

# Behaviour of bismuth during simulated processing of model aluminium capacitor foils

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The production of high specification, aluminium-based, electrolytic capacitors requires optimization of material composition and heat and surface treatments in order to maximize the area available for formation of the dielectric, anodic film. Commercial foils contain low additions of copper and lead in order to achieve this goal. The present study examines the effects of heat and surface treatments on aluminium foil containing either 50 or 1000 ppm bismuth, as a replacement for lead, by a combination of Rutherford backscattering spectroscopy and scanning electron microscopy. Heat treatment at 823 K results in segregation of bismuth to the surface regions of the foils, with enrichments in the range  $4\text{--}8 \times 10^{14}$  Bi atoms  $\text{cm}^{-2}$ , localized mainly just beneath the thermal oxide, for the selected treatment conditions. The enrichment reduces following alkaline etching, to the range  $1\text{--}4 \times 10^{14}$  Bi atoms  $\text{cm}^{-2}$ . This level of enrichment is maintained during subsequent anodizing, with the enrichment partitioned between the metal and the outermost layers of the anodic films. The enrichment of the metal is about  $4 \times 10^{13}$  Bi atoms  $\text{cm}^{-2}$ . Electropolishing in perchloric acid solution eliminates the enrichment developed during the heat treatment, probably due to activation during the polishing process. The enrichment remains very low or negligible during subsequent anodizing. The general behaviours of bismuth and lead are similar in aluminium foils subject to the selected heat and surface treatments. However, additional studies are needed of tunnel etching to determine the feasibility of substitution of lead by bismuth in commercial foils.

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## 1. Introduction

The production of aluminium-based electrolytic capacitors uses tunnel etching of the aluminium foil as one stage of the manufacturing process [1]. The aluminium foil, which is approximately 100  $\mu\text{m}$  thick, is first heat-treated to produce grains of about 100  $\mu\text{m}$  size, with the {100} planes parallel to the surface of the foil, and then pre-treated in either an acid or an alkaline bath. The subsequent tunnel etching, using d.c. polarization in chloride-containing electrolyte, results in crystallographic pits, which propagate approximately at right angles to the foil surface, along <100> directions, with occasional orthogonal branching [2]. The pits have an approximately square section, with the section area decreasing slightly with distance from the surface [3]. Finally, anodizing of the tunnel-etched foil forms the dielectric layer on the extensively pitted surface, with resultant devices having greatly increased capacitance

compared with that available from the original foil surface.

The achievement of high specification capacitors requires optimization of the surface area available for growth of the dielectric layer. An important factor in achieving this objective is control of the composition of the aluminium foil. Studies have identified elemental additions that lead to high capacitance devices [4]. For instance, a frequently preferred composition contains 50 ppm (by wt) copper and 0.5 ppm Pb. Although such additions realize enhanced capacitances, there remains uncertainty in the precise roles of the alloying elements. However, the improved distribution of tunnels indicates an influence of the alloying elements on the initiation of tunnel nuclei.

The initiation of pitting in aluminium is generally associated with the presence of flaws in the residual oxide film [5]. The origins of the flaws can be due to physical

factors, for example the presence of scratches, or chemical factors, for example the presence of second phase material. In the case of capacitor foil, it is likely that the alloying elements are particularly influential with respect to the distribution of the latter kind of flaws. Thus, the authors are examining the effects of the various types of pre-treatment on the composition of the surface regions of foils of selected compositions. The first objective of the studies is to determine quantitatively the distributions of alloying elements across the macroscopic surface. Later studies will determine the local influences of alloying elements, especially on the cellular structure of the foils and nucleation of pits during tunnel etching.

The present paper reports results of a range of pre-treatments on the compositions of aluminium foils containing 50 and 1000 ppm (by wt) bismuth. The selected compositions assist analyses of surface regions of foils, although optimum additions of bismuth for capacitor applications are probably a few ppm [4]. Such an element, with a relatively low melting point and low solid solubility (max. 0.2 wt% at 930 K), can segregate to the aluminium surface during heat treatment [6], and hence may affect tunnel-etching behaviour.

## 2. Experimental

### 2.1. Preparation of materials and specimens

Two series of 100  $\mu\text{m}$  thick aluminium foils, with grain sizes about 100  $\mu\text{m}$ , were prepared with nominal bismuth contents of 50 and 1000 ppm respectively. The foils contained additions of copper to 45 ppm, and 10 ppm iron and 10 ppm silicon as impurities, as determined to an accuracy of 0.5 ppm by inductively coupled plasma spectroscopy. The concentration of copper was similar to that in commercial capacitor foils. The foil materials were prepared by melting >99.999% aluminium with separate additions of Al-Bi and Al-Cu mother alloys. The subsequently cast materials were homogenized at 873 K for 7 ks and cold rolled from 15 mm to 100  $\mu\text{m}$  thickness. The foils were later heat treated at 823 K for 20 ks in a vacuum of  $10^{-3}$  Pa, resulting in grains of mainly {100} orientation. The amounts of bismuth in the foils of nominal composition 50 and 1000 ppm, determined by atomic absorption spectroscopy (AAS), to an accuracy within 1 ppm, were 47 and 881 ppm (6.1 and 114 ppm) respectively.

There are about  $3.67 \times 10^{15}$  and  $6.86 \times 10^{16}$  Bi atoms  $\text{cm}^{-2}$  for the foils containing 47 and 881 ppm bismuth respectively, assuming foils of density  $2.7 \text{ g cm}^{-3}$ . If all the bismuth in the foils segregated in equal amounts to each surface of the individual foils during either heat or surface treatments, then about  $1.84 \times 10^{15}$  and  $3.43 \times 10^{16}$  Bi atoms  $\text{cm}^{-2}$  would be present at each surface of the respective foils. In later consideration of results, these quantities are referred to as the amounts of available bismuth.

Specimens of heat-treated foil, of dimensions  $50 \times 10 \times 0.1 \text{ mm}$ , were either alkaline etched for 60 s in 0.25 M sodium hydroxide solution at 348 K or electropolished at 20 V for 120 s in perchloric acid/ethanol (20/80 by vol.) at approximately 278 K. Selected etched and electropolished specimens were anodized indi-

vidually at  $5 \text{ mA cm}^{-2}$  to 150 V in stirred, aqueous 0.1 M ammonium pentaborate electrolyte at 293 K. The voltage-time responses were recorded during anodizing of each foil. The responses for electropolished foil were linear with slopes similar to that for anodizing high purity aluminium at approaching 100% efficiency, namely about  $2.3 \text{ V s}^{-1}$ , under the same conditions. The response for the alkaline etched foil, containing 50 ppm bismuth, also indicated a high efficiency. However, a reduced efficiency, to  $\sim 70\%$ , was revealed for the foil containing 1000 ppm bismuth. The latter material revealed an initial period, to about 20 V, of growth at high efficiency, before the slope diminished.

### 2.2. Specimen examination

Foils were examined by scanning electron microscopy (SEM), using an Amray 1810 instrument equipped with energy dispersive X-ray (EDX) analysis facilities, and by Rutherford backscattering spectroscopy (RBS), using a 2.08 MeV  $\text{He}^+$  beam supplied by the Van de Graaff accelerator of the University of Paris. The beam current and beam diameter were 60 nA and 0.5 mm respectively. Alpha particles were detected at  $165^\circ$  to the direction of the incident beam, and data were interpreted by the RUMP program [7]. Two specimens of the foil containing 1000 ppm bismuth were usually analysed in order to assess the reproducibility of the influences of the various treatments. The individual results are accurate typically to within 10%, mainly due to counting statistics and uncertainty in the background due to pile-up.

## 3. Results

### 3.1. Scanning electron microscopy

In the following section, examples of typical micrographs are presented for the foil containing 1000 ppm bismuth following various heat and surface treatments. The micrographs for the foil containing 50 ppm bismuth revealed similar features, but with the expected reduced numbers of bismuth particles evident in the surface regions.

Cross sections of heat-treated foils, polished to 0.1  $\mu\text{m}$  alumina finish, reveal approximately spherical bismuth particles of about 1  $\mu\text{m}$ , or less, diameter (Fig. 1a). The composition of the particles was confirmed by EDX analysis. The particles are present throughout the thickness of the foil. Plan views of the original surface of the foil reveal rolling lines and bismuth particles, located either at or close to the surface of the foil, with typical separations of 10s to 100s of microns (Fig. 1b).

Alkaline etching of the heat-treated foil resulted in numerous, fine etch pits of approximately square section, and edge dimension about 0.5  $\mu\text{m}$  (Fig. 1c). Rolling features remained, but were less defined due to the loss of material during etching. Larger pits, of approximately circular shape, occur at bismuth particles. The edges of the pits often had straight sections, suggesting local crystallographic attack of the matrix, possibly due to activation. The bismuth particles may also act as local cathodes during etching. Often these larger pits were empty, possibly because the bismuth particles

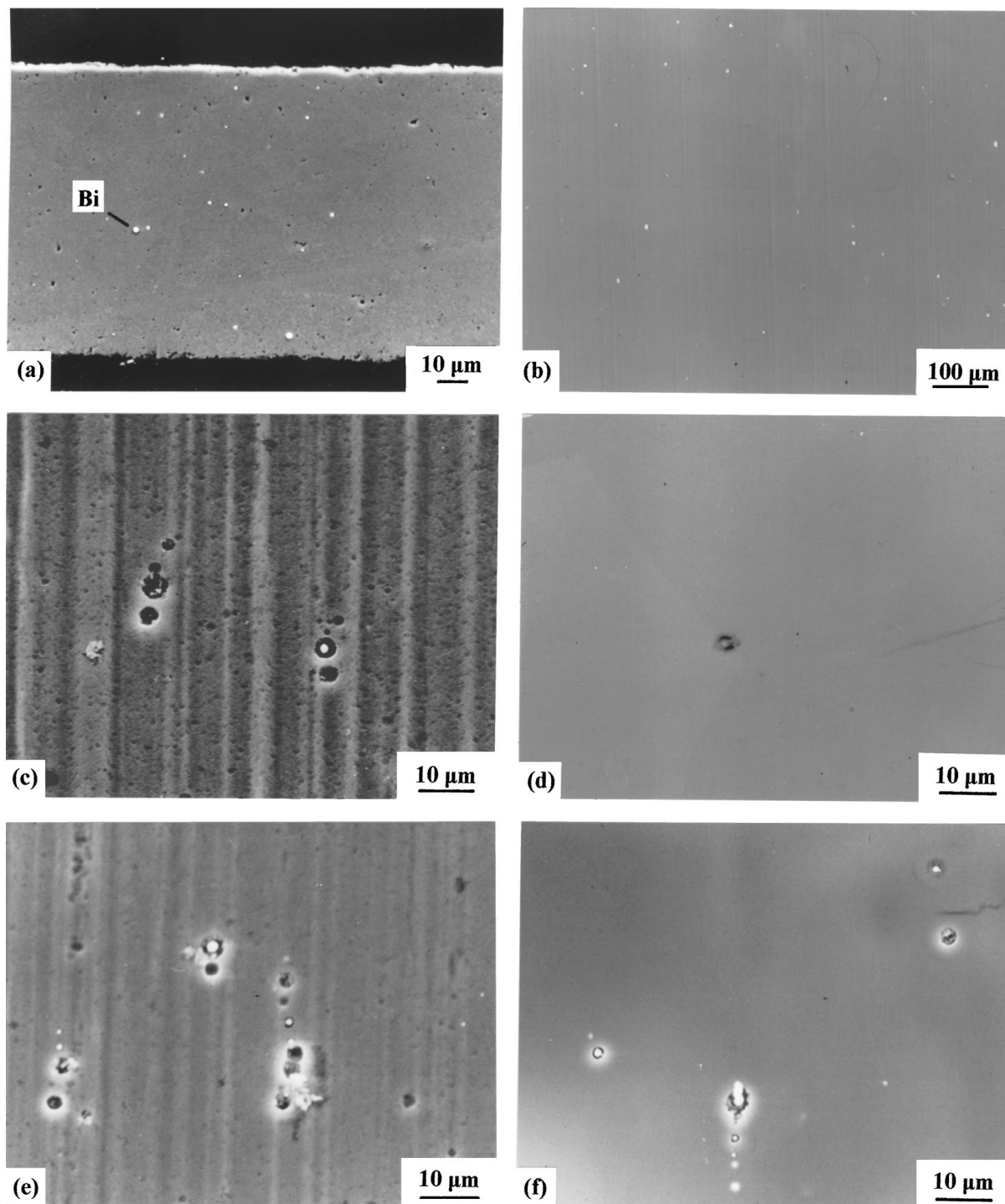


Figure 1 Scanning electron micrographs of the aluminium foil containing 1000 ppm bismuth. Backscattered electron images of the heat-treated foil in (a) section and (b) plan views. Secondary electron images of the heat-treated foil following subsequent (c) alkaline etching, (d) electropolishing, (e) alkaline etching and anodizing and (f) electropolishing and anodizing.

were lost due to undermining by the local corrosion. The particles may also be attacked by the etch solution.

Electropolishing of the heat-treated foil led to a relatively smooth surface, compared with the alkaline etched condition (Fig. 1d). Pits, associated with bismuth particles, similar to those identified following alkaline etching, were occasionally present.

Following anodizing, the features of the etched and electropolished surfaces were retained, although less distinctively due to the growth of the anodic film over the macroscopic surfaces (Fig. 1e and f). Occasional bismuth particles appeared to be located at the surface of the anodized foils. These may be filmed due

to anodizing of bismuth. The particles may also be associated with film cracking and generation of oxygen, which is suggested by the reduction in efficiency of anodizing of the etched and anodized foil containing 1000 ppm bismuth.

### 3.2. Rutherford backscattering spectroscopy

The RBS spectra for the variously treated bismuth-containing foils, here illustrated mainly by representative examples for the foil containing 1000 ppm bismuth, reveal edges due to scattering from aluminium and oxygen at the surfaces of the specimens (Fig. 2a).

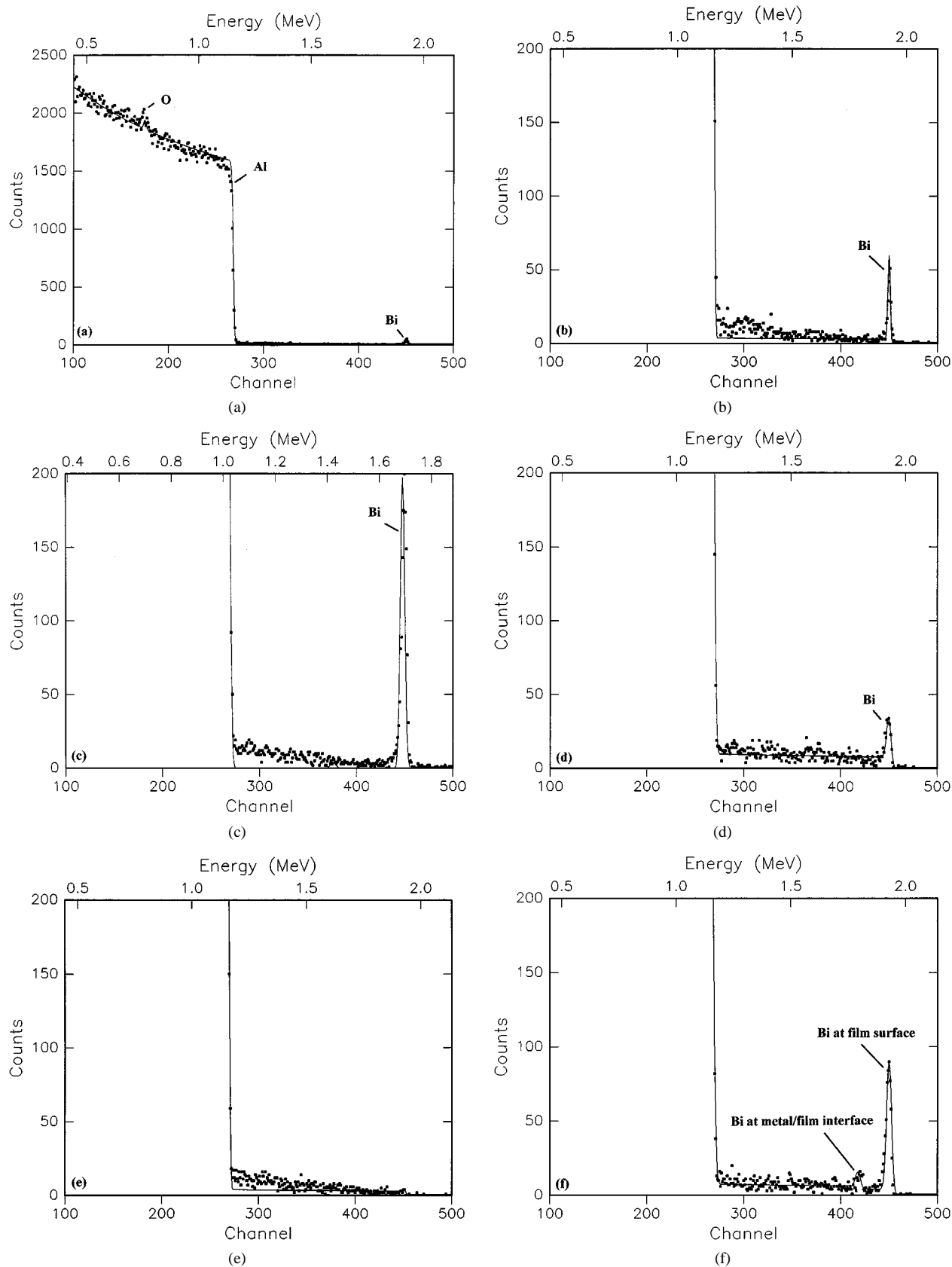


Figure 2 Experimental and simulated (solid line) RBS spectra for aluminium foil containing 1000 ppm bismuth. (a) Hard foil – showing scattering from aluminium and bismuth. (b) Hard foil – showing scattering from bismuth in more detail. (c) Heat-treated foil. (d) Heat-treated and alkaline-etched foil. (e) Heat-treated and electropolished foil. (f) Heat-treated, alkaline-etched and anodized foil.

The oxygen peak in each spectrum is located on the background yield from aluminium in buried layers of the foil. The magnitude of the oxygen peak reflects the thickness of the film developed during each treatment of the foil. The films were less than about 10 nm thick for all specimens, except for the anodized foils,

with films approximately 190 nm thick, and the heat-treated foil containing 1000 ppm bismuth, which had a hydrated layer, about 500 nm thick, as explained later. Steps were evident in the aluminium yield for foils with the relatively thick films, but not for thinner films due to limitations of detector resolution. The film thicknesses

TABLE I Results of RBS analyses of aluminium foils containing either 50 or 1000 ppm bismuth following heat and surface treatments

50 ppm Bi	Bi enrichment (atoms cm <sup>-2</sup> )	Bi atoms cm <sup>-2</sup> at F/E
H	$\leq 1.5 \times 10^{13}$ (0.8)	-
HT	$4.6 \times 10^{14}$ (25.0)	-
HT + E	$3.9 \times 10^{14}$ (21.2)	-
HT + EP	$< 1 \times 10^{12}$ (<0.1)	-
HT + E + A	$3.7 \times 10^{13}$ (2.0)	$4.1 \times 10^{14}$ (22.3)
HT + EP + A	$< 3 \times 10^{12}$ (<0.2)	$< 1 \times 10^{12}$ (<0.1)
1000 ppm Bi		
H	$1.5 - 2.3 \times 10^{14}$ (0.6)	-
HT	$7.8 \times 10^{14}$ (2.3)	$9.2 \times 10^{14}$ (2.6)
HT + E	$1.3 - 2.5 \times 10^{14}$ (0.6)	-
HT + EP	$< 4 \times 10^{12}$ (<0.1)	-
HT + E + A	$4.1 - 4.6 \times 10^{13}$ (0.13)	$1.4 - 4.6 \times 10^{14}$ (0.9)
HT + EP + A	$\leq 9 \times 10^{12}$ ( $\leq 0.03$ )	$< 2.7 \times 10^{13}$ (<0.1)

The following designations identify the treatments of the foils: *H* = hard foil (before heat treatment); *HT* = heat-treated only; *HT + E* = heat-treated and then etched; *HT + EP* = heat-treated and then electropolished; *HT + E + A* = heat treated, then etched and finally anodized; *HT + EP + A* = heat-treated, then electropolished and finally anodized. The numbers in brackets indicate the approximate percentages of the available bismuth. The final column indicates the amounts of bismuth at the film/electrolyte (F/E) interface, which were identified for relatively thick hydrated films and anodic films. For other specimens, the separate enrichments in the metal and overlying thin ( $\leq 10$  nm) films were not resolved.

were derived from fits to the experimental spectra, with the assumption that the ionic density in the films is that of anodic alumina of density  $3.1 \text{ g cm}^{-3}$ .

Most pertinently, the spectra reveal scattering from bismuth nuclei, often in the form of either one or two peaks at high scattering energies (Fig. 2b–f). These peaks arise from bismuth in the surface regions of the specimens, which is of increased concentration relative to the amount of bismuth in the underlying foil material. The yield from bismuth in the immediately underlying foil material is low, with the signal unresolved from the level of the background pile-up. The latter sets an upper limit of 300 appm on the concentration of bismuth.

The foils reveal enrichments of bismuth in the initial condition, i.e. before heat treatment (Fig. 2b), (Table I). The widths of the bismuth peaks are determined by the detector resolution. The enrichments amount to less than 1% of the available bismuth in the foil. A thin film, up to 10 nm thick, covers the foils. The depth resolution of the analyses, about 30 nm, is insufficient to separate distributions of bismuth within the foil and film. Heat treatment enhances the enrichment of bismuth by a factor of about 30 for the foil containing 50 ppm bismuth. The enhancement factor is about 4 for the foil of higher bismuth content (Fig. 2c). For the latter, a  $\sim 500$  nm film was present on the heat-treated surface, which fitting of the spectrum indicated was composed of hydrated alumina of approximate composition  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . The relatively thick layer of hydrated alumina gave a dull grey appearance to the heat-treated foil. Similar hydration occurs with bismuth-implanted aluminium [8], and appears to be due to stimulation of corrosion of the bismuth-rich foil surface in the ambient air. Bismuth was present close to the metal/film interface ( $7.8 \times 10^{14} \text{ Bi atoms cm}^{-2}$ ) and within the

film ( $2.9 \times 10^{15} \text{ Bi atoms cm}^{-2}$ ) with an increased concentration at the surface of the film ( $9.2 \times 10^{14} \text{ Bi atoms cm}^{-2}$ ) (Table I). The total amounts of bismuth in the surface regions of the foils were about 25 and 13% of the available bismuth for the foils containing 50 and 1000 ppm bismuth respectively. The amount for the latter foil includes that in the hydrated layer.

Alkaline etching of the heat-treated foils, containing either 50 or 1000 ppm bismuth, results in an enrichment of bismuth in the approximate range  $1-4 \times 10^{14} \text{ Bi atoms cm}^{-2}$  (Fig. 2d). The enrichment represents about 21% and 0.6% of the available bismuth in the foils containing 50 and 1000 ppm bismuth respectively. The widths of the bismuth peaks are determined by the detector resolution.

Distinct from the result of alkaline etching, electropolishing leaves no detectable enrichment of bismuth, with an upper limit of  $1 \times 10^{12}$  and  $4 \times 10^{12} \text{ Bi atoms cm}^{-2}$  for the foils containing 50 and 1000 ppm Bi atoms  $\text{cm}^{-2}$  respectively (Fig. 2e). Following anodizing, there is evidence of slight enrichment, to about  $1 \times 10^{13} \text{ Bi atoms cm}^{-2}$ , near the metal/film interface for the foil containing 1000 ppm bismuth. The pile-up background sets an upper limit of  $4.7 \times 10^{14} \text{ atoms cm}^{-2}$  for bismuth within the anodic film. The anodized foil containing 50 ppm bismuth revealed no significant enrichments of bismuth in either the foil or the anodic film. In contrast, a low enrichment,  $\leq 9 \times 10^{12} \text{ Bi atoms cm}^{-2}$ , developed in the metal during anodizing of the foil containing 1000 ppm bismuth. Any presence of bismuth species in the anodic film could not be distinguished from the pile-up background.

Contrasting with the electropolished and anodized foils, the alkaline etched and anodized foils revealed enrichments of bismuth near the metal/film and film/electrolyte interfaces, within layers of thickness less than the depth resolution of the analyses (Fig. 2f). The former enrichments correspond to about  $4 \times 10^{13} \text{ Bi atoms cm}^{-2}$  for both compositions of foil. The latter enrichments are in the range  $1-5 \times 10^{14} \text{ Bi atoms cm}^{-2}$ . The films may also contain bismuth throughout their thicknesses. The upper limits are in the range  $2.9 \times 10^{13}-1.1 \times 10^{14} \text{ Bi atoms cm}^{-2}$  for the foils containing 50 and 1000 ppm bismuth respectively. The combined enrichments of the metal/film and film/electrolyte interfaces associated with the alkaline etched and anodized foils amount to about 24 and 1% of the available bismuth in the foils containing 50 and 1000 ppm bismuth respectively.

#### 4. Discussion

The RBS analyses of the two compositions of foil in the initial condition and following the various heat and surface treatments reveal the following behaviours: a low enrichment of bismuth in the initial foil, which is enhanced to  $4-8 \times 10^{14} \text{ Bi atoms cm}^{-2}$  following heat treatment; enrichment to  $1-4 \times 10^{14} \text{ Bi atoms cm}^{-2}$  following alkaline etching; retention of similar enrichments after anodizing of etched foil, with an enrichment of about  $4 \times 10^{13} \text{ Bi atoms cm}^{-2}$  in the metal and the remainder in the anodic film; negligible enrichment,

i.e.  $<1-4 \times 10^{12}$  Bi atoms  $\text{cm}^{-2}$  following electropolishing, with slight enrichment developing during subsequent anodizing. In all cases, the enrichments are low relative to the total quantity of bismuth in the original foils, indicating substantial amounts of bismuth remain within the foils. The analysis of duplicate specimens of foil containing 1000 ppm bismuth reveals that enrichment levels are reproduced within about a factor of 2.

The heat treatment of the foils contributes significantly to the enrichments of the foil of lower bismuth content. A previous study of heat-treated foil revealed by ion microanalysis, that the bismuth enrichment is located just beneath the surface oxide [9]. The subsequent alkaline etching treatment of the present foils results in oxidation of about  $1 \mu\text{m}$  of metal. A metal layer of this thickness contains about  $3.67 \times 10^{13}$  Bi atoms  $\text{cm}^{-2}$ , based on the measured composition of the bulk foil containing nominally 50 ppm bismuth. This amount of bismuth is less than that present after alkaline etching, indicating the significant contribution from the prior heat treatment stage. In the case of the foil containing 1000 ppm bismuth, etching may result in an enrichment of  $6.86 \times 10^{14}$  Bi atoms  $\text{cm}^{-2}$ , which exceeds the measured enrichment. Thus, significant contributions to the measured enrichment may arise from both the heat treatment and etching stages.

The results reveal losses of bismuth following alkaline etching of the heat-treated foils, with a negligible change following subsequent anodizing of the etched foils. However, after anodizing, the enrichment is divided between the metal and the anodic film. A similar division of the enrichment, between metal and film, is probable for the heat-treated and the etched foils, although the depth resolution of the analysis is insufficient to separate the enriched metal and film layers. Electropolishing of the heat-treated foil has a dramatic effect on the level of enrichment of bismuth, reducing it by at least two orders of magnitude.

The behaviour of bismuth during the various treatments of the foils follows expected patterns from studies of influences of alloying elements in other alloys [6, 10]. Thus, heat treatment of binary alloys containing relatively low-melting point additions of low solid solubility causes segregation of the alloying element to the alloy surface, with transport by diffusion from the bulk alloy [6]. The enrichment of binary aluminium alloys by surface treatments such as electropolishing, alkaline etching and anodizing arises from the necessity of establishing a sufficient amount of the alloying element in a layer of alloy about 1–2 nm thick before oxidation of the alloying element can occur [10]. The enriched alloy layer is located immediately beneath the alumina-based, amorphous film developed on the alloy surface by the particular treatment process. The enrichment accumulates during the initial formation of the alumina-based film, free of alloying element species, which leads to consumption of the alloy. Hence, the rate of accumulation of alloying element in the enriched alloy layer is dependent upon the rate of oxidation of the alloy. Alkaline etching, electropolishing and anodizing treatments usually develop such enriched alloy layers whenever the Gibbs free energy per equivalent for formation of

the alloying element oxide is less than that for formation of alumina. These treatments would normally produce similar levels of enrichment in a particular alloy. The thermodynamic data for Bi/Bi<sub>2</sub>O<sub>3</sub> and Al/Al<sub>2</sub>O<sub>3</sub> indicate that significant enrichment of bismuth should occur during surface treatments of Al-Bi alloys [10]. The presumption of formation of units of Bi<sub>2</sub>O<sub>3</sub> during anodizing of the alloy is consistent with formation of amorphous Bi<sub>2</sub>O<sub>3</sub> during anodizing of bismuth [11].

A distinctive feature of the present foils, compared with many other alloys that reveal enrichments, is the absence of a significant amount of enriched bismuth following electropolishing. A similar effect of electropolishing occurs for Al-Pb [12, 13] and Al-Ga [14] alloys, which has been attributed to loss of alloying element by local activation of the surface. The mechanism of activation and the associated loss of alloying elements have not been examined in detail. However, the loss of bismuth from the present foils probably occurs by the same type of process.

The results for the anodized foils suggest an enrichment of about  $4 \times 10^{13}$  Bi atoms  $\text{cm}^{-2}$  is sufficient for the oxidation of bismuth atoms in the two compositions of foil. This is the measured level of bismuth adjacent to the metal/film interface for both compositions of foil. The higher measured enrichments of the alkaline etched foils are probably due to the additional presence of bismuth in the film developed during the alkaline etching treatment. This additional bismuth appears to be retained during the subsequent anodizing of the etched foils, where it is located mainly at the surface of the anodic film. The amount of bismuth at the film surface constitutes no more than the equivalent of a monolayer of Bi<sub>2</sub>O<sub>3</sub>, assuming a uniform distribution rather than formation of islands. The presence of bismuth at the surface of the film is consistent with the stability of Bi<sub>2</sub>O<sub>3</sub> in alkaline electrolytes [15]. The amount of bismuth in the surface region should be enhanced during anodizing, since the low energy of the Bi<sup>3+</sup> - O bond, namely about  $145 \text{ kJ mol}^{-1}$ , relative to that of the Al<sup>3+</sup> - O bond, namely about  $281 \text{ kJ mol}^{-1}$ , favours a higher mobility of Bi<sup>3+</sup> ions, relative to that of Al<sup>3+</sup> ions, in the anodic film [16].

The distribution of bismuth in the enriched layer of metal beneath the anodic film is uncertain. Presuming the enriched layer to be about 1 nm thick, the average concentration of bismuth within the layer is about 6600 appm. This represents factors of about 1080 and 58 increase in bismuth concentration with respect to the initial composition of the foils, containing 50 and 1000 ppm bismuth respectively. However, it is possible that the distribution of bismuth is non-uniform within the enriched layer, with local regions of high bismuth content, possibly involving clusters of bismuth atoms. The anodic oxidation of non-uniformly distributed bismuth would result in non-uniform distributions of bismuth species within the bulk of the anodic film material and possibly also at the bismuth-rich surface region. Such non-uniformities may also be present for heat-treated and for alkaline etched foils.

The behaviour of bismuth in the present foils has strong parallels with that of lead in aluminium foils, which reveal lead enrichments following heat

treatment, alkaline etching and anodising [13] broadly similar to those found for bismuth. Bismuth and lead species are also distributed similarly in the anodic films. Thus, the segregation and enrichment of bismuth resulting from the various heat and surface treatments suggests possible beneficial influences in tunnel etching, akin to the influence of lead.

## 5. Conclusions

1. Heat treatment at 823 K of aluminium foils containing either 50 or 1000 ppm bismuth results in segregation of bismuth to the near surface regions of the foil. The segregation is associated with the relatively low melting point and low solid solubility of bismuth compared with that of aluminium.

2. Alkaline etching of the previously heat-treated foils maintains a substantial enrichment of bismuth, about  $1-4 \times 10^{14}$  Bi atoms  $\text{cm}^{-2}$ , although the amounts of enriched bismuth are less than in the heat-treated foils. The enrichment is associated with accumulations of bismuth both in the film developed by the etching process and in the metal layer immediately beneath this film.

3. Electropolishing of the previously heat-treated foils, in perchloric acid/ethanol solution, leads to elimination of the bismuth enriched-layers, i.e.  $<4 \times 10^{12}$  Bi atoms  $\text{cm}^{-2}$ , probably due to local activation in the electropolishing bath.

4. Anodizing of the alkaline etched foils results in enrichments of bismuth in the metal and at the surface of the anodic film. The enrichment in the metal is about  $4 \times 10^{13}$  Bi atoms  $\text{cm}^{-2}$ . This level of enrichment is probably that required for oxidation of bismuth and hence, is probably similar to the enrichment of the metal during alkaline etching. The total amounts of enriched bismuth in the etched and anodised foil, including enrichments in both the film and the metal, are similar to that associated with the etched foils.

5. Anodizing of the electropolished foils leads to negligible,  $<4 \times 10^{12}$  Bi atoms  $\text{cm}^{-2}$ , or very low,  $\leq 9 \times 10^{13}$  Bi atoms  $\text{cm}^{-2}$ , enrichments of bismuth in

the metal, with no significant amounts of bismuth in the overlying films.

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## References

1. N. F. JACKSON, *Electrocomp. Sci. Technol.* **2** (1975) 33.
2. E. MAKINO, K. TAKEDA, T. YAJIMA, T. SATO and E. SUGANUMA, *J. Met. Finish. Soc. Jpn* **39** (1988) 446.
3. R. S. ALWITT, H. UCHI, T. R. BECK and R. C. ALKIRE, *J. Electrochem. Soc.* **131** (1984) 13.
4. O. IWAO, A. MIZUNO, K. YAMAGUCHI and M. MEHATA, *Jpn Pat.* 501, 249 (1987).
5. J. A. RICHARDSON and G. C. WOOD, *Corros. Sci.* **10** (1970) 313.
6. E. D. HONDROSS, *Scr. Metall.* **14** (1980) 345.
7. L. R. DOOLITTLE, *Nucl. Instrum. Meth.* **B9** (1985) 344.
8. A. JARANY, MSc Dissertation, University of Manchester Institute of Science and Technology, 1980.
9. K. ARAI, T. SUZUKI and Y. ATSUMI, *J. Electrochem. Soc.* **132** (1985) 1667.
10. H. HABAZAKI, K. SHIMIZU, P. SKELDON, G. E. THOMPSON, G. C. WOOD and X. ZHOU, *Trans. Inst. Met. Finish.* **75** (1997) 18.
11. I. MASON and L. YOUNG, *Can. J. Chem.* **44** (1966) 2409.
12. Z. ASHITAKA, G. E. THOMPSON, P. SKELDON, G. C. WOOD, H. HABAZAKI and K. SHIMIZU, *J. Electrochem. Soc.* **146** (1999) 1380.
13. *Idem.*, *ibid.* **147** (2000) 132.
14. N. MARGADANT, P. SKELDON, M. TEXTOR, G. E. THOMPSON, J. WAN, H. HABAZAKI, K. SHIMIZU, N. D. SPENCER and G. C. WOOD, *Corros. Sci.* **42** (2000) 405.
15. M. POURBAIX, "Atlas of Electrochemical Equilibria in Aqueous Solutions," National Association of Corrosion Engineers (Houston, TX, 1974).
16. K. SHIMIZU and K. KOBAYASHI, *J. Surf. Finish. Soc. Jpn* **46** (1995) 402.

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