 and 0.014 g/cm\textsuperscript{2}/min for alloys AlGa250, AlGa500 and AlGa1000, respectively.

![Figure 3.18. Variation in the corrosion potential during etching of pure Al and AlGa alloys in 12 wt% NaOH at 45°C.](image)

**Heat-treated and alkaline-etched (HT+E) samples in chloride solution**

Potentiodynamic polarisation curves, obtained in 5% NaCl solution after heat treatment for 1 h at 600°C and 2 min etching of alloys in alkaline solution, are shown in Fig. 3.19. Alkaline etching caused lowering of $E_p$ by about 70 mV for alloys AlGa50 and AlGa100. Alloy AlGa250 exhibited reduced and unstable passivity above $E_c$. 

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characterised by a couple of active peaks. Stable pitting initiated at about $-0.8 \text{ V}_{\text{SCE}}$, i.e., at about the same $E_p$ as alloys AlGa50 and AlGa100. However, $E_c$ of higher Ga alloys AlGa500 and AlGa1000 was significantly depressed with increasing Ga content. The variations in $E_p$ as a function of Ga content, annealing temperature and alkaline etching are summarised in Fig. 3.20.

![Figure 3.19](image1.png)

Figure 3.19. Potentiodynamic polarisation curves (after 1 h heat treatment at 600°C and etching for 2 min in 12wt% NaOH at 45°C and desmutting in nitric acid) in 5% NaCl solution at 25°C.

![Figure 3.20](image2.png)

Figure 3.20. Effect of annealing temperature, alkaline etching and Ga concentration on the pitting potential ($E_p$) in 5% NaCl solution.
Fig. 3.21a shows current-time data for heat-treated (600°C) and etched (HT+E) AlGa alloys at an applied potential of -0.8 V_{SCE} in 5% NaCl solution. Alloy AlGa1000 was active throughout the test period at a current density of about 50 mA/cm². Alloy AlGa500 was more passive than alloy AlGa1000 at the outset. It became increasingly active during the test period, reaching the same current level as alloy AlGa1000 after about 5 min. In comparison, these alloys without pre-etching (HT condition) exhibited passive behaviour at the outset at the same applied potential (Fig. 3.17a), and they activated gradually to about the same steady-state current value as the etched sample of about 50 mA/cm². The higher initial activities of the etched samples are clearly related to Ga enrichment by alkaline etching. The steady-state current density of the active surface is determined by the steady-state enriched Ga concentration of the surface at the given applied potential.

Alloys with lower Ga concentration were more passive than alloy AlGa500 at the outset, with current densities at about 10⁻² mA/cm² (Fig. 3.21a). The current density increased to a maximum after about 2-3 min of polarisation as a result of Ga enrichment by dealloying, the value depending on the Ga content of the alloy. However, Ga enrichment by dealloying could not be maintained on these alloys, and the current density decreased to a more passive steady state value of about 0.1 mA/cm². This value was still much higher than the steady-state current densities of the unetched alloys, polarised under identical conditions (Fig. 3.17b). This indicated that higher amount of Ga remained enriched on the surface as a result of alkaline etching prior to the polarisation test in chloride solution.

Figure 21b shows potentiostatic data for heat-treated and etched AlGa1000 alloy at applied potentials more negative than -0.8 V_{SCE}. The short-time current transients were not too reproducible. At potentials of -1.2 and -1.3 V_{SCE}, the current density decayed to small values, indicating passivation of the surface.

Reheating the etched samples of alloys AlGa50 and AlGa1000 for 1 h at 600°C (HT+E+HT) caused repassivation of the active surface, which was caused by etching, as indicated by the potentiodynamic polarisation curves shown in Fig. 3.22a and 3.22b, respectively. After reheating, the polarisation behaviour of both samples became similar to that of the HT condition. The potentiostatic polarisation results for alloy AlGa1000 at -0.8 V_{SCE}, shown in Fig. 3.23, also indicated similar behaviour for conditions HT and HT+E+HT. The current density for these cases was small at the outset, indicating passive behaviour as discussed earlier (Fig. 3.17b) in comparison to the stable high current density for the HT+E condition.
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Figure 3.21. a) Potentiostatic data for heat-treated (1 h at 600°C) and two-minute alkaline etched AlGa alloys, containing different amounts of Ga, at an applied potential of -0.8 V\textsubscript{SCE} in 5% NaCl solution. Alloys AlGa500 and AlGa1000 were etched for one minute to avoid embrittlement. b) Potentiostatic data for alloy AlGa1000 (heat treated for 1 h at 600°C, followed by alkaline etching for 60 s) at different applied potentials in 5% NaCl solution. Data for alloy AlGa500 at -1.3 V\textsubscript{SCE}, treated similarly, are included for comparison.
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Figure 3.22. Potentiodynamic polarisation curves for alloys a) AlGa50, b) AlGa1000, in the HT (heat treated for 1 h at 600°C), HT+E (etched after heat treatment) and HT+E+HT (heat treated again after etching) conditions in 5% NaCl solution. AlGa1000 was etched for 60 s to avoid embrittlement.
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3.4.4 Corrosion morphology obtained by potentiostatic polarisation in chloride solution

As heat-treated samples

Alloys with Ga content equal to or smaller than 500 ppm, in as-polished or heat treated condition, were passive and did not corrode at an applied potential of -0.8 V\text{SCE} in 5% NaCl solution. Corrosion morphology obtained on the as-heat-treated alloy resulting from potentiostatic polarisation for 4 h at -0.8 V\text{SCE} is shown in Fig. 3.24a and 3.24b (magnified area marked in Fig. 3.24a). Corrosion initiated at a few locations and spread across the surface in the form of filaments by some branching. The attack in the filaments appeared cellular (blunt edges) than crystallographic (sharp edges) features. No preferential attack of the grain boundaries was observed. The cellular morphology suggests stepwise propagation from one cell to the next. Undermining of the oxide was observed at the boundary of cellular attack and uncorroded area (Fig. 3.24c). Light grey features at the bottom of the cells were corrosion products, giving only Al and O signals on the EDS spectrum. Ga was detected by EDS spot analysis around these oxide deposits, as shown in Fig. 3.24d.
3. Effect of Gallium on Anodic Activation and Embrittlement of Aluminium
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Figure 3.24. Localised corrosion morphology observed after potentiostatic polarisation of heat-treated (600°C) alloy AlGa1000 at -0.8 V_{SCE} for 4 h. (b-d) shows (a) at successively increasing magnifications of marked areas. (d) shows also Ga enrichment at the X-marked spot by EDS analysis.

**Heat-treated (1 h at 600°C) and alkaline etched samples**

Alkaline etched pure Al was passive at an applied potential of -0.8 V_{SCE} in chloride solution, and the scalled surface morphology formed by etching treatment prior to the polarisation test was not affected, as shown in Fig. 3.25a. Superficial crystallographic attack, with directional propagation based on grain orientation, was observed on alloy AlGa50 after 4 h exposure at the same potential (Fig. 3.25b). This type of attack spread at a faster rate over the surface with increasing Ga content. Appearance of submicron-sized pits on the etched surface, as shown for alloy AlGa100 in Fig. 3.25c, indicated propagation in depth in addition to the superficial attack. Fig. 3.25d shows that the etch morphology was no longer dependent on the grain orientation for alloy AlGa250. In addition, the density of submicron pits increased (Fig. 3.25e). Entire exposed surface of AlGa1000 sample was excessively corroded, as shown in Fig. 3.25f, and at a higher magnification in Fig. 3.25g.

Alkaline etch morphology (scalloped) was similar for pure Al and AlGa alloys containing 50-250 ppm Ga (Fig. 3.3a-c). However, potentiostatic polarisation of the etched alloys at -0.8 V_{SCE} resulted in deeper corrosion attack for AlGa100 and AlGa250 than that for pure Al and AlGa50. Pitting at -0.8 V_{SCE} was attributed to areas activated by Ga enriched during alkaline etching of these alloys. Applying the same potential (-0.8 V_{SCE}) caused uniform corrosion attack on alloy AlGa1000 removing the etch morphology formed by previous alkaline etching (Fig. 3.3d). Corrosion morphology became more localised at more negative potentials.

Corrosion on alloy AlGa1000, as a result of polarisation for 4 h at the lower potential -1.1 V_{SCE} in chloride solution, occurred also in the form of filaments along the grain boundaries and in grain bodies in cellular steps, as shown in Fig. 3.26a. Small pits of size 30-35 μm were formed during polarisation for 4 h at -1.2 V_{SCE} (Fig. 3.26b).
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Similar pits of a smaller number density were initiated as a result of potentiostatic polarisation at -1.3 $V_{\text{SCE}}$. *In situ* video observation indicated that initiation occurred within a few minutes of application of the potential. These pits grew in circular shape without the initiation of new pits until the maximum current density was attained within 10 min (cf. Fig. 3.21b), as shown in Fig. 3.26c, and at a higher magnification in Fig. 3.26d. These pits eventually repassivated, as indicated by the current density-time shown in Fig. 3.21b.

Stepwise propagation of the filaments was similar for as-etched and as-annealed surface condition of alloy AlGa1000 (Fig. 3.26a and Fig. 3.24, respectively). The filaments formed at a more negative potential for the as-etched condition than for the as-annealed condition, because the surface was already activated by Ga enrichment during alkaline etching. Such stepwise filament formation for both cases was attributed to significant enrichment of Ga during corrosion of Al, i.e. dealloying. When the potential was too negative (-1.2 $V_{\text{SCE}}$ and less) to cause sufficient dealloying, areas with the highest Ga enrichment by alkaline etching corroded and then passivated (Fig. 26b-d) because replenishment of Ga was not sufficient to prevent passivation.
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Figure 3.25. Surface morphology of the heat treated and alkaline-etched AlGa samples after 4 h potentiostatic test at -0.8V_{SCE}. a) Pure Al, b) AlGa50, c) AlGa100, d) and e) AlGa250 and f, g) AlGa1000.
Figure 3.26. Surface morphology of pre-etched alloy AlGa1000 after potentiostatic polarisation for 4 h at a) -1.1 V_{SCE} and b) -1.2 V_{SCE}, and c, d) for 1.5 h at -1.3 V_{SCE}, at two different magnifications.
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3.5 Discussion

This work has shown that the Ga present in Al at concentrations up to 1000 ppm is stable in solid solution at temperatures up to 600°C (maximum heat treatment temperature used in this work) without any possibility of segregation. This conclusion is in accordance with the available thermodynamic data for the AlGa system [16]. Aluminium can accommodate even at higher concentrations of Ga without the danger of thermal segregation, although not investigated in the present study, but reported to be the case in other studies [35]. The effect of a second activating element and certain transition elements and Si, which are present in commercial alloys, will be discussed in the following chapters.

The effect of Ga metal (not alloyed with Al), in metallic contact with Al, on liquid metal embrittlement of Al, although discussed briefly earlier in the chapter, is outside the scope of this thesis. However, it is shown that embrittlement can occur readily on AlGa binary alloys if Ga is enriched on the surface by dealloying, occurring effectively by deep alkaline etching. Gallium becoming enriched at the surface then readily diffuses into the grain boundaries, which causes the embrittlement. This process is enhanced by surface diffusion. Ga does not segregate directly to the grain boundaries. The embrittled grains are also readily bound together by diffusion of Ga into the grains, thereby eliminating embrittlement. The mechanism, by which the bonding of the grain occurs, is not known and worth investigating. The governing mechanism in this case is volumetric diffusion, and the rate is enhanced by heat treatment. Embrittlement of Al by Ga is significantly reduced in the presence of other alloying elements, as will be discussed later in the thesis (Ch. 6 and 7).

Activation of Al containing Ga occurred as a result of dealloying during corrosion in chloride solution and etching in alkaline solution. Enrichment of the AlGa alloys to a critical amount of Ga was required for activation to occur. The critical amount was not determined in the present study. However, it is believed, with reference to Tuck et al. [5], that the critical amount is that required to form a liquid GaAl phase at the surface. No significant activation occurred in chloride solution on AlGa alloys containing less than 1000 ppm Ga, probably because of limited amount of corrosion during the corrosion experiments conducted in this study. However, activation occurred on alloys containing smaller amounts of Ga by alkaline etching because of significantly larger amount of Al corroding in a shorter period of etching to obtain the critical amount of Ga.

The critical amount of Ga at the surface, or the formation and maintenance of liquid GaAl phase at the surface, was determined by the balance between the rate of formation of the Ga phase by dealloying, diffusion of Ga back into Al metal and removal of the liquid phase from the surface during corrosion. The unstable corrosion behaviour during potentiostatic polarisation and unstable corrosion potential during alkaline etching are attributed to this balancing phenomenon. In the case of potentiostatic polarisation, alloy AlGa1000, which contained more Ga than required for maintaining a stable amount of amalgam at the surface at a sufficiently high applied potential (-0.8 V SCE) for the dealloying rate, reached and maintained a highly active current density of 25 mA/cm².
within a few hours (Fig. 3.17). Establishment of an active current of similar magnitude on alloy AlGa500 required much longer period of polarisation at the same potential. Alloys containing lower amounts of Ga remained essentially passive, although the passive current depended on the amount of Ga in the alloy.

In the case of the pre-etched specimens, potentiostatic polarisation in chloride solution at -0.8 V_{SCE} gave only a temporary active period for alloys AlGa50, AlGa100 and AlGa250 because of enriched liquid Ga already present at the surface at the outset. The alloys passivated after prolonged polarisation, while alloys with higher Ga content remained stably active (Fig. 3.21a). However, the critical amount of Ga could not be maintained on alloys AlGa500 and AlGa1000 at applied potentials more negative than -1.1 V_{SCE}, causing repassivation after a few hours of polarisation (Fig. 3.21b). This demonstrated the role of applied potential as the driving force for maintaining a sufficiently high rate of corrosion to provide sufficient enrichment of Ga by dealloying.

The balancing effect is evident also during alkaline etching, as reflected by the quick stabilisation of the corrosion potential at a highly negative level of -2.05 V_{SCE} for alloys AlGa250, AlGa500 and AlGa1000, indicating establishment of stable liquid GaAl alloy at the surface. For alloys with lower Ga content, an oscillatory behaviour of the corrosion potential was established, characterised by almost periodic surges to about -2.1 V_{SCE} from a more stable value around -1.9 V_{SCE}, which was close to the corrosion potential of pure Al in the same environment (Fig. 3.18). The frequency of surges decreased with decreasing Ga content in the alloy. This behaviour indicated enrichment of Ga and ensuing activation of the surface, possibly locally, occurring only in periods for low Ga alloys. The activating GaAl layer was quickly destroyed, returning the surface to the less active state of pure Al. The activated areas were possibly destroyed by high rate of hydrogen evolution observed to occur at these sites corresponding to the negative potential surges, or the situation was similar to the behaviour of AlMgSnGa alloys in chloride solution, as described by Birkin et al.[36]. Similar periodic oscillations of the current during potentiostatic polarisation and potential oscillations during galvanostatic polarisation have been discussed for AlIn alloys related to similar phenomena [37]. Passivation state can also be due to accumulation of corrosion products at the active sites and inhibition of H\textsubscript{2} evolution, and the unstable corrosion products in alkaline environment can be dissolved again increasing gas evolution again [38].

In view of the foregoing, it can be concluded that the activation mechanism is similar to that caused by a mercury drop in contact with the Al metal surface [39, 40], as also suggested to apply to Al alloys containing Ga by Flamini et al. [41]. In the light of this theory, aluminium is envisaged to dissolve into Ga enriched at the oxide film-aluminium metal interface. Dissolved Al is rapidly transported to the opposite surface of the GaAl liquid alloy, where it oxidizes. The eutectic point in the AlGa phase diagram is 26.6°C, which is slightly below the melting point of Ga with the liquid composition containing approximately 3 at% Al.

The cellular corrosion morphology observed on alloy AlGa1000, heat-treated at 600°C, after potentiostatic polarisation at -0.8 V_{SCE} has also been reported in earlier studies [5,
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The corrosion morphology observed in this study can be discussed more suitably with reference to corrosion morphology formed in the mercury-drop experiment [40]. Gallium enriched at the oxide-metal interface by dealloying destroyed the passivity of the oxide in the presence of chloride at the applied potential, which was more negative than the pitting potential of pure Al [11, 15]. Entrainment of Al in Ga in the absence of passivity and formation of a liquid GaAl phase (amalgamation) increased the corrosion rate. Increase in the volume of the amalgam by segregation of additional Ga by dealloying contributed to the corrosion rate. Spreading of the amalgam over the surface occurred in a stepwise, rather than a continuous fashion, probably controlled by the surface tension of the amalgam in determining its wetting of the aluminium metal [42].

3.6 Conclusions

- Gallium is highly stable as a trace element in solid solution with aluminium. It does not segregate as a result of heat treatment at temperatures up to 600°C.
- Gallium in solid solution segregates by dealloying of aluminium during corrosion in chloride or alkaline solution, which activates the surface anodically. A critical level of segregation is required for stable activation. This is determined by the amount of gallium in the alloy and the corrosion rate. Activation becomes significant if the amount of Ga in the binary AlGa alloys exceeds 250 ppm.
- Significant Ga enriched at the surface during etching in alkaline solution can readily diffuse into the grain boundaries and cause liquid metal embrittlement. The metal recovers to its original mechanical condition by heat treatment, which enhances removal of Ga from the grain boundaries by diffusion into the grains back to solid solution with aluminium.

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References

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4 Anodic Activation of Aluminium Containing Trace Elements Gallium and Tin

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Abstract

In this study, anodic activation of pure aluminium caused by segregation and interaction of trace elements Ga and Sn was investigated. Model AlGaSn alloys containing 50 to 1000 ppm Ga and 100 ppm Sn were heat treated for 1 h at 300°C and 600°C before potentiodynamic and potentiostatic polarisation in 5 wt% NaCl and 5 wt% Na₂SO₄ solutions. Surface characterisation before and after corrosion was performed using glow discharge optical emission spectroscopy (GD-OES), scanning electron microscopy (FEG-SEM) and further study on the corroded surfaces was performed using Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS). Sn segregated to the surface as a result of annealing at 300°C, while Ga was stable in solid solution because of its high solubility in Al. Both elements became homogenised by annealing at 600°C, giving a homogenous surface close to the bulk properties. Potentiodynamic polarisation after annealing at 300°C in 5% NaCl solution resulted in highly active surfaces giving a very negative passivity breakdown potential and high anodic current density. The ternary AlGaSn alloys were far more active than their binary counterparts AlGa and AlSn, containing the same amount of Ga or Sn. Similar activation did not occur on the alloy homogenised by heat treatment at 600°C because of the absence of thermally segregated Sn for the initiation. During potentiodynamic polarisation, the samples annealed at 300°C developed localized corrosion patterns consisting of nearly concentric circular etch marks, while samples annealed at 600°C did not show this type of corrosion patterns. Potentiostatic polarisation at -0.8 V_SCE after annealing at 600°C caused Ga enrichment at grain boundaries due to selective corrosion of Al and subsequent enrichment of Ga caused by dealloying. Passivity breakdown of the AlGaSn alloys annealed at 600°C occurred at a significantly higher potential and corrosion propagated at an enhanced rate by the anodic segregation of Sn and Ga above the breakdown potential. Presence of segregated Sn at the surface was involved in catalysing the dealloying process during propagation, such that Ga was also enriched on the corroding surface. Same phenomenon did not occur without the presence of Sn in the alloy.
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4.1 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.

Anodic activation of commercial alloys AA8006 [4, 5] and AA3102 [6] 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 [7, 8], was the cause of activation as the corrosion propagation followed the film, thereby undermining the passivating oxide [9]. 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 temperatures as low as 350°C. This result was attributed to the segregation of other elements in the group with lower melting points [10-12].

Work with model binary alloys showed that Sn [13] and In [14], 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 points and limited solubility of these elements at this temperature. Adding Mg to AlPb model alloys increased activation by annealing at 450°C at lower annealing temperatures [15]. Al-Bi model alloys exhibited activation by annealing at 600°C by segregation of Bi in the form of nearly continuous metallic nano-film at the oxide-metal interface [16] similar to Pb.

Gallium is known to activate Al in alkaline and neutral chloride solutions [2, 17-20]. It has a low melting point of 29.8°C and high solid solubility of up to ~20 wt% in aluminium [21]. However, higher amount of gallium than the other activator elements is required for significant activation depending on the application. The critical amount of alloyed Ga needed was 0.26 wt% according to Tuck et al. [17] for Al/air anodes and 500 ppm for sacrificial anodes according to Despic et al. [2] in NaCl. Homogenised AlGa alloys, investigated in Chapter 3, did not cause significant activation for Ga concentrations below 1000 ppm Ga. However, etching for 2 min at 45°C in 12 wt% NaOH caused activation of AlGa alloy containing as low as 50 ppm Ga. Lower gallium contents activated only after pre-polarisation at -2 V_{SCE} [18-20] or after immersion for 30 s at 60°C in 4M NaOH solution at open circuit condition [17], resulting from surface segregation of Ga by dealloying.

Gallium was suggested to facilitate adsorption of aggressive halide ions as the reason for activation of aluminium [20]. However, activation by formation of a liquid AlGa surface alloy, which destroyed the passivating oxide film, has later been shown to be a more viable mechanism [22, 23]. This is similar to the mechanism based on the classical Hg-drop experiment on aluminium in humid environment [24]. If the natural oxide layer of aluminium under the Hg drop becomes damaged, mercury wets the bare Al surface.
and prevents the direct contact of the surface with oxygen. Aluminium dissolves into mercury which enables the transport of aluminium to the liquid mercury-moisture (or humid air) interface, where Al oxidizes and repassivation of Al surface is prevented [24-26].

Solubility and diffusivity of Al in the liquid 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 [21], in comparison to only ~1.35x10⁻⁵ wt% in Hg [27]. Aggressive ions were not necessary for activation in aqueous environment if liquid phase GaAl alloy was formed at the surface [22, 23]. These data suggest that Ga must be at least as active as Hg in activating Al by the amalgamation mechanism.

Activation of aluminium as a result of alloying small amounts of gallium, tin and magnesium (0.4 wt.% Mg, 700 ppm Sn and 500 ppm Ga) for battery applications has recently been studied [28-30]. The presence of gallium and tin together caused high activation, by lowering the corrosion potential down to -1.5 V_{SCE} and increasing the corrosion rate of the aluminium alloy with hydrogen evolution during applying current density of 1 mA/cm² in 2 M NaCl solution [30]. Corrosion was claimed to initiate around tin inclusions present at the surface, since the amount of Sn in the alloy was above its solid solution solubility in aluminium. Corrosion propagation occurred superficially around Sn inclusions, resulting in round shallow pits. Tin particles were found in the pits after corrosion of Al. However the role of gallium on increased activation and corrosion morphology could not be explained even though its contribution was evident from the electrochemical results [28].

Gallium is commonly present as a trace element up to 200 ppm depending on the source of the primary aluminium production [31], while tin is considered to be due to 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.

4.2 Experimental

**Materials.** Model ternary AlGaSn alloys containing 100 ppm Sn and two different concentrations of Ga (50 and 1000 ppm) were cast from pure components. 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 μm diamond paste finish. The alloy designations used in this paper and 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.
Electrochemistry and corrosion. Electrochemical characterisation was performed in 5 wt% NaCl and 5 wt% Na₂SO₄ 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/Hg₂SO₄ electrode was used in Na₂SO₄ 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. The cell geometry, solution volume and the stirring rate in the solution were identical in all runs. The sample area exposed to the solution was 0.64 cm². When required, thick oxide formed after annealing and water quenching was removed by immersing the sample in standardised hot chromic-phosphoric acid (Cr-P) solution (ASTM G1-90) for 30 min at 90°C. Alkaline etching of the specimens was conducted for 2 min at 45°C in 12 wt% NaOH solution.

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).

Auger Electron Spectroscopy (AES) was used for determining the chemical state of the enriched Ga at the surface after alkaline etching. A JEOL 9500F Auger Microprobe instrument, equipped with a hemispherical electron spectrometer, was used. The spectra were obtained at 10 keV accelerating voltage and a primary electron beam current of 20.4 nA at energy resolution of 0.35%. The depth profiling area was about 500 μm x 500 μm.

Secondary Ion Mass Spectroscopy (SIMS) analysis was also performed for better lateral resolution than AES and GD-OES for elemental mapping of corroded surfaces using a Cameca IMS 7f dynamic SIMS with elemental mapping capability and sub-micron lateral resolution. O₂⁺ 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 μm x 500 μm and 100 μm x 100 μm with image lateral resolution of about 10 μm.
4.3 Results

4.3.1 Characterisation of as-annealed surface

SEM. Fig. 4.1 shows the surface morphology of sample AlGa1000Sn100 after 300°C and subsequent water quenching, which was also representative for alloy AlGa50Sn100. Fig. 4.1a-d- show clusters of oxide mounds formed on sample AlGa1000Sn100 with increasing magnification. FEG-SEM investigations confirmed that the bright contrast was due to small clusters of thick oxide formed randomly in these regions. The mounds were nearly circular in shape, up to 10 μm in diameter, either discrete (Fig. 4.1b) or merged with other mounds in a cluster (Fig. 4.1c). The oxide mounds was cracked (Fig. 4.1d), probably while it was being formed during water quenching. Fig. 4.1e shows a magnified back-scattered electron image of a crack in the oxide mound. The bright contrast indicated Sn enrichment in the crack. At a higher magnification, nano-sized Sn segregations were observed on top of the oxide mound, as shown in Fig. 4.1f. These observations are similar to those reported for AlSn model alloys, containing 30 and 100 ppm Sn, earlier after similar heat treatment [32].

Pits and blisters, smaller than 1 μm in size, were observed on other areas of alloy AlGa1000Sn100 not yet covered with oxide mounds after 1 h treatment at 300°C, as shown in Fig. 4.2a. Bright Sn segregations of size 10 to 100 nm decorated the backscattered SEM images of such an area in Fig. 4.2b and 4.2c. These areas have been shown, after longer periods of annealing, followed by quenching in water, also to form coalescing oxide mounds, leading eventually to the coverage of the surface by a thick oxide scale [32].

Gallium could not be detected on samples heat treated at 300°C, by using EDS. Oxide mounds did not form by cooling the samples in air instead of water quenching. However, pitted surface decorated with particulate nanoscale Sn segregations was still observed.

Tin or gallium segregation could not be detected by EDS on any of the samples prepared by heat treatment at 600°C, followed by water quenching. Oxide mounds were not observed either.

Grain size was within the range of 20-500 μm after annealing at 300°C, while annealing at 600°C produced grain sizes in the range 500 μm to 3 mm.

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Figure 4.1. SEM images of thick oxide formation on the surface of alloy AlGa1000Sn100 after annealing at 300 °C and quenching in water. a-c) Oxide mounds on the surface at increasing magnification, d) Oxide mounds in white frame in (c) at higher magnification, revealing cracks. e) Higher magnification back-scattered image of the area in the black frame in (c), showing Sn segregation in the crack. f) Higher magnification back-scattered image of the oxide mound near cracks showing nanoscale Sn particles embedded at the oxide surface.
Figure 4.2. FEG-SEM morphologies of the surface free from oxide mounds on alloy AlGa1000Sn100 formed after annealing for 1 h at 300 °C, followed by water quenching. a) Secondary electron image obtained at 1 kV accelerating voltage. b) Back-scattered image of mound-free area obtained at 5 kV accelerating voltage, revealing nanoscale Sn particles in bright contrast. The dark contrast spots are the pits. The straight lines (also in (a) are polishing scratches. c) Higher magnification of (b) obtained at an accelerating voltage of 7 kV.
GD-OES. Qualitative GD-OES depth profiles for Al, O, Ga and Sn are given for all three alloys in as-polished and annealed conditions at varying temperatures in Fig. 4.3. The Ga profiles for the Ga containing alloys (columns 2 and 3 in Fig. 4.3) were nearly uniform. Sn was enriched slightly at the oxide surface for all samples. The highest Sn enrichment occurred on samples annealed at 300°C, at the metal-oxide interface, as inferred from the appearance of a peak on the Sn profile at the intersection of the O and Al profiles (Fig. 4.3d-f). Annealing at 450°C caused less Sn enrichment at the surface, while annealing at 600°C resulted in homogenisation of Sn.

Thickening of the oxide with respect to pure Al occurred for all alloys with increasing annealing temperature. For the cases which showed Sn segregation (all alloys annealed at 300 and 450°C), the Sn peak location corresponded well with the intersection of the O and Al profiles. Thus, the oxide-metal interface was reached after about 0.3 s of sputtering for samples annealed at 300°C (Fig. 4.3d-f), corresponding to an oxide thickness of about 10 nm, and after about 0.5 s sputtering for samples annealed at 450°C (Fig. 4.3g-i), corresponding to a thickness of about 20 nm. Increase in the oxide thickness at 300°C, was attributed to formation of the oxide mounds at areas activated locally by thermally segregated Sn. Despite the surface roughness caused by the oxide mounds, the oxide thickness measured by this approach gave similar results for all samples corresponding to annealing at 300 and 450°C, possibly a slight thickening at the higher temperature. Since Sn peak could not be detected at the oxide-metal interface on samples annealed at 600°C, the oxide thickness was determined as about 30 nm from the intersection of O and Al curves, which corresponded to an inflection point on the Al curves (Fig. 4.3j-l). The oxide thickness was independent of Ga content of the alloys for a given annealing temperature. Oxide growth could be attributed to γ-aluminium oxide formation at the applied annealing temperature [33]. Since no oxide mounds were observed at this temperature, Sn content (100 ppm) did not contribute to oxide growth. These results indicate, therefore, that segregation of Sn during heat treatment at this temperature range and subsequent water-quenching was the main factor determining the oxide thickness and morphology. The results for the AlGaSn alloys were similar to the results for AlSn alloys containing Sn in the range 30-1000 ppm [32]. The presence of Ga in the alloy did not affect the results significantly. Air-cooled samples after annealing at 300°C showed a similar depth profile as the water-quenched condition regarding tin or gallium segregation and oxide thickness, though not shown here.

The effect of surface treatments, alkaline etching, grinding-polishing and stripping in Cr-P solution, was investigated for alloy AlGa1000Sn100 after annealing at 300°C and water quenching. GD-OES results could not distinguish any difference in the oxide thickness of the etched, polished and annealed conditions, i.e., the oxide thickness were 10±5 nm for these conditions. The weight loss data indicated that the etched thickness was about 0.5 μm after 2 min exposure at 45°C in 12 wt% NaOH. Alkaline etching caused significant enrichment of Ga, while most of the Sn segregated during annealing was removed from the surface (Fig. 4.4a). No significant Sn or Ga enrichment was observed after re-grinding and polishing of the annealed sample, as shown in Fig. 4.4b. Stripping removed the oxide mounds (Fig. 4.1a) while segregated Sn remained at metal-oxide interface and Ga remained homogenised according to the depth profiles shown in Fig. 4.4c.
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Figure 4.3. Qualitative GD-OES depth profiles for alloys AlSn100, AlGa50Sn100 and AlGa1000Sn100 in as-polished (a, b, c) and heat-treated conditions at 300°C (d, e, f), 450°C (g, h, i) and 600°C (j, k, l). The heat treated samples were subsequently quenched in water.
Figure 4.4. Qualitative GD-OES depth profiles for alloy AlGa1000Sn100, annealed at 300°C and water quenched, followed by a) alkaline etching (at 45°C for 2 min in 12 wt% NaOH), b) metallographic polishing, or c) stripping in Cr-P solution.
4.3.2 Electrochemical characterisation

Potentiodynamic polarisation. Potentiodynamic polarisation in NaCl solution indicated that gallium containing ternary alloys AlGa50Sn100 and AlGa1000Sn100 were much more active than the binary alloys AlSn100, AlGa50 and AlGa1000 (all heat treated at 300°C and quenched in water), as shown in Fig. 4.5. Passivity breakdown of the binary alloys AlGa50 and AlGa1000 occurred at about -0.8 V$_{SCE}$, not too different from the pitting potential of pure Al. In contrast, passivity breakdown of the ternary alloy AlGa50Sn100 occurred at -1.3 V$_{SCE}$, and the anodic current density reached 1 mA/cm$^2$ at -1.25 V$_{SCE}$. The passivity breakdown potential of alloy AlGa1000Sn100 was about -1.45 V$_{SCE}$, and the current density reached 1 mA/cm$^2$ already at -1.38 V$_{SCE}$. The passivity breakdown potential was -1.2 V$_{SCE}$ for the binary alloy AlSn100. The polarisation curve showed partially passive behaviour after an anodic peak current density of about 1 mA/cm$^2$ at -1.1 V$_{SCE}$. The current density then decreased by two orders of magnitude with increasing potential. The passive behaviour disappeared completely by the added presence of only 50 ppm Ga. Gas evolution during polarisation was observed only at potentials more positive than the passivity breakdown potential for all alloys.

Figure 4.5. Potentiodynamic polarisation curves for the model binary and ternary alloys after annealing at 300°C and quenching in water.
Annealing at 450°C gave -0.95 V$_{SCE}$ and -1 V$_{SCE}$ as the breakdown potentials for alloys AlSn100 and AlGa50Sn100, respectively, as shown in Fig. 4.6. Annealing at 600°C resulted in a slight increase of breakdown to -0.8 V$_{SCE}$ and -0.91 V$_{SCE}$, respectively. Thus, activation of these alloys was reduced with increasing annealing temperature relative to 300°C. Activation was always higher in the presence of Ga at a given annealing temperature. The decrease in activation with increase in the annealing temperature was attributed to decrease in the amount of Sn segregation. Segregation of Sn at 450°C was less than the segregation at 300°C, while Sn homogenised by annealing at 600°C, as indicated by the GD-OES data in Fig. 4.3.

Fig. 4.6. Potentiodynamic polarisation curves for alloys AlSn100 and AlGa50Sn100 after annealing at 450°C and 600°C, followed by quenching in water.

Fig. 4.7 shows potentiodynamic polarisation of alloy AlGa1000Sn100 annealed at temperatures in the range 200°C-600°C. As-polished sample and the sample annealed at 200°C showed polarisation behaviour similar to pure aluminium, i.e., no significant activation. Maximum activation was obtained by annealing at 300°C as judged by the significant shift in the breakdown potential and current output. Activation decreased again with increasing annealing temperature, and it was insignificant at 500°C and 600°C. This behaviour of alloy AlGa1000Sn100 was qualitatively similar to that of the binary alloy AlSn100 [34], although the activation introduced by the presence of Ga was much larger.
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Surfaces of samples, which were annealed at 300°C and quenched in water, were modified by mechanical polishing, alkaline etching or stripping in hot chromic-phosphoric acid bath in order to see the effect of these mechanical and chemical processes on the activity of the surface. Potentiodynamic polarisation data, shown in Fig. 4.8, indicate that none of the treatments affected surface activation significantly. Alkaline etching caused slightly more negative passivity breakdown potential relative to the as-annealed sample. The other processes increased it. In all processed cases, the anodic current density decreased relative to the as-annealed sample. These results indicate that surface processing by these methods reduced the activity of the surface somewhat. The significance of these changes in the surface composition on the electrochemical behaviour will be discussed further in the Discussion section below.

**Potentiostatic polarisation.** The time dependence of activation of as-polished and heat treated samples was investigated further by potentiostatic polarisation at -0.8 V_{SCE} in NaCl solution. The current transients obtained for the as-polished samples are shown in Fig. 4.9. None of the samples were active for the first 2 min of polarisation. The current density at the outset was of order $10^{-2}$ mA/cm² for alloy AlSn100, $10^{-3}$ mA/cm² for the AlGaSn alloys, and $10^{-5}$ mA/cm² for alloy AlGa1000. The current densities of alloys AlSn100 and AlGa50Sn100 remained at this level throughout the test, which lasted for 3 h. The current density of samples containing 1000 ppm Ga increased with time, reaching the same steady-state value of approximately 5 mA/cm² after about 2 h. The higher initial current density of alloy AlGa1000Sn100 than that for alloy AlGa1000 is attributed to its Sn content. The Ga content of alloy AlGa50Sn100 was not sufficient to cause increased activation with the time of polarisation.
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Figure 4.8. Potentiodynamic polarisation curves for alloy AlGa1000Sn100 after annealing at 300°C and quenching in water, followed by different surface modification procedures.

Figure 4.9. Current density - time curves for model binary and ternary alloys in the as-polished condition, obtained by potentiostatic polarisation at -0.8 V_{SCE}.
The effect of annealing temperature on alloys AlGa50Sn100 and AlGa1000Sn100 were investigated by potentiostatic polarisation at -0.8 V_{SCE} as shown in Fig. 4.10a and 4.10b, respectively. The initial current density was highest for those annealed at 300°C. It was by an order of magnitude lower for the alloys annealed at 450°C and by yet another order of magnitude for alloys annealed at 600°C. The current density on AlGa50Sn100 samples decreased rapidly to a steady-state current density of order 0.1 mA/cm², independent of the heat treatment temperature. The current density of alloy AlGa1000Sn100, annealed at 300°C, remained relatively stable at about 10² mA/cm² during the test period. The current densities of alloys annealed at 450 and 600°C remained stable at about their initial levels for about 1 h and then increased gradually to steady-state values of about 75 and 50 mA/cm², respectively.

Figure 4.10. Potentiostatic polarisation results at -0.8 V_{SCE} for alloys a) AlGa50Sn100 and b) AlGa1000Sn100 after annealing at different temperatures, followed by quenching in water.
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Potentiostatic polarisation results for alloy AlGa1000Sn100, annealed at 300°C, at applied potentials more negative than -0.8 V SCE, are shown in Fig. 4.11. Active current densities were measured down to -1.3 V SCE, although the steady-state current density decreased by an order of magnitude in this potential range. At -1.4 V SCE, the current density reached a maximum value of 5 mA/cm² after 60 min and then decreased to 0.3 mA/cm² after about 1 h, indicating onset of passivation. The current density was still positive at -1.45 V SCE. However, it showed sharp peaks in the negative direction to very low values in the range 0.05 - 10 μA/cm² from a quasi-steady level of order 100 μA/cm², indicating unstable active-passive transitions.

Figure 4.11. Potentiostatic polarisation results for alloys AlGa1000Sn100 annealed at 300°C, at different applied potentials.

**Polarisation in sulphate solution.** Potentiodynamic polarisation results for the binary AlGa, AlSn and ternary AlGaSn alloys (annealed and water quenched) in Na₂SO₄ solution are shown in Fig. 4.12a. Alloy AlGa1000Sn100, annealed at 300°C, was active also in the absence of chloride, although the current output was lower than that in NaCl solution (Fig. 4.5). The binary alloys and alloy AlGa50Sn100 showed passive behaviour in Na₂SO₄ solution. None of the samples were active after annealing at 600°C, exhibiting much smaller current densities than those observed in NaCl solution. The binary alloys AlGa1000 and AlSn100, annealed at 300°C, also showed passive behaviour. Ga and Sn at these compositions had to be present together in the alloy to cause activation. However, annealing the same alloy (AlGa1000Sn100) at 600°C did not cause activation. Reducing the temperature of the test solution to 5°C did not change the active behaviour of alloy AlGa1000Sn100 annealed at 300°C (not shown).

Potentiostatic polarisation results for alloys AlGa1000Sn100, annealed at 300°C, obtained separately in Na₂SO₄ and NaCl solutions are compared in Fig. 4.12b. At the two potentials -1.3 V SCE and -1.4 V SCE, the initial activation behaviour indicated with
the increase of the current density to a maximum was similar to that observed in NaCl solution. It was a bit higher in chloride solution than in sulphate solution during most of the test period. The corroded thickness estimated from the current transients for 3600 s of polarisation at -1.3 V\textsubscript{SCE} was about 9.5 μm in sulphate solution and 15.5 μm in chloride solution. After about 10\textsuperscript{4} s of polarisation at -1.4 V\textsubscript{SCE}, passivation occurred in sulphate solution, while the current density stabilised at about 0.3 mA/cm\textsuperscript{2} in chloride solution.

Figure 4.12. a) Potentiodynamic polarisation results for selected alloys annealed at 300°C and 600°C. b) Potentiostatic polarisation data for alloy AlGa1000Sn100, annealed at 300°C, at potentials -1.3 V\textsubscript{SCE} and -1.4 V\textsubscript{SCE} in sulphate and chloride solutions at 25°C.
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4.3.3 Post-mortem analysis

4.3.3.1 SEM

Potentiodynamically polarised samples. The potentiodynamic polarisation conducted in the manner described above were terminated at predetermined potentials, the samples were removed from the cell, washed and dried, and they were examined by SEM. Fig. 4.13a and 4.13b show the circular corrosion morphology formed during potentiodynamic polarisation of alloys AlGa50Sn100 and AlGa1000Sn100 (annealed at 300°C), respectively, up to -1.3 V_{SCE} in chloride solution. Corrosion propagated by forming concentric circular ditches and ridges, indicating a stepwise process starting from the centre of the circles. The corroded area was also decorated with pits of order 10 μm in size. The growing circular corrosion cells eventually coalesced, as shown in Fig. 4.13b. Fig. 4.13c shows the centre of one of the concentric cells, marked in Fig. 4.13b, at a higher magnification, showing the uncorroded ridges, flat on top, appearing in dark grey contrast. The area marked by the black frame in Fig. 4.13c, is shown in Fig. 4.13d as a backscattered electron image at a higher magnification, revealing a cellular structure. EDS spot analysis of the marked bright particle in the figure revealed enrichment of Ga. Since Ga enrichment did not occur as a result of heat treatment, it must have segregated as a result of dealloying during polarisation. On samples polarised up to -1 V_{SCE}, deep-penetrating pits were observed at the boundaries formed by coalescing cells, as shown in Fig. 4.14.
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Figure 4.13. Corrosion morphology on alloy AlGa1000Sn100 (annealed at 300°C) after potentiodynamic polarisation up to -1.3 $V_{SCE}$, showing a) circular etch patterns and b) merged circular patterns. c) Area marked in (c) near the centre of circles at a higher magnification. d) Area marked in (d) at a higher magnification together with a point EDS analysis of the point marked in (d).

Figure 4.14. Alloy AlGa1000Sn100 (annealed at 300°C) after potentiodynamic polarisation up to -1 $V_{SCE}$. 
Corrosion morphology on alloy AlGa50Sn100 was similar to that on alloy AlGa1000Sn100 at sweep termination potentials lower than -1.2 V\text{SCE}. At more noble potentials, discrete and deep pits were formed, as shown in Fig. 4.15a for termination at -1 V\text{SCE}. The pit bottoms, shown at higher magnification in Fig. 4.15b, revealed bright particles (Fig. 4.15b), which were identified as Sn particles by EDS, as marked on Fig. 4.15b. Ga could not be detected.

Figure 4.15. Corrosion morphology on alloy AlGa50Sn100 (annealed at 300°C) resulting from potentiodynamic polarisation up to -1 V\text{SCE}, showing a) a large circular pit containing smaller deeper pits. b) Higher magnification of the bottom of the pit marked in (a).
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Potentiostatically polarised samples. The corrosion morphologies obtained on alloy AlGa50Sn100 (annealed at 300°C), polarised for 2000 s at -1.3 V SCE, which was very close to its breakdown potential in chloride solution (Fig. 4.5), are shown in Fig. 4.16. Both pitting and superficial etching were observed, as shown in Fig. 4.16a. Pits varied widely in size and depth as can be seen in the figure. Superficial etching was crystallographic in nature, morphology depending on the grain orientation, and it occurred by undermining the oxide, as shown in Fig. 4.16b. The crystallographic facets, containing remnants of the oxide, are shown at a higher magnification in Fig. 4.16c. Tin or gallium could not be detected on the superficially etched areas.

Alloy AlGa1000Sn100, annealed at 300°C, was similarly polarised at -1.45 V SCE, close to its breakdown potential. The corrosion morphology resulting after polarising for 2000 s is shown in Fig. 4.17. The general morphology, shown in Fig. 4.17a, reveals both pitting and filament-formed superficial attack. Fig. 4.17b shows that pits were associated with the oxide mounds (Fig. 4.1) formed by heat treatment and quenching. The mounds were first attacked around their periphery forming ditches around yet uncorroded areas at the centre. These morphologies then developed into pits as the centre areas also corroded. Extending the polarisation to 4 hours at -1.45 V SCE caused circular corrosion attack propagating from a centre, similar to that discussed for potentiodynamically polarised samples in Fig. 4.13. This morphology developed by undermining the oxide, such that it can be observed only partially where the oxide was destroyed.
Figure 4.16. Corrosion morphology on alloy AlGa50Sn100 (annealed at 300°C) resulting from potentiostatic polarisation for 2000 s at -1.3 V_SCE, showing a) both deep pits and superficial corrosion. b) Higher magnification micrograph of the superficially corroded area, marked by a black frame in (a), showing that corrosion propagated by undermining the oxide (arrows).
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Figure 4.17. Corrosion morphology on alloy AlGa1000Sn100 (annealed at 300°C) resulting from potentiostatic polarisation at -1.45 V\textsubscript{SCE}. a) General appearance of a corroded area after polarising for 2000s. b) Corrosion at oxide mounds marked in (a). c) Concentric circular corrosion morphology developing by undermining the oxide after polarising for 4 h at -1.45 V\textsubscript{SCE}.

With increasing applied potential, the undermining circular morphology was increasingly favoured, as shown in Fig. 4.18a, which was obtained by 10 min polarisation at the slightly higher potential of -1.4 V\textsubscript{SCE}. The areas exposed by destruction of the undermined oxide were characterised by successive ditches and ridges.
of the concentric circle morphology. This type of morphology became more clearly visible with increasing time of polarisation as the oxide became peeled off the surface, as shown in Fig. 4.18b. Visible gas evolution occurred at the propagating circular fronts, while the corroded areas passivated. Rate of propagation at the circular fronts decreased as the circles became larger, causing increased passivation of the surface in accordance with the electrochemical data shown in Fig. 4.11.

Figure 4.18. Corrosion morphology on alloy AlGa1000Sn100 (annealed at 300°C) resulting from potentiostatic polarisation at -1.4 V_{SCE}. a) after 10 minutes and b) 4 hours.
Both types of AlGaSn alloys investigated in this work were passive at potentials more negative than -0.8 V\textsubscript{SCE}, as a result of annealing at 600°C. Alloy AlGa100Sn100, when polarised at -0.8 V\textsubscript{SCE}, showed crystallographic pitting near the grain boundaries and in the grains, as shown in Fig. 4.19a. Fig 4.19b is the magnified form of the black frame in Fig. 4.19a. Fig. 4.19b shows one of the propagating corrosion fronts. The analysis of the area marked by the black frame is shown in Fig. 4.20a as EDS maps of the elements Al, Ga, Sn, O and C. The maps indicate enrichment of Ga, O and C at the corrosion front, while Sn could not be detected. Line scan as marked in Fig. 4.20a also showed Ga segregation with high O signal, as shown in Fig. 4.20b.

Figure 4.19. Corrosion morphology on alloy AlGa100Sn100 (annealed at 600°C) resulting from potentiostatic polarisation for 1 h at -0.8 V\textsubscript{SCE}, showing a) crystallographic attack at and near a grain boundary and b) higher magnification image of the corrosion front marked by a black square in (a).
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Figure 4.20. a) EDS elemental maps and b) EDS line scan of the corrosion cell in Fig. 19c along the black line shown on the top left corner micrograph in Fig. 20a.
Samples polarised in sulphate solution. Potentiostatic polarisation of alloy AlGa1000Sn100 (annealed at 300°C and water-quenched) for 1 h at -1.3 V_SCE in 5% Na_2SO_4 solution gave a current-time relationship quite similar to the polarisation of an identical sample in 5% NaCl solution, as reported above (Fig. 4.12). The resulting corrosion morphology of circular patterns, shown in Fig. 4.21a, was similar to that obtained in chloride solution (cf. Fig. 4.13a). No significant pitting was observed. The valleys between the circular ridges formed in sulphate solution were wider than those formed in chloride solution, and parts of the etched surface were covered by an oxide layer, as shown in Fig. 4.21b. Ga was detected by EDS spot analyses of areas with corrosion products such as the spot marked with an arrow on a ridge in Fig. 4.21c, while Na and S were found on the thick layer (area marked by a black rectangle in Fig. 4.21c). Position of Ga particles could not be shown clearly by EDS.
4.3.3.2 **GD-OES**

Circular corrosion cells formed on AlGa1000Sn100 as a result of potentiostatic polarisation for 1200 s at -1.3 V\text{SCE} in NaCl (cf. Fig. 4.12 and 4.13) and in Na\textsubscript{2}SO\textsubscript{4} (cf. Fig. 4.12 and 4.21) was investigated further by GD-OES depth profiling, as shown in Fig. 4.22a and 4.22b, respectively. The profiles in the two figures were measured under identical conditions, such that the intensities are comparable. Gallium became enriched significantly as a result of dealloying in both solutions. Ga enrichment shown in Fig. 4.22a and Fig. 4.22b gave two peaks, the first larger than the second. However, the size and position of the peaks, as well as the thickness of the oxide, could not be reproduced due to varying roughness at the corroded surface. Sn appeared to be slightly enriched on top of the oxide.
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Figure 4.22. GD-OES depth profiles obtained on AlGa1000Sn100 alloy (annealed at 300°C and water quenched) after potentiostatic polarisation for 1200 s at -1.3 V\textsubscript{SCE} in a) NaCl and b) Na\textsubscript{2}SO\textsubscript{4} solutions.

4.3.3.3 AES

An AlGa1000Sn100 sample, identically treated as above in chloride solution, was analysed by AES in order to obtain additional information about the chemical composition of the corroded and uncorroded areas on the surface. Comparison with the reference spectra for metallic Ga and Ga\textsubscript{2}O\textsubscript{3} presented in Chapter 3 indicated that the
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enriched Ga was in the metallic state. Fig. 4.23a shows the SEM micrograph of the sample area analysed, which corresponded to a circular corrosion cell. The AES depth profile is shown in Fig. 4.23b. The profiles are qualitatively similar to the corresponding GD-OES profiles for enrichment of Sn and Ga in the near surface region of the corroded area (cf. Fig. 4.22a). Fig. 4.23c shows the uncorroded area marked on the same sample, which was similarly analysed, with the results shown in Fig. 4.23d. Enrichment of tin was evident near the surface, while Ga exhibited a uniform depth profile. Sn enrichment, probably at the metal-oxide interface, resulted from the heat treatment process.

Figure 4.23. AES data after polarisation up to -1.3 V_{SCE} in NaCl solution of AlGa1000Sn100 after annealing at 300°C and quenching in water. a) The corroded area analysed. b) Qualitative depth profile of the area in (a). c) Area analysed outside the corroded region. d) Qualitative depth profile of the area in (c).
4.3.3.4 SIMS

GD-OES has poor lateral resolution, and the AES method was not sensitive enough to obtain the lateral distribution of the enriched Ga and Sn on the corroded surface. Surface mapping of these elements was achieved by SIMS on the same type of sample as used for GD-OES and AES. The elemental intensity maps for Al, Ga and Sn over a corroded area of 500 x 500 μm are shown in Fig. 4.24a and 4.24b for polarisation times of 300 and 600 s in chloride solution, respectively. In order to distinguish differences between intensity changes due to composition and roughness on the corroded surface, coinciding areas where both Ga and Sn were traced. Polarisation for 300 s resulted in enrichment of Ga and Sn mostly at the edges of the circular corrosion cells, marked by large circles in Fig. 4.24a. Smaller areas of Ga and Sn enrichment were observed also inside the cells, which are marked by the smaller circles in Fig. 4.24a. The two elements were enriched over the entire corroded surface after 600 s, as shown in Fig. 4.24b. Higher concentrations of gallium and tin were observed near the corrosion front also in this case, as shown in the areas marked by circles and arrows at the edges in Al map in Fig. 4.24b. The area of Ga and Sn enrichment near the corrosion front was larger than the segregated Sn particles observed in the SEM micrographs in Fig. 4.1-3 for the uncorroded surface. This was probably due to dealloying at the corrosion front, while Ga and Sn segregated earlier by the same mechanism spread over a larger corroded area, mixed with corrosion products and became diluted.

4.4 Discussion

4.4.1 Effect of heat treatment

The fact that Ga does not segregate by heat treatment (Chapter 3) was confirmed also in this chapter, where the added presence of Sn as trace element was investigated. It was demonstrated again that segregation of trace element Ga and its contribution to anodic activity of the surface of Al depend on additional factors which cause dealloying, such as alkaline etching and, as shown particularly in this chapter, the initial step of Sn segregation causing passivity breakdown.

Annealing at 300°C resulted in enrichment of Sn at the surface, while Ga did not segregate due to its high solubility in Al. Annealing at 450°C caused a larger amount of Sn to remain in solid solution with Al, and annealing at 600°C caused all Sn to dissolve in Al, as expected from the solubility of Sn in Al [35]. Consequently, the highest anodic activation among these heat treatment processes was obtained after annealing at 300°C, leading to the formation of oxide mounds.

The mechanism of formation of oxide mounds as a result of water quenching, following heat treatment at 300°C, has been discussed for AlSn model binary alloys [32]. In summary, the mounds form by oxidation of aluminium around Sn particles, which segregate locally during heat treatment. This is the temperature at which maximum Sn segregation occurs, as determined by low solubility of Sn in Al and sufficiently high
Figure 4.24. SIMS Elemental maps over the corroded area of alloy AlGa1000Sn100 – annealed at 300°C – for Al, Ga and Sn after potentiostatic test at -1.3 V vs. a) for 300 s at the area of 500 μm x 500 μm, b) for 600 s at the area of 500 μm x 500 μm.
mobility of liquid phase Sn in Al. The number density of the mounds increases as the sites for segregation of Sn increase with increasing Sn content of the alloy, leading ultimately to the formation of a hydrated oxide of order 1 μm thick for AlSn alloy containing 1000 ppm Sn, covering the entire surface of the specimen. In addition to the Sn particles segregated during heat treatment, the enhancement of oxidation during quenching was attributed to segregation of Sn in the form of an interfacial nanofilm as a result of selective oxidation of the Al component of the alloy. This resulted in significant activation of the surface in contact with superheated steam in the absence of chloride. The formation of the oxide mounds for the present AlGaSn alloys is attributed to Sn segregation alone according to the same mechanism, in view of the fact that no simultaneous Ga segregation was detected (Fig. 4.2 and 4.3) resulting from heat treatment and water quenching. The air-cooled samples did not form oxide mounds. However, they contained Sn particles formed during heat treatment.

### 4.4.2 Passivity breakdown during electrochemical polarisation

The oxide mounds were the initiation sites for circular corrosion morphology obtained by potentiodynamic and potentiostatic polarisation. Although the Sn particles, which segregated during heat treatment, were lifted up from the metal surface by the growing oxide, the surface was still active by formation of a fresh Sn film (or Sn-rich surface layer) as a result of dealloying, as described for binary AlSn alloys [32] and summarised above. Corrosion initiated by activation of the surface by Sn enriched during heat treatment.

Segregation of Sn by heat treatment at 300°C thus caused passivity breakdown and Al oxidation first during water quenching after heat treatment and then by electrochemical polarisation in chloride or sulphate solution. These oxidation processes caused Ga enrichment by anodic segregation (dealloying). Homogenised binary AlGa alloys containing 50-1000 ppm Ga did not activate as a result of annealing, as discussed in Chapter 3, since passivity breakdown did not occur in the absence of Sn.

In the polarisation curve of AlSn100 (Fig. 4.5) a small passivation plateau appeared just after the passivity breakdown. This behaviour was attributed to needle-shaped propagation of corrosion limited to Sn-segregated crystallographic sites. Since only the needle tips following the Sn-rich sites were active, the anodic current was limited by the active area available, giving a quasi-passive behaviour [32]. With the added presence of Ga (even only 50 ppm), this quasi-passive zone in the polarisation curve vanished, and the corrosion morphology was rounded instead of the crystallographic needle shapes. This was attributed to better wetting of Al surface by segregating liquid Ga by dealloying during anodic polarisation than thermally segregated Sn restricted to its crystallographic sites.

In the absence of segregated Sn at the surface after annealing at 600°C, the passivity breakdown potential of the AlGaSn alloys was increased to more noble values closer to the pitting potential of pure Al, although the current density output was much higher than that of pure aluminium. This resulted from the segregation of Ga and Sn, by dealloying of the corroding surface. This conclusion is restricted to Sn content limited to
100 ppm as in the present work. Higher Sn concentrations, especially 1000 ppm, lead to high oxidation rates during water quenching after heat treatment at 600°C, as shown in Ref. 32. This phenomenon is also expected to cause segregation of Ga and enhanced activation of the surface, although this was not investigated explicitly in the present study.

The present description of Sn segregation by heat treatment and its effect in passivity breakdown supports the earlier work on binary AlSn alloys [13, 32] and, with reference to that work, explains the effect of heat treatment on Sn segregation and its role in passivity breakdown of AlGaSn alloys. Furthermore, it clarifies previous discussions of the combined roles of Sn and Ga in the activation of Al alloys [3] and shows that Ga segregation by dealloying on the surface activated by Sn and resulting significant increase in activation. It is not possible to invoke hydride formation [36] in this mechanism, which would cause pH increase at the surface. This is explained by the observation that significant hydrogen evolution does not occur on the passive surface below the breakdown potential (Fig. 4.5), as discussed further in Section 4.4.7. During potentiodynamic polarisation in the positive potential direction, hydrogen evolution starts with passivity breakdown and increases with increasing potential, related instead to pH drop, resulting from hydration of the corroding Al metal, as is the case in the classical electrochemical theory of propagation of localised corrosion in aqueous solution [37].

In view of the foregoing, the presence of Ga alone is therefore not a big threat for passivity breakdown because it is stable in solid solution with aluminium in significant amounts. An additional factor has to exist, such as the added presence of Sn, which causes passivity breakdown and ensuing Ga segregation by dealloying, resulting in a synergistic form of activation as described above. Alkaline etching is another example of the necessary additional factor for activation with undesirable consequences, as discussed in Chapter 3.

These comments apply to binary and ternary alloys discussed in Chapter 3 and the present chapter. The effect of the added presence of other alloying and impurity elements, relevant for commercial alloys, will be discussed later in Chapter 7.

4.4.3 Significance of amalgamation

Another important factor in the activation mechanism by the presence of Sn and Ga together in Al as trace elements is the existence of segregated Ga in the liquid state at room temperature and the likelihood of formation of lower melting point GaSn amalgam as a result of the segregation or enrichment mechanisms described above. As argued in earlier papers [9, 13, 38, 39], activation of aluminium separately by higher melting point elements In, Sn, Bi and Pb was a result of fluidization of the nanoparticle and nanofilm segregations of these elements at the aluminium metal-oxide interface leading to passivity breakdown. For this process, the presence of chloride in the solution was an additional requirement [7, 39]. In the present mechanism of activation by the combined presence of Ga and Sn in the alloy, however, the presence of chloride as an aggressive factor contributing to passivity breakdown is not a requirement. As long as
the segregation at the metal-oxide interface is in the liquid metallic state at room temperature, passivity breakdown occurs in the absence of chloride. In such a situation, the conditions required by the classical mechanism for passivity breakdown by Hg or Ga drop on the Al surface, viz., mechanical contact between the Al substrate and the liquid metal droplet and the presence of humidity, are satisfied [24, 40].

4.4.4 Circular corrosion morphology

The cause of the circular morphology has to be attributed to the segregation of Ga as discussed above. The circular shape is possibly enhanced by initiation of the attack in the oxide mounds with circular shape by undermining of the oxide. High rate of etching caused by continually increasing potential as the driving force probably favours spreading in the most efficient circular pattern from the point of initiation, with corrosion occurring in the periphery, as in the case of two dimensional pitting [41]. The propagation may follow a stepwise process of enrichment of the activating elements to form the liquid phase GaSnAl alloy on a ring-shaped corrosion front, which becomes a groove by corrosion and increased enrichment.

The factors contributing to the driving force for this type of attack are the applied potential, as already mentioned, and Sn and Ga content in the alloy. With decreasing applied potential (Fig. 4.11) and decreasing Ga content (Fig. 4.15a and 16a), the circular attack tends to become more occluded. This occurs in the form of undermining the oxide, which is not as easily destroyed as in high rate of etching accompanied by vigorous hydrogen evolution at the corrosion front. The morphology appearing as stepwise filamental attack during polarisation at -1.4 V\textsubscript{SCE} (Fig. 4.18) (and at potentials more positive than -1.4 V\textsubscript{SCE} (Fig. 4.13) results by cracking of the undermined film in the radial propagation direction of a circular cell. The grooves also become deeper with decreasing driving force, which provides better conservation of the acidic anolyte needed for the process.

4.4.5 Effect of surface processing

Chemical and mechanical treatments followed by annealing at 300°C did not cause significant changes in the activation behaviour of alloy AlGa1000Sn100 other than moderate reduction in the anodic current density relative to the as-annealed sample (Fig. 4.8). The reduction in the current density can be explained for the mechanically-polished surface, since this is expected to remove the activating segregations Sn from the surface. However, the reduction was more moderate than expected. The GD-OES results indicated also that not all Sn segregated by heat treatment could be removed (Fig. 4.4). Perhaps, some Sn remained segregated along the grain boundaries. The remaining Sn was sufficient to maintain surface activity according to the synergistic autocatalytic mechanism described above (Section 4.3.2).

Active behaviour of the alkaline etched surface is expected in view of that the noble elements Ga and Sn should become enriched by dealloying. GD-OES data (Fig. 4.4) confirmed this to be the case for Ga. However, the data did not indicate a significant enrichment of Sn relative to the as-annealed case. Broadening of a shallow peak close to
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the oxide-metal interface, probably by surface roughening by etching (Fig. 4.4a) relative to the sharper interfacial Sn peak for the as-annealed sample (Fig. 4.3f) suggested either removal of a certain fraction of Sn or its redistribution by etching. Since Ga alone is not an effective activator, possible reduction in the concentration of enriched/segregated Sn at the surface by alkaline etching decreased its anodic activation.

Based on earlier results for the binary AlSn alloy [32], stripping of the alloy surface in hot chromic-phosphoric acid was not expected to affect Sn segregated by heat treatment. However, a certain broadening of the Sn peak by stripping (Fig. 4.4c), relative to the as-annealed condition (Fig. 4.3f) is evident, and this may have caused reduction in activity, similar to that described above for the etched surface. The significant increase in the breakdown potential may suggest increased passivity by the converted oxide containing Cr.

This discussion indicates that the effect of surface processing was not sufficiently clarified with the data obtained. Further work in this area was outside the present scope, and further investigation is needed.

4.4.6 Inhibition of hydrogen evolution

Earlier work by different research groups has indicated that the rate of hydrogen evolution, or water reduction, on Sn in aqueous media is very low (high hydrogen overpotential) [42], such that the presence of Sn in Al inhibits water reduction in aqueous solution [32, 43] to quite negative applied potentials. This phenomenon was also observed in the present polarisation experiments of the Sn containing alloys. Reduced hydrogen evolution often implies also slow kinetics for the oxygen reduction reaction [44]. The lowering of the passivity breakdown potential, as long as it is equal to the corrosion potential defined by the anodic dissolution and total rate of the reduction processes, can partly be attributed to this phenomenon.

The passivity breakdown potential is depressed even further by increase of Ga concentration in the AlGaSn alloy from 50 to 1000 ppm both in chloride and sulphate solutions. Ga is also known to have high hydrogen overpotential [44-45], and probably contributes to further inhibition of hydrogen evolution, resulting in further depression of the passivity breakdown potential, which can be viewed as a mixed potential as argued above. Contribution of Ga in this case can be attributed to i) Ga in solid solution, ii) a monolayer segregation of Ga during after quenching after heat treatment, which could not be detected by the present characterisation techniques, iii) instantaneous monolayer segregation of Ga in contact with aqueous chloride or sulphate solution, or a combination of these.

4.5 Conclusions

- The model ternary AlGaSn alloys were anodically more active in chloride solution than the binary alloys AlGa and AlSn with same Ga or Sn content as the ternary alloy and identical thermal treatment.
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- AlGa1000Sn100 alloy, with highest Ga content investigated, activated also in sulphate environment, i.e., the presence of aggressive chloride was not necessary for activation of this alloy with relatively high Ga content.
- The highest anodic activation of model AlGaSn alloys was obtained as a result of annealing at 300°C. This is the temperature at which maximum segregation of Sn occurs, indicating important role of Sn in the activation process.
- In chloride solution, passivity breakdown was initiated by thermally segregated Sn. Subsequent propagation of corrosion at an enhanced rate was caused by enrichment of Ga by dealloying. Similar activation was not possible on the binary AlGa alloy under similar conditions, and it was not as enhanced on alloy AlSn, indicating the synergy of the two elements in the observed behaviour of the ternary alloy.
- Annealing at 600°C resulted in homogenisation of Sn and preservation of the passivity of the surface. However, enrichment of Sn occurred by prolonged exposure of the ternary alloy to chloride solution, causing increased anodic activity according to the mechanism above.
- Segregation of both Sn and Ga formed a liquid phase alloy rich in Ga and Sn (amalgamation) spreading over the surface as a thin film, which destroyed the passivity of the aluminium oxide underneath and autocatalytic corrosion of the Al substrate by uninhibited transport of dissolving Al atoms through the amalgam film. The same phenomenon did not occur without the presence of one of the components, Ga or Sn, in the alloy.
- Corrosion followed the spreading of the amalgam film from Sn-rich initiation sites in the form of nearly circular corrosion cells. This geometry was also enhanced by the nearly hemispherical oxide mounds formed around Sn segregations during heat treatment and subsequent quenching in water. At the higher applied potentials, this type of corrosion propagation occurred superficially. It became more occluded with decreasing applied potential by undermining of the oxide.
- Another role played by segregated Sn and Ga was the inhibition of hydrogen evolution that reduced the passivity breakdown potential significantly to very negative values.

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References

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Effect of Trace Elements Gallium and Lead on Anodic Activation of Aluminium in Chloride Solution

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Abstract

The objective of this study is to investigate the combined effect of small amounts of lead and gallium in aluminium on surface segregation by heat treatment and ensuing anodic activation of aluminium, in relation to the known behaviour of the binary alloys AlPb and AlGa. For this purpose, model ternary alloys containing gallium (50 and 1000 ppm) and lead (50 ppm) were prepared from pure components. After cold rolling and mechanical polishing, the alloys were heat treated in the temperature range 300-600°C, followed by quenching in water. The samples were subsequently characterised electrochemically in 5% NaCl solution maintained at 25°C. Annealing at 600°C resulted in significant segregation of insoluble lead while gallium was homogenised in solid solution due to its high solid solubility in aluminium. Segregated lead was dominant in determining the anodic behaviour in this condition. In all thermal conditions, small Ga content (50 ppm) had only a small contribution to activation by Pb, if any. However, the presence of 1000 ppm Ga contributed significantly to activation by becoming enriched at areas around Pb segregations, where passivity breakdown occurred initially by presence of Pb. Gallium, which was stable in solid solution with Al in all thermal conditions, became activating as a result of segregation by dealloying at sites activated by Pb. This started an autocatalytic spread of activation over the surface by continuing enrichment of Ga by dealloying, as long as the alloy contained sufficiently high Ga (1000 ppm). Lower Ga content could not sustain activation by this process, and repassivation occurred after removal of the activating Pb particles from the Al surface by corrosion.

5.1 Introduction

Lead and gallium are ubiquitous trace elements in commercial aluminium alloys, originating from the raw material bauxite [1-3]. The surface segregation of Pb by heat treatment of binary [4-7] and ternary [8-10] model alloys has recently been investigated, along with its role on anodic activation of the alloy in chloride media [11, 12]. Solubility of Pb in solid Al is nearly zero (< 5 ppm) [4], and its presence even at ppm level was sufficient to cause enrichment of the element at the surface by heat treatment at 600°C, giving anodic activation. A similar study of model binary AlGa alloys verified the existing thermodynamic data in Chapter 3 that solubility of Ga in solid aluminium is significant. Trace element Ga is therefore stable in solid aluminium. Ga can activate
aluminium anodically in chloride solution by dealloying if its concentration exceeds 500 ppm in the binary alloy [13-15].

Anodic activation of model and commercial Al alloys by Pb occurred within a reasonable period of heat treatment time (1 h) at 600°C, a temperature significantly above its melting point [5]. The period of heat treatment required for similar level of activation at 600°C increased significantly with decreasing temperature. Activation was attributed to the formation of a continuous nanofilms of Pb, which was trapped at the aluminium metal – γ Al₂O₃ interface by diffusion of Pb to the surface and growth of γ Al₂O₃ into the metal [6]. Pb segregated also at lower temperatures, but mostly in the form of nanoparticles, which did not give sufficient coverage of the metal surface by Pb, a necessary condition for anodic activation.

Anodic activation caused by Pb in chloride solution was characterized by two oxidation peaks at the potentials of about -0.91 V SCE and -0.88 V SCE in the polarisation curve of the AlPb alloy heat treated at 600°C [4-7, 10, 16]. Each peak was related to superficial etching of the surface, causing multilayered attack during potentiodynamic polarisation [7]. The first layer of corrosion was attributed to the undermining of the thermally formed oxide film along the Pb nano-film [6, 7]. The second layer was a result of crevice corrosion in the crevice formed between the undermined oxide and metal surface with acidified anolyte still present. Activation by Pb was a temporary effect [6]. The surface passivated after the Pb nanolayer was destroyed by corrosion.

The investigation of the model AlPb alloys did not explain the observation that certain commercial alloys become anodically active by heat treatment at temperatures significantly lower than 600°C, e.g., 450°C for alloy AA8006 [10, 11, 16], and the attention was directed toward the possible added presence of the lower melting point elements In [17], Sn [18], Bi [19] and Ga (Chapter 3). The elements Ga, Sn and In are known to be more effective than Pb as activators [4, 20-22]. This was attributed to their lower melting points than Pb and higher solubility of Al in these elements [18, 23].

The theory, which is often referred to in explaining activation of aluminium by the low melting point elements in Group IIIA-VA elements, is the formation of a liquid phase alloy (amalgam) of the segregated element and aluminium, as is the case for Hg [24, 25] and Ga [26, 27]. According to this theory, Al corrodes by dissolving into the amalgam where it is in contact with it and oxidizing at the surface of the amalgam, where it is in contact with the ambient atmosphere. The amalgam wetting the surface of Al metal prevents its oxidation to recover the passivating oxide. Since the elements of the group other than Hg and Ga have their melting points significantly higher than room temperature, melting point depression [28-30], known to occur with decreasing size of solid material to nanometer dimension, is invoked to justify the applicability of the theory to the higher melting point elements. Amalgamation theory for the activation effect of these elements was suggested to occur by melting point depression of the segregated nano-sized Pb [6] film and Sn [18] particles, constituting a liquid phase with the assistance of Joule heating generated by corrosion of aluminium.
The presence of a second element that can contribute to melting point depression is also of concern. Combined presence of 20 ppm Pb and 20 ppm Sn in Al model alloys caused activation at 450°C by segregation of a nanofilm, rich in Pb and Sn, at the metal-oxide interface [31, 32]. This was attributed to the lower melting point of the PbSn film than the melting points of Pb and Sn segregated alone. Combined presence of 1000 ppm Ga and 100 ppm Sn activated Al as a result of annealing at a lower temperature of 300°C even in the absence of chloride ions in the solution (Chapter 5). This was attributed to the formation of a GaSnAl amalgam by dealloying in aqueous solution.

It can be concluded from the foregoing that Pb is probably the least effective activator of aluminium among the Group IIIA-VA elements. However, it is also evident that the presence of combination of these elements in aluminium can cause higher activation than expected by synergistic effects, e.g., the combined effect of Pb and Sn. No information is available about the combined effect of Pb and Ga. The objective of this study is, therefore, to investigate whether Pb and Ga, when present together at small concentrations in model ternary alloys, can cause a similar synergistic increase in anodic activation of aluminium in relation to the effect of these elements when they are present alone in model binary aluminium alloys.

5.2 Experimental

Materials. Model ternary alloys were prepared by adding 50 and 1000 ppm of gallium and 50 ppm of lead to high purity aluminium. The alloys were denoted as AlGa50Pb50 and AlGa1000Pb50 based on their Pb and Ga content in ppm. The cast alloys were scalped and cold rolled from 20 mm to a final thickness of approximately 2 mm. The compositions of the rolled samples were verified within 5-15% error by glow discharge mass spectrometry (GDMS). Samples were ground with SiC paper and polished metallographically to 1 μm diamond paste finish. Heat treatment was conducted for 1 h in the temperature range 300-600°C in an air-circulating furnace, followed by quenching in water.

Surface characterisation. Elemental depth profiles of the samples were determined after heat treatment and electrochemical testing by glow discharge optical emission spectrometry (GD-OES), using a Horiba Jobin Yvon instrument in radio frequency (RF) mode with a standard 4 mm diameter copper anode. The measurements were quantified for Al and O by using the standards available for pure Al and oxygen. The data for Ga was calibrated by using the linear relationship between the amount of gallium in the bulk and the measured intensity (V) of Ga emission (Chapter 3). The data was collected every 5 ms during sputtering. The sputtering rate was 70 nm/s in the metal and 40 nm/s in the oxide [33].

Samples were characterised before and after electrochemical tests in plan-view by using a field emission gun scanning electron microscope (FE-SEM) of type Zeiss Ultra 55, equipped with Inca (Oxford Instruments) X-ray electron diffraction spectrometer (EDS) capability.
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**Electrochemistry.** All specimens were degreased in acetone and ethanol before potentiodynamic polarisation in stirred 5 wt% NaCl solution at 25°C, which was exposed to ambient air. Earlier work showed that the anodic current was not affected significantly by the presence of dissolved oxygen in the solution [34]. The sample area exposed to the solution was 1.33 cm². The cell geometry, solution volume and the stirring rate in the solution were identical in all runs. Anodic polarisation curves were acquired with respect to saturated calomel reference electrode (SCE) at a sweep rate of 0.1 mV/s in the positive potential direction, starting 50 mV below the corrosion potential. Selection of the solution concentration and the sweep rate were based on a previous attempt to optimize these for best observation of the active behaviour, which is an unstable process [11]. Potentiostatic runs were performed at selected potentials to investigate the transient processes between active and passive conditions.

Changes in the corrosion potential of alloy AlGa1000Pb50 were investigated for a period of 20 h in synthetic seawater whose pH was adjusted to 3 by adding glacial acetic acid. This procedure has often been used in the past to observe changes in the corrosion potential of binary alloys of Al and Group IIIA-VA elements, as the surface of the alloy was lightly and slowly etched layer by layer in the presence of a weak acid.

**5.3 Results**

**5.3.1 SEM**

No observable change occurred in the surface morphology of the alloys after heat treatment at 300°C and 450°C, as observed by SEM. After annealing at 600°C, formation of γ-Al₂O₃ was verified by observation of its typical porous morphology [35] and segregated Pb particles of size less than 50 nm [5] (not shown).

**5.3.2 GD-OES**

Elemental depth profiles shown in Fig. 5.1 indicate that Ga segregation did not occur on any of the two AlGaPb alloys investigated in any of the heat treatment temperatures used, in accordance with the thermodynamic properties of the AlGa system discussed above, indicating high solubility of Ga in solid Al. Segregation of Pb was not detected both for the as-polished condition (Fig. 5.1a and 5.1b) and after annealing at 300°C (5.1c and 5.1d). The oxide thickness for both alloys was about 5 nm after heat treatment at this temperature as in the as-polished condition. After annealing at 450°C (Fig. 5.1e and 5.1f), Pb peak appeared at the metal-oxide interface. The oxide thickness obtained was about 20 nm at this temperature, as determined by assuming that the position of the Pb peak corresponded to the oxide-metal interface [4]. The size of the Pb peak increased by heat treatment at 600°C for both alloys AlGa50Pb50 and AlGa1000Pb50 (Fig. 5.1g and 5.1h, respectively) and became about 50 nm. The GD-OES data for heat treatment
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Figure 5.1. GD-OES elemental depth profiles for alloys a) AlGa50Pb50 and b) AlGa1000Pb50 in as-polished condition, c) AlGa50Pb50 and d) AlGa1000Pb50 after heat treatment at 300°C, e) AlGa50Pb50 and f) AlGa1000Pb50 after heat treatment at 450°C and for g) AlGa50Pb50 and h) AlGa1000Pb50 after heat treatment at 600°C. All heat-treated samples were quenched in water after heat treatment.
at 600°C agreed with the earlier data for binary model AlPb alloys [4, 5], indicating that the observed effect of heat treatment was determined by segregation of the trace element Pb. Area under the Pb enrichment curves were identical for both samples at each annealing temperature indicating that Ga, still in solid solution with Al, had no effect on the thermal segregation of Pb.

5.3.3 Electrochemistry

Potentiodynamic polarisation

Figure 5.2 shows potentiodynamic polarisation curves for the binary and ternary alloys in the as-polished condition (Fig. 5.2a) and after heat treatment at 300°C (Fig. 5.2b) and 600°C (Fig. 5.2c). Figure 5.2c includes also curves for alloy AlGa50Pb50 and AlGa1000Pb50 heat treated at 450°C. The polarisation curves for alloy AlGa50 were almost identical to that for pure Al in all conditions reported in Fig. 5.2, unaffected by heat treatment. The curve for alloy AlGa1000 showed a slight shift in the negative potential direction by about 50-100 mV relative to the curve for alloy AlGa50 in all conditions. The effect of Ga content on the anodic behaviour of the binary AlGa is discussed in more detail elsewhere (Chapter 3). The curves for alloys AlPb50 and AlGa50Pb50 showed slight shifts in the negative potential direction (about 50 mV) relative to the curve for alloy AlGa50 after heat treatment at 300°C (Fig. 5.2b). However, these shifts did not indicate significant activation. Activation became significant for alloy AlGa1000Pb50. The ternary alloy was already active in the as-polished condition (Fig. 5.2a). Heat treatment at 300°C did not give a significant effect relative to the as-polished condition. This is in agreement with the GD-OES data, which did not indicate significant difference between the elemental depth profiles of the two conditions (Fig. 5.1a-b and 5.1c-d).

Heat treatment at 450°C gave further increase in the activation of alloys AlGa50Pb50 and AlGa1000Pb50 relative to the 300°C condition (Fig. 5.2b), which was attributed to Pb segregation during annealing at 450°C, as shown by the GD-OES depth profile in Fig. 5.1e and 5.1f. Nevertheless, it did not cause as high activation as annealing at 600°C (Fig. 5.2c).

After heat treatment at 600°C, the alloys containing Pb were significantly activated (Fig. 5.2c) in accordance with the mechanism described earlier in detail [4, 5]. The added presence of 1000 ppm Ga caused increase in the activation by mainly increasing the current output. Corrosion potential data as a function of immersion time in acidified seawater for alloys AlGa1000Pb50, AlGa1000 (Chapter 3) and AlPb20 [5], identically heat treated at 600°C, are shown in Fig. 5.3. Among the heat-treated alloys, the presence of Ga gave a slightly decreasing trend to the large-time behaviour of the corrosion potential, while the corrosion potential of alloy AlPb20 increased at large times. The corrosion potential of alloy AlGa1000Pb50 was about only 50 mV more negative than that of AlPb20 at the outset, while the difference increased to about 150 mV at the end of test (about 20 h).
Figure 5.2. Polarisation curves for samples in conditions a) as-polished, b) annealed at 300°C and c) annealed at 450°C and 600°C. The curves without the temperature label in (c) were annealed at 600°C.
Figure 5.3. Corrosion potentials of alloys AlGa1000Pb50, AlGa1000 and AlPb20 (reproduced from Ref. 5) in acidified synthetic seawater.

**Potentiostatic polarisation**

The potential selected for polarisation was -0.8 \( V_{SCE} \), such that most alloy-heat treatment combinations showed some degree of activation to make comparison possible. AlGa alloys were passive below this potential at all heat-treatment conditions (Fig. 5.2). Current transients at -0.8 \( V_{SCE} \) are shown in Fig. 5.4. Alloy AlGa50Pb50, heat-treated at 300°C, showed passive behaviour, as indicated by anodic current output at \( \mu \)A level in Fig. 5.4a. A similar result was obtained for the binary alloy AlGa treated identically, as discussed in Chapter 3. The current level increased with increasing annealing temperature. These results are in agreement with the potentiodynamic data shown in Fig. 5.2b and 5.2c. For all annealing temperatures, however, the current density went through a maximum before decaying to a much lower steady-state level. With reference to the anodic behaviour of the binary AlGa (Chapter 3) and AlPb [4, 5, 7] alloys, increased activation of alloy AlGa50Pb50 at the outset with increasing heat treatment temperature was attributed to segregation of Pb at the metal-oxide interface during annealing, as also indicated by the present GD-OES data (Fig. 5.1). However, the binary AlGa50 alloy, when annealed in the temperature range 300-600°C, was passive at -0.8 \( V_{SCE} \) (Chapter 3). In the case of AlPb alloys, passivation occurred after temporary active behaviour at the outset [5] as the Pb active layer, segregated at the metal-oxide interface by heat treatment, was removed by corrosion. Therefore, the initial active behaviour in Fig. 5.4a is attributed to Pb, and increasing steady-state current density with increasing annealing temperature is attributed to Ga, as will be discussed further in the Discussion section.

In the case of alloy AlGa1000Ga50, the current density at the same applied potential increased with time for all heat-treatment temperatures, as shown in Fig. 5.4b. The sample annealed at 600°C gave the highest current density initially. The current density
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remained quite stable for about 30 min before increasing gradually as a function of time. Maintenance of active current levels after prolonged polarisation was attributed to high Ga content of the alloy, with reference to the anodic behaviour of the binary alloy AlGa1000 (See Ch. 3), which is also shown in Fig 5.4b for the annealing temperature of 300°C. High Ga content maintained AlGa1000Pb50 alloys at all heat treatment conditions in active state with high current densities, while all AlGa50Pb50 alloys passivated after short active behaviour at the outset. The current density for the AlGa1000Ga50 samples, annealed at 300°C and 450°C, was lower than those annealed at 600°C at the outset. The current density for all cases then increased gradually to a similar level of about 65 mA/cm² after 4 h of polarisation.

At the more negative potential of -0.9 V_SCE, the binary alloy AlGa1000 was passive. The current density of alloy AlGa1000Pb50 (annealed at 300°C), initially at 0.1 mA/cm², increased to about 30 mA/cm², as shown in Fig. 5.4c. Conversely, the same alloy, annealed at 600°C, was initially active at a current density of 7.5 mA/cm² at this potential, and it passivated to a current density of 0.2 mA/cm² after 10 min. Alloy AlGa50Pb50, annealed at 300°C, was not as active as alloy AlGa1000Pb50 because of its low Ga content. However, it was more active than alloy AlGa1000. These differences between the annealing temperatures of 300°C and 600°C are attributed to Pb segregation, as will be discussed further in the Discussion section.

Pb containing binary and ternary alloys, annealed at 600°C, were polarised at potentials -0.93 V_SCE and -0.88 V_SCE, corresponding to the two oxidation peaks typically measured during potentiodynamic polarisation of the Pb containing alloys (Fig. 5.2c). At -0.93 V_SCE, the current density attained a maximum of about 3 mA/cm² after about 1 min for alloys AlPb50 and AlGa50Pb50, while alloy AlGa1000Pb50 attained a maximum current density of about 7 mA/cm² after 8 s, as shown in Fig. 5.5a. Alloys AlPb50 and AlGa50Pb50 then passivated to a current level of about 150 μA after 5 min and alloy AlGa1000Pb50 after 10 min. At -0.88 V_SCE, two successive peaks were observed in the current transients of the three Pb containing alloys, as shown in Fig. 5.5b. The current transients for alloys AlPb50 and AlGa50Pb50 were similar. The peaks correspond to the corrosion mechanisms, which cause the current peaks observed in the corresponding potentiodynamic polarisation curves (Fig. 5.2c), as discussed in detail earlier for the binary alloy AlPb [7]. The trend in the current transient for alloy AlGa1000Pb50 was similar to that of alloys AlPb50 and AlGa50Pb50. However, the current level was higher. The charge passed until passivation during polarisation at -0.87 V_SCE, was about 2 times higher for AlGa1000Pb50 than the other two alloys.
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Figure 5.4. Potentiostatic polarisation results a) for alloy AlGa50Pb50 at an applied potential of -0.8 $V_{SCE}$ and for alloy AlGa100Pb50 at potentials b) -0.8 $V_{SCE}$ and c) -0.9 $V_{SCE}$ after annealing at different temperatures.
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Figure 5.5. Potentiostatic polarisation results for samples annealed at 600°C at applied potentials of a) -0.93 $V_{SCE}$ and b) -0.88 $V_{SCE}$.

5.3.4 Corrosion morphology: 600°C-annealed specimens.

Corrosion behaviour of alloy AlGa50Pb50, annealed at 600°C, during potentiodynamic polarisation was nearly identical to the well-documented behaviour of the binary AlPb alloys [5-7]. In summary, the surface was passive below the corrosion potential. The $\gamma$-$Al_2O_3$ layer was undermined nearly completely as a result of superficial etching, as the first anodic peak was formed (Fig. 5.2c). However, the film remained loosely attached to the surface, forming a crevice. The second layer, corresponding to the second anodic peak, occurred in the form of crevice corrosion. Each layer of corrosion was accompanied by hydrogen evolution and followed by relative passivity indicated by termination of the etching process and hydrogen evolution.
During polarisation of alloy AlGa1000Pb50 (annealed at 600°C), the first layer of corrosion was similar to that on alloy AlPb50 and AlGa50Pb50. However, pitting also occurred with intensive gas evolution. Although undermining of the film spread over most of the exposed area as on alloy AlGa50Pb50 with resulting passivation of the etched area, pits continued to propagate. Pitting resulted in higher current density for alloy AlGa1000Pb50 in the polarisation curve in Fig. 5.2c, as well as in the potentiostatic polarisation data in Fig. 5.5a and 5.5b, in relation to alloy AlGa50Pb50. The focus in the remainder of this section is the corrosion of alloy AlGa1000Pb50.

Potentiodynamic polarisation of AlGa1000Pb50 samples annealed at 600°C was terminated at predetermined potentials, and the resulting corrosion morphology of the sample was investigated ex-situ by FE-SEM. Fig. 5.6 shows corrosion morphologies obtained by sweeping the potential up to -0.93 V_{SCE}, which corresponded to the first oxidation peak in Fig. 5.2c. Fig. 5.6a shows a general view at low magnification. The slip planes seen were formed during heat treatment and cooling, as discussed in Ref. 33. The light grey areas, marked A, remained uncorroded at this potential. The dark grey areas, marked as B, were formed by superficial etching along the metal-oxide interface, undermining the thermally-formed γ-alumina layer [7].

Areas marked by white squares in Fig. 5.6a are shown at higher magnification in Fig. 5.6b-e. The propagation front under the oxide, seen in Fig. 5.6b, is not affected by the grain boundary (line with bright contrast). The undermined oxide and the etched surface, probably exposed by removal of part of the loosely attached film during rinsing of the sample after the run, is seen more clearly in Fig. 5.6c. Ga could not be detected by EDS at the surface. However, Pb particles were detected as bright spots in the back-scattered image (Fig. 5.6e) of the corroded area shown in Fig. 5.6d.
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Figure 5.6. Surface morphology of alloy AlGa1000Pb50 (annealed at 600°C) after potentiodynamic polarisation to -0.93 \( V_{SCE} \), investigated ex-situ by SEM. a) General view of the corroded area marked A for uncorroded areas and B for corroded areas. b) Undermined oxide at higher magnification of area marked in (a). c), d) Propagation of corrosion at corresponding areas marked in (a). e) Back-scattered electron image of (d) where bright spots are Pb particles.

An AlGa1000Pb50 sample polarised up to -0.915 \( V_{SCE} \), which corresponded to the minimum between the two oxidation curves, is shown in Fig. 5.2c. At this potential, the first layer of attack, which consisted of undermining of the oxide, covered most of the surface exposed to corrosion. The undermined oxide began to be detached locally from the surface during polarisation, as shown in Fig. 5.7a. The corroded metal with etched morphology (light grey), marked as C in Fig. 5.7b, also showed crystallographic pitting before the undermined oxide was removed. This is in contrast to the pitting of the binary alloys and alloy AlGa50Pb50, which initiated at higher potentials close to the pitting potential of pure Al [7] (Fig. 5.2c). As the undermined oxide was removed from the surface, corrosion continued propagating by forming crystallographic pits instead of passivation of the entire surface as was the case for the other alloys.

Fig. 5.8a shows the corrosion morphology obtained by potentiostatic polarisation at -0.88 \( V_{SCE} \) until the surface passivated. Most of the undermined oxide was detached from the surface, revealing crystallographic etching. Crystallographic pits were also observed on the etched surface, as shown in Fig. 5.8b. Pb or Ga segregation could not be indicated by EDS analysis.
Figure 5.7. Surface morphology of alloy AlGa1000Pb50 (annealed at 600°C) after potentiodynamic polarisation to -0.915 V_{SCE}, investigated by ex-situ SEM. a) General view of corroded area. b) Area marked in (a) at a higher magnification.
Figure 5.8. Corrosion morphology of alloy AlGa1000Pb50 (annealed at 600°C) after potentiostatic polarisation at -0.88 $V_{SCE}$ for 10 min. a) General view. (b) Area marked in (a) at a higher magnification.

5.3.5 Corrosion morphology: 300°C-annealed and as-polished specimens.

The post mortem analysis of samples heat treated at 300°C is limited to alloy AlGa1000Pb50, which was significantly more active than the other alloys annealed at this temperature. This alloy remained active after potentiostatic polarisation for 2 h at -0.9 $V_{SCE}$ (Fig. 5.4c). The corrosion morphology obtained after polarisation is shown...
in Fig. 5.9a and 5.9b at different magnifications. The attack was in the grains rather than grain boundaries. The attack was deep and localized in contrast to the superficial etching of the sample annealed at 600°C. Ga was detected by EDS of the area in Fig. 5.9c, as shown by the spectrum in Fig. 5.9d.
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Figure 5.9. The surface morphology after the potentiostatic polarisation of alloy AlGa1000Pb50 (annealed at 300°C) for 2 h at -0.9 V_{SCE}. a) General appearance of the corroded area. b) Marked area in (a) at a higher magnification. c) Marked area in (b) at a higher magnification. c) EDS analysis of the spot marked in (c).

Potentiostatic polarisation of the as-polished AlGa1000Pb50 alloy for 4 h at -0.8 V_{SCE} gave corrosion around the grains elongated along the rolling direction, as shown in Fig. 5.10. This morphology indicated inhomogeneity of the as-cast material, especially along the grain boundaries. The nature and cause of inhomogeneity could not be investigated further. However, possible causes will be discussed later in the chapter.
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5.3.6 GD-OES analysis on corroded surface

GD-OES analysis of samples polarised potentiostatically for 10 min at -0.93 \( V_{SCE} \) revealed similar depth profiles for Pb on alloys AlPb50, AlGa50Pb50 and AlGa1000Pb50, with enrichment of Pb at a depth of about 125 nm, as shown in Fig. 5.11a, 5.11b and 5.11c, respectively. No Ga segregation could be detected for AlGaPb alloys. Judging from the inflection and intersection points of the O and Al profiles this time, instead of the location of the Pb peak (Section 5.3.2), and considering the increased roughness of the surface, the thickness of the undermined oxide must be about the same as the thickness of \( \gamma \)-Al2O3 on as-heat treated samples (Fig. 5.1g and 5.1h). The deeper position of the Pb peak, in relation to the as heat-treated surface, is probably determined by the remnants of Pb film, originally at the metal-oxide interface, collecting in the form of particles on etched aluminium metal surface, as discussed earlier [5]. The location of Pb at 125 nm should include the crevice height formed by undermining of the oxide [7].

GD-OES depth profiles for the same three alloys, polarised at -0.88 \( V_{SCE} \), shown in Fig. 5.12a, 5.12b and 5.12c, respectively, indicate that Pb enrichment was much closer to the surface, at a depth of a few nm. This resulted from the removal of the thermally formed oxide nearly completely from the sample surface. Ga was also enriched at the surface of Ga containing alloys, especially on alloy for AlGa1000Pb50, as seen in Fig. 5.12c. The Ga profile followed the depth profile of Pb.

Depth profile of alloy AlGa1000Pb50, annealed at 300°C and, potentiostatically polarised at -0.8 \( V_{SCE} \) is shown, in Fig. 5.13. The figure indicates that the surface was enriched with Ga within a broader region of about 20 nm. Broadening was caused by surface roughness. Pb profile was similar to that for the as-annealed condition shown in Fig. 5.1d.
Figure 5.11. GD-OES analysis after polarising alloys a) AlPb50, b) AlGa50Pb50 and, c) AlGa1000Pb50 (annealed for 1 h at 600°C) for 10 min at -0.93 V_{SCE}. 
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Figure 5.12. GD-OES analysis after polarising alloys a) AlPb50, b) AlGa50Pb50 and c) AlGa1000Pb50 (annealed for 1 h at 600°C) for 10 min at -0.88 V$_{SCE}$.
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Enrichment of Ga and Pb was calculated from the area under the GD-OES profiles for as-annealed and as-corroded conditions of alloy AlGa1000Pb50, as shown in Fig. 5.14. Pb enrichment increased with increasing annealing temperature for 1 h of annealing time, while the Ga concentration remained constant at its homogenised bulk concentration (Fig. 5.14a). However, the amount of Pb remaining at the surface of the sample (annealed at 600°C) after potentiostatic polarisation at \(-0.8\ \text{V}_{\text{SCE}}\) was smaller than that for the as-annealed state, while Ga was enriched (Fig. 5.14b). The amount of Ga enriched was similar for samples annealed at 300 and 600°C. The same was true for the amount of charge passed for the two thermal conditions after polarisation under similar conditions (Fig. 5.14c). These results verify that Pb segregation by heat treatment, which increased with annealing temperature, did not affect the stability of Ga in solid solution with Al. Ga became segregated by dealloying during corrosion, albeit affected by the amount of Pb already present due to segregation during heat treatment. Although an appreciable amount of segregated Pb was removed by corrosion, its contribution to the dealloying process, resulting in significant Ga enrichment is evident from these results.

5.4 Discussion

In the presence of Ga alone in Al, significant activation occurred only for sufficiently high Ga concentration, viz., about 1000 ppm according to the literature [13, 14] and present results (Chapter 3). However, this occurred after a certain induction period in potentiostatic testing, if the underlying oxide was not destroyed mechanically, which was required for segregation of sufficient Ga on the Al surface by dealloying in chloride solution (Chapter 3 and Fig. 5.4b above). The role of added presence of Pb was to cause activation all the way from the start of the experiment at increasing rate with increasing annealing temperature, according to the mechanism discussed in Ref. 7.
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Figure 5.14. Comparison of Ga and Pb enrichment on alloy AlGa1000Pb50 after annealing at different temperatures, calculated by integrating the GD-OES Ga and Pb profiles in a) Fig. 5.1b, 5.1d, 5.1f and 5.1h before, and b) Fig. 5.12c and 5.13 after potentiostatic polarisation at -0.8 V\textsubscript{SCE}. c) Amount of charge passed by potentiostatic polarisation of alloy AlGa1000Pb50 after annealing at 300 and 600\degree C, calculated by integration of the data in Fig. 5.14 (data during first 10 min) and 5.5b.

The initial activation is therefore attributed to Pb segregated by heat treatment, although this occurred only in particulate form at temperatures lower than 600\degree C. Despite particulate Pb causes very limited activation, the amount, probably occurring locally around the segregated particles still in contact with the Al surface, appears to be sufficient to cause appreciable liquid Ga enrichment by dealloying, which then starts contributing to the activation of the surface at an increasing degree with respect to time of potentiostatic polarisation, as is evident from the curves for 300\degree C and 450\degree C in Fig. 5.4b (and 5.4c for alloy AlGa1000Pb50, annealed at 300\degree C). The mechanism of activation is related to formation of a liquid phase alloy wetting the aluminium surface, preventing the formation of a protective oxide film and high rate of Al dissolution through the liquid phase alloy (amalgamation theory) discussed in Chapter 3. For alloy AlGa50Pb50, the initial activation observed during potentiostatic runs (Fig. 5.4a) is again due to only Pb. However, the initial activation cannot be maintained because the Ga content of the alloy is not sufficient, and passivation occurs after a short period of polarisation, as the segregated Pb at the surface is removed by corrosion. Segregation of Pb by dealloying is not significant because the near-surface region has become nearly depleted of Pb by thermal segregation [6]. The foregoing mechanism is reflected also by the potentiodynamic data, which include also the effect of the driving force, the potential.

For samples annealed at 600\degree C, the Pb nanofilm is formed at the metal-oxide interface, providing the well-known conditions for maximum activation of the Al surface by Pb. The electrochemical behaviour under the conditions of potentiodynamic polarisation is more or less dominated by Pb (Fig. 5.2). Behaviour of alloy AlGa1000Pb50 was slightly different (higher current output than the other Pb-containing alloys) because of
high Ga content contributing to activation as discussed above. During potentiostatic polarisation involving prolonged exposure, removal of the interfacial film after a few minutes causes a decrease in the corrosion rate until the amount of Ga needed to sustain the active surface state becomes enriched at the surface by dealloying (Fig. 5.4b). This also depends on the applied potential as the driving force. While an increase is observed after a shallow minimum in the current density at an applied potential of -0.8 \text{ V}_{\text{SCE}} for alloy AlGa1000Pb50, the current increases again due to Ga enrichment. A similar recovery of current density does not appear to occur at a lower applied potential of -0.9 \text{ V}_{\text{SCE}} (Fig. 5.4b). With further decrease in the applied potential, all Pb-containing alloys showed tendency for passivation as the activating Pb film was removed, and the driving force was not high enough to cause sufficient Ga enrichment by dealloying (Fig. 5.5).

The foregoing discussion is reflected also in the corrosion potential data for alloys annealed at 600°C in acidified synthetic seawater (Fig. 5.3). This solution was selected for the corrosion potential (E_{\text{corr}}) measurements because the evolution of the mixed potential can be observed as the removal of the surface layers occurs in an accelerated fashion [4, 36]. As-polished alloy AlPb20 is not active, and E_{\text{corr}} stabilises at the critical pitting potential of pure Al [37], indicating that corrosion mechanism is controlled by pitting of the pure Al matrix alloy. Since Pb has no solubility in Al, all Pb content of the alloy is assumed to be segregated as particles with minimal activating effect. The E_{\text{corr}} of the same alloy, alloyed at 600°C, shows a complex behaviour, related to the sequence of film breakdown, exposure of the interfacial Pb-rich nanofilm and ensuing activation (undulating behaviour up to 600 min) and passivation as the film is destroyed by corrosion (increasing E_{\text{corr}} after 600 min), as discussed in detail elsewhere [5]. The AlGa1000 binary alloy shows a similar tendency at the outset, reflected by the increasing E_{\text{corr}}. However, E_{\text{corr}} starts to decrease slowly after reaching a maximum. We interpret this behaviour as activation initiated by Ga enrichment of the surface as a result of dealloying. Similar behaviour of alloy AlGa1000Pb50, but at a significantly more negative level than that for alloy AlGa1000, demonstrates the activation mechanism of Pb and Ga together as discussed in detail above.

We believe that the role of the two elements in the activation of Al is evident from the corrosion morphology observed on the as-polished (not heat-treated) alloy AlGa1000Pb50, showing severe near grain boundary attack during potentiostatic polarisation at -0.8 \text{ V}_{\text{SCE}} (Fig. 5.10). Although the cause of this type of corrosion was not investigated further in this study, the cause is believed to be segregation of Pb along the grain boundaries during solidification and remaining at the elongated grain boundaries during cold rolling. Because Pb has no solubility in Al [38], it readily segregates to the grain boundaries at temperatures above its melting point [39] and then becomes incorporated in the growing grains, but remains concentrated near the grain boundaries [8, 39]. The corrosion morphology in Fig. 5.10 indicates, similar to that described above, that active corrosion starts around the Pb segregations, causing Ga segregation by dealloying, resulting in accelerated active corrosion at and near grain boundaries. The fact that susceptibility to this type of corrosion is eliminated by heat treatment is attributed to recrystallization of the alloy, leading to further incorporation
(not homogenisation) of the Pb particles into the grains [39]. The properties of the as-polished surface of alloy AlGa1000Pb50 deserve further study.

Corrosion morphology obtained by polarisation of alloy AlGa1000Pb50 (annealed at 300°C) by potentiostatic polarisation at -0.8 V_SCE (Fig. 5.9a) indicated tendency for cellular (blunt edged) attack as discussed in Chapter 3 for binary AlGa alloys. Such morphology was attributed to formation of a GaAl liquid-phase alloy (amalgam) by dealloying of Ga and its stepwise spreading in the radial direction, autocatalytically activating the surface. On alloy AlGa1000Pb50, segregated insoluble Pb particles on the surface probably contributed to passivity breakdown and resulted in a more irregular propagation than on the AlGa binary alloy, both in depth and superficially, depending on the location of the segregations.

Alloy AlGa1000Pb50, annealed at 600°C, showed pitting corrosion, producing deep pits (Fig. 5.7) well below the pitting potential of the Al bulk (Fig. 5.2), while AlPb50 [7] and AlGa50Pb50 exhibited only superficial etching of the active layer (not shown) during potentiodynamic and potentiostatic polarisation. Passivation of alloy AlGa1000Pb50 between the two steps of multilayer corrosion [7] (see also Section 5.1) did not occur due to sustained activation caused by Ga enrichment. The two oxidation peaks were still present on the anodic polarisation curves of alloys AlPb50 and AlGa50Pb50 (Fig. 5.2).

Melting point depression of segregated Pb in form of nano-sized particles or interfacial film of nanometer thickness [28, 29, 40] was suggested to have a possible role on formation of amalgam and cause anodic activation [41]. Dissolution of the Pb film or particles in liquid Ga, which segregates by dealloying, may form a GaPb liquid alloy at nano-scale, with a much lower melting point than the bulk alloy [42], as discussed in Chapter 2. Such an effect may be speculated to play a role in increased activation of the ternary alloy AlGa1000Pb50 in relation to the binary AlPb and AlGa alloys.

5.5 Conclusions

- For Ga content lower than 1000 ppm, the added presence of Pb in aluminium caused electrochemical behaviour very similar to that of binary AlPb alloys reported earlier. For these cases anodic activation in chloride environment was significant only if the samples were annealed at 600°C.
- In the case of high Ga content (1000 ppm), the added presence of small amounts of Pb (50 ppm) significantly enhanced activation for all heat treatment conditions investigated. This occurred by passivity breakdown around Pb particles exposed at the surface causing Ga segregation by dealloying and spreading of corrosion to larger areas over the surface. Similar activation was caused initially by Pb according to the same mechanism, passivation occurred after corrosion detached the segregated Pb film from the surface, and the amount of segregated Ga was not sufficient to sustain activation.
- The higher activation occurring on the ternary AlGa1000Pb50 alloy in relation to the binary alloys AlGa1000 and AlPb50 under identical conditions was
attributed to the formation of liquid phase GaPb alloy at the surface, which is expected to cause rapid failure of the passivating Al oxide.

References

5. Effect of Trace Elements Gallium and Lead on Anodic Activation of Aluminium...

6 Anodic Activation and Embrittlement of AlGaPb Alloy by Alkaline Etching

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Abstract

The effect of alkaline etching and heat treatment was investigated on anodic activation and grain boundary embrittlement of model AlGaPb alloys (containing 50 ppm Pb together with 50 and 1000 ppm Ga), with reference to the behaviour of binary model alloys AlGa (containing 50 and 1000) studied in Chapter 5. Ternary AlPbGa alloys were activated significantly in relation to the binary AlPb and AlGa alloys as a result of Pb segregation to the surface during heat treatment at 600°C and subsequent Ga enrichment by dealloying during etching in alkaline solution. Grain boundary embrittlement of the susceptible alloy AlGa, containing 1000 ppm Ga, by diffusion of enriched Ga into the grain boundaries was also reduced by segregated Pb. In chloride solution, the effect of 50 ppm Pb in the alloy was to enhance activation of alloy containing 50 ppm Ga by reducing the breakdown potential and stabilise the passive state of alloy containing 1000 ppm Ga by increasing the breakdown potential of the etched surface. Once breakdown occurred, the anodic current output was enhanced by the presence of Pb in comparison to the binary AlGa alloys, as a result of the synergistic role of Pb in increasing the rate of Ga segregation by dealloying.

6.1 Introduction

It was concluded in Chapter 3, that trace amounts of Ga up to 1000 ppm was stable in solid solution with Al in model binary AlGa alloys and did not segregate by annealing at temperatures up to 600°C. Limited segregation by dealloying and resulting slight activation occurred for alloy AlGa1000 by anodic polarisation in chloride solution. AlGa alloys with smaller Ga content investigated did not show significant activation as a result of anodic polarisation in chloride solution. However, significant Ga segregation by dealloying and subsequent anodic activation in chloride solution occurred as a result of alkaline etching of AlGa model alloys, as well as liquid metal embrittlement resulting from diffusion of Ga enriched at the surface into the grain boundaries. It was also observed that reheat treatment at 600°C after alkaline etching dissolved segregated Ga into solid solution with Al, thereby restoring the passivity of the surface and rebind the grain boundaries to restore the material also back to its original strength. It was further shown in Chapter 5 that the added presence of 50 ppm Pb enhanced anodic activation of the model AlGa alloys. The purpose of this chapter is to investigate the effect of small addition of Pb to AlGa alloys and subsequent alkaline etching on their
activation behaviour in chloride solution and embrittlement by Ga penetration into the grain boundaries.

6.2 Experimental

Model binary AlGa containing 50 and 1000 ppm of gallium (AlGa50 and AlGa1000) and ternary alloys by adding 50 ppm Pb (AlGa50Pb50 and AlGa1000Pb50) were prepared as mentioned in the previous chapters. The procedures used for surface finishing (metallographic polishing) and annealing (1 h at 600°C, followed by quenching in water) of the samples and surface and electrochemical characterisation were also identical. Etching was performed for 2 min in 12 wt% NaOH solution maintained at 45°C. The etching temperature was chosen to be higher than the melting point of gallium in order to cause its enrichment in liquid form. The specimens were thereafter desmutted in concentrated HNO3 and rinsed in distilled water and alcohol.

6.3 Results

The effect of annealing on the surface microstructure and morphology of AlGa and AlGaPb alloys were discussed in detail in Chapters 3 and 5, respectively. Briefly, annealing of AlGa alloys at 600°C did not cause any remarkable effect on the surface morphology, structure and composition due to stability of Ga in the bulk. After annealing AlGaPb alloys for 1 h at 600°C, Pb segregated to the surface as nanosized particles and film, the latter at the metal-oxide interface, as reported for similarly-annealed AlPb alloys [1]. The grain size for the binary and ternary samples was similar at about 3 mm in average.

6.3.1 Etching morphology

Fig. 6.1 shows the surface morphologies of the alloys AlGa50, reproduced from Chapter 3 (Fig. 6.1a), and AlGa1000 (Fig. 6.1b and 1c) after annealing and etching as described above. Compared to the scalloped etching morphology of alloy AlGa50, which was identical to the etched surface of pure Al [2-4], alloy AlGa1000, etched under identical conditions, showed coarser cell morphology.

The etch morphology of alloy AlGa50Pb50 and AlGa1000Pb50 annealed at 600°C, shown at different magnifications in Fig. 6.2a-c, changed from one grain to another, indicating crystallographic etching depending on grain orientation. Coarse cell-like morphology was still evident (Fig. 6.2b), with a nanoscale striated attack on the protruding cell walls, as shown in more detail in Fig. 6.2c. The etch morphology on alloy AlGa1000Pb50 was similar in terms of cellular nature and grain orientation dependence, as shown in Fig. 6.3a-3c at different magnifications.
Figure 6.1. Etch morphology of AlGa alloys annealed at 600°C and etched for 2 min. in 12 wt% NaOH solution at 45°C. a) Scalloped morphology of AlGa50. b) Coarser morphology of alloy AlGa1000 (note lower magnification). c) Cell morphology on alloy AlGa1000 at the same magnification as (a).
Figure 6.2. Etch morphology of alloy AlGa50Pb50 annealed at 600°C and etched for 2 min. in 12 wt% NaOH solution at 45°C. a) General surface appearance including a triple point, b) Area marked in (a) at higher magnification. c) Area marked in (b) at higher magnification, showing striated morphology.
Figure 6.3. Etch morphology of alloy AlGa1000Pb50 annealed at 600°C and etched for 2 min. in 12 wt% NaOH solution at 45°C. a) General surface appearance with orientation-dependent morphology at neighbouring grains. b) Area marked in (a) at higher magnification. c) Area marked in (b) at a higher magnification.
6. Anodic Activation and Embrittlement of AlGa and AlGaPb Alloys by Enrichment…

6.3.2 Liquid metal embrittlement during etching

In contrast to alloy AlGa1000 (Chapter 3), alloy AlGa1000Pb50 did not exhibit embrittlement after etching under identical conditions. Etching of AlGa1000Pb50 for an extended period of 5 min caused formation of a white layer along the grain boundaries, as shown in Fig. 6.4a. After 12 min the grain boundaries separated and fracture occurred (Fig. 6.4b).

Figure 6.4. The etched surface of alloy AlGa1000Pb50 after a) 5 min and b) 12 min of etching. The light brown material is the specimen holder, and the tube is the Luggin probe (reference electrode). Hydrogen evolution from the sample can be observed.

SEM images of grain boundaries of alloy AlGa50Pb50 after alkaline etching for 30 min and of alloy AlGa1000Pb50 after 10 min are shown in Fig. 6.5a and 6.5b, respectively. Pits were formed in certain grains of alloy AlGa50Pb50 in addition to grain boundary attack. Alloys AlGa50 and AlGa50Pb50, which contain low amount of Ga, did not undergo grain boundary fracture after etching for 30 min.

6.3.3 Surface characterisation by GD-OES

Fig. 6.6 shows the depth profiles of alkaline etched AlPb and AlGaPb alloys, which will be interpreted with reference to the depth profile data for binary AlGa alloys reported in Chapter 3 (Fig. 3.5) and annealed AlGaPb (Fig. 5.1.) alloys reported in Chapter 5. Peak concentration of Pb was about 0.75 wt% for both AlPb50 (Fig. 6.6a) and AlGaPb (Fig. 6.6b) alloys. The oxide thickness, based on the position of the peak [5] was also similar for the two cases at about 8-12 nm. The concentration and position of the Ga peak was quite similar to that of the Pb peak, possibly slightly deeper into the metal (about 12-15 nm).

The position of the peaks was similar for the etched alloy AlGa1000Pb50 (Fig. 6.6c), with significant broadening of the Pb peak to varying degrees from grain to grain, attributed to varying roughness. Enrichment of Ga was much higher on alloy AlGa1000Pb50 than on alloy AlGa50Pb50, varying significantly also from grain to
grain. However, broadening due to roughness was not significant relative to alloy AlGa50Pb50.

Figure 6.5. Surface appearance after alkaline etching of alloys a) AlGa50Pb50 (30 min) and b) AlGa1000Pb50 (10 min).

The etching rate of alloys AlGaPb and AlPb50 were similar to that of pure Al and alloy AlGa50, while etching rate of alloy AlGa1000Pb50 was twice as fast, based on 2 min of etching. According to weight loss data for this period, approximately 0.5 μm of metal was removed from the surface of AlPb50. Therefore the Pb peak in the figures cannot be attributed to the Pb film that segregates at the metal - γ-Al2O3 film interface by annealing. The 50 nm thick γ-Al2O3 film was obviously removed during etching. The Pb peak still present at the metal-oxide interface must therefore correspond to the remnants of the Pb film and Pb segregating as a result of the etching process (dealloying).
Figure 6.6. GD-OES elemental depth profile of alloys a) AlPb50, b) AlGa50Pb50 and c) AlGa1000Pb50 after alkaline etching.
A second heat treatment at 600°C after etching of AlGa50Pb50 and AlGa1000Pb50 alloys resulted in the dissolution of segregated Ga back into the solid solution, as shown in Fig. 6.7a and 6.7b, respectively. Pb enrichment and the thickness of the oxide film increased to that expected for γ-Al2O3 film [1, 5]. However, the Pb peak was broadened for both samples, probably due to a significant increase in the surface roughness resulting from etching prior to the second heat treatment. Increase in Ga concentration toward the oxide surface indicates that some Ga enriched during etching was entrapped in the growing oxide during heat treatment.

Figure 6.7. GD-OES depth profiles of alloys a) AlGa50Pb50 and b) AlGa1000Pb50 after re-heat treatment at 600°C following alkaline etching.
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6.3.4 Corrosion potential during etching

Corrosion potential, \( E_c \), of AlGaPb alloys were compared to that of their binary counterparts in Fig. 6.8a and Fig. 6.8b. The data for the binary AlPb alloys were not reported earlier, and data for binary AlGa alloys were shown in detail in Chapter 3. The figures indicate that the steady-state \( E_c \) was attained after 2 min for most alloys. Longer time was required for \( E_c \) of alloy AlPb to reach a steady state (Fig. 6.8a). The steady-state values of \( E_c \) for the binary alloys AlGa50 and AlPb50 were not too different from that of pure Al at about -1.85 \( V_{\text{SCE}} \). \( E_c \) for alloy AlGa50 showed unstable behaviour with negative periodic surges (about every 1 min) from the steady-state value by 0.3 V in the negative direction. \( E_c \) for alloy AlGa100 was about 0.2 V more negative due to higher activation caused by Ga segregating by dealloying (Chapter 3). Intense gas evolution was observed visually during etching of the samples, especially on alloy AlGa1000 and during the negative potential surges on alloy AlGa50. The added presence of 50 ppm Pb decreased the steady-state \( E_c \) of alloy AlGa50 by about 0.25 V, while the addition of the same amount of Pb to alloy AlGa1000 increased it by about 0.1 V (Fig. 6.8b). The \( E_c \) of alloy AlPb50 was stably negative at about -2.15 \( V_{\text{SCE}} \) for 4 min before increasing to more positive values. \( E_c \) values after 2 min of etching and at steady state are shown in Table 6.1 together with the average etching rates after 2 min of immersion. The etching rate was much lower for AlGaPb alloys relative to the AlGa alloys. However, the etching rate of alloy AlGa1000Pb50 was still larger than that for pure Al.

Since Ga was homogenised during annealing, the negative corrosion potential of alloys AlPb50 and AlGaPb at the outset is related to activation by Pb segregated during heat treatment prior to etching. Ga enrichment occurred by dealloying during etching, which also contributed to the negative shift in the corrosion potential. The corrosion potential of alloy AlGa1000Pb50 with high Ga concentration was close to the potential of alloy AlGa1000 (Fig. 6.8a). The corrosion potential of alloy AlGa50Pb50, at -2.1 \( V_{\text{SCE}} \), was close to that of alloy AlPb50 for about 2 min (Fig. 6.8b). Corrosion potential of AlGa50Pb50 remained low at about this value at steady state, whereas that of AlPb50 increased significantly to -1.83 \( V_{\text{SCE}} \), close to the steady state value of pure Al.
Figure 6.8. Variation of the corrosion potential of alloys a) AlGa50 and AlGa1000 and 
b) AlPb50, AlGa50Pb50 and AlGa1000Pb50 in relation to pure Al during alkaline 
etching.
Table 6.1. Summary of results for etching rate, corrosion potential and liquid metal embrittlement (LME) conditions of the model alloys after etching in 12 wt% NaOH at 45°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Corrosion potential (±0.05 V) after 2 min etching (V\text{SCE})</th>
<th>Steady-state corrosion potential (±0.02 V) (V\text{SCE})</th>
<th>Etching rate (mg/cm²/min) after 2 min</th>
<th>LME Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>-1.92</td>
<td>-1.85</td>
<td>0.5 ± 0.1</td>
<td>No LME.</td>
</tr>
<tr>
<td>AlGa50</td>
<td>-1.98</td>
<td>-1.86</td>
<td>0.5 ± 0.1</td>
<td>No LME after 30 min etching.</td>
</tr>
<tr>
<td>AlGa1000</td>
<td>-2.04</td>
<td>-2.00</td>
<td>14 ± 1</td>
<td>LME after 2 min etching.</td>
</tr>
<tr>
<td>AlPb50</td>
<td>-2.15</td>
<td>-1.83</td>
<td>0.6 ± 0.1</td>
<td>No LME.</td>
</tr>
<tr>
<td>AlGa50Pb50</td>
<td>-2.1</td>
<td>-2.05</td>
<td>0.6 ± 0.1</td>
<td>No LME after 30 min etching.</td>
</tr>
<tr>
<td>AlGa1000Pb50</td>
<td>-2.01</td>
<td>-1.94</td>
<td>1 ± 0.1</td>
<td>LME after 10 min etching.</td>
</tr>
</tbody>
</table>

6.3.5 Polarisation behaviour

The polarisation curves of alloys AlGa50Pb50 and AlGa1000Pb50 for heat-treated (HT), heat treated and etched (HT+E) and reheat treated after heat treatment and etching (HT+E+HT) conditions are shown in Fig. 6.9a and Fig. 6.9b, respectively. These curves are compared with the identically treated AlGa50 and AlGa1000 alloys. Passivity breakdown potentials of alloys AlGa50Pb50 and AlGa1000Pb50 in HT+E condition were depressed significantly to -1.1 V\text{SCE} and -1.15 V\text{SCE}, respectively, relative to their potentials at HT condition (-0.95 V\text{SCE} for both alloys). The two oxidation peaks, which were typical for the as-heat treated (600°C) unetched surface (HT), did not appear.

For alloy AlGa50Pb50 (Fig. 6.9a), the current density was slightly less than the HT+E+HT condition in the potential range -0.95 V\text{SCE} to -0.85 V\text{SCE}. After pitting initiated at -0.85 V\text{SCE}, the magnitude of the current density was similar for HT+E and HT+E+HT conditions. An anodic current plateau of about 0.1 mA/cm² was observed in the range -1.05 – -0.93 V\text{SCE} in the HT+E condition.

A similar plateau of about 0.25 mA/cm² was observed for alloy AlGa1000Pb50 (HT+E) in the range -1.12 – -1.06 V\text{SCE} (Fig. 6.9b). The current density then increased significantly following the polarisation curve for alloy AlGa1000 (HT+E). Alloy AlGa1000 (HT+E) had a much lower passivity breakdown at -1.38 V\text{SCE} and a broader current plateau at the same level as that for alloy AlGa1000Pb50 (HT+E).
Second heat treatment at 600°C after annealing and etching (HT+E+HT) restored the polarisation curves of AlGaPb alloys back to the original heat-treated (HT) condition. The current density level of the HT+E+HT condition was a bit smaller than that for the HT condition. The significance of the shape of the polarisation curve for the HT condition of the AlGaPb alloys was discussed in Chapter 5.

Figure 6.9. Potentiodynamic polarisation results for alloys a) AlGa50Pb50 and AlGa50 and b) AlGa1000Pb50 and AlGa1000, in the heat treated (1 h at 600°C) (HT), heat treated and etched (HT+E) and heat treated, etched and re-heat treated (HT+E+HT) conditions.
6.4 Discussion

Variation of the corrosion potential as a function of time in alkaline solution (Fig. 6.8a) can be explained by the combined effect of conventional theory of anodic activation by Group IIIA-VA elements [1, 5-8] and kinetics of water reduction on metals. The corrosion potential of alloy AlGa50 followed that of pure Al at about -1.85 $V_{SCE}$, except for the brief negative surges, which probably corresponded to brief periods of Ga enrichment above a threshold, probably locally, giving increased activation. Increase in $H_2$ evolution indicates corresponding increase in the etching rate, according to the mixed potential theory. Enriched Ga was probably removed from the surface as a result of high local rate of corrosion, so that the corrosion potential returned to that of pure Al, which corresponded to a reduced active state. As a result, the etching rate of alloy AlGa50 was not too different from that of pure Al (Table 6.1). In contrast the corrosion potential of alloy AlGa1000 remained stable at a lower value of about -2.05 $V_{SCE}$, indicating that the alloy had a stable coverage of enriched Ga, which resulted in a much higher etching rate (Table 6.1). Effect of Ga concentration on the corrosion potential of AlGa binary model alloys during alkaline etching was discussed in Chapter 3.

In the presence of 50 ppm Pb, $E_c$ and corrosion rate of alloy AlGa50Pb50 were not significantly affected relative to binary alloy AlGa50. In the case of alloy AlGa1000Pb50, however, the presence of Pb caused an appreciable decrease in both quantities relative to alloy AlGa1000 (Fig. 6.8b, Table 6.1). The reduction in the etching rate is attributed partly to the reduction in grain boundary embrittlement by the presence of Pb. The role of Pb can be explained by examining the corrosion potential of alloy AlPb50 in alkaline solution (Fig. 6.8b). Alloy AlPb50 has the most negative potential at about -2.15 $V_{SCE}$ during the first 4 min of immersion. This is attributed to the high overpotential for water reduction on Pb enriched surface [9, 10], applicable especially to the original heat-treated (HT) alloy initially supporting the Pb-rich nanofilm. Increase in $E_c$ for this alloy after 4 min of immersion is attributed to the destruction of the Pb film during etching, as discussed in earlier papers [5, 7, 11]. Remnants of the film and new segregations during etching, detected by GD-OES (Fig. 6.6), are in particulate form, not giving the necessary wetting of the aluminium metal surface. In the case of alloy AlGa1000Pb50, sustained effect of Pb in inhibiting the water reduction reaction can be attributed to coexistence of segregated Pb and Ga (Chapter 5), possibly as a liquid phase alloy. Since a certain part of water reduction is expected to occur on this phase, the presence of Pb would also have an inhibiting role on alloy AlGa1000Pb50.

The oxidation peaks which were caused by “multilayer corrosion” of Al [6] observed in the polarisation curve of the as-annealed AlPb50 [1, 5, 7, 11] and AlGaPb alloys in Chapter 5 in chloride solution disappeared for their as-annealed and etched state HT+E (Fig. 6.9a and 6.9b). This showed again that the thermally formed Pb-film was removed or destroyed during etching. As a result, corrosion in the activated potential region consisted of etching of a single layer. During alkaline etching, fresh Pb became enriched at the surface, as detected by GD-OES (Fig. 6.6a-c). However, enrichment probably occurred in the form of particles rather than a film. Previously it was reported that AlPb alloys, activated by heat treatment at 600°C, repassivated as a result of subsequent deep alkaline etching [5]. This was shown to be caused by the destruction of the interfacial
6. Anodic Activation and Embrittlement of AlGa and AlGaPb Alloys by Enrichment...

Pb film. Even though Pb existed in particle form at the surface, the contact area provided by nearly spherical Pb particles and Al metal was too small to produce activation that could be measured electrochemically. However, alkaline etching did not passivate the AlGaPb alloys. Instead, activation increased by alkaline etching. This was caused by enrichment of Ga in addition to Pb during etching. Liquid phase Ga probably wetted the Al surface to a much larger degree than the Pb particles, such that significant activation occurred. However, after re-heat treatment of the etched samples (HT+E+HT condition), the electrochemical behaviour was reverted to the behaviour of the as-heat treated (HT) condition (Fig. 6.9) by re-formation of the interfacial Pb-film, while Ga dissolved back into solid solution.

Corrosion potentials of the binary AlGa alloys in chloride solution were much more negative than those of the corresponding AlGaPb alloys containing 50 ppm Pb in the HT+E condition (Fig. 6.9). The addition of 50 ppm Pb caused about 200 and 250 mV increase in the corrosion potential of alloys AlGa50Pb50 and AlGa1000Pb50, respectively. Inspection of the polarisation curves in Fig. 6.9 indicates that the rate of reduction at potentials more negative than E_c was higher in the presence of Pb than without for the same amount of Ga in the alloy. However, this explanation does not agree with the above argument that the hydrogen overpotential of Pb is one of the highest among pure metals [12]. The other alternative, which would give a similar shift in the corrosion potential, is the increased passivity of the surface by the presence of Pb, which gives an increased breakdown potential in chloride solution. Further shift in the breakdown potential in the positive direction for the HT+E+HT condition supports this mechanism since all Ga is in solid solution, and activation is a result of Pb segregation alone.

The anodic current density of alloy AlGa1000Pb50 increased to the same current-density level as alloy AlGa1000 after passivity breakdown in chloride solution (Fig. 6.9b). Thus, the current output in the activated condition was controlled by Ga enrichment by anodic segregation (dealloying). The corrosion potential of alloy AlGa50Pb50, although higher than that of alloy AlGa50, was equal to its breakdown potential, above which the current output became significantly higher than that for alloy AlGa50 in the HT+E condition. This indicates that the amount of Ga enriched on alloy AlGa50 by alkaline etching was not sufficient for passivity breakdown at the corrosion potential. Activation occurred gradually between the corrosion potential and pitting potential, as additional Ga became gradually enriched at the surface with increasing potential during potentiodynamic polarisation. Contrary to alloy AlGa1000Pb50, the presence of 50 ppm Pb significantly enhanced the current output of alloy AlGa50Pb50 above its breakdown potential to a much higher level than that of alloy AlGa50. This indicates that the presence of Pb contributes synergistically to enrichment of Ga by anodic segregation if the amount of Ga is too low to control activation alone. This probably occurs by enhanced corrosion around Pb segregations at the surface, which gives accelerated enrichment of Ga by dealloying.

The etching morphology of alloy AlGa1000Pb50 shown in Fig. 6.3 was similar to that of binary AlGa1000 alloy (Chapter 3, Fig. 3.3d). Roughening of cellular morphology was caused by Ga segregation on both samples. However, the etching morphology of
alloy AlGa50 and AlGa50Pb50 was quite different. Besides the cellular structure, the protruding cell walls with sharp edges (Fig. 6.3b) and dependence of etching on grain orientation (Fig. 6.2a for AlGa50Pb50 and Fig. 6.3a for AlGa1000Pb50) were not observed on AlGa alloys.

6.5 Conclusion

- Presence of small amount of Pb (50 ppm) in AlGa alloys reduces the etching rate in alkaline solution. As a result, the rate of enrichment of Ga by dealloying is also reduced, decreasing in turn the risk of liquid metal embrittlement.
- Reduction of alkaline etching rate by Pb is caused by decrease in the rate of water reduction reaction, related to the high overpotential of the reduction reaction on Pb segregations.
- Pb segregations, which are not stable on Al during etching of AlPb alloys are stabilised at the surface by coexistence of anodically segregated Ga, possibly in the form of a GaPb liquid phase alloy.
- Presence of Pb has a relative passivating effect on the anodic behaviour of etched AlGa alloys in chloride solution by increasing the breakdown potential. Once breakdown occurs, however, Pb segregations enhance Ga segregation by dealloying, causing increased anodic current output, especially on alloy with low (50 ppm) Ga content. Corrosion of alloy with high Ga content (1000 ppm) is mainly controlled by the anodic segregation (dealloying) of Ga.

References

7 Possible Effects of Trace Element Ga on Electrochemical Properties of Alkaline-Etched Commercial Aluminium Alloy AA6060

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Abstract

Effect of surface enrichment of Ga by dealloying as a result of alkaline etching and its effect on the electrochemical activation in chloride solution and grain boundary embrittlement of aluminium alloy AA6060 was studied. Commercial AA6060 alloy (nominally wt% 0.371 Mg, 0.448 Si, and 0.182 Fe) containing 130 ppm Ga was investigated together with a higher Ga containing (500 ppm) variant (Alloy 6060-Ga500). Model binary AlGa (500 ppm) and ternary AlGaMg (500 ppm Ga, 200 ppm Mg), prepared from the pure components were also studied. Etching for 2 min in 12 wt% NaOH solution at 45°C caused significant Ga enrichment at the surface of all model alloys and their subsequent embrittlement as a result of enriched Ga diffusing into the grain boundaries. Ga enrichment by etching caused also anodic activation of all model alloys in subsequent polarisation measurements in chloride solution, characterised by a significant reduction in their breakdown potential and large increase in their anodic current output. Enrichment of Ga by alkaline etching occurred to a smaller degree on alloy 6060-Ga500. Liquid metal embrittlement did not occur, and resulting activation in chloride solution was minimal. The behaviour of alloy 6060-Ga500 was attributed to the simultaneous enrichment of the noble alloying and impurity elements Si, Fe and Cu during alkaline etching, which counteracted the activation effect of Ga. As a result, the etching rate was smaller than on the model alloys, and the breakdown potential was maintained close to that of pure Al in chloride solution.

7.1 Introduction

Alloying aluminium with gallium has been proposed for activation of Al anodes for Al/air batteries [1-3]. Because of high solid solution solubility of Ga in Al [4], the amount of Ga required for this purpose has to exceed 1000 ppm in chloride solution [1-2]. The background for the present study is the concern for trace element Ga segregation as a result of deep alkaline etching of commercial Al alloys as a pretreatment step in chemical surface processing, such as anodizing and application of organic coatings [5-9], and causing liquid metal embrittlement (LME).
Available work on the effect of alloyed Ga on the etched surface is limited to model alloys. For example, alkaline etching of model binary AlGa alloys for 2 min at 45°C in 12 wt% NaOH caused significant anodic activation if the Ga content was at least 250 ppm Ga (Chapter 3). Ga, enriched at the surface by alkaline etching, diffused into the grain boundaries causing liquid-metal embrittlement. Alkaline etching of Al0.5% Mg-85 ppm Ga alloy decreased the corrosion potential in chloride solution, depending on the period of alkaline etching [10]. Annealing of Al-1000 ppm Ga-50 ppm Pb (AlGa1000Pb50) model alloy for 1 h at 600°C caused segregation of Pb to the surface. Subsequent alkaline etching for 2 min did not cause embrittlement. Corrosion potential and etching rate during alkaline etching were lower for the AlGa1000Pb50 alloy than that for AlGa1000 alloy because Pb segregated by heat treatment delayed Ga enrichment by dealloying during subsequent alkaline etching.

Other alloying and impurity elements, such as Cu, Fe, Mn, Mg, Si and Zn are known to become enriched in metallic or oxide form on Al [11-14] and AlMgSi alloys [6-8, 15-16] as a result of caustic etching. The effect of these elements on activation and embrittlement by trace element Ga is not known. However, Si and transition elements Cu, Fe, Mn and Zn, which are more noble than Al reduce activation caused by trace element Pb in chloride solution [17] without the need for pre-etching in alkaline solution, while Mg may contribute to activation [18].

In view of the foregoing, the purpose of this work is to study the effect of trace element Ga on the electrochemical and mechanical properties of the commercial alloy AA6060 as a result of alkaline etching. The behaviour of alloy AA6060 was compared to alloy AA6060 with increased amount of Ga and to model alloys containing Ga, investigated in the previous chapters. In addition, ternary model AlMgGa alloys were prepared and investigated for any specific effect of the alloying element Mg in the activation process.

7.2 Experimental

Materials. Commercial AA6060 alloy was received as a chill-cast, homogenised billet of diameter of 95 mm, containing 130 ppm Ga. Alloy AA6060 with increased Ga concentration (500 ppm) was prepared by melting the as-received material, adding extra Ga and re-casting in chilled copper moulds. The re-cast alloy was homogenised at 575°C for 2 h, followed by cooling at a rate of 300°C/h in the furnace, identical to the procedure used for the original 6060 alloy. It was then cold rolled from 20 mm thick slabs to a final thickness of 2 mm. A slice of thickness of 20 mm from the original AA-6060 alloy billet was also cold rolled similarly for comparison.

Model ternary AlGaMg alloys were prepared from pure components, cast, homogenised for 20 h at 600°C, scalped and cold-rolled from 20 mm to a final thickness of 2 mm. Composition of the test materials, measured by spark optical emission spectroscopy, along with their assigned notations are given in Table 7.1.
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Table 7.1. Notations and compositions of the test samples. The number after the element in the notation is the intended composition of the element in ppm.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Si (wt%)</th>
<th>Fe (wt%)</th>
<th>Cu (wt%)</th>
<th>Mn (wt%)</th>
<th>Mg (wt%)</th>
<th>Ga (ppm)</th>
<th>Pb (ppm)</th>
<th>Sn (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6060</td>
<td>0.45</td>
<td>0.18</td>
<td>0.001</td>
<td>0.05</td>
<td>0.37</td>
<td>130</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>6060Ga500</td>
<td>0.42</td>
<td>0.17</td>
<td>0.001</td>
<td>0.05</td>
<td>0.34</td>
<td>440</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>AlGa150Mg200</td>
<td>0.01</td>
<td>0.002</td>
<td>-</td>
<td>-</td>
<td>0.022</td>
<td>160</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AlGa500Mg200</td>
<td>0.01</td>
<td>0.002</td>
<td>-</td>
<td>-</td>
<td>0.038</td>
<td>775</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Samples were ground with SiC paper and polished metallographically through 1 μm diamond paste finish. Heat treatment was conducted for 1 h at 600°C in an air-circulating furnace, followed by quenching in water, in order to compare with the results for the model alloys reported in the previous chapters.

Etched samples were prepared from specimens which were heat-treated at 600°C. Etching was performed for 2 min in 12 wt% NaOH solution maintained at 45°C. The specimens were thereafter desmutted in concentrated HNO3 and rinsed in distilled water and alcohol.

**Electrochemistry and corrosion.** All specimens were degreased in acetone and ethanol before potentiodynamic polarisation in stirred 5 wt% NaCl solution at 25°C, which was exposed to ambient air. Specimens were mounted in screw cap holders [19] giving an area of 0.64 cm² exposed to the electrolyte. Anodic polarisation curves were measured with respect to calomel electrode (SCE) at a sweep rate of 0.1 mV/s in the positive direction, starting 50 mV below the corrosion potential. The cell geometry, solution volume and the stirring rate in the solution were identical in all runs. Selected samples were polarised potentiostatically at -0.85 V SCE. The corrosion morphologies resulting from 4 h polarisation were investigated by FEG-SEM and EDS. Corrosion potential was measured during alkaline etching for an extended period of 10 min. The sample holder used was similar to that described above giving an exposed sample area of 1.33 cm². Hg/HgO reference electrode (-129 mV with respect to saturated calomel electrode) was used in order to avoid chloride contamination.

**Surface characterisation.** Elemental depth profiles after heat treatment were measured qualitatively by using glow discharge optical emission spectrometry (GD-OES). The measurements were quantified for Al, O, Si, Fe, Cu, Mg and Pb by using the standards available. The depth profiles of Ga was quantified as described in the previous chapters, while those of Sn, which could not be quantified, were included as intensity in arbitrary units (a.u.) together with the quantified data. The depth profiles were obtained by Ar-beam sputtering at a rate of about 70 nm/s in the metal and 40 nm/s in the oxide [20]. Sample surfaces were characterised also after heat treatment and etching by using a field emission gun scanning electron microscope (FE-SEM).
Auger electron spectroscopy (AES) was used for high lateral resolution chemical analysis of the alkaline etched surfaces, using a JEOL 9500F Auger Microprobe instrument, equipped with a hemispherical electron spectrometer. The spectra were obtained at 10 keV accelerating voltage and a primary electron beam current of 20.4 nA at energy resolution of 0.35%. For depth profiling, an area of approximately 20x20 μm was sputtered at 15 s cycles at a rate of about 6.3 nm/min. The depth profile data were quantified by calculating the peak-to-peak intensities of the differentiated peaks and using JEOL database for the relative sensitivity factors (RSFs) of the elements. Reference spectra for Ga metal and Ga2O3 powder were measured in the laboratory by using high purity materials. For quantification of Al-oxide and metallic Al, the first and the last cycles of the depth profile were used as reference, respectively.

**Mechanical testing.** Changes in the mechanical properties of the samples resulting from Ga embrittlement and recovery from embrittlement were characterised by three point bending test using a 0.2 kN load cell. Load was applied at a constant rate of 0.05 mm/s for 18 mm. The sample size was 53 x 30 x 2 mm and the opening between two dies below the sample was 35 mm.

7.3 Results

7.3.1 SEM investigation

Figure 7.1a shows the as-polished surface morphology revealing the dominant α-Al(Mn,Fe)Si phase particles. After annealing at 600°C, the surface was covered with a thermally-formed oxide, consisting of a mixture of γ-Al2O3 and MgO, i.e. the spinel MgAl2O4 [21] (Fig. 7.1b). This oxide could not be entirely removed by etching at the specified conditions. The etched surface of commercial alloy 6060 showed (Fig. 7.1c) the scalloped morphology reported in earlier work [6]. The remnants of the oxide were also visible. The particles remaining on the surface after annealing (at 600°C) and etching (Fig. 7.1c and 7.1d) were similar to those on the as-polished surface (Fig. 7.2a). Alloy 6060Ga500 showed the same type of scalloped appearance and particles as on 6060 alloy, as shown in Fig. 7.2. In addition, large pits at the grain boundaries and triple points were observed. Remnants of the thermal oxide could not be observed after etching. Ga enrichment could not be detected by EDS.

The etch morphology of alloy AlGa150Mg200, shown in Fig. 7.3a, was crystallographic in nature, rather than the scalloped morphology mentioned above, with small pits becoming visible at higher magnification (Fig. 7.3b). Ga was detected around the pits by EDS analysis. Alloy AlGa500Mg200 was etched only for 1 min because longer etching caused unravelling of the sample due to severe embrittlement. Fig. 7.3c shows deep attack close to the grain boundaries and initiation of fracturing at the grain boundaries similar to that reported for AlGa alloys in Chapter 3. The grain surfaces were more severely etched and pitted than for alloy AlGa150Mg200, as shown at a higher magnification in Fig. 7.3d.
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Figure 7.1. Surface morphology of alloy 6060 (a) in the as-polished condition, b) after annealing at 600°C, c) annealed at 600°C and etched for 2 min in 12 wt% NaOH at 45°C, showing remainder of spinel oxide (white arrows) and intermetallics (black arrows). d) Back scattered electron image of (c).

Figure 7.2. Surface morphology of alloy 6060Ga500 after etching as in Fig. 7.3b, showing etched grain boundaries and scalloped appearance together with intermetallics (arrows).
Figure 7.3. a) Etched surface of 600°C-annealed alloy AlGa150Mg200 b) revealing pits and crystallographic etch patterns at higher magnification. Etched surface (etched for 1 min) of 600°C-annealed alloy AlGa500Mg200 c) showing pit formation with fracture at the triple point. d) Etch pattern on the same surface at higher magnification.
GD-OES depth profiles of elements Si, Fe, Mg and Cu for etched alloys 6060 and 6060Ga500 were identical. Therefore profiles only of these elements are shown on alloy 6060 for as-polished, annealed (at 600°C) and annealed and etched conditions, respectively, in Fig. 7.4a, 7.4b and 7.4c. Profiles for the trace elements Ga, Pb and Sn are shown separately for the two alloys in Fig. 7.5.

The profiles of Si and Fe on the as-polished surface, shown in Fig. 7.4a, were attributed to α-Al(Fe,Mn)Si intermetallics (Mn is not shown). Significant Mg enrichment, probably in the form of an oxide, was observed on the annealed surface, as shown in Fig. 7.4b. The oxide thickness was estimated from the intersection of the O and Al profiles as about 65 nm. Cu enrichment was detected at the outer surface of the oxide, probably resulting from Cu contamination prior to heat treatment. The Si profile after annealing was similar to the as-polished condition giving a broad mild peak following the Fe profile.

After etching of the annealed samples, a small peak of Mg was detected due to oxidized Mg that remained after etching the annealed sample, as shown in Fig. 7.4c. The Fe profile indicated enrichment close to the surface. Si was enriched even closer to the surface. These probably relate to the enrichment of the components of the α-Al(Mn,Fe)Si phase as a result of dealloying of Al. Cu, which is expected to be in solid solution with Al in the heat-treated sample, was enriched at the metal-oxide interface by dealloying of the matrix during etching.

The trace element Pb became enriched at the metal-oxide interface as a result of annealing alloy 6060 at 600°C, while Ga and Sn were homogenised in Al and did not indicate any surface enrichment, as shown in Fig. 7.5a. The depth profiles of these elements on alloy 6060Ga500 were very similar to those on alloy 6060 and are not shown. Fig. 7.5b and 7.5c show the profiles for the annealed-and-etched condition of alloys 6060 and 6060Ga500, respectively. These profiles indicate that the trace elements Ga and Sn became enriched at about metal-oxide interface, while the Pb peak became reduced in relation to the as-annealed surface, as a result of alkaline etching. Etched alloy 6060Ga500 showed a significantly higher Ga enrichment (Fig. 7.5c), as expected. Location of the Pb peak was closest to the surface in all cases, probably in the oxide adjacent to the interface, since it segregated during annealing at 600°C rather than as a result of dealloying during subsequent etching. The Ga peak was at about the metal-oxide interface, and the Sn peak was located more on the Al substrate side of the interface. Since Ga and Sn were in solid solution with Al as a result of annealing at 600°C, segregation of these elements was due to dealloying during etching.
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Figure 7.4. GD-OES depth profiles of elements Si, Fe, Mg and Cu on alloy 6060 in a) as-polished, b) annealed at 600°C and c) annealed and etched conditions.
Figure 7.5. GD-OES depth profiles of trace elements Ga, Pb and Sn for annealed (600°C) and annealed-and-etched alloys a) 6060 and 6060Ga500.
Heat treatment of model alloy AlGa500Mg200 at 600°C resulted in enrichment of Mg in the oxide, while Ga remained homogenised in the metal, as shown in Fig. 7.6a. Oxide thickness was about 70 nm, thicker than that expected for pure Al [22, 23], which was attributed to oxidation of Mg and formation of a spinel MgAl$_2$O$_4$ oxide [18]. Surface analysis after alkaline etching, shown in Fig. 7.6b, indicated that Ga became enriched at the metal-oxide interface at a very high concentration at a thickness of about 15 nm. High Ga intensity was measured similarly for the binary alloy AlGa1000 in Chapter 3 and attributed to Ga segregation in the form of a liquid-phase film. Most of the oxidised Mg was removed by etching. Oxide thickness remained at about 10 nm, probably because of the activating effect of segregated Ga. Ga and Mg in alloy AlGa50Mg200 showed similar behaviour as a result of annealing at 600°C and subsequent alkaline etching.

Figure 7.6. GD-OES depth profiles for alloy AlGa500Mg200 a) in the as heat-treated (600°C) condition and b) after alkaline etching.
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7.3.3 AES analysis

AES depth profile was obtained at about 1.5 nm depth intervals for 20 μm x 20 μm area of an 6060Ga500 sample, annealed at 600°C and etched, as shown in Fig. 7.7. Al-oxide was removed after sputtering for 30 s, corresponding to about 3.2 nm. Metallic Ga peak became visible clearly after sputtering for 15 s and existed for 75 s, corresponding to a thickness of 8 nm. The Ga peak was located at the metal-oxide interface at a depth of about 2.5 nm. Metallic Ga was detected also on the intermetallic particles by point analysis.

![AES depth profile](image)

Figure. 7.7. AES depth profile of alloy 6060Ga500 annealed at 600°C and etched for 2 min in 12 wt% NaOH at 45°C.

7.3.4 Bending test

Caustic etching of alloy 6060Ga500 did not cause any embrittlement along the grain boundaries. No significant difference was detected between alloys 6060 and 6060Ga500 in terms of strength and elongation as a result of caustic etching. Grain boundaries of these alloys did not show any crack initiation at the surface of the test section. Etched alloy AlGa500Mg200 did not exhibit embrittlement either. However, alloy AlGa500Mg200 showed complete loss of strength by embrittlement after 2 min of etching. Fig. 7.8 shows the condition of the specimens AlGa500Mg200 and 6060500 after the bending test.
Figure 7.8. Photographs of bent samples of alloys a) AlGa500Mg200 and b) 6060500Ga that were heat treated at 600°C and alkaline etched for 2 min prior to mechanical testing.

7.3.5 Corrosion potential during alkaline etching

The corrosion potential showed the transient behaviour depicted in Fig. 7.9 during the first few minutes of etching, before stabilising to the values reported in Table 7.2. Corrosion potential of alloy 6060 was not significantly affected by increased Ga content. Corrosion potential of annealed alloys 6060 and 6060Ga500 increased by about 100 mV from the outset to a steady-state potential of about \(-1.66 \text{ V}_{\text{SCE}}\) during the first 2 min of etching, whereas that of as-polished 6060 reached a steady-state already during the first seconds of etching. However, steady-state values were not influenced by the thermal history of the samples. Corrosion potential of the model alloys AlGa500 and AlGa500Mg200 and pure Al were initially around \(-2.0 \text{ V}_{\text{SCE}}\) and then decreased briefly to a minimum of \(-2.1 \text{ V}_{\text{SCE}}\) before stabilising at a steady-state value of \(-2.05 \text{ V}_{\text{SCE}}\), while the potential of pure Al increased to a steady-state value of \(-1.85 \text{ V}_{\text{SCE}}\). Annealing did not influence the corrosion potential of AlMg200Ga500 significantly. The small difference shown in the figure was within the error limits given in the Table 7.2. Liquid metal embrittlement started on alloys AlGa500 and AlGa500Mg200 after 2 min of etching. The etching rate was also much higher than on the 6060 alloys, for which the etching rate was much higher than that for pure Al. The highest etching rate occurred on alloy AlGa500Mg200 with intensive hydrogen evolution.
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Figure 7.9. Corrosion potential of alloys AlGa500Mg200, 6060 and 6060-Ga500 during alkaline etching (P: as-polished).

Table 7.2. Average etching rate based on weight loss after 2 min of alkaline etching and steady-state corrosion potential in alkaline solution of all test materials investigated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Etching rate (g/cm²/min)</th>
<th>Corrosion potential ±0.02 (V_SCE)</th>
<th>LME* condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>0.0005±0.0001</td>
<td>-1.86</td>
<td>No LME</td>
</tr>
<tr>
<td>AA6060</td>
<td>0.003±0.0005</td>
<td>-1.67</td>
<td>No LME</td>
</tr>
<tr>
<td>AA6060Ga500</td>
<td>0.003±0.0005</td>
<td>-1.66</td>
<td>No LME</td>
</tr>
<tr>
<td>AlGa500</td>
<td>0.014±0.001</td>
<td>-2.05</td>
<td>LME</td>
</tr>
<tr>
<td>AlGa500Mg200</td>
<td>0.02±0.001</td>
<td>-2.05</td>
<td>LME</td>
</tr>
</tbody>
</table>

*: LME: Liquid metal embrittlement after 2 min etching.

7.3.6 Electrochemical characterisation of etched samples in chloride solution

Potentiodynamic polarisation

Alloy 6060, annealed at 600°C and alkaline etched, showed significant activation in chloride solution, while annealing at 300°C and 450°C caused passive behaviour, as shown in Fig. 7.10. AlGaMg alloys showed polarisation behaviour similar to pure Al [22, 24] independent of annealing temperature and Ga content, as represented by alloy AlGa500Mg200, annealed at 600°C, in the figure. Activation at 600°C is attributed to Pb segregation (Fig. 7.5a), however, the polarisation behaviour of alloy 6060 was nobler than that for AlPb [19, 22, 25] and AlPbCu [25] model alloys under identical conditions.
Figure 7.10. Potentiodynamic polarisation curves in chloride solution for annealed alloys 6060 and AlGa500Mg200.

Potentiodynamic polarisation of alloy 6060 and the model AlGa and AlGaMg alloys in chloride solution, all previously annealed at 600°C and then etched, are compared in Fig. 7.11. Alloy 6060Ga500 exhibited more active behaviour than alloy 6060, with a lower passivity breakdown potential and higher current density output for the annealed (at 600°C) condition. For the annealed samples of alloy 6060Ga500, the passivity breakdown potential was at about -0.87 V\text{SCE}. An active peak and pseudo-passivation after the breakdown potential was followed by pitting at about -0.78 V\text{SCE}. Active condition observed on alloy 6060, resulting from Pb segregation by annealing at 600°C (Fig. 7.10), was removed by alkaline etching, and the pitting potential increased to about -0.7 V\text{SCE} (Fig. 7.11). Alloys 6060 and 6060Ga500 were significantly less active than the model alloys with comparable Ga content. Etching of AlGa500 and AlGa500Mg200 was limited to 1 min since 2 min of etching caused embrittlement at the grain boundaries. The added presence of Mg in the ternary model alloy AlGa500Mg200 gave increased activation in comparison to the binary AlGa500 alloy at the potential range of -1.4 V\text{SCE} – -1.35 V\text{SCE}. Above -1.35 V\text{SCE}, corrosion rate of AlGa500Mg200 decreased relative to that of AlGa500.

\textit{Potentiostatic polarisation}

Figure 7.12 shows potentiostatic polarisation data for alloys 6060, 6060Ga500 and AlGa150Mg200, all annealed at 600°C and alkaline etched and then polarised at -0.85 V\text{SCE}. Alloy 6060 was passive at this potential. The presence of 500 ppm Ga in the alloy caused temporary activation. Etching of AlGa500Mg200 was limited to 1 min since 2 min of etching caused embrittlement at the grain boundaries. The applied potential -0.85 V\text{SCE} was also too high for the active alloy AlGa500Mg200. Therefore, results for this alloy polarised at -1.3 V\text{SCE}, close to its passivity breakdown potential (Fig. 7.11), are shown in Fig. 7.12. Still, AlGa500Mg200 alloy had the highest current
density at the outset, and it passivated the latest in comparison to the other alloys in Fig. 7.12, polarised at -0.85 V\textsubscript{SCE}. Thus, the model alloys AlGa150Mg200 and AlGa500Mg200 were significantly more active than the 6060-based alloys. The activation of the etched model alloys was enhanced by segregated Ga.

Figure 7.11. Potentiodynamic polarisation in NaCl solution of AlGa500, AlGa150Mg200 and AlGa500Mg200 model alloys compared with 6060 and 6060Ga500 alloys after annealing at 600°C and alkaline etching.

Figure 7.12. Potentiostatic polarisation data for alloys 6060, 6060Ga500 and AlGa150Mg100 at -0.85 V\textsubscript{SCE} and for alloy AlGa500Mg200 at -1.3 V\textsubscript{SCE}. All samples were annealed at 600°C and alkaline etched for 2 min at 45°C.
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7.3.7 **SEM analysis after potentiostatic polarisation**

After potentiostatic polarisation at -0.85 \( V_{SCE} \) in chloride solution, alloy 6060Ga500 (annealed at 600°C) showed slight attack along the grain boundaries and orientation depended etching in the grains and along the scallop ridges (Fig. 7.13a). The scallop ridges which were susceptible to attack were possibly enriched in Ga during alkaline etching. The attack was shallow undermining the oxide, as shown in Fig. 7.13b. Alloy 6060 alloy, since it was passive at -0.85 \( V_{SCE} \), did not show any evidence of corrosion.

Potentiostatic polarisation of alkaline etched alloy AlGa500Mg200 (annealed at 600°C) for 3600 s at -1.3 \( V_{SCE} \) in chloride solution caused superficial pitting, as shown in Fig. 7.14a. Ga was detected inside the pits by EDS. Crystallographic propagation along selected planes was observed at the etching front, as shown in Fig. 7.14b.

![Figure 7.13. Corrosion morphology of alloy 6060Ga500 (annealed at 600°C and etched for 2 min in 12 wt% NaOH at 45°C) after potentiostatic polarisation for 3600 s at -0.85 \( V_{SCE} \) in chloride solution, showing corrosion a) on different grains and b) at the scallop ridges, undermining the oxide.](image-url)
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Figure 7.14. Corrosion morphology of model alloy AlGa500Mg200 (annealed at 600°C and etched for 1 min in 12 wt% NaOH at 45°C) after applying -1.3 V_{SCE} for 3600 s showing a) a shallow pit in round form and b) corrosion front propagating in crystallographic patterns.

7.4 Discussion

The activation behaviour of model AlGaMg alloys as a result of etching in alkaline solution was quite different from that of commercial alloy 6060 and the high Ga modification 6060Ga500. Enrichment of Ga on alloy 6060Ga500 by alkaline etching is appreciable (Fig. 7.5b and Fig. 7.5c), however not as copious as on alloy AlGa500 (Chapter 3) and AlGa500Mg200 (Fig. 7.6b) by identical treatment. The main conclusion of this chapter is, therefore, that the other alloying and impurity elements, especially the transition elements and Si, reduce Ga segregation during alkaline etching. Enrichment of these elements ennoble the surface, as was observed for AlPb alloys [17] in cancelling activation by segregated Ga. Significantly more noble corrosion potential
observed for alloys 6060 and 6060Ga500 in relation to the model alloys AlGa500 and AlGa500Mg200 (Fig. 7.9) indicates the existence of the ennobling effect. This is confirmed by much higher breakdown potentials observed for etched alloys 6060 and 6060Ga500 in relation to the model alloys in chloride solution (Fig. 7.11). Lower etching rates of 6060-base alloys in relation to AlGaMg alloys by an order of magnitude (Table 7.2) caused by this ennoblement result in smaller Ga enrichment (Fig. 7.5) in relation to the model alloys (Fig. 7.6) by dealloying.

The factors discussed above also removed the danger of grain boundary embrittlement of alloy 6060Ga500. Although Ga was enriched by alkaline etching, it did not diffuse into the grain boundaries, possibly due to α-Al(Fe,Mn)Si (Fig. 7.1a) intermetallic precipitates that decorate the grain boundaries. This may occur slowing down or prevention of surface diffusion of Ga by the surface segregations or by arresting penetration of Ga into the grain boundaries by the grain boundary segregations. Pitting caused by Ga at the triple points of grain boundaries may indicate that Ga collecting at such locations are prevented from further penetration into the grain boundaries.

Since the amount of Sn present in alloy 6060 is very small (7 ppm), its effect on activation by annealing or alkaline etching cannot be discerned. The only element, which activates alloy 6060, and that only after annealing at the high temperature 600°C is Pb (Fig. 7.5 and Fig. 7.10), as has been shown to be the case for many commercial Al alloys [5, 26-28]. However, the activating effect of Pb became reduced by segregation of ennobling elements.

### 7.5 Conclusions

Alkaline etching of commercial aluminium alloy 6060, containing about 130 ppm Ga, and its higher Ga-content (500 ppm) modification, caused enrichment of Ga by dealloying at the surface. However, mechanical properties, due to possible liquid metal embrittlement, and electrochemical properties characterised in chloride solution, subsequent to etching, were not significantly affected. In contrast, model binary AlGa and ternary AlGaMg alloys containing similar amounts of Ga showed significant anodic activation in chloride solution. Model alloys containing 500 ppm Ga were embrittled after 2 min of alkaline etching as a result of enriched Ga diffusing into the grain boundaries. Resistance of the commercial alloys to activation and embrittlement was attributed to the ennobling effect of the noble alloying and impurity elements Si, Fe and Cu, which reduced the etching rate in alkaline solution, thereby reducing the amount of Ga enrichment by dealloying. More importantly, the enrichment of the noble elements themselves during alkaline etching, maintained the passivity breakdown potential close to that of pure Al in chloride solution, thereby significantly reducing activation by Ga.

### References

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8 Discussion

The present work verified the frequently used thermodynamic data for the binary AlGa system [1] that Ga is stable in solid solution with Al in the Ga concentration (50-1000 ppm) and temperature (100-600°C) ranges of interest. The thermodynamic properties of Ga as a trace element in Al are in this respect very different from the other low melting point trace elements of interest, such as Pb [2], In [3], Sn [4] and Bi [5], which are known to segregate in this temperature range even if their concentration in Al may be lower than 50 ppm. Stability of Ga in Al under the given conditions is further not affected by the added presence of Pb and Sn, studied in this work, and probably neither by the presence of In and Bi, although not investigated in this work. That is to say, Ga is expected to remain in solid solution with Al although the other elements mentioned may segregate by heat treatment in the specified temperature range. Therefore, certain recently published theoretical studies (e.g., [6, 7]), which may suggest segregation of Ga from AlGa alloys under the specified conditions, in disagreement with the established thermodynamic data, should be viewed with care.

Gallium can, however, segregate as a result of selective corrosion (dealloying) of Al, depending on the concentration of Ga in Al, the presence of other alloying and trace elements and the rate of dealloying. For example, at a concentration of 500 ppm, Ga in binary AlGa alloys is critical in terms of anodic activation in chloride environment. A concentration of 250 ppm becomes critical in alkaline environment. Ga segregated in this manner can then readily diffuse into the grain boundaries of the aluminium substrate, causing embrittlement.

In the added presence of Sn the Al surface becomes quite active as a result of Sn segregation during heat treatment in the temperature range 300-450°C and subsequent segregation of both Sn and Ga by dealloying in aqueous environment. In the presence of Sn, the presence of Ga at concentrations as low as 50 ppm in aluminium becomes detrimental. Pb, the other element studied together with Ga in trace amounts alloyed with Al, was not as effective as Sn in activating the surface, probably because of its higher melting point and ennobling effect than Sn. The added presence of more noble transitions elements, such as Cu, Mn and Fe, and Si reduce activation by Ga by simply ennobling the surface and thereby increasing the breakdown potential and the anodic dissolution rate above this potential. Moreover, the presence of additional elements appears to hinder diffusion of Ga into the grain boundaries and thereby reduce the risk of embrittlement. As a result, the activating and embrittlement effects of Ga, alone or together with the other low melting point activating elements in Group IIIA-VA in model ternary alloys, is not commonly observed in most commercial alloys containing up to 500 ppm of Ga as a trace element.

The mechanisms related to the main findings of the thesis will be discussed in more detail below.
8. Discussion

8.1 Anodic activation by gallium

By definition, anodic activation causes both depression of passivity breakdown potential and increased anodic current output at which aluminium is expected to be passive. Annealed AlGa alloys are not activated by Ga up to 1000 ppm Ga content. However, prolonged polarisation of alloy AlGa1000 at -0.8 V_{SCE}, which is close to the pitting potential of pure Al, for about 2 h caused activation. Activation of alloys with smaller Ga content required longer times of polarisation, e.g., about 22 h for alloy AlGa500. Activation is attributed dealloying of Al and enrichment of Ga at the surface at a rate commensurate to the Ga content of the alloy in solid solution. Corrosion of Al at a slow rate and deposition of Ga in the mean time until a critical level of enrichment which enhances corrosion rate is attained at the surface. Once initiated, the corrosion rate increased in direct proportion to the polarisation time with sudden step increases, as discussed in Chapter 3. The current steps occurred each time a new pit initiated, observable from in-situ video recordings of the corroding surface, probably when a critical net Ga surface concentration was attained locally [8, 9].

The eutectic point in the Al-Ga binary phase diagram, corresponding to about 3 at.% Al [1], is 26.6°C, which is slightly below the melting point of pure Ga. Activation occurred by formation of GaAl liquid phase (amalgamation) similar to the well-known mechanism of HgAl amalgamation [10, 11]. Rapid corrosion of Al was observed when a liquid drop of Ga was similarly placed on Al, and the surface of Al was scratched through the Ga droplet, causing direct metallic contact between Al and Ga. Corrosion occurred by chemical dissolution of Al in the Ga droplet and its oxidation once it reached droplet surface exposed to ambient air. Corrosion rate increased in the presence of moisture. Wetting the Ga droplet by water caused intensive H₂ gas evolution. Aluminium oxide and hydroxide formed as corrosion products accumulated around the corroding area [12, 13].

Ga that readily enriched during alkaline etching caused significant activation. Enrichment of Ga was uneven with highly concentrated areas locally. The Ga enriched layer is believed to be liquid at room temperature, not allowing formation of a passivating oxide at the location. AlGa alloys had the activating GaAl amalgamated areas already present on their surfaces when placed in chloride solution immediately after etching. However, alloys containing 500 and 1000 ppm maintained their active states in chloride solution, whereas AlGa alloys containing 250 ppm and less were passivated. Continuous anodic activation was thus dependent on both Ga enrichment by alkaline etching prior to polarisation and replenishment of the surface with fresh Ga, which segregated by dealloying of the aluminium component during potentiostatic polarisation.

Activation of AlGa alloys did not depend on the annealing temperature, in contrast to the activation of the ternary AlGaSn and AlGaPb alloys, discussed below.
8.2 Activation by gallium and tin

Sn segregation and its effect on anodic activation was studied comprehensively [14]. In this thesis, Sn concentration was held constant at 100 ppm. Oxide mounds 1-10 μm in diameter were formed at the surface of AlGaSn alloys after annealing at 300°C and subsequent water quenching similar to AlSn alloys containing 100 ppm Sn [14]. Ga was not detected at the surface after annealing. It is expected to be stable in solid solution under the stated conditions as discussed above and to have no significant influence on the segregation of Sn. Thus, Sn, segregating locally during heat treatment, activated the surface and caused the formation of the oxide mounds by metal oxidation during water quenching at the locations where Sn was enriched. It was argued that this is a process catalysed by formation of super-heated steam on the surface [14]. The amount of oxidation on the AlGaSn alloy was higher than that on the binary alloy AlSn100. This was also true for activation as a result of subsequent polarisation in chloride solution. Activation of alloy AlGa1000Sn100 occurred also in chloride free solutions. AlGaSn alloys with low and high Ga concentration were, thus, far more active than the binary alloys of each component after annealing at 300°C, at which the highest Sn segregation was obtained.

This indicates a synergy between Ga and Sn in anodic activation of Al by amalgamation. It is believed that Ga was segregated anodically during quenching on the surface activated by Sn segregation during subsequent annealing, forming a GaSnAl liquid phase alloy already at that stage. GD-OES analysis after cleaning the oxide mounds by treatment in hot chromium-phosphoric acid bath showed slight Ga enrichment (Fig. 4.3). This may be smaller than the actual enrichment during water quenching since some of the Ga may have diffused back into the metal before surface analysis. However, this development must have contributed to a higher rate of oxidation on the AlGaSn alloy in relation to the corresponding binary AlGa. Activation effect of such a ternary amalgam becomes so high with increasing Ga content of the alloy, and therefore of the amalgam, that alloy AlGa1000Sn100 is active even when it is polarised in chloride-free solutions, in contrast to alloys AlSn100 and AlGa50Sn100.

In view of the foregoing, the mechanism described in Chapter 4 can be discussed further with reference to the schematic representation shown in Fig. 8.1a. The oxide mounds were essentially where corrosion attack initiated during heat treatment and subsequent water quenching, as described above. When immersed in aqueous solution, activation is observed at a much more negative potential than the binary alloys because of the presence of the GaSnAl amalgam. The liquid alloy then spreads in the radial direction undermining the oxide in the manner sketched in Fig. 8.1b. The radial propagation was stepwise rather than continuous, the latter as in the case of alloys activated by formation of a continuous Pb-rich film at the oxide-metal interface by annealing at 600°C [15]. The stepwise propagation was suggested by the formation of concentric grooves and ridges along the radial path. It appears that a certain amount of corrosion in a groove, probably undermined by the surrounding oxide, was required to produce sufficient dealloying and segregation of Sn and Ga, as well as acidification of the adjacent solution, to cause passivity breakdown of the film at the periphery of the circular attacks to initiate the next propagation step.
8. Discussion

Figure 8.1. Schematic summary of the mechanism of passivity breakdown at Sn rich locations formed during heat treatment of alloy AlGa1000Sn100 at 300°C. The process is enhanced by Ga enrichment by resulting dealloying during water quenching at the activated sites and formation of a GaSnAl liquid phase segregation at the location, and further propagation by undermining of the oxide in the radial direction.

The above mechanism depends on the Ga concentration in the alloy. A similar activation leading to the type of corrosion morphology described did not occur for alloys containing 50 ppm of Ga. It must also be dependent on the Sn concentration with reference to the work on the binary AlSn alloys [14]. Sufficient Ga and Sn have to be present together to sustain the synergistic mechanism described in maintaining sufficient activity and acidity needed to obtain the radial etching of the surface. Below the necessary concentrations, the activation imparted to the surface in chloride solution is only temporary, as was observed presently for alloys AlSn100 and AlGa50Sn100,
while activation of AlGa1000Sn100 increased autocatalytically as the corrosion propagated.

Annealing at 600°C homogenised Sn and Ga in the alloy and the segregation and oxidation phenomena described above for alloys annealed at 300°C did not occur. However, similar activation, as judged by the current transient at an applied potential of -0.8 V SCE (Fig. 4.10b) occurred on alloy AlGa1000Sn100 by dealloying as a result of an extended period of polarisation in chloride solution, while alloy with lower Ga content (50 ppm) remained passive under similar conditions.

8.3 Activation by gallium and lead

Ternary AlGaPb alloys were activated by segregation of Pb by annealing at 600°C, similar to the binary AlPb alloys, leading to a multilayer etching process [16]. Electrochemical behaviour and corrosion morphology of AlGaPb alloys were very similar to those of AlPb alloys annealed at 600°C. Alloy AlGa1000Pb50 was different with significantly increased current density despite minor change in the passivity breakdown potential. Effect of increased current density was observed to be a result of pitting in addition to etching at potentials well below the potential at which pitting initiated on AlPb alloys. Corrosion propagated in the form of superficial etching along the oxide-metal interface for the AlPb alloys during polarisation from -0.93 V SCE to -0.88 V SCE, which corresponded to the first layer of etching along the Pb film at the oxide-metal interface. However, pits initiated on alloy AlGa1000Pb50 shortly past the passivity breakdown potential of the alloy at -0.915 V SCE. This is attributed to enrichment of Ga during corrosion of the first layer along the interfacial Pb film as in the binary AlPb alloy. Ga enrichment was probably localised, causing pitting, although this could not be documented. Gas evolution was also higher on alloy AlGa1000Pb50 than on alloys AlPb50 and AlGa50Pb50, as observed by in-situ video. Larger gas bubbles formed on the pits than on the etching parts of the surface. These phenomena are sketched schematically in Fig. 8.2.

Pb is insoluble in Al [17] remaining as crystalline inclusions precipitated along crystallographic planes [18]. Trace element Pb alone is well known to cause significant changes in electrochemical behaviour of Al after annealing at 450°C and above [19]. The reason for the highest activation after annealing at 600°C is Pb segregation in form of continuous film [15, 16], while Pb in particle form was of no significance. The present study showed, however, that alloy AlGa1000Pb50 exhibited significant activation in as-polished and as-annealed at 300°C conditions. Preferential corrosion attack along the grain boundaries of elongated grains of as-polished AlGa1000Pb50 must be due to Pb particles segregated near and at the grain boundaries. Corrosion of Al caused Ga enrichment in the form of GaAl amalgam, which caused increased activation and corrosion in these areas. AlGaPb alloys, even in as-polished state, were more active than AlGa alloys because the presence of Pb particles made the surface less stable and easier to initiate corrosion than the homogeneous surface of AlGa alloys.
Pb segregation in the form of a continuous film causes higher anodic activation than segregations in particle form because the film gives a much higher coverage of the Al surface [15]. Ga enrichment of the surface may increase the contact angle of the Pb particles and their coverage of the Al metal surface. The monotectic point of Ga-15 at% Pb particles of size few hundreds of nanometres was reported to be in the range 226-261°C [20]. Further melting point depression [21] of smaller nano-sized PbGaAl particles or liquid-phase film at the Al metal-oxide interface may contribute to activation of the surface, as claimed to occur for alloys AlPb50 and AlGaPb (Chapter 5).

### 8.4 Grain boundary embrittlement

The available literature on grain boundary embrittlement of Al by Ga is based on situations where bulk Ga in liquid state is brought in direct contact with bulk Al metal [22-24]. In the present work, the possibility of grain boundary embrittlement by segregation of Ga alloyed with Al at amounts not exceeding 1000 ppm is investigated. The amount of trace element Ga present in commercial alloys seldom exceeds a few hundred ppm. The present results for the binary model AlGa alloys (Chapter 3) indicated that 1000 ppm Ga is stable in solid solution with the Al matrix in the temperature range 300 to 600°C used in the study.

Segregation of Ga to the alloy surface occurs as a result of dealloying during corrosion in aqueous solution. Segregated Ga can cause grain boundary embrittlement by diffusing into the grain boundaries, *i.e.* segregation does not occur directly to the grain...
boundaries. Diffusion of Ga into the grain boundaries is believed to occur once a critical amount of Ga accumulates on the surface by de-alloying. The nature (morphology, state, composition) could not be determined by the present results. It was determined by the Ga composition of the alloy and the rate of de-alloying, in turn determined by the corrosion process, such as alkaline etching and corrosion in chloride solution. Alloys with smallest Ga content (50-100 ppm) investigated did not undergo embrittlement due to insufficient Ga enrichment during etching for 2 min in 12 wt% solution at 45°C, whereas 250 ppm Ga in the bulk was sufficient for embrittlement after identical treatment.

The resulting embrittlement may cause opening up of the grain boundary at the surface in the presence of tensile stress, allowing the corrosive environment enter between the grains causing corrosion and further Ga enrichment by de-alloying, as shown schematically in Fig. 8.3. Embrittled grain boundaries were probably covered by several atomic layers of Ga [25]. A small force was sufficient to separate the grains coated with Ga [26]. When the embrittled sample was re-annealed, the grains were bound again as strong as before etching, as long they were not separated by force in the embrittled condition. Re-annealing for 1 h at 600°C was necessary in order to diffuse Ga from the grain boundaries back into solid solution with Al for rebinding of the grains to occur. Since this is a diffusion controlled process, the annealing time and temperature are important parameters in this process.

![Figure 8.3. Schematic representation of grain-boundary embrittlement caused by diffusion of Ga, segregated during alkaline etching, into the grain boundaries.](image)

In the added presence of trace element Pb in AlGaPb ternary model alloys, the Pb rich interfacial film formed by annealing at 600°C reduced the etching rate of Al in alkaline solution and consequently reduced the segregation of Ga by de-alloying compared to the binary AlGa alloys. Grain boundary embrittlement did not occur until the Pb layer was removed by alkaline etching. Effect of Sn on grain boundary embrittlement was not
studied. However, a similar inhibition of the etching rate and Ga enrichment is expected.

### 8.5 Effect of gallium in commercial alloys

Ga did not have any influence on the electrochemical behaviour of AA6060 alloys containing 120 and 500 ppm Ga after annealing in temperature range 300-600°C. Annealing at 300°C did not cause activation by segregated Sn, probably due to very low amount of Sn in the bulk. Activation occurred after annealing at 600°C by Pb segregation. However, the anodic behaviour in chloride solution was more noble than model AlPb alloys [16]. This is in accordance with the earlier work on AlPbCu alloys where addition of Cu increased nobility of the surface and reduced the activating effect of Pb [2, 16, 19, 27-29].

Corrosion potentials of alloys 6060, containing 130 ppm Ga and 500 ppm Ga (alloy 6060Ga500), which were similar during alkaline etching, were significantly more positive than that of AlGa model alloys. Significant Ga enrichment documented at the surface of alloy 6060Ga500 by etching caused slight activation during polarisation in chloride solution. However, the surface passivated after the Ga enriched layer was removed during polarisation. This indicates that Ga can only activate if it can be segregated continuously by dealloying. In commercial alloys containing ennobling alloying elements, Ga enrichment by dealloying will not give the critical Ga segregation required for sustained activation. This critical amount could not be determined in this study. The presence of other elements further prevented diffusion of segregated Ga into the grain boundaries and thereby grain boundary embrittlement. This probably occurred by grain boundary precipitates, containing noble elements, acting as diffusion barriers. The intermetallic particles at the surface and enrichment of the noble elements at the surface by alkaline etching may also reduce surface diffusion of Ga to the grain boundaries.

### 8.6 Recommendations for further work

Further work is needed for clarifying

1. the mechanism of segregation of solid solution Ga together with other activating elements, especially Sn, in multicomponent multiphase Al alloys, including commercial alloys, by dealloying during exposure to an aqueous environment, including super-heated steam (during water quenching) and electrolytic solutions and the resulting surface compounds formed and their microstructure,
2. the critical concentration of segregated Ga at the surface which causes activation and grain boundary embrittlement, the effect of other activating elements and more noble elements, and the underlying mechanisms,
3. the effect of the indigenous oxide and its modification during indicated thermal and chemical processing of the surface,
4. recovery of grain boundary embrittlement by annealing, and
5. the details of the mechanism of activation of aluminium and its alloys by surface segregations forming a liquid phase metallic film at the oxide-metal interface.
As far as item 5 is concerned, a working theory of activation exists, based on studies with Hg or Ga droplets placed on pure Al. The details as to how and why the repair of the damaged oxide is prevented by a small particle or thin film is not known. It is further not clarified as to how Al metal dissolves into the amalgam, the solubilities and diffusion coefficients required for Al transport in the amalgam, effect of convection, surface diffusion and tension, type and role of galvanic coupling, amongst many other factors.

The study of the above phenomena requires the type of experimental methods used in the present work. Aberration corrected TEM is expected to contribute in characterising the microstructure and composition of the segregated activating elements at nanoscale. *In-situ* characterisation would be of great help. However, it is difficult to propose *in situ* methods which would give useful analytical results at nanoscale dimensions.

In view of the number of alloying/trace elements and environmental factors and numerous coupling possibilities of these, pure experimental approach is expected to give limited results. The use of first-principles simulations would probably be required at this stage to generalise the experimental results.

An important contribution of this work was to clarify that trace amount of Ga present in the commercial alloy 6060 (a few hundred ppm) is harmless insofar as surface activation and grain-boundary embrittlement. An important recommendation for further applied work would be a test program to determine the limits of safe Ga levels in different commercial alloys.

References

9 Conclusions

- Trace level of gallium (≤ 1000 ppm) is stable in aluminium solid solution confirming thermodynamic data available for the AlGa system. It does not segregate at the surface or cause embrittlement of aluminium as a result of heat treatment at temperatures up to 600°C. Annealing gives homogenisation of Ga in Al solid solution.

- Trace amounts of Ga dissolved homogeneously in Al matrix cause a negligible change in the anodic behaviour of aluminium in chloride solution. Anodic activation by Ga becomes significant when Ga concentration is 500 ppm. 250 ppm is sufficient for causing activation if the binary alloy is etched in alkaline solution (for 2 min in 12wt% NaOH at 45°C) before polarising in chloride solution. This results from segregation of Ga by selective corrosion of aluminium (dealloying), in chloride or alkaline solution.

- Ga segregated at the surface as a result of alkaline etching may diffuse into the grain boundaries and cause liquid metal embrittlement. If the embrittled grains are not separated by strain, original mechanical properties are recovered by heat treatment. This enables Ga to diffuse into the grain bodies from the grain boundaries enabling rebinding of the grain boundaries.

- The added presence of Sn causes a significant increase in the activation of AlGa alloys in chloride solution, especially after annealing at 300°C and water quenching. Thermally segregated Sn during annealing plays an important role in passivity breakdown and sustained activity. Ga segregation by dealloying significantly contributes autocatalytically to higher surface activity and increased rates of dealloying. Ternary AlGaSn alloys were more active than the binary AlSn and AlGa alloys containing the same amount of Ga or Sn.

- Segregation of Sn and Ga leads to the formation of a liquid phase GaSnAl alloy at the surface, which prevents the formation of a passivating oxide at locations where the alloy is in physical contact with the Al substrate. Dissolution of Al in the liquid phase alloy and its oxidation when it comes in contact with the aqueous solution is the cause of high corrosion rates observed. The presence of chloride is not necessary for activation of the surface under these conditions.

- Annealing the ternary model AlGaSn alloys at 600°C causes homogenisation of both Ga and Sn in solid solution with Al and consequently a significant reduction in surface activation in chloride solution.

- Corrosion of AlGaSn alloys initiates already during heat treatment at 300°C and subsequent quenching in water at localised sites where Sn and Ga segregate, forming discrete oxide mounds. During subsequent polarisation in aqueous solution, corrosion propagates radially from these mounds by undermining the oxide film. Radial attack is driven by continuing Sn and Ga segregation by
dealloying at the periphery of the circular attack. Formation of circular ditches and ridges in the propagation path indicates some sort of intermittent propagation mechanism.

- Ternary model AlGaPb alloy are more active than the binary AlGa and AlPb alloys depending on the Ga content and annealing temperature. The behaviour of low Ga content of 50 ppm is similar to that of the binary the AlPb alloy, showing activation by annealing only at 600°C as a result of formation of the Pb nanofilm at the oxide-metal interface. High Ga content (1000 ppm) causes a significant increase in the corrosion rate of aluminium despite a minor depression on the passivity breakdown potential compared to AlPb systems for all heat treatment conditions investigated. This is caused by enhanced Ga segregation by dealloying in chloride solution in the presence of Pb segregations formed during earlier annealing step.

- Segregated Pb at the surface of annealed AlGaPb alloys reduces the etching rate in alkaline solution and the rate of Ga enrichment by dealloying, decreasing in turn the risk of liquid metal embrittlement. This was attributed to high overpotential of the reduction reaction on Pb in alkaline solution.

- Alkaline etching of commercial aluminium alloy 6060, containing about 100 ppm Ga, and its higher Ga-content (500 ppm) modification, causes enrichment of Ga by dealloying at the surface. However, Ga enrichment does not cause anodic activation or liquid metal embrittlement in contrast to model binary AlGa and ternary AlGaMg alloys containing similar amounts of Ga. Resistance of the commercial alloys to activation and embrittlement is attributed to the ennobling effect of the alloying and impurity elements Si, Fe and Cu. Effect of Ga enrichment is reduced by their presence in solid solution in the bulk alloy and enrichment at the surface during alkaline etching.