Characterization of Electrochemically Activated Surface on Rolled Commercial AA8006 Aluminium

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ABSTRACT

Commercial alloy AA8006 (nominal composition in wt% 1.5Fe, 0.4Mn, 0.2Si) exhibits electrochemical activation in chloride media as a result of annealing at temperatures above 350 ºC. Activation is manifested by a significant negative shift in the corrosion potential and a significant increase in the anodic current when polarized above the corrosion potential in aqueous chloride solution. This phenomenon was correlated with the enrichment of trace element Pb at the oxide-metal interface. For fixed annealing time, maximum activation and Pb-enrichment are obtained at an annealing temperature of 450 ºC independent of the original surface condition. Reduced activation with increasing temperature is attributed to increasing density of the spinel crystalline phase to cause the passivity of the surface.

INTRODUCTION

Thermomechanical processing has a significant role in the determination of the surface properties of aluminum alloys. Electrochemical activation of various commercial aluminum alloys resulting from high temperature heat treatment has been a subject of attention for the past several years because of its importance in galvanic and filiform corrosion [1-9]. The phenomenon is observed by heat treatment at temperatures above 350 ºC. 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 [10]. In addition, anodic polarization in neutral chloride solutions gave a high anodic current output with oxidation peaks corresponding to the potential arrests, as also confirmed by potentiostatic data [5-7, 11]. Recent work on commercial alloys AA8006 and AA3102 has shown the cause of activation to be the enrichment of the material surface by lead, which was present in the material as a trace element only at the ppm level [5-7]. Further work on model-binary AlPb alloys verified the role of Pb in activation [11, 12].

The present work was undertaken to obtain a more detailed chemical and microstructural information on hot-rolled commercial alloy AA8006 in the activation behavior. It is further desirable to obtain additional evidence of Pb segregation resulting from heat treatment of a commercial alloy, specifically the actual location and state of the segregated Pb, the effect of heat treatment in general on the near surface chemistry and microstructure of the alloy and the effect of these factors on the electrochemical and corrosion behavior.

EXPERIMENTAL DETAILS

The commercially rolled AA8006 material was supplied in the form of fully annealed O temper with 0.8 mm thick sheets. Samples were heat-treated at different selected temperatures in an air circulation furnace for 2 h, followed by quenching in distilled water at room temperature and degreasing in acetone. Some samples packaged inside high-purity aluminum (99.98%) foil were also heat-treated for 2 h under Ar gas protection at 600 ºC followed by slow cooling. This
procedure was reported to promote metallic Pb particle segregation on the surface in contrast to air annealing and subsequent water quenching [13]. For both as-received and heat-treated samples, alkaline etching was carried out in 10 wt.% NaOH at 60 °C for 10 s, removing approximately 1 µm material from the sample surface, and then desmutted for 1 min in concentrated nitric acid at 25 ºC.

Electrochemical polarization measurements were performed at a potential sweep rate of 6 mV/min in a 5 wt% NaCl electrolyte exposed to ambient air at 25 ±1 ºC, and stirred by a mechanical stirrer at a fixed rate. In all cases, polarization curves were recorded at least twice in order to ensure reproducibility of the plotted results. In preparing TEM cross-sectional specimens, four strips of sample material, 4 mm wide, were first glued together with epoxy and the final electron transparency achieved by ion-milling [12]. Some TEM cross-sectional specimens were also generated by ultramicrotomy, with final sectioning with a diamond knife, using well-documented procedures [14]. Stripped surface oxide specimen was prepared by immersing an annealed sample into a mercuric chloride-methanol solution to remove the thermal oxide film from the aluminum substrate.

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. Surface morphology was investigated by using a Hitachi Field Emission Gun SEM (FEG-SEM) equipped with an EDS detector operated at 5 kV.

RESULTS

Figure 1(a) shows the effect of 2 h annealing in the range 350 – 600 ºC on the anodic behavior of as-extruded AA8006 in 5 wt.% NaCl solution. In comparison to the behavior of an etched sample as shown in Fig. 1(b), the material was already active in the as-received condition as a result of hot rolling and annealing during fabrication. Therefore, the polarization curve for the sample annealed at 350ºC was nearly identical to that of the as-received condition [6]. If the surface was first etched and then annealed, the anodic behavior obtained was quite similar to those for the as-received samples, as shown in Fig. 1(b). Maximum activation, as judged by the general anodic current level, appeared to be attained by annealing at 450ºC for the etched surface.

**Figure 1.** Effect of annealing temperatures on the polarization behavior of as received (a) and etched (b) alloy 8006 in 5% NaCl solution. The samples were annealed for 2 h annealing followed by quenching in water.
Annealing at higher temperatures gave reduced activation as shown by the 600ºC annealed curve in Fig. 1(b). Increasing the annealing periods beyond 2 h did not significantly affect the shape of the polarization curves in the annealing range 350 to 600 ºC. It should be reiterated that these results differ from those for the binary model AlPb alloys [11, 12] in the fact that activation of alloy 8006 occurs much easier at lower temperatures of annealing.

GD-OES elemental depth profiles obtained from the as-received and air-annealed AA8006 alloy verified earlier data insofar as the enrichment of Pb together with significant Mg enrichment at the surface. The profiles for the etched surface indicated that Pb was removed from the metal surface.

Since the thick thermal oxide layers covered the sample surfaces after high temperature air-annealing, it was difficult to visualize the segregated Pb particles by SEM investigation [12]. However, Pb-containing particle was visible by SEM analysis, as shown in Fig 2, after promoting Pb segregation at 600 ºC for 2 h annealing under oxygen-lean Ar atmosphere followed by slow cooling in air. The enlarged figure (b) shows the SEM EDS analysis of the Pb-rich particle as insert.

Figure 2. Plan-view morphology of the as-received sample, annealed for 2 h at 600 ºC under oxygen-lean Ar atmosphere, followed by slow cooling in air. The enlarged figure (b) shows the SEM EDS analysis of the Pb-rich particle as insert.

Figure 3. TEM cross-sectional micrographs of (a) as-received sample (b) and as-received sample annealed for 2 h at 600 ºC, followed with water quenching. Nanocrystals of aluminum remaining from the original GRSL are indicated by arrows on the annealed sample.
confirmed by the corresponding EDS spot analysis. TEM selected area electron diffraction (SAED) pattern inserted in Fig. 4(a) was recorded from the top oxide surface region which demonstrated amorphous alumina together with spinel and γ-Al₂O₃ microcrystalline phases inside the oxide layer. As indicated by the high resolution TEM (HRTEM) image shown in figure 4(b), this particle was located at the metal-oxide interface and in contact with the Al metal surface. The inserted HRTEM micrograph in Fig. 4(b), enlarged from the arrow-marked area in the figure, indicated that the particle lattice fringes in two perpendicular directions were both 0.287 nm, as determined by using the bulk Al (111) lattice 0.234 nm as internal reference [12]. Such lattice-fringe configuration indicated that this particle was not in metallic Pb state. HRTEM data of the observed Pb-rich particle did not reveal further information about the composition and structure.

Figure 5(a) and (b) show the TEM micrographs of surface oxides stripped from sample
surfaces annealed for 2 h at 500 and 600 °C, respectively. TEM SAED pattern of the dark contrast crystalline phases in both figures revealed the spinel structure MgAl₂O₄ [15]. Only a tiny fraction of the oxide crystals were characterized as γ-Al₂O₃ crystals. Both the spinel and γ-Al₂O₃ crystals were embedded in an amorphous aluminum oxide matrix which corresponded to the well known oxide structures for Mg containing aluminum alloys discussed in the literature [16]. As shown in Figures 5(a) and (b), it demonstrated the significant increasing size of the spinel crystalline phase with increasing annealing temperature from 500 to 600 °C.

DISCUSSION

If the segregation of the trace element Pb is a normal activation controlled diffusion process, increase of both the surface enrichment of Pb and anodic activation of the surface would be expected by increasing annealing temperature. However, annealing temperature did not seem to have such an effect on alloy 8006. The results verified, in fact, that alloy 8006 became electrochemically activated at a lower annealing temperature [5] than the model binary alloy AlPb [12] for a fixed time of annealing. The present work indicated furthermore that Pb enrichment of the surface occurred most effectively at 450°C than at 600°C for alloy 8006, whereas the higher annealing temperature was more effective for Pb enrichment of the surface of the binary model AlPb alloy. Among the commercial alloys investigated earlier, alloys 3005 [7], 5754 [6] and an "Alloy X" [3] with the nominal composition 0.4% Fe, 0.2% Si, 0.2% Mn, 0.1% Mn exhibited behavior similar to alloy 8006, while alloys, 1050, [3] 1080, [3] 1200 [3] and 3102 [9] were similar to the binary AlPb.

One difference which could give this distinction between the two alloy groups is the fact that the first group contained Mg, and the second group did not. A direct role of Mg in the activation mechanism was ruled out because it existed in a stably oxidized state at the surface. However, magnesium is known to diffuse readily to the surface by heat treatment [4-9, 11, 12, 15, 16], if it is present in the alloy, probably by diffusion of the metal along the grain boundaries. The metal oxidizes readily once it becomes in contact with oxygen close to the alloy surface.

It is difficult to discuss the factors affecting the rate of Pb transport to the surface, nature of Pb segregation at the surface, and effect of these on surface activation because appreciable Pb was enriched already as a result of the thermomechanical history of the as-received sample. The present results verify again that most of the Pb near the alloy surface was removed by deep alkaline etching. The most significant enrichment in terms of the peak concentration of Pb was obtained by annealing at around 450°C. Highest anodic activation, as judged by the anodic current output, was also obtained at this temperature. The solid solution concentration of Pb in aluminum metal is limited at this temperature. Even in a supersaturated state at the metal surface, the results so far indicated a maximum possible solid solution concentration of about 1 wt%. HRTEM analysis of cross-sectional foils seemed to support this hypothesis although the present HRTEM data were not enough to allow determination of their exact microstructure and composition. Furthermore, the probability of capturing Pb-containing particles of adequate size and number in cross-sectional TEM foils is small. Whether Mg enhances Pb diffusion, since the two elements have a certain affinity to one another in terms of solid solution solubility and formation of intermetallic compounds, remains to be shown. Work is in progress by use of ternary model AlMgPb alloys.

The reduced activation resulting from annealing at temperatures higher than 450°C is difficult to explain based on the view that the Pb in solid solution with the aluminum matrix is responsible for the activation, since the solid solution concentration should increase with
increasing temperature. However, this study could not ascertain the type of Pb containing phases formed by annealing at 450ºC, which may be responsible for the activation, and their stability with increasing temperature. Furthermore, formation of the spinel oxide with increasing density with increasing annealing temperature may contribute to the passivity of the surface [16]. In addition, evaporation of the surface Pb with increasing temperature may become possible [12].

CONCLUSIONS

The data presented for the rolled commercial AA8006 aluminum alloy and data available for various other commercial and model alloys in the literature indicated that segregation of the trace element Pb as a result of heat treatment requires annealing at lower temperatures (450ºC) on Mg-containing aluminum alloys than on Mg-free alloys (600ºC) for fixed annealing time (2 h). The presence of magnesium in the alloy enhanced enrichment and segregation of Pb at the surface, thereby increased anodic activation of the alloy in chloride environment. Although the bulk concentration was at the ppm level, the trace element Pb became enriched at the surface of rolled alloy 8006, probably in solid solution with the aluminum matrix, at a supersaturated concentration of 1 wt%. Reduced activation with increasing temperature is attributed to increasing density of the spinel crystalline phase to cause the passivity of the surface.

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REFERENCES