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Effect of small concentrations of gallium and lead on anodic activation of aluminium in chloride solution

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ABSTRACT

The presents objective is to investigate the combined effect of alloyed Pb and Ga on surface segregation by heat treatment and ensuing anodic activation of aluminium in chloride solution. Model alloys containing Pb and Ga, which were heat treated in the range 300–600 °C, were characterized electrochemically in 5% NaCl solution. Annealing at 600 °C resulted in significant segregation of Pb causing limited activation, while Ga remained in solid solution. The presence 50 ppm Ga had only a small contribution to activation, while 1000 ppm Ga contributed significantly by becoming enriched at areas around Pb segregations and spreading radially by dealloying.

1. Introduction

Lead and gallium are ubiquitous trace elements in commercial aluminium alloys, originating from the raw material bauxite [1–3]. While Pb is normally present at the ppm level by weight as a trace element in most commercial alloys, the Ga concentration is in the range 50–200 ppm. However, these elements may become enriched at the surface by orders of magnitude as a result of heat treatment and dealloying, respectively. The surface segregation of Pb by heat treatment of binary [4–7] and ternary [8–10] model alloys has been under investigation by this group, along with its role on anodic activation of the alloy in chloride media [11,12]. Anodic activation was defined as significant depression of the anodic breakdown (pitting) potential and significant increase in the anodic current density output in the potential range where aluminium is normally expected to be passive [12]. Solubility of Pb in solid Al is nearly zero [5], and its presence even at ppm level is sufficient to cause enrichment of the element at the surface by heat treatment at 600 °C, giving anodic activation. Solubility of Ga in solid aluminium is significant. Trace element Ga is therefore stable in solid aluminium even at high temperatures. However, Ga can become enriched at the surface because of selective corrosion of Al (dealloying), such as during alkaline etching or anodic polarization in chloride solution. Ga enriched in this manner may activate aluminium anodically in chloride solution especially 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 the melting point of Pb [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 nanofilm of Pb, which was trapped at the aluminium metal – γAl_2O_3 interface by diffusion of Pb to the surface and growth of γAl_2O_3 into the metal [6]. Most of the Pb in the alloy segregated in the form of nanosized, nearly spherical particles. These particles were either detached from the metal or did not contribute significantly to the metallic contact area between segregated Pb and the underlying Al matrix, a necessary condition for anodic activation. Pb segregated also at lower temperatures, but mostly in the form of nanoparticles.

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 polarization curve of the AlPb alloy heat-treated at 600 °C [4–7,10]. Each peak was related to superficial etching of the surface, causing multi-layered attack during potentiodynamic polarization [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. Presence of these oxidation peaks in the anodic potentiodynamic polarization of Al alloys were shown to be a clear indication of the segregated Pb nanofilm at the Al metal-oxide interface. Activation by Pb was a temporary effect [6]. The surface passivated after the Pb nanolayer was destroyed by corrosion.

Investigation of the model AlPb alloys did not explain the

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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 attention was directed toward the possible additional presence of the lower melting point elements In [17], Sn [18,19], Bi [20] and Ga [21]. The elements Ga, Sn and In are known to be more effective than Pb as activators [4,22–24]. This was attributed to their lower melting points than Pb and higher solubility of Al in these elements [18,25].

The theory, which is often referred to in explaining activation of aluminium by the low melting point elements in Group IIIA-VA, is the formation of a liquid phase alloy (amalgam) of the segregated element and aluminium, as is the case for Hg [26,27] and Ga [28,29]. 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 [30–32], known to occur with decreasing size of solid material to nanometre 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 film [6] and Sn particles [18], constituting a liquid phase amalgam with aluminium.

The presence of a second element that can contribute to melting point depression is also of concern. Combined presence of the trace elements Pb and Sn in the commercial alloy 8006 caused activation at 450 °C (instead of 600 °C for Pb alone) by segregation of a nanofilm, rich in both Pb and Sn, at the metal-oxide interface [33]. 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 [34]. This was attributed to the formation of a GaSnAl amalgam by dealloying of the Al component in aqueous solution.

Although Pb is probably the least effective activator of aluminium among the Group IIIA-VA elements, its presence together with other elements in the Group can cause higher activation of aluminium than expected from the single element alone. This may arise from synergistic effects, as demonstrated, *e.g.*, for the element pairs Pb-Sn [33] and Ga-Sn [34]. 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.

2. Experimental

2.1. Materials

Model ternary alloys were prepared by adding 50 and 1000 ppm of gallium and 50 ppm of lead to high purity aluminium by casting in chilled copper moulds. The alloys were denoted as AlGa50Pb50 and AlGa1000Pb50 based on their Pb and Ga content in ppm. The choice of alloy compositions was based on the earlier extensive work on the binary AlPb [4–11] and AlGa [21] alloys. The anodic activation of the Al surface caused by Pb was not significantly affected by the Pb concentration in the range 5–50 ppm. The cause of this was related to the segregation of a limited and constant amount of Pb in the form of a nanofilm by heat treatment at 600 °C, and the rest of the Pb in the alloy segregated in the form of nearly spherical particles. While the film was the main cause of anodic activation, the contribution of the segregated particles was relatively small, as determined by anodic polarization measurements in chloride solution. The upper extreme of 50 ppm was selected since the chemical and morphological characterization of the element becomes easier with increasing concentration. The presence of 50 ppm Ga alone did not change the electrochemical and corrosion properties of the binary alloy significantly in anodic polarization experiments, and Ga concentration had to be increased to 1000 ppm to observe appreciable changes in the electrochemical properties of the binary AlGa alloy. The effect of the intermediate concentrations for the binary alloy are demonstrated in detail elsewhere [21].

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 by glow discharge mass spectrometry (GD-MS). Samples were ground with SiC paper and polished metallographically to 1 μm diamond paste finish. “As-polished” samples were not treated any further. For the heat treated samples, the treatment was conducted for 1 h in the temperature range 300–600 °C in an air-circulating furnace, followed by quenching in water.

2.2. Surface characterization

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 certified oxide (CE 650) [35]. The data for Ga was calibrated by using the direct proportionality shown to exist between the known amount of gallium in the bulk and the measured intensity of Ga emission at concentration levels of interest [36]. 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 [37].

The surface morphology and microstructure of samples were characterized before and after electrochemical tests by using a field emission gun scanning electron microscope (FE-SEM) of type Zeiss Ultra 55, equipped with Inca (Oxford Instruments) energy dispersive X-ray spectroscopy (EDS) capability.

2.3. Electrochemistry

All specimens were degreased in acetone and ethanol before potentiodynamic polarization in stirred 5 wt% NaCl solution at 25 °C, which was exposed to ambient air. Earlier work showed that the anodic current density was not affected significantly by the presence of dissolved oxygen in the solution [5,9]. The sample area exposed to the solution was 1.33 cm^2. The cell geometry, solution volume and the stirring rate in the solution were identical in all runs. Anodic polarization curves were measured 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, time-dependent process [11]. Potentiostatic runs were performed at selected potentials to investigate the transient processes between active and passive conditions.

Change in the corrosion potential of alloys AlGa1000 and AlGa1000Pb50 were investigated for a period of 20 h in synthetic seawater (ASTM D1141-98), whose pH was adjusted to 3 by adding glacial acetic acid. This procedure has often been used in the past [4,5] 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.

3. Results

3.1. SEM

No observable change occurred in the surface morphology of the