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A MICROCHEMICAL STUDY OF SURFACE FILMS ON ALUMINUM ALLOY FOILS FOR AEM

P. J. Lee

To realize the full spatial resolution potential of thin-foil microanalysis one must work at thicknesses below 100 nm. The thinner the foil the greater the proportion of the signal analyzed that is generated by the surface layers. Earlier work has shown that STEM-EDX analyses in thin regions are significantly influenced by such layers.[1-6]

The aim of this study has been to investigate the nature of the surface films produced on aluminum-copper and aluminum-silver alloys so as to develop an understanding of the factors controlling the formation, composition and thickness of the film, and if possible to use this knowledge to overcome its limiting effect on thin-foil microanalysis.

Experimental

The principal study was carried out on an Al-1.45 at.% Cu alloy produced from high-purity Al and Cu, age-hardened so that almost all the Cu was precipitated in the form of $\theta'(CuAl_2)$. Al-0.59 at.% Cu, Al-1.7 at.% Ag, Mg-1 at.% Ag, Ti-1.52 at.% Cu, and commercial Al-Cu alloys were also prepared so as to produce similar precipitation.

A number of electropolishing techniques and conditions were used to prepare thin films of these alloys.[7] The optimum bath-electrolytes and conditions for the Al-1.45 at.% Cu materials were found to be a 50% nitric acid, 50% methanol solution at -20 C and 20 V or with the addition of 2% hydrochloric acid (-25 C and 15 V). After polishing, the foils were immediately rinsed in cold water or methanol and repeatedly washed in methanol and ethanol. Alternative postpolishing treatments included washing in 50% ammonia solution and a more elaborate technique which used a standard cyanide plating solution as an electrolytic etch.

Jet polishing was carried out using 3% perchloric acid (60%), and 32% 2-n-butoxyethanol and 65% methanol solutions at -30 C and 40 V, in both a commercial Tenupol device and a simple laboratory apparatus.

All the specimens were examined in a Philips EM400T TEM/STEM with a single-tilt beryllium holder. Energy-dispersive x-ray microanalysis was carried out in the STEM mode at 100 kV with a spot size of approximately 12 nm. Convergent-beam electron diffraction patterns were used to calibrate x-ray intensities in terms of foil thickness. Analysis areas were selected in the matrix away from grain boundaries and precipitates. If the matrix composition is homogeneous, the contribution to the measured x-ray intensities from this source should decrease linearly with thickness (providing there are no absorption or fluorescence effects). However, the x-ray contribution from a uniform surface layer remains constant, independent of the foil thickness. Thus the effect of a surface layer can be observed by analysis of the specimen at a range of foil thicknesses.

Auger electron spectroscopy was performed at the National Physical Laboratories, Teddington, England. A 5keV primary electron beam was rastered over an area of 0.01 cm^2. The normal sputtering conditions were 2.5×10^{-5} T and an accelerating voltage of 1 kV; the resulting sputter rate was 0.12 nm/min.

Results

X-ray microanalysis in STEM suggested the presence of a uniform and continuous surface layer, enriched in Cu, on all the electropolished θ' Al-1.45 at.% Cu specimens. The

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variation in resulting EDX analyses is illustrated in Fig. 1. The error bars correspond to the 95% confidence limits for the measured intensities. A highly simplified model has been used to generate concentration levels for varying amounts of Cu enrichment so as to gauge the magnitude of the surface enrichment and to ease comparison of different sets of data. The model assumes that the foil is coated with a uniform layer of pure Cu. It can be seen that the enrichment is equivalent to between one and two atomic layers of Cu on each surface and that the enrichment is uniform within the analytical resolution of the probe used.

The θ' precipitate spacing was approximately 200 nm compared with estimated probe sizes of 6 and 12 nm (hence 90% x-ray source diameters of approximately 12 to 22 nm) It was found that such probes could be reliably positioned so that analyses were not influenced by the precipitates. The Tenupol jet-polished specimens exhibited a lower level of enrichment than those prepared in polishing baths. Studies using a range of electrolyte flow speeds indicated that the level of enrichment was between 0.5 and 1 atomic layers of Cu independent of the flow rate. Foils polished in a bath with the jet electropolishing solution were enriched to levels similar to those polished with the other solutions.

It was found that polishing a high-purity Al specimen in a Cu-rich polishing bath could also produce a Cu enrichment. Therefore further jet polishing was carried out by means of a different apparatus that was fed only with clean electrolyte. The results of this experiment are shown in Fig. 2. The enrichment level for the θ' foils was similar to the best Tenupol-produced specimens but in the case of the grossly over-aged specimens containing large θ ($CuAl_2$) precipitates (typically 1000 nm spacing), no enrichment was found.

The AES depth profiles (typical profiles are shown in Fig. 3) reveal that the copper enrichment is localized at the oxide-metal interface. Study of the Cu LMM peak morphology indicates that the Cu is not oxidized but is combined with the Al. The chemical state of the Cu may have been altered, however, by the baking of the AES vacuum chamber (100 C for 4 h). An attempt at studying the foils without baking resulted in the profile shown in Fig. 4 (a). The background pressure in this case was 10^{-8} Torr. The Al is being continuously oxidized. The Cu enrichment was not removed until the vacuum was improved to 10^{-10} Torr by baking of the system. A parallel can be drawn here between the 10^{-8} Torr case and the failure of commercial ion-beam thinners (which rarely have backing pressure of better than 10^{-6} Torr) to remove surface enrichment on aluminum alloys.

The nitric acid-based chemical polish was successful in producing foils apparently free of Cu enrichment. Unfortunately these foils were heavily etched and were otherwise unusable. The phosphoric acid-based chemical polish produced foils similar to those obtained by electropolishing.

Variations in the post-polish washing procedure did not reduce the enrichment. The electrolytic cyanide etch was only partially successful as it was not possible to judge when the surface Cu had been removed and when the specimen itself was being attacked.

STEM-EDX analysis of the foils after sputtering in the AES apparatus at high vacuum gave no indication of surface enrichment.

Of the other systems studied Al-0.59 at.% Cu produced surface layers similar to the Al-1.45 at.% Cu, the Al-Ag had a surface enrichment equivalent to 0.5 atomic layers of Ag on each side, and the Mg-Ag foils were coated with a surface enrichment equivalent to 1 atomic layer of Ag on each surface. Again, AES revealed that the enrichment was localized at the metal-oxide interface. However, no enrichment was discovered on the Ti-Cu alloy foils.

Conclusions

The mechanism of electropolishing requires the presence of a solid oxide layer at the specimen surface.[8-11] By selective oxidation the elements with the lower rates of oxidation (Cu and Ag) may become trapped under those which oxidize at a much faster rate (Al and Mg). This mechanism may also be used to explain the enrichment produced by ion-beam thinning (Fig. 4). Such a situation occurs for some alloys in dry corrosion,[12] where there is a large difference in the oxygen affinity among the constituents or sufficient difference in the diffusivity of the constituents through the oxide. Care must be taken in this comparison, however, as the oxide layer on a foil being electropolished is produced by an acid rather than a gaseous medium and the thickness of the electropolishing oxide, once it has been formed, remains constant during the process. The study of the over-aged specimens (Fig. 2) indicates that the distribution of the alloying element in the foil is also important.

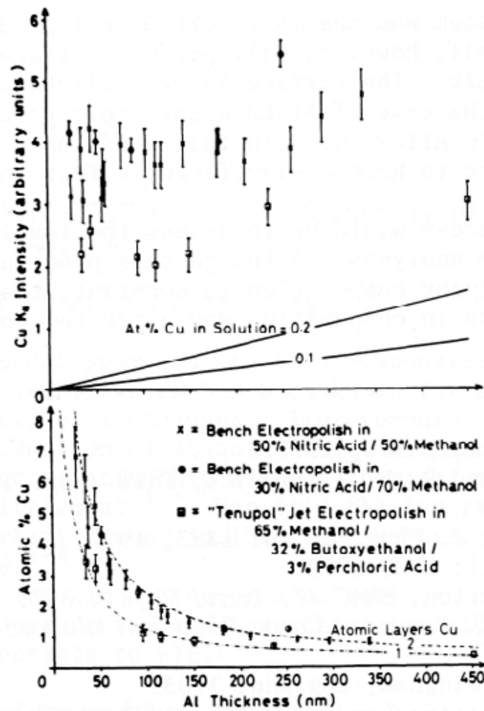

FIG. 1.--Comparison of STEM EDX analyses of three electropolishing conditions for Al-1.45 at.% Cu (θ' condition): (a) normalized Cu Ka intensity vs Al thickness; (b) atomic % Cu vs Al thickness.

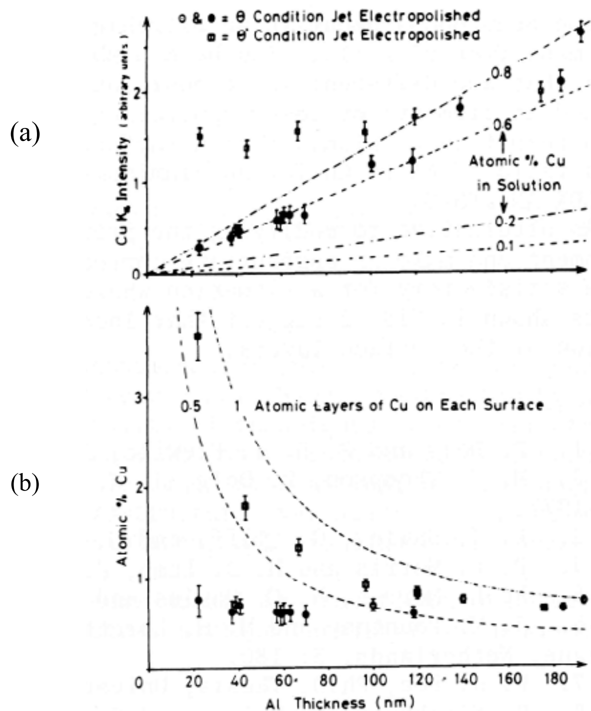

FIG. 2.--STEM-EDX analyses of Al-1.45 at.% Cu foils in θ' and θ conditions jet electropolished in clean electrolyte; 50 V at approximately —60 C.

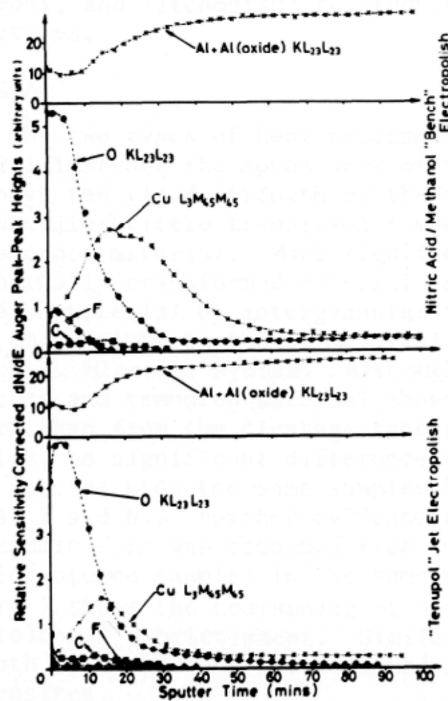

FIG. 3.--Combined AES/argon ion sputter depth profiles of electropolished Al-1.45 at.% Cu (θ') foils: (a) bath electropolished in nitric acid and methanol solution; (b) "Tenupol" jet electropolished in methanol, butoxyethanol, and perchloric acid solution. Estimated profiling rate of 0.12 nm/min.

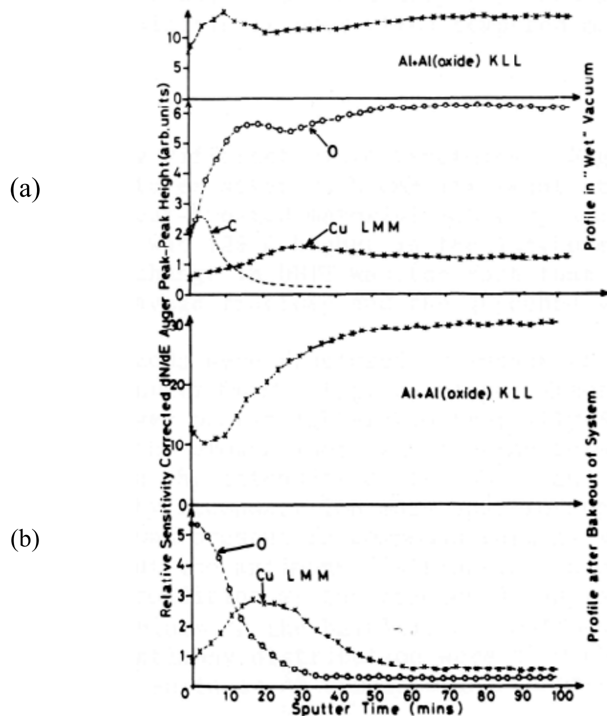

FIG. 4.--Combined AES and Ar ion sputter depth profile of bath electropolished Al-1.45 at.% Cu (θ') foil: (a) background pressure, 10^{-8} Torr; (b) after bake-out of vacuum chamber, background pressure better than 10^{-10}

Ion beam bombardment in an ultrahigh-vacuum system was the only method that produced enrichment-free θ' foils. Ion beam bombardment itself, however, will produce surface layers that are different in composition from the bulk. The surface layers will become enriched in elements of lower sputtering rates; in the case of Al-Cu alloys this process should result in an aluminum-rich surface. The Al-Cu alloys used in this study have too high a ratio of Al to Cu for an aluminum-rich surface to have a significant effect on the STEM-EDX Analyses.

An alternative to modifying the preparation process would be to assess the level of enrichment and make an appropriate correction to the analyses. Although this procedure may be satisfactory for a situation where the underlying composition is constant, the results shown in Fig. 2 suggest that local variations in composition may alter the composition of the surface layers.

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