Enriched alloy layer on an Al-Cu alloy studied by cyclic voltammetry

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Abstract. The behaviour of enriched Al-0.7at.%Cu alloy is investigated using cyclic voltammetry. Enriched alloy layers at the interface between the alloy/oxide film were developed by alkaline etching at 5mA cm\(^{-2}\) in 0.1M sodium hydroxide solution at 298K, with the time of etching determining the extent of enrichment. Cyclic voltammograms were recorded at a scan rate of 10mV s\(^{-1}\) in naturally aerated 0.1M ammonium pentaborate solution at 298K. The current overshoot of the enriched alloys was different from that for non-enriched alloy. The latter material revealed the usual single peaks, which are very similar. In contrast, the overshoot comprised two or more components for the enriched alloys. The behaviour is suggested to be associated with the atomic bonding of aluminium in copper-rich and aluminium-rich regions of the enriched alloy layer, with influence on the activation potentials for oxidation of aluminium.

1. Introduction
Oxidation of many aluminium alloys by anodizing leads to formation of a thin layer of alloy, which is highly enriched in the alloying element with respect to the bulk alloy [1,2]. However, enrichment can be generated also by surface pre-treatments, such as chemical polishing [3], electropolishing [4] and alkaline etching [5], making the enrichments of general relevance to preparation of alloy surfaces and their subsequent performance. In particular, the corrosion potential of Al-Cu alloys is affected by the presence of the enriched alloy layer [6,7].

In the present study, the effect of the copper enriched layer on the transient behaviour of an Al-0.7at.%Cu alloy is investigated using cyclic voltammetry. Dilute aluminium alloys containing relatively noble alloying elements offer the ability to change the composition of the alloy at the metal/oxide interface, without affecting the composition of the oxide. For a single alloy composition, a wide range of local alloy compositions can be developed by anodic pre-treatment of the alloy. The possibility of control of the local alloy composition arises because copper is not oxidized until it is sufficiently enriched in the alloy. In the case of the alloy of interest, enrichment to about 40at.% Cu in an enriched alloy layer of 2nm thickness is necessary [8]. The copper enriches in the initial stages of oxidation of the alloy, during which only aluminium atoms are oxidized, forming an alumina film. When copper later begins to oxidize, it enters the oxide as Cu\(^{2+}\) ions that migrate through the oxide faster than the Al\(^{3+}\) ions, by about a factor of 2 [9]. At this stage of the oxidation process, the average composition and thickness of the enriched alloy layer do not change significantly with time, indicating...
that copper and aluminium atoms enter the oxide in proportion to their concentrations in the bulk alloy rather than their concentrations in the enriched layer [10].

2. Experimental details
The Al-0.7at.%Cu alloy was deposited onto electropolished high purity aluminium sheet by magnetron sputtering. Targets were composed of 99.999% aluminium and 99.99% copper. The deposited layers were about 400-500nm thick. In order to develop enrichments of the alloy, anodic etching was carried out at 5mA/cm² in 0.1M NaOH at 293K for different times, followed by an immersion in nitric acid. Cyclic voltammograms were then recorded at a scan rate of 10mV s⁻¹ in naturally aerated 0.1M ammonium pentaborate electrolyte at 293K. The cell comprised a platinum counter electrode and a saturated calomel reference electrode (SCE). All potentials are expressed with respect to SCE. Compositions of enriched alloy layers were determined by Rutherford backscattering spectroscopy, using 2.0MeV He⁺ ions produced by the Van de Graaff accelerator of the University of Paris, with spectra interpreted using the RUMP program [11].

3. Results and discussion
The enrichments of copper in the Al-0.7at.%Cu alloy following anodic etching are summarized in Table 1. The average compositions of the enriched layer are given, assuming a layer of thickness of 2nm and a weighted average of the atomic densities of aluminium and copper. The thickness of the alloy is reduced by 110nm after 41s of etching, indicating an etching rate of about 2.7nm s⁻¹. Typical RBS spectra showing enrichments of Al-Cu alloys have been presented in previous work [6]. It can be seen that the copper enrichment increases as the etching time increases and that for the longer times the oxidation of copper at the alloy/oxide interface took place. The latter is evident from the differences between the experimental and expected enrichment values.

| Time of etching (s) | Enrichment in alloy (Cu atoms cm⁻²) | Average composition of enriched layer (at.%Cu) |
|---------------------|------------------------------------|---------------------------------------------|
|                     | RBS | Expected |                                  |
| 0                   | 0   | 0        | 0                               |
| 12                  | 0.9×10¹⁵ | 0.9×10¹⁵ | 7.2                             |
| 25                  | 1.8×10¹⁵ | 1.8×10¹⁵ | 15.2                            |
| 41                  | 2.9×10¹⁵ | 2.9×10¹⁵ | 24.3                            |
| 71                  | 4.7×10¹⁵ | 5.2×10¹⁵ | 38.7                            |
| 110                 | 5.1×10¹⁵ | 8.0×10¹⁵ | 42.5                            |

The first anodic cycle of the voltammograms for Al-0.7at.%Cu alloy in the as-deposited condition disclosed the transient peak in current density, centred at about -100mV, followed by a shallow dip and gradual approach to a steady value of about 33μAcm⁻² that is maintained from about 500mV until the anodic limit of 1V (Figure 1). The final current density corresponds to the steady-state oxide growth. The current density on reversal of the anodic scan fell rapidly to a low value as oxide growth declined rapidly. The anodic current density remained low on subsequent cycles, with a small rise towards the anodic limit, when some film growth occurred.

Different behaviour is observed for the alloy after the anodic etching. The transient peak is shifted to more positive potentials as the etching time increases, achieving an increment of about 500mV after 71s of etching. The height of the transient peak is significantly reduced. In contrast, the steady current density was relatively unaffected. The transient peak appears to comprise at least two sub-peaks separated by about 200-300mV. The shape of the peak often differed in repeat measurements. However, consistently, the potential range between the initial rises in current density to the tail of the
Transient peak was from 500-700mV compared with about 300mV for the as-deposited alloy. In the cathodic scan only the hydrogen evolution is evident after -1.7V.

![Cyclic voltammograms (First cycle) of Al-0.7at.%Cu alloy after anodic etching in 0.1M sodium hydroxide, in 0.1M ammonium pentaborate electrolyte at 298K.](image)

**Figure 1.** Cyclic voltammograms (First cycle) of Al-0.7at.%Cu alloy after anodic etching in 0.1M sodium hydroxide, in 0.1M ammonium pentaborate electrolyte at 298K.

The copper-enriched alloy layer appears to have a significant effect in the initial anodic oxidation. For an Al-0.7at.%Cu alloy, the required level of enrichment of the alloy for oxidation of copper to take place is about $6 \times 10^{15}$ Cu atoms cm$^{-2}$, in a layer about 2nm thick. Assuming an average atomic density of the enriched layer of $7 \times 10^{22}$ atoms cm$^{-3}$, between those of copper and aluminium of $8.4 \times 10^{22}$ and $6.0 \times 10^{22}$ respectively, the average concentration of copper is 43at.%. During etching, copper enriches initially at a rate of about $9 \times 10^{13}$ Cu atoms cm$^{-2}$ s$^{-1}$, thus achieving the maximum enrichment at about 67s. This stage follows oxidation of about 142nm of the alloy. By 12 s of etching, the enrichment corresponds to an average copper concentration of 7at.%, with levels of 15 and 24at.% after 25 and 41s, respectively. The enriched layer is composed of aluminium-rich and copper-rich region. Some aluminium atoms are bound to copper atoms, while others are bound to other aluminium atoms, and probably some copper atoms are bound to others copper atoms. The previous considerations suggest that the developing enriched alloy layer alters the local lattice structure of the metal.

The aluminium atoms in the various locations will require different activation potentials for their oxidation and incorporation into the oxide. The altered transient of the etched alloy may relate to oxidation of aluminium atoms at local sites of relatively low copper content, when a low activation potential is sufficient, and at sites of relatively high copper content, where an increased activation potential is necessary. The shape of the peak will depend upon the contribution to the current from oxidation of aluminium at the various sites. Although there is experimental evidence in some voltammograms for two peaks in the overshoot, there may be a range of types of site that contribute to the observed behaviour. The aluminium ions would be generated preferentially from the sites with low activation potential, but these would be more limited as enrichment proceeds, which in broad terms is consistent with the experimental observation of a smaller contribution to the overshoot of the lower potential contributions for longer etching times. However, the experimental data do not reveal a systematic change with time of etching, and in some cases, differences in data occurred for repeated measurements at a single etching time.
The maximum current density in the overshoots of the etched alloys moves to higher potentials with longer times of etching up to the point at which copper can oxidize, when there is no further increase. The magnitude of the potential shift for the etched alloys, about 400-500mV, is very similar to the increase in the open-circuit potential of etched alloys with increasing enrichment of copper in the alloy. The similarity suggests that the potential shift at the open-circuit potential is largely determined by the increase in potential of the anodic reaction due to the enrichment of copper.

4. Conclusions
The initial stages of anodic oxidation of sputtering-deposited Al-0.7at.%Cu alloy in ammonium pentaborate solution is associated with a current overshoot, comprising a single relatively narrow peak over a potential range of about 300mV.

Anodic etching of the alloy in sodium hydroxide solution leads to enrichment of copper in the alloy, which modifies the form of the current overshoot. The overshoot occurs over an extended potential range, approximately 500-700mV, and consists of two or more components.

The differing behaviour resulting from enrichment of copper is suggested to be due to altered bonding of aluminium atoms in the alloy, leading to a range of activation polarization for oxidation of aluminium.

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