EIS study of anodic oxide films formed by DC, AC and combined AC/DC methods on Al alloy AA2219

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Introduction

Our studies have focused on the electrochemical passivation of Al alloys containing Cu and on the AA2219 alloy (6%-wt Cu), in particular. Al alloys containing Cu are of interest to the aerospace industry due to their good strength-to-weight ratio. However, the large amount of Cu in AA2219 leads to the formation of intermetallic inclusions with sizes up to 100 µm, making this alloy particularly susceptible to corrosion and to loss in fatigue strength. As opposed to the more common AA2024 alloy (4%-wt Cu), standard chronic and sulfuric acid DC anodizing techniques applied to AA2219, while successfully bestowing corrosion protection, significantly reduce the alloy strength.

Previous literature has suggested that the use of AC instead of DC anodization methods may generate more benign conditions under which it might be possible to retain the intermetallic inclusions, while also generating a thick oxide film [1271]. However, some uncertainty seems to exist in the literature regarding the actual applied potential during AC anodizing, as the rectifying nature of the Al oxide introduces an unknown anodic DC bias and makes it difficult to compare data from two electrode AC anodization experiments with data from potentiostat-controlled single-electrode work.

The main goal of this work has been to form a protective oxide film on AA2219, while also retaining and passivating the Cu-rich inclusions. Thus our research has focussed on determining the reasons for the strength loss during DC anodization and on investigating the suitability of AC and biased AC (AC/DC) anodizing methods to achieve these goals.

Experimental Methods

Disc samples of AA2219-T851, intended for electrochemical studies, were polished using 600 grit SiC emery paper, while samples for SEM imaging were polished with diamond slurry to a 1 µm finish. DC anodization was carried out using a Solartron 1287 potentiostat, a RHE reference electrode and a Pt mesh counter electrode. Disc samples of AA2129-T851, with an exposed area of 0.43 cm², were mounted in a glass cell, and anodized under sweep and hold conditions in unbuffered acid and neutral buffer solutions.

AC/DC anodization was carried out using a variable DC power supply (0-60 VDC) and a Varies (0-140 VAC), utilizing a Pt mesh as the secondary electrode.

The corrosion resistance of the resulting oxide films was determined using Electrochemical Impedance Spectroscopy (EIS), both in the anodizing electrolyte and in 5%-wt NaCl solution.

The surface composition and morphology of diamond-polished AA2219 samples were examined both in the SE and BSE modes. EDX was used to qualitatively assess any changes in composition of the intermetallic particles.

Results and Discussion

From the SEM imaging of the diamond polished samples, and consistent with the electrochemical evaluation, we were able to determine that, as a result of standard DC anodization, all exposed Cu-rich inclusions were removed from the surface in both neutral and acidic electrolytes. Further studies showed that this removal occurred after less than 10 min and at voltages significantly below the typical anodization range for Al alloys (18-25 V). Taking into account the average particle size of 10-100 µm, this would predict the formation of pits up to 100 µm deep in the anodized surface, thus explaining the subsequent loss in fatigue strength.

Our AC/DC work suggests that the ratio of anodic peak voltage, Ua, and cathodic peak voltage, Ub, has a significant effect on the oxide film formed. In particular, we found that no anodic film would be formed for Ua/Ub > 1 in sulfuric acid. Further, EIS results indicate that, when formed in neutral buffer solutions, the film thickness increases with decreasing Ua/Ub, suggesting that film dissolution occurs as a result of cathodic exposure.

The corrosion behavior of the AC/DC anodized AA2219 samples in 5%-wt NaCl solution, using EIS and linear polarization methods, will be discussed in this presentation as a function of the anodizing solution composition, pH and temperature, as well as the AC peak potentials employed.

Fig. 1: SEM image of polished AA2219-T851. (a) Before DC anodizing. The bright spots are Cu-rich inclusions (elemental contrast) with a composition close to Al12Cu.
(b) After DC anodization, the majority of the Cu-rich bright regions are no longer present, indicating the removal of the inclusions under these conditions.