

Dioxygen Reduction at AA2024 Causes Base-Induced Loss of Passivation

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Several aluminum alloys contain intermetallic compounds that influence their corrosion behavior. In particular, AA2024-T3 has intermetallic inclusions that variously contain Al, Cu, Fe, Mn and Mg [1]. These cause corrosion of AA2024 by virtue of galvanic cells that arise because of compositional variations across the surface [2]. One of the key reactions at this alloy surface is dioxygen reduction, which is thought to be the cathodic part of the electrochemical process causing corrosion. We report here that, under buffered conditions, dioxygen reduction at AA2024 follows microelectrode behavior. In contrast, under unbuffered conditions it causes local production of hydroxide, leading to severe attack on the surface oxide film near the inclusions and resulting loss of passivation.

AA2024-T3 samples were cleaned and polished using standard procedures, except that polishing was done in aprotic solvents to inhibit corrosion during the polishing. The reduction of dioxygen at the alloy surface was studied in a wall-jet flow cell [3]. Figure 1 shows the current observed for an experiment in which the AA2024 substrate was held at a potential of -0.95 V vs. SCE and the flow was alternated between N_2 -saturated and O_2 -saturated buffer solutions. The diffusion-limited reduction current for dioxygen at the AA2024 surface was 13 microamp/cm². Calculations will be presented that show this current to be in good agreement with expectations for an array of microelectrodes (i.e. the micron-sized intermetallic particles). Under unbuffered conditions, the observed currents are much larger, in the range of hundreds of microamps/cm², and much less stable. These much larger currents result from wholesale attack by hydroxide at the surface, where the hydroxide is the product of dioxygen reduction. No attack is observed in the absence of O_2 . Figure 2 shows a scanning electron micrograph of the surface after a limited period of attack of the surface by hydroxide produced *via* reduction of dioxygen. The image clearly shows attack around both the Fe-rich and Cu-rich inclusions as well as pitting at various locations across the surface. These results and other details of these measurements will be discussed in this presentation.

ACKNOWLEDGMENT

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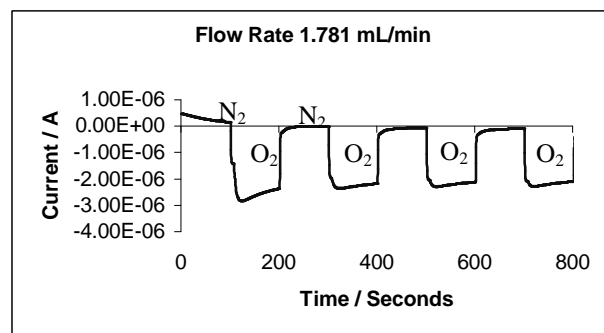


Figure 1 Time dependent current in wall-jet flow cell at AA2024 sample. Flow is alternated between N_2 -saturated and O_2 -saturated buffer solution (80 mM BES, pH 6.5), showing repeatability. O_2 reduction current is 13 microamp/cm².

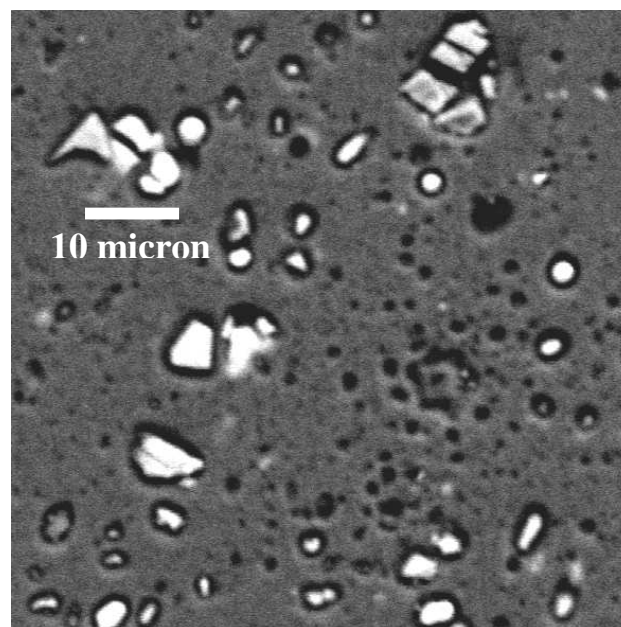


Figure 2 - SEM image of AA2024 surface showing hydroxide-induced trenching around both the Fe-rich and Cu-rich intermetallic inclusions. Note also substantial pitting across the surface.