

Effect of Lead on Anodic Behavior of Aluminum

Y. W. Keuon, S. Ono,* J. H. Nordlien,⁺
and K. Nisancioglu¹

Department of Electrochemistry, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

*Department of Applied Chemistry, Faculty of Engineering, Kogakuin University, 1-24-2 Nishishinjuku, Shinjuku-ku, Tokyo 163-8677, Japan

⁺Hydro Aluminium R&D Materials Technology, N-4265 Håvik, Norway

Recent work on filiform corrosion of certain rolled commercial alloys¹⁻³ indicated that the metal surface can be electrochemically activated as a result of high temperature processing with consequences for electrochemical properties and general corrosion behavior. The active behavior is characterized by deep, negative corrosion potential transients in a slightly etching chloride solution, indicating polarization of the surface to the usual pitting potential as the activating material is removed and the bulk structure of the material is exposed to the solution. Furthermore, potentiostatic polarization of the active surface well below the pitting potential leads to significant current density transients.³ Potentiodynamic sweeps give active anodic activation peaks, again well below the usual pitting potential. These anodic events lead to superficial etching of the surface, rather than pitting in the usual manner, indicating the removal of thin patches of apparently active surface layer. Preliminary work⁴ indicated that surface activation can be attributed to the enrichment of the surface layer by metallic Pb, in the same manner as the well-known effect of a number of other Group IIIA and IVA elements in the development of sacrificial aluminum anodes for cathodic protection and Al-air batteries.

In this work, the causes of this activation phenomenon was investigated further by use of the commercial rolled alloy AA8006 and model binary alloys prepared from the pure components. Alloy 8006 contained nominally 1.5% Fe, 0.4% Mn, 0.2% Si, and about 200 ppm each of the elements Mg, Cu and Zn. It was hot and cold rolled to 0.8 mm thickness and delivered in the fully annealed O condition. The binary alloys were AlFe0.04, AlMn1, AlSi0.1, AlMg3, AlZn1, and AlPb0.1. These materials were available from various earlier projects, and therefore, compositions of the alloying elements do not correspond to those presents in the commercial alloy 8006. The present objective was to obtain a first hand opinion about the possible role of these elements on the electrochemical behavior of the commercial material. The binary samples were prepared by cold rolling mold-cast slabs on a laboratory roller followed by heat treatment at about 600°C to dissolve as much of the alloying elements in solid solution as possible.

As indicated in the earlier work, negative E_{corr} values recorded at the outset of open-circuit transients can be attributed to electrochemical activation or cathodic control resulting from unavailability of cathodic sites at the surface. E_{corr} transients then result from the etching of the active layer or exposure of the cathodes, respectively, as the sample surface is polarized in the positive direction toward the pitting potential. E_{corr} transients for the first type of surface are also characterized by several potential arrests, indicating occurrence of successive electrochemical phenomena as the surface is polarized. E_{corr} transients for the second type of surface are usually faster and

monotonic. This type of surface is essentially passive in terms of both anodic and cathodic processes. Originally active surfaces give the high anodic current outputs, characterized by several oxidation peaks, as a result of anodic potential sweep, as summarized earlier. The peaks roughly correspond to the potential arrests in the corresponding E_{corr} transients. The passive type of surfaces typically exhibit the usual passive behavior, followed by steep current increase above the pitting potential.

The electrochemical data for alloy 8006 in the as-received and annealed conditions and the binary AlPb0.1 could readily be classified as corresponding to an active type of surface, while the data for other binary model alloys were more characteristic of the passive type of surface. The E_{corr} transients, including the potential arrests, and the potentiodynamic data, including the oxidation peaks, were strikingly similar for the two active materials. Deep caustic etching and metallographic polishing removed the active behavior. Subsequent heat treatment restored electrochemical activity. The electrochemical data, therefore, indicated that activation of the surface can be attributed to enrichment of the surface by metallic Pb as a result of heat treatment, although Pb is present at an impurity (ppm) level in alloy 8006. However, Pb enrichment of Al surfaces by heat treatment is a well known phenomenon,⁵ even if Pb is present at a ppm level in the alloy.

In order to document Pb enrichment further, elemental depth profiles of 8006 surfaces were performed by glow discharge emission spectroscopy (GD-OES). A qualitative analysis achieved so far of the results revealed a clear enrichment of Pb near the surface of the as-received material. There was a slight increase in the enrichment level as a result of annealing for 2 h at 450°C. Deep caustic etching removed the enriched Pb, although this is in apparent disagreement with earlier results.⁵ Re-annealing of the etched surface caused enrichment of the surface again with Pb. However, Pb enrichment was confined to a thinner surface layer in this case. This difference in the Pb profiles for the as-received and etched-and-annealed samples does not affect their electrochemical behavior significantly.

It is anticipated that activation of the aluminum surface in the manner described will become important in future studies of electrochemistry and corrosion of aluminum alloys because of increase in the content of Group IIIA and IVA impurity elements as a result of recycling. Despite ample electrochemical data available regarding the effect of such elements on the electrochemical behavior of aluminum, the actual mechanism by which these elements activate the surface still remains unresolved. The successive oxidation processes in the presence of Pb are a newly observed phenomenon, which also requires further investigation.

References

1. H. Leth-Olsen *et al.*, *Corr. Sci.*, **40**, 1179, 1195 and 2051 (1998).
2. A. Afseth, J. H. Nordlien, G. Scamans, and K. Nisancioglu, *Corr. Sci.*, in press.
3. Y. W. Keuon, J. H. Nordlien, and K. Nisancioglu, submitted to *J. Electrochem. Soc.*
4. K. Nisancioglu, J. H. Nordlien, A. Afseth, and Y. W. Keuon, presented at the 198th Meeting of The Electrochem. Soc., Abs. No. 306, Abs. Vol. 2000-2.
5. Z. Ashitaka, G. E. Thompson, P. Skeldon, G. C. Wood, H. Habazaki, and K. Shimizu, *J. Electrochem. Soc.*, **147**, 132 (2000).