

Anodic Film Formation on Al-Ag Alloys

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The incorporation of alloying elements species into anodic films formed on dilute binary aluminum alloys reveals an interesting pattern of behavior [1]. Thus for alloying elements which form oxides with Gibbs free energies of formation per equivalent similar to, or more negative than, that for alumina, the alloying element atoms are oxidized at the alloy/film interface in their alloy atoms from the commencement of anodizing. Conversely, alloying elements with less negative $\Delta G^\circ/n$ values show enrichment in the alloy prior to oxidation at the alloy/film interface. For such latter alloying elements, a thin layer of alloy, immediately adjacent to the alloy/film interface, is highly enriched by initial oxidation of aluminum atoms. The thickness of the enriched layer varies with the particular alloying element, but is usually in the range 1-3 nm[1-3]. The composition of the enriched alloy layers is known, but the precise structure is unclear; however for observation of the oxidation of tungsten in dilute Al-W alloys, the presence of clusters of nanometre dimensions is suggested [4].

Al-Ag alloys are of interest because of the strong tendency towards enrichment of silver in the alloy, occurring as a consequence of film growth, suggested by a survey of the $\Delta G^\circ/n$ values for oxide formation of a wide range of alloying elements in aluminium [1]. In the present study, the anodic oxidation of a series of Al-Ag alloys has been examined by a combination of Rutherford back scattering spectroscopy (RBS) and transmission electron microscopy of ultramicrotomed sections.

The anodic oxidation of Al-Ag alloys, containing 1, 2, 3 and 4 wt% Ag, proceeds initially by the formation of an anodic alumina film containing no silver species, as revealed for anodizing in ammonium pentaborate solution under the selected conditions. In parallel, the alloy layer immediately beneath the anodic film enriches progressively in silver as a consequence of the initial formation of relatively pure alumina. With sufficient enrichment of silver, oxidation of the clusters proceeds with Ag units entering the amorphous alumina film. Additionally the reduced slope of the voltage-time transient, together with the observation of voids in the film, suggest development of oxygen gas in the amorphous film. The extent of alloying element enrichment of the alloy for the production of oxygen gas is dependent upon the alloy composition. Further, the extensive generation of oxygen within the film at, or near, the alloy/film interface, leads to the formation of oxygen-gas filled voids within the anodic alumina, which subsequently rupture and release oxygen gas.

The results of transmission electron microscopy of ultramicrotomed sections of the alloys and their attached films, together with RBS analyses of the corresponding samples, have been used to derive compositional models for the layered morphologies. Further, as indicated previously, the initial suggestion of a relationship between the $\Delta G^\circ/n$ value relative to that of aluminium and the extent of interfacial enrichment, of nanometre dimensions, is confirmed. Finally, the reduced extent of mobility of Ag^+ cations relative to Al^{3+} ions is predicted from the magnitudes of the corresponding single metal-oxygen bond strengths.

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References

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