Characterization of Lead Enrichment on Electrochemically Activated Binary AI-Pb Model Alloy

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Abstract

Commercial aluminum alloys can become electrochemically activated by heat treatment as a result of segregation of the trace element Pb at the surface. Pb segregation was investigated on an AIPb binary model alloy annealed at 600°C in air. Most of the segregated Pb was enriched near the oxide film - aluminum matrix interface, probably in solid solution with aluminum. Segregated metallic Pb particles in the order of 10 nm in size were also detected at the oxide-metal interface. The electrochemical activation is suggested to be related to reduced passivity of the overlying oxide by Pb enrichment.

1. Introduction

Electrochemical activation of various commercial aluminium alloys resulting from high temperature heat treatment has been a subject of attention for the past several years [1]-[7] because of its importance in galvanic and filiform corrosion. The phenomenon is observed by heat treatment at temperatures above 400°C. The anodic activation was characterized by deep corrosion potential transients in slightly acidified chloride solutions, starting from highly negative potentials in relation to the usual pitting or corrosion potential of about $-0.75 V_{SCE}$ [8]. In addition, anodic polarization in neutral chloride solutions gave high anodic current output [4]-[7],[9].

Recent work on commercial AA 8000 and 3000 series alloys related the cause of activation to the enrichment of the material surface by lead, which was present in the material as a trace element only at the ppm level [6],[7]. Work on model binary AIPb alloys indicated that the surface concentration of enriched Pb reached the order of 1 wt % independent of the bulk Pb content in the test range of 5 to 50 ppm, as revealed by quantitative glow discharge optical emission spectroscopy (GD-OES). Mechanical polishing or caustic etching appeared to remove most of the lead from the surface. However, the etched surfaces were enriched again with Pb as a result of reannealing.

TEM work [9] on heat-treated model binary AIPb alloy containing 50 ppm Pb indicated enrichment of Pb at the surface and at the grain boundaries near the surface. No phase segregation was observed, and the exact location of enrichment could not be determined.

No Pb was detected along the grain boundaries and the grain bodies in the bulk of the material, starting at a distance of about 0.5 μ m from the oxide-metal interface.

For electrochemical activation to occur, it was postulated that segregated Pb has to be in contact with the aluminum metal surface and exist in the metallic state [6],[9].

In addition to Pb enrichment, chloride has to be present in the solution, to which the metal is exposed, for activation to occur.

The present work aims to obtain additional microstructural information about the nature of Pb segregation resulting from heat treatment, specifically the location and state of the segregated Pb, by use of transmission electron microscopy (TEM) and glow discharge optical emission spectroscopy (GD-OES). The study is restricted to ambient air as the heat treatment environment.

2. Experimental

The binary AIPb alloys used in this work, containing 20 and 50 ppm Pb, were prepared from high-purity aluminum (99.98%) and lead (99.99%). These materials are designated as AIPb20 and AIPb50, respectively. The alloys were cast as 20 mm thick sheets and subsequently scalped and cold rolled to a final thickness of about 2 mm. Samples were metal-lographically polished through 1 μ m diamond paste. This was followed by heat treatment at 600°C in an air circulation furnace for 1, 2 and 4 h, quenching in distilled water at room temperature and degreasing in acetone.

Electrochemical polarization measurements were performed at a potential sweep rate of 0.1 mV/s in a 5 wt% NaCl electrolyte exposed to ambient air at 25 \pm 1°C and stirred by a mechanical stirrer at a fixed rate. The cell geometry, including the container size, electrode holders and locations, the stirrer geometry and location were identical in all electrochemical runs to obtain identical hydrodynamic conditions in the test solution.

In preparing the TEM cross-sectional specimens, two strips of metal were first glued together with epoxy. These were cut into 0.5 mm thick slices perpendicular to the glued surfaces, mechanically ground to about 120 μ m thickness, and then further thinned using a dimple grinder, yielding a sample thickness of about 30 μ m at the oxidized surface region. Finally, the electron transparency was achieved by ion-milling at an angle of 3.5°.

TEM observations were carried out using a Philips CM30 microscope with a point-to-point resolution of 0.23 nm. The microscope was equipped with an energy dispersive x-ray spectroscopic (EDS) detector, operated at an accelerating voltage of 300 kV. Quantitative depth profiling was performed by using a LECO GDS-750A optical emission spectrometer (GD-OES) in the direct current mode.



Figure 1: Polarisation data for pure aluminium and alloy AIPb20 in 5 wt% NaCl solution at 25°C. Ht = heat treated.

3.1 Electrochemical Data.

Figure 1 shows typical anodic polarization curves for pure aluminum and alloy AIPb20 in 5% NaCl solution. More detailed studies of the electrochemical behavior of various commercial and laboratory-made alloys can be found in references [1] through [7] and reference [9]. The data for polished AIPb20 is without heat treatment, whereas all other curves represent heat-treated samples. The data in this figure verify the earlier results, and they are representative of the following facts which we wish to emphasize before presenting the surface-analytical data.

Pure AI and non-heat-treated AIPb20 exhibited similar polarization behavior insofar as corrosion and pitting potential are concerned. However, the AIPb alloy had a much higher passive current than the pure AI in the range -0.9 to -0.7 V_{SCE}. In the heat treated condition the corrosion potential was shifted in the negative direction relative to pure AI and non heat treated AIPb. The heat-treated samples exhibited a high oxidation current at the potential range where the other specimens were passive, indicating an active surface relative to the non-heat treated state and pure AI. Increasing heat treatment time from one hour to four hours did not affect the polarization curve significantly. The results were not significantly different for Pb concentration in the range 5-50 ppm investigated in the binary model alloy system [9], although the data shown here are limited to the AIPb20 alloy for electrochemical measurements and GD-OES analyses and AIPb50 alloy for TEM investigation.



Figure 2: GD-OES elemental depth profiles for alloy AIPb20 heat treated in air for two different periods. The Al curve corresponds to 1 h annealed sample.

3.2 GD-OES Data.

Elemental depth profiles obtained for the air-annealed binary AIPb20 alloy also verify earlier data [9] insofar as significant Pb enrichment of the surface, as shown in figure 2. The data were obtained from two samples which were heat treated at the same temperature for different periods of time. Aluminum and oxygen profiles for the two samples were similar in shape. Al (not shown) and O curves for the 4 h annealed sample were slightly higher than for the 1 h sample, indicating a slight increase in the density and thickness of the oxide for the 4 h annealed sample. Judging from the shape of Al and O profiles, the enrichment is thought to be at a maximum at the metal-oxide interface, and the enriched region extended a certain distance into the metal. Thus, the thickness of Pb-enriched region in the metal phase appeared to increase with the time of annealing from 1 to 4 h. However, the peak concentration was not increased significantly with annealing time, indicating possibly a near-surface saturation value for the Pb in aluminum.

3.3 TEM Data.

Observations of the cross-sectional specimens revealed that the increase in the oxide film, if any, was small in the range 1 - 4 h of annealing and remained in the order of 50 nm, in good agreement with the earlier results [9]. Nanoprobe EDS analysis indicated increasing Pb enrichment with increasing annealing time as shown in figure 3. These data were obtained by using the same nanoprobe spot size centralized at the metal-oxide interface with the spectrum collection time of 100 s. TEM pole piece produced an unavoidable Cu K background peak. This peak was exploited to gain-normalize the EDS as an internal reference for comparing the spectra acquired from different annealed sample metal-oxide interfaces regions. In the resulting spectra both of Pb L and M peak intensities are clearly observed to increase with increasing annealing time from 1 to 4 h. The oxygen peak also increased with increasing annealing time indicating densification of the oxide at the oxide-metal interface.





The foregoing observations were typical for most of the cross-sectional TEM samples from the near surface region, probably representing Pb in solid solution with the aluminum matrix. Lead segregation in the form of discrete particles was detectable on a few samples as shown in figure 4 and in the high resolution TEM (HRTEM) images, figure 5. As can be discerned from the examples shown in the figures, particles of about 5-10 nm in size were segregated at the oxide-metal interface. These particles were unstable under TEM electron beam during HRTEM observation. As a result, the lattice image could be recorded only in one direction as shown in the figure 5.

The lattice plane value was determined accurately as 0.286 nm by using the (111) lattice plane (0.453 nm) of γ -Al₂O₃ crystals in the same image as internal reference, as illustrated in figure 5c. This value agrees exactly with the (111) lattice plane of metallic Pb.

Inspection of Pb particles in figures 4 and 5 reveals that some are in contact with the aluminum metal, *e.g.*, figure 5b, while some are incorporated in the growing oxide layer, *e.g.*, figure 5c. Since the particles in the oxide in almost all cases exhibit flat surfaces facing the aluminum metal, it is clear that they were in contact with the aluminum metal at a certain point during heat treatment. As a result of oxide growth, which is well known to occur at the metal-oxide interface [17], some of these particles became encompassed in the aluminum oxide.



Figure 4. TEM bright-field micrographs of the segregated Pb containing particles at the metal-oxide interface of the specimen annealed for 1 h at 600°C.

Figure 5. HRTEM images of the segregated Pb particles on specimen annealed for 1 h at 600°C.

4. Discussion

We believe that the Pb detected at the surface is in most cases in solid solution with aluminum. The solid solution solubility of Pb in aluminum is 0.2 wt% at 659°C [16]. However, the GD-OES data indicated Pb concentrations above this level. This result may be due to the added presence of segregated Pb particles scattered over a much larger analysis area, super saturation of Pb in solid solution, or problems with the standard used in calibrating the GD-OES instrument. These matters are under investigation.

Segregation of metallic Pb in the liquid state along the low energy grain boundaries of AIPb alloys as a result of heat treatment above the melting point of Pb metal has been demonstrated by *in situ* TEM studies of alloys containing much higher Pb than the present sample [12]. Based on this information, it is possible to envisage such particles to migrate along the grain boundaries further toward the lower energy metal-oxide interface during heat treatment and further spreading along this interface.

It is more difficult to suggest a mechanism by which a similar surface enrichment can occur in solid solution. One possibility is enrichment in solid solution simply as a result of selective oxidation of the more active aluminum during heat treatment. Another possible mechanism is the segregation and migration of the Pb particles, which are shown to be fast processes [12], as the temperature of the sample increases from room temperature to 600°C in the air circulation furnace. The Pb droplets segregating along the grain boundaries near the surface and then along the metal-oxide interface in this manner probably go subsequently into solid solution as a result of prolonged heat treatment at 600°C. This hypothesis, in turn, fails to give a fully satisfactory explanation of increasing Pb enrichment of the surface as a function of annealing time, which is indicated by GD-OES data to be in the form of increasing thickness of the enriched metal layer rather than increased concentration, while the TEM data suggest more of the latter. A possible problem is the fact that we have been using these instruments close to their detection limits. Nonuniform etching of the surface during argon sputtering would broaden the peaks. The work in sorting out such mechanistic details is in progress by obtaining a better statistical basis for the existing data and use of analytically more sensitive instruments such as FEG-TEM.

The observation that the surface peak concentration of Pb remained constant from 1h to 4h heat treatment is in agreement with the fact that the anodic behavior was not altered by the time of annealing in the range 1 to 4 h. Existence of a surface saturation concentration

by annealing in air is also in agreement with the results of Aloni and Polak [14]. These authors suggested that the saturation concentration is determined by the surface sites available for Pb segregation in competition with oxygen adsorption.

As argued in earlier papers [6],[9], we believe that the segregated Pb has to exist in metallic state and in contact with the aluminum matrix to cause electrochemical activation. The present TEM images give concrete evidence that the segregated Pb particles are in contact with the aluminum surface before they become incorporated in the thermal oxide as a result of continuing oxidation. As long as the Pb particles are in contact with the aluminum surface, it is thermodynamically impossible for the particles to become oxidized. Nevertheless, the present data indicate that the particles, which are embedded in the oxide, are also metallic Pb. We believe further, with reference to the work on AIGa alloys in chloridefree alkaline solution [18], that the Pb, which exists in solid solution with the Al matrix also segregates as metallic Pb nanoparticles or film as a result of anodic polarization in chloride solution. These particles, together with those segregated as a result of heat treatment cause activation of the surface as long as the particles touch the aluminum surface. The role of chloride here must be similar to that in localized corrosion, in further destruction of the oxide film whose passivating properties are reduced by the presence of underlying Pb particles giving rise to the enhanced dissolution of aluminum. The surface is passivated again after the Pb-rich surface layer is corroded and Pb particles detached from the surface.

The extremely small size of the particles demonstrated by the present data may contribute to the understanding of the activation mechanism in ways different from that considered in earlier studies. For example, the physical properties may change significantly as a function of size. Metals are known to undergo significant melting point depression with decreasing size at nanoscale [19],[20] if the segregated particle forms incoherent grain boundary with the surrounding matrix, as is the case between Pb particles and the surrounding aluminum metal and γ -Al₂O₃ crystals. One possible explanation of the observed instability of the particles exposed to the electron beam during TEM investigation may be the onset of melting. The possibility of liquid AIPb alloy formation as a result of local heat generation during anodic polarization and possible consequences of such a phenomenon in destabilizing the passivity of the aluminum oxide are under investigation.

5. Conclusions

Enrichment of the oxide-aluminum interface by lead as a result of high temperature heat treatment was demonstrated. Lead segregation at the metal surface occurs both in solid solution with the aluminum matrix and in the form of metallic Pb nanoparticles. The surface concentration of Pb, segregated as a result of annealing in air, reaches an apparent saturation level independent of the bulk concentration. The degree of anodic activation of the surface, as characterized by anodic polarization, is therefore independent of bulk Pb concentration and annealing time. The fact that the segregated Pb particles were in contact the aluminum metal is considered to be an important factor in explaining the mechanism of electrochemical surface activation by Pb.

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