

Development of Porous Anodic Films on an Al-1.5 at % Cu in Phosphoric acid

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With regard to aluminium alloys, barrier type oxide growth has been widely studied [1-3], however, brief reference is made to the growth of porous anodic film on these materials [4-6]. From these works it is clear that the oxide morphology and efficiency of anodizing is influenced by local composition of the metal substrate, generally determined by the type of alloying elements present in the material and the metallurgical history of the material.

In order to understand the roles of alloying elements during film growth in neutral electrolytes, alloy oxidation have been undertaken, using compositionally uniform alloys developed by magnetron sputtering.[7] Such studies have revealed conditions for interfacial enrichment of alloying elements prior to oxidation at the alloy/film interface. Thus, alloying elements with Gibbs free energies of oxide formation per equivalent less negative than alumina show enrichment prior to oxidation, whereas those with more negative $\Delta G^\circ/n$ values reveal immediate oxidation, along with aluminium, at the alloy/film interface. Subsequent mobilities of alloying element cations within the amorphous alumina film depend largely on the metal-oxygen single bond energy relative to that of the Al-O single bond energy.

From the limited, detailed studies of porous anodic film formation on binary Al-Cu alloys, aged to produce θ' precipitation, it is evident that porous film growth proceeds relatively uniformly over the macroscopic alloy surface (of relatively low copper content); however, when the receding alloy/film interface encounters θ' platelets, of high copper concentration relative to the matrix, oxygen gas generation occurs within the film, with sufficient pressures developed to cause cracking [7]. Such cracking allows electrolyte access to the precipitate at high potential, with its subsequent rapid dissolution, and eventually re-anodizing of the underlying alloy. As a consequence of these overlapping and interacting processes, films of enhanced porosity develop at reduced current efficiency to produce a relatively rough, anodized alloy substrate. A recent study has confirmed the low efficiency, the prior enrichment of copper below the alumina film and the high porosity of oxides grown in acid solution (8). However, film formation was undertaken in sulphuric acid generating fine features porous oxides, where discrimination of the various features is difficult. Consequently, in the present work, relatively large featured films formed in phosphoric acid have been examined by transmission electron microscopy (TEM), of plan views of stripped anodic films and ultramicrotomed cross. sections, Rutherford backscattering spectroscopy (RBS) and nuclear reaction

analysis (NRA) have also been employed for compositional studies.

In this work, the development of porous anodic films on an Al-1.5 at% Cu has been studied by transmission electron microscopy of ultramicrotomed sections and Rutherford backscattering analysis. Particular attention has been focused on the location and origin of the non uniform thickening of the initial barrier oxide. From TEM examination of the anodic films formed on the alloy substrate at 5 mA cm⁻² to different voltages reveals the dynamic evolution of numerous features in the thickening film in the initial stages of anodising. Such features appear related to oxygen bubbles in the film, which arise from oxidation of O²⁻ ions above copper clusters in the copper enriched layer, at the alloy-oxide interface and, from oxygen generated above second phase and impurity regions in the metal substrate. As a consequence of oxygen gas generation, film growth proceeds at efficiencies lower than that on superpure aluminium under similar conditions.

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