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A contribution to the understanding of a.c. anodizing of aluminium

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Commercial aluminium has been anodized in 10% v/v sulphuric acid using alternating current. At 20 V no significant differences in colour and thickness between specimens anodized at the neutral and live terminals were detected. At higher voltages the oxide on the neutral specimens was always more yellow and thinner than that on the live specimens. The colouration was attributed to the reduction of sulphate to sulphide during the cathodic half-cycle, no other sulphur-containing species being detected by XPS. EPMA has shown that the total sulphur distribution across the film was practically uniform and independent of the operating conditions, except in thin films, where it was greatest at the free surface. With additions of ferric sulphate to the solution the reduction to sulphide was inhibited and the differences between live and neutral specimens were avoided. The total amount of sulphur remained unchanged at approximately 5% weight and no iron was incorporated in the film.

1. Introduction

The anodizing of aluminium using an alternating current (a.c.) is a process that, although known for over 50 years, has never reached the industrial importance of d.c. anodizing. The sulphuric acid solution is the most widely used but one of its problems is the occurrence of yellow discolouration that renders the workpieces unsuitable for decorative purposes. The colour is due to the incorporation of sulphur, either in the form of sulphide or elemental sulphur [1], as a result of reduction of sulphate ions during the cathodic half-cycle. This difficulty can be overcome by the use of suitable modifying agents, which normally consist of salts of transition metals, e.g. ferric ammonium oxalate, ferric sulphate, chloride or nitrate, nickel sulphate and also sodium sulphate.

The chemical species responsible for the yellow colouration of the anodized films has not been positively identified but early analysis by Cook [2] indicates that about 60% of the total sulphur is present as sulphide. The possibility of sulphur being in other oxidation states cannot be excluded. The distinction between them can be easily recognized by X-ray photoelectron spectroscopy (XPS) but until recently only Treverton and Davies [3] have employed it for this purpose. Although their results indicate that, apart from sulphate, only sulphide is present, the use of ion bombardment to profile through the film could have resulted in the decomposition of sulphate thus casting some doubts on the validity of the findings.

The action of solution modifiers in preventing the reduction of sulphate can be interpreted as either: (i) providing an alternative cathodic reaction; (ii) depolarizing the hydrogen evolution reaction, thus increasing the rate of hydrogen evolution and in this way decreasing the need for sulphate reduction; (iii) preventing the electrode potential from dropping below the equilibrium potential for the reduction process. Experimental distinction between these mechanisms has not yet been achieved.

The understanding of the process involved is rendered even more problematic by the lack of fundamental electrochemical studies under alternating current. Some solution modifiers used in a.c. electrolytic colouring, e.g. nickel [4] and silver [5] salts, show clear signs of reduction of the cation within pores formed by d.c. anodizing. The pattern of distribution of the solution modifiers used in a.c. anodizing has not been reported, and although some ions like Fe^{2+}, Fe^{3+} or Ni^{2+} can be reduced during the cathodic half-cycle, the mechanism by which Na^+ (or the associated anion) acts [6] must be a non-reductive reaction in normal aqueous electrolysis.

The main objectives of the present investigation were threefold: (i) to investigate the patterns of sulphur distribution; (ii) to establish the oxidation state of the species responsible for the yellow colouration; (iii) to determine the extent of incorporation of solution modifiers in the oxide.

The basic unmodified solution was 10% vol. H_2SO_4 to which ferric sulphate was subsequently added. The

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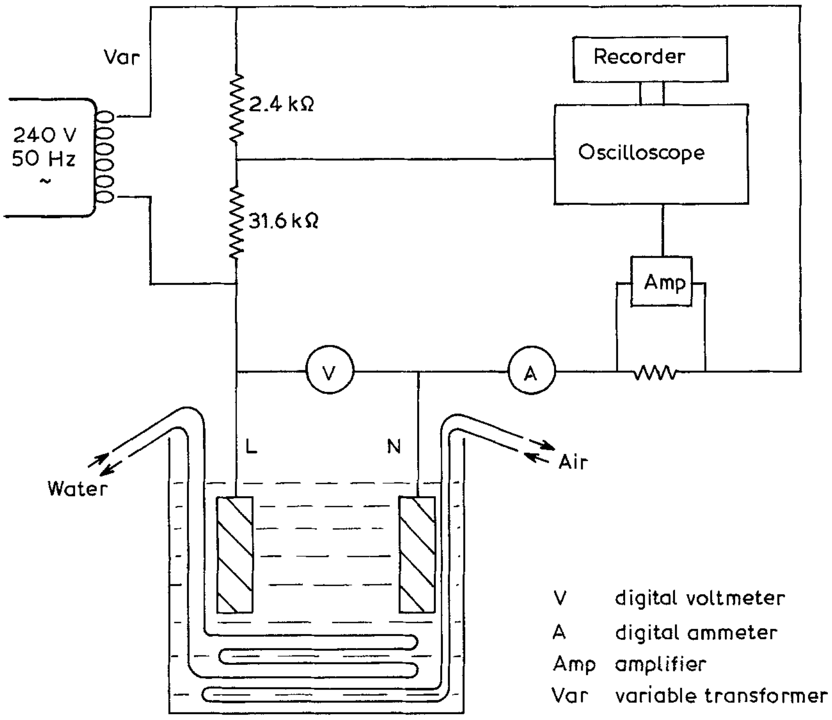

Fig. 1. Experimental arrangements and circuitry for a.c. anodizing.

above concentration of H_2SO_4 appears most suitable [7], and ferric ions are normally considered the most effective modifiers [8, 9]. Ferric sulphate was used in order not to introduce other extraneous anions. The composition of the oxides was determined by electron microprobe analysis, Auger and XPS techniques. In the XPS studies the composition through the oxide was determined by using an abrasion method that removed controlled amounts of oxide, as described later. The aim was to prevent decomposition of sulphate that might occur during ion bombardment. Carbon replicas of the oxide surfaces were examined on a TEM.

2. Experimental details

Commercial quality aluminium sheet (type 1080), 1.0 mm thick, was used in the investigation. Test strips 10 × 100 mm were cut from this material, were degreased in acetone and chemically polished in a 70% H_3PO_4 + 20% H_2SO_4 + 10% HNO_3 (v/v) + 5 $g l^{-1}$ $Cu(NO_3)_2$ solution at 80°C for 40 s. Subsequently, they were thoroughly rinsed in running water and further cleaned by immersion in a 30% (v/v) HNO_3 solution followed by rinsing with water and alcohol. Electrical contact was made to the specimens by bending and tightly clipping one end to a copper electrical wire, the area of the contact being covered with PTFE tape. Finally a protective lacquer (Lacomit) was painted over the PTFE tape and down to half the length of the specimen giving a total electrode area of 10 cm^2.

Two specimens were anodized simultaneously, being kept at a distance of 60 mm. In order to avoid burning of the aluminium at the water line the specimens were immersed in the electrolyte to about two thirds of their length. One side of the original material had a mirror finish and in each test the sides with this finish were placed facing each other. It was found during the tests that no significant differences in thickness existed between both sides of the same sample, indicating that the 'throwing power' of the solution was good.

The anodizing solution consisted of 10% (vol.) H_2SO_4 prepared with SLR grade sulphuric acid and de-ionized water. Ferric ions, in two concentrations, 3 and 10 $g l^{-1}$, were added in the form of Analar grade $Fe_2(SO_4)_3 \cdot 9H_2O$. The experimental arrangement is given in Fig. 1. The anodizing experiments were carried out in a plastic tank containing 18 l of solution which was continuously agitated with a stream of air bubbles coming from four plastic tubes perforated at regular intervals and placed at the bottom of the tank. Cooling could be carried out be passing tap water through a lead coil placed at the periphery of the bath. All the tests were conducted at a temperature of 20 ± 1°C.

A variable transformer (Variac, 0–270V, 15 A max.) was used to control the applied voltage, the current being derived directly from the mains (50 Hz). The minimum voltage was 20 V, below which film growth was very slow in the unmodified solution. Current and voltage were monitored with two multi-meters (Thandar TM 355). In some experiments a dual channel digital storage oscilloscope (Gould OS 4200) was connected to a dual pen recorder to obtain voltage and current traces. The latter was recorded by measuring the voltage drop across a high precision 1 Ω resistor placed in series in the circuit.

The specimens were immersed in the bath with the voltage at 0 V, in order to avoid the occurrence of burning. Over a short period (typically 10 s) the

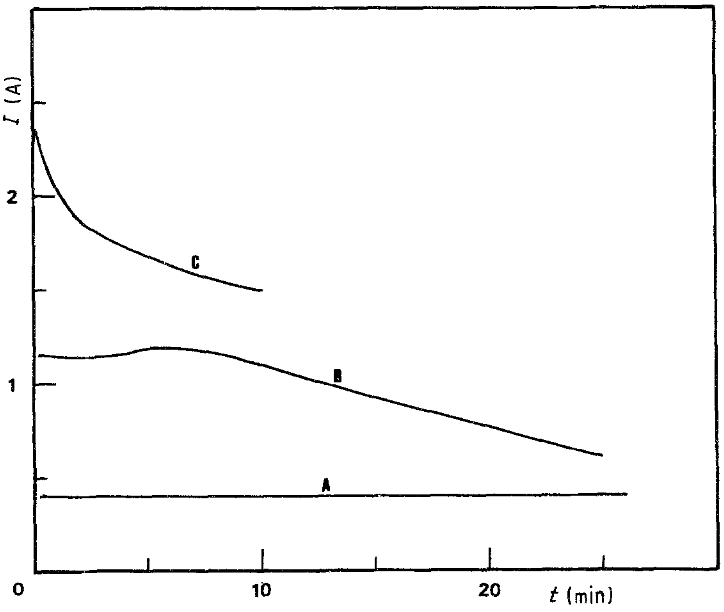

Fig. 2. Current–time curves in unmodified solution: (A) 20 V; (B) 25 V; (C) 40 V.

voltage was increased to the desired value. At the end of the tests the voltage was rapidly turned down to 0 V and the specimens were washed with cold running water and rinsed in alcohol. The thickness of the oxide on each specimen was measured at three points on each side with a Permascope type EW8 (Fischer Instrumentation). In most cases the thickness was quite uniform but those films that had been grown at the highest voltages, i.e. at the fastest rates, were normally 10% thicker at the bottom than at the top: this is presumed to result from uneven agitation along the specimens.

Some specimens were selected for the analytical work with an electron microprobe (Cambridge Microscan 5), Auger (Varian) and XPS (VG Escalab) spectrometers. The specimens for the microprobe were mounted in an epoxy resin (Araldite), at right angles to the surface to be polished. The analysis was carried out on both sides of the anodized sheet at a voltage of 25 kV and a beam current of 0.2×10^{-7} A. The concentrations of Al, S and Fe (in this case only for those specimens anodized in modified solutions) were measured. The amounts of sulphur and aluminium were calculated using ZnS and pure Al as standards, respectively, and the results were corrected using the NBS (COR2) programme [10]. The XPS analyses were obtained at various depths after abrading the oxide with 180 grit SiC paper under a dry nitrogen atmosphere in a glove box placed adjacent to the entrance chamber of the instrument. The amount of film removed before each analysis was estimated by measuring the thicknesses of the remaining oxide, using the Permascope inside the glove box. (Abrasion and thickness measurements were carried out under a dry nitrogen atmosphere to minimize the oxidation of the sulphur species with low oxidation numbers.) The XPS spectra were recorded using aluminium K_α radiation. Compositions were determined using relative sensitivity factors derived from chemical standards. Binding energies were referenced to surface carbon at 284.6 eV. The Auger electron spectra (AES) were obtained using a primary electron beam of 3 keV, 1 μA and a spot size of ca 250 μm. The samples were sputtered by argon ion bombardment (3 keV, 75 μA cm^{-2}).

Direct carbon replicas of the surface were examined in a TEM (Jeol JEM 100 CX). Prior to replicating the surface some specimens were bent in order to crack the oxide, hence allowing a short cross-section of the film to be observed.

3. Results and discussion

3.1. *Current–time curves*

Figures 2 and 3 give the evolution of current with time, respectively, for unmodified and modified solutions. In both cases the current remains constant for long periods of time at 20 V (the lowest voltage

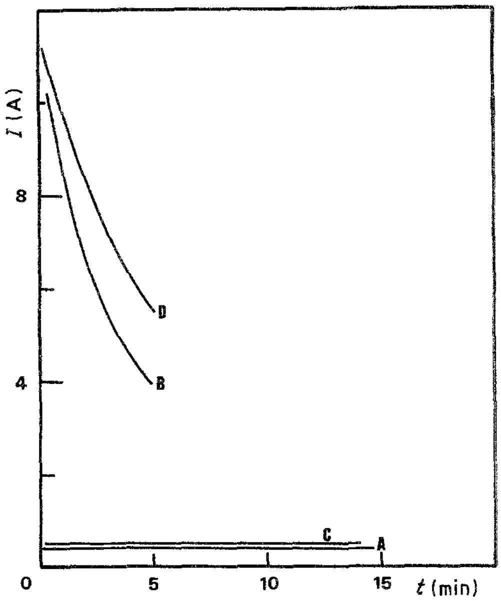

Fig. 3. Current–time curves in modified solutions; (A) 3 g l^{-1} Fe^{3+}, 20 V; (B) 3 g l^{-1} Fe^{3+}, 30 V; (C) 10 g l^{-1} Fe^{3+}, 20 V; (D) 10 g l^{-1} Fe^{3+}, 30 V.

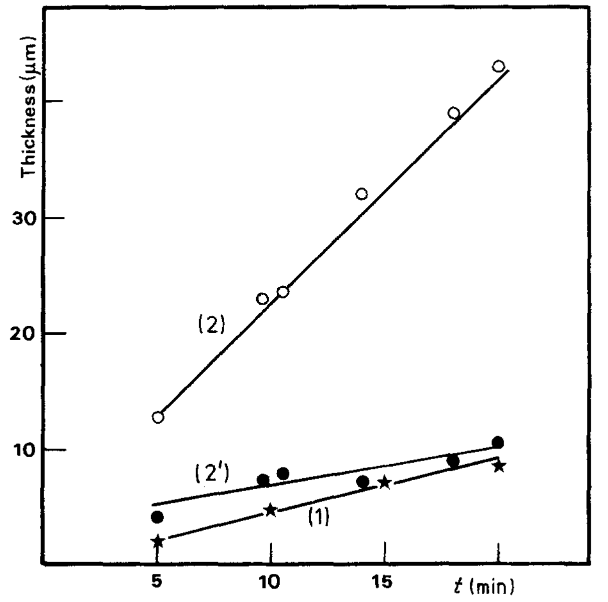

Fig. 4. Variations of thickness with anodizing time in unmodified solution for neutral (N) and live (L) specimens: (1) 20 V, L and N specimens; (2) 40 V, L specimens: (2′) 40 V, N specimens.

used). For higher voltages a decrease, similar to that reported by Gabe [9, 11] is found. The constancy of the current is probably associated with a process of growth that does not necessarily involve a significant increase in resistance of the oxide layer. The growth rate at 20 V was found to be constant, as expected from results obtained under fixed current conditions [12]. The growth rate was relatively low (ca 1 μm min^{-1}) but thicknesses of the order of 30 μm could be produced without the current showing any tendency to fall. This is indicative of a low electrolyte resistance with the pores. The behaviour of the current at the higher potentials probably reflects an increase in resistance within the pores resulting from the more rapid growth kinetics of the oxide. It is worth noting that the rate of current decay is higher in the modified than in the unmodified solutions which agrees with the fact that thick films can be produced faster in the former [11]. In unmodified solutions at 40 V the specimens connected to the neutral terminal were consistently yellower and had a thinner oxide than those connected to the live, whereas at 20 V no differences were found. This can be seen in Fig. 4, which gives the variation of thickness with time at 20 and 40 V. This behaviour was totally unexpected but consistently reproduced under experimental conditions used. The imbalance in film growth rate and colouration were maintained for long periods of time and only after prolonged anodizing (typically 30 min at 40 V) was this tendency reversed. The possibility of the lead piping used for cooling the cell creating earth loops was excluded in a separate group of experiments in which the bath was not cooled.

To elucidate the causes for these differences, the current was monitored with an oscilloscope. Figure 5 gives traces recorded at 30 s, 60 s and 45 min for $V = 40$ V. At 30 s, although some rectification is apparent, on crossing the zero line no difference is noticed between both cycles. At 60 s, however, the current flowing from neutral to live in the half-cycle marked A is lower than the current flowing from live to neutral in the following half-cycle (marked C). This implies that a higher anodic current is passing through the live specimen than through the neutral, thus explaining their relative thicknesses. At 45 min, a deliberately long time, not employed in any other anodizing tests, an interesting phenomenon has occurred as indicated in Fig. 5c. The neutral specimen is now being anodized faster than the live. This inversion in anodizing tendency was confirmed in several other experiments and through thickness measurements. No difference between the positive and negative half-cycles was detected at 20 V for unmodified solutions and at any voltage in modified solutions. In all experiments voltage and current were in phase. From traces similar to those of Fig. 5, graphs showing the evolution of the anodic and cathodic maximum currents with time were drawn. They are given in Fig. 6 for two voltages, 20 and 40 V, in the unmodified solution. This figure shows that at 40 V the inversion in anodizing tendency occurs at ca 25 min, with the higher anodic currents passing through the specimens connected to the neutral terminal after this time. For 20 V this current is identical in both cycles and starts dropping only after 30 min.

The average currents in each half-cycle were calculated from the oscilloscope traces obtained in unmodified solution, by graphic integration of the I–t curves and dividing the charges by the duration of a half-cycle. The absolute values of the anodic and cathodic currents calculated in this way were then used to calculate the mean current flowing in a complete cycle $|I|_{\text{mean}}$. This current is plotted in Fig. 7, together with the readings from the current meters. For a perfect sinusoidal wave, the latter read the root-mean square of the current I_{rms}, but when the shape of the wave changes the reading has no straightforward meaning. The relationship between $|I|_{\text{mean}}$, represented in Fig. 7, and I_{rms} can be deduced considering that for one half-cycle

$$I_{\text{mean}} = \frac{2}{\pi} I_{\text{max}} \tag{1}$$

where I_{max} is the maximum current attained in a particular half-cycle.

Since

$$I_{\text{rms}} = \frac{I_{\text{max}}}{\sqrt{2}} \tag{2}$$

then

$$I_{\text{rms}} = 1.1 I_{\text{mean}} \tag{3}$$

or, for a perfect sinusoidal wave

$$I_{\text{rms}} = 1.1\ |I|_{\text{mean}} \tag{4}$$

This implies that if the waves were perfectly sinusoidal I_{rms}, read on the meter, should be only 10% higher than $|I|_{\text{mean}}$, calculated by the method described above. Figure 7, however, shows that at 20 and 40 V

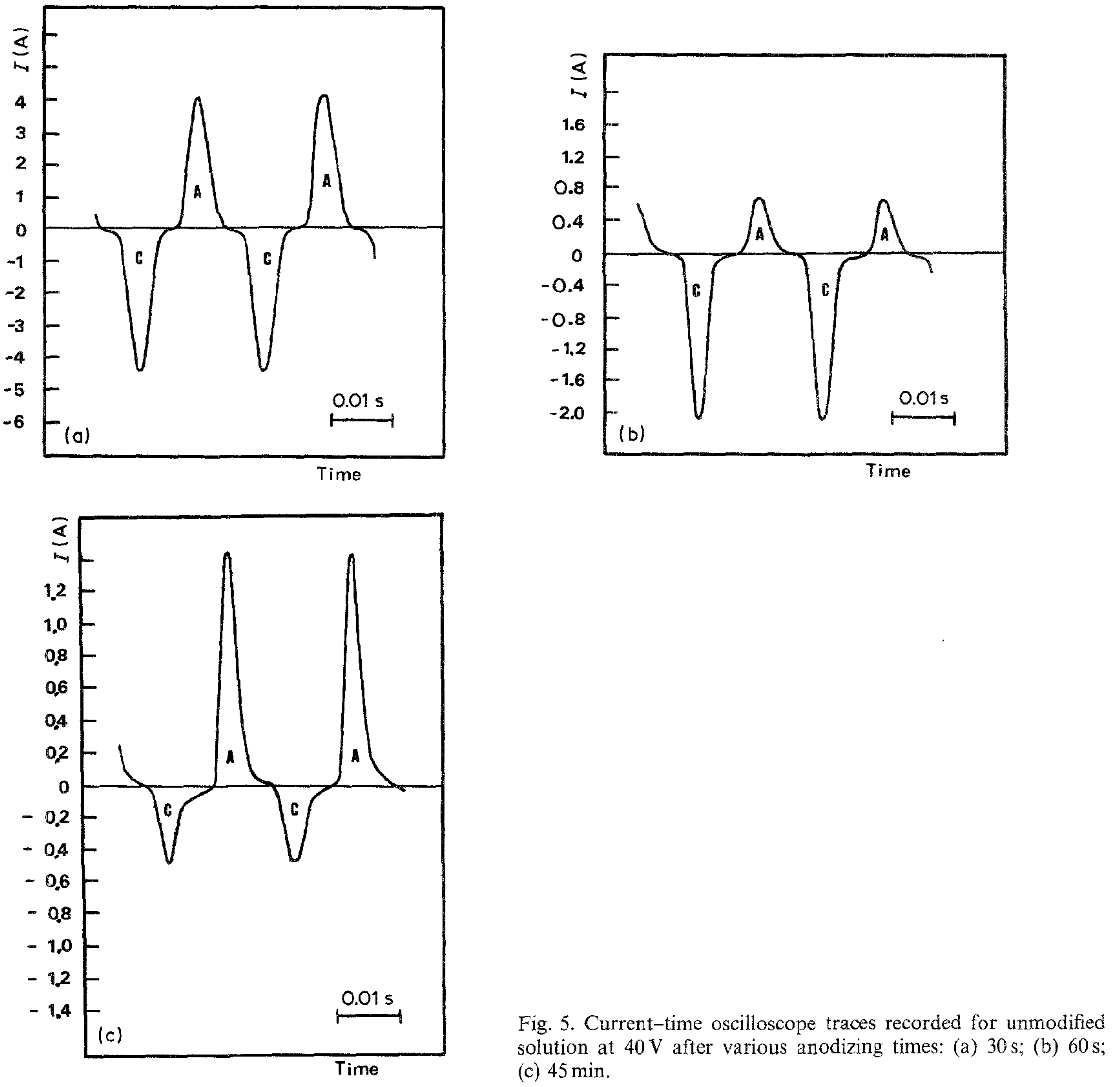

Fig. 5. Current–time oscilloscope traces recorded for unmodified solution at 40 V after various anodizing times: (a) 30 s; (b) 60 s; (c) 45 min.

the currents read on the meter are respectively 4 and 5 times higher than $|I|_{\text{mean}}$. The possibility of instrumental errors can be ruled out on the account that the equipment was first calibrated with sinusoidal current inputs. If the results in Fig. 7 are accepted the implication is that the current actually used in the a.c. anodizing process is significantly lower than that indicated by normal current meters.

The above observations were made with unmodified solutions but in those with ferric ions a similar effect was found. Table 1 indicates that I_{meter} can be substantially higher than I_{rms} calculated from Equation 2, the difference increasing with an increase in applied voltage. Their ratio is nearly as high as 8 at 25 V. In modified solutions, the waves were symmetrical but not sinusoidal and this has resulted in large differences.

*Table 1. Comparison between the currents read on a current meter, I_{METER}, and I_{RMS} *Modified solution (10 g l^{-1} Fe^{3+})*

Applied voltage (V)	I_{meter} *(A)*	I_{max} *(A)*	$\frac{I_{\text{meter}}}{I_{\text{rms}}}$
10	0.07	0.03	2.3
15	0.17	0.045	3.8
20	0.68	0.17	4.0
25	4.13	0.75	5.5

*I_{rms} was calculated from the maximum current recorded on a digital storage oscilloscope, I_{max}.

3.2. *Electron microprobe analysis*

The interest in this part of the work was to establish whether the sulphur distribution in the yellow specimens was any different from that found in the non-yellow ones. Figure 8 shows two sulphur composition profiles recorded for two specimens anodized at 40 V. The oxide thickness on the live specimen (Fig. 8a) was 48 μm, whereas on the neutral specimen (Fig. 8b) it was only 7 μm. The sulphur concentration is smaller on the latter in spite of its yellow colouration being stronger. The lower sulphur level could be associated with poor resolution of the electron microprobe beam but since this is of the order of 1 μm the above result represents a genuine decrease. In other similar comparisons the sulphur levels were also approximately identical and the amounts present on the yellower specimen were never higher than those found on the other one. For films thicker than about 10 μm the percentage of sulphur was approximately constant all across the oxide, as seen in Fig. 8 for the live specimen.

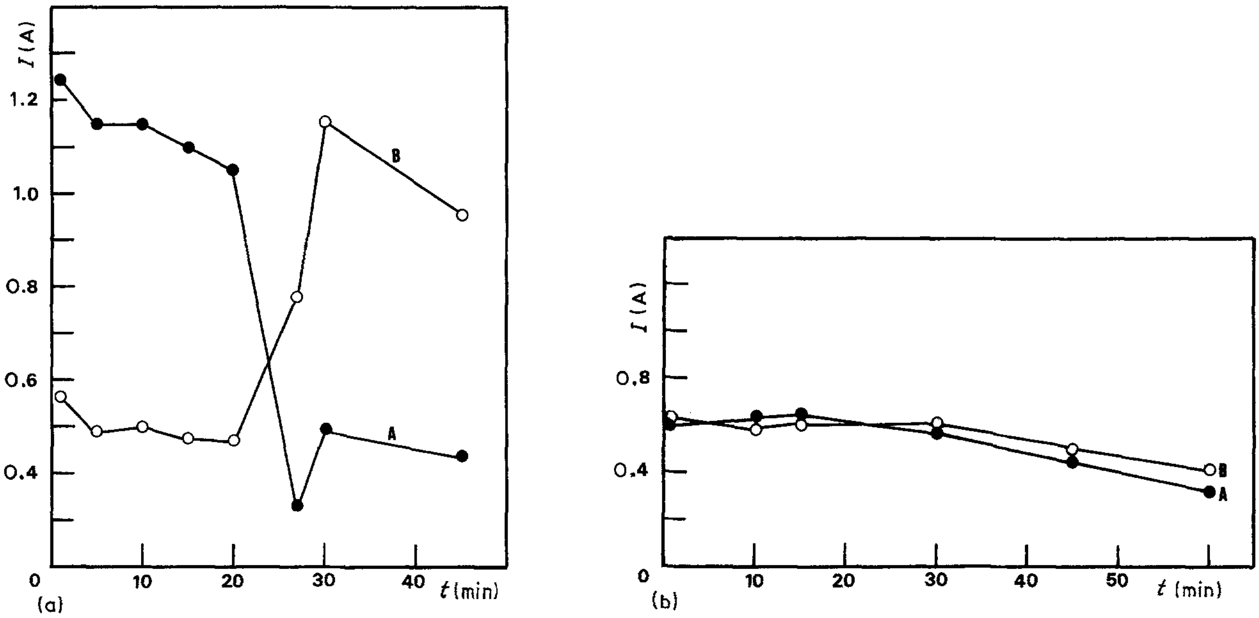

Fig. 6. Evolution of the cathodic (A) and anodic (B) peak current with time of anodizing obtained from oscilloscope traces similar to those given in Fig. 4: (a) 40 V; (b) 20 V. Unmodified solution.

The sulphur content for low voltages was no different from those obtained at higher voltages. The addition of iron did not change the amount and the pattern of sulphur distribution, as illustrated in Fig. 9 for a concentration of 10 g l^{-1} of Fe^{3+} and an applied voltage of 20 V. In the same figure is also represented the variation of the iron content across the film, which does not increase above the background level of the metallic substrate. In every case there was, in fact, a continuous decrease of iron from the metal interface to the solution interface as indicated in Fig. 9. Identical contents were detected within films formed in iron-free solutions.

The results of the microprobe analysis obtained under various experimental conditions are summarized in Table 2. The differences between the aluminium and sulphur contents are too small to legitimately ascribe them to the variations in the anodizing conditions – if anything there is more sulphur in the live than in the neutral specimens. Furthermore, there is no direct correspondence between the aluminium and the sulphur contents, high percentage of one corresponding sometimes, but not always, to high percentage of the other.

3.3. *XPS and Auger electron spectroscopy (AES)*

The sulphur contents estimated from XPS measurements are in reasonable agreement with those obtained from EPMA, as seen in Table 3. The only

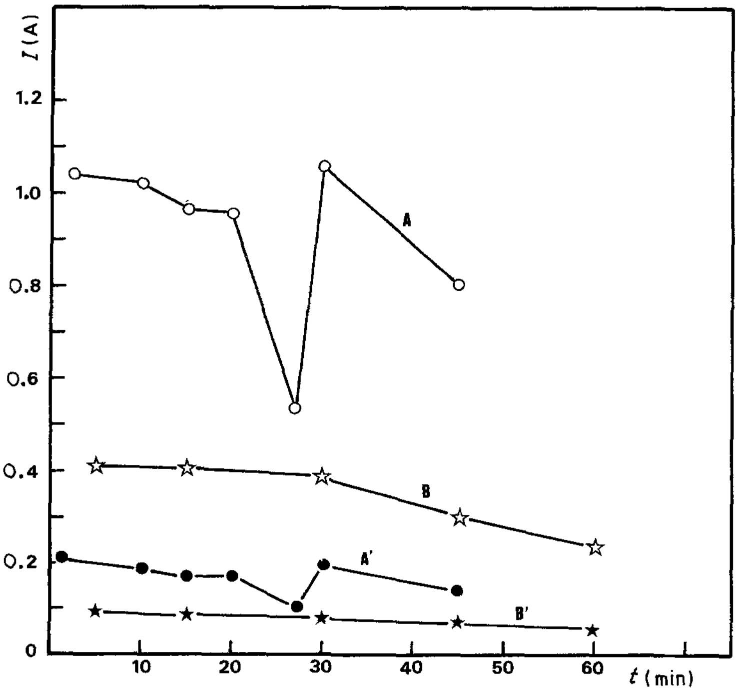

Fig. 7. Variation of the calculated, $|I|_{\text{mean}}$, and measured, I_{meter}, currents as a function of time for two anodizing voltages. (A) I_{meter}, 40 V; (A′) $|I|_{\text{mean}}$, 40 V; (B) I_{meter}, 20 V; (B′) $|I|_{\text{mean}}$, 20 V. Unmodified solution.

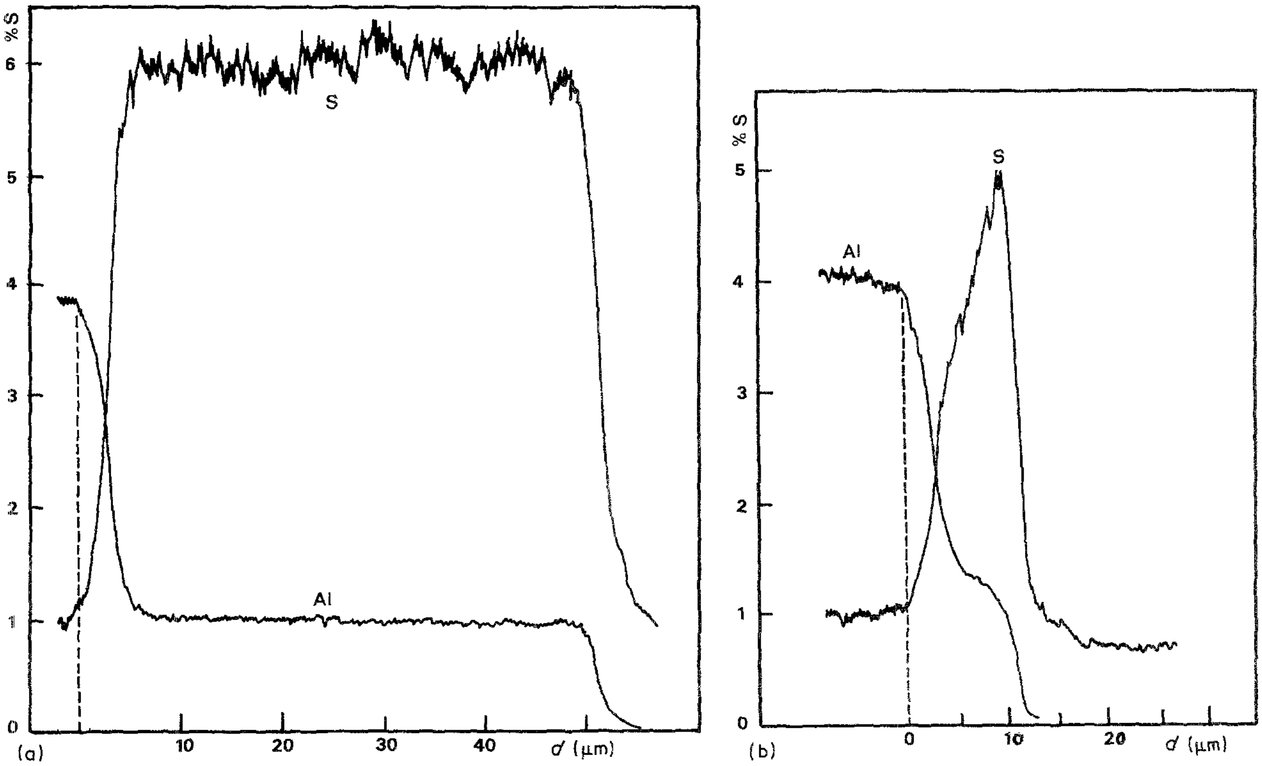

Fig. 8. Sulphur and aluminium distribution across anodic films produced in unmodified solution at 40 V during 15 min: (a) live terminal; (b) neutral terminal. The distance is measured from the Al–oxide interface. EMPA results.

sulphur species found in films with a yellow colouration were sulphide and sulphate, as indicated in the XPS spectrum of Fig. 10 obtained on a specimen anodized at 25 V for 30 min. In this case the proportion of sulphur present as sulphide is considerable, of the order of 30%. All the films produced in unmodified solutions, even those without an apparent discolouration, had some quantity of sulphide present. For example, Fig. 11 compares the amounts of sulphide present in two films obtained in unmodified solution, one slightly yellow (curve A) and the other with a normal appearance. Whereas the former contains 30–40% of sulphur as sulphide the latter shows a maximum of 20% near the air interface which rapidly drops down to 5% at half thickness. The low sulphide content of the yellow film found near the interface is probably the result of oxidation to sulphate due to exposure to air. Even in thin films, with thicknesses of the order of 1 μm, grown at low voltage (20 V), sulphide was present. It amounted to about 15% of the total sulphur.

Table 2. Composition (wt %) of anodized films for various experimental conditions (epma results)

Solution	*Voltage V*	*Time min*	*Polarity*	*Al*	*S*
Unmodified	20	30	live	38.8	4.8
	30	5	live	41.5	5.6
	30	5	neutral	38.6	5.9
	30	10	live	41.0	6.0
	30	10	neutral	39.3	6.1
	40	15	live	37.1	4.8
	40	15	neutral	36.1	6.2
3 g l^{-1} Fe^{3+}	20	30	live	37.5	4.4
	30	1	live	34.7	4.8
	30	5	live	34.6	4.9
10 g l^{-1} Fe^{3+}	30	1	live	35.1	5.0
	30	5	live	35.0	6.1

No sulphide was detected after anodizing in modified solutions, both for 3 and 10 g l^{-1} ferric sulphate, at the highest voltage used (30 V). At this voltage film growth was already very rapid, with thicknesses of the order of 60 μm being attained in 5 min. This very rapid growth frequently results in cracking of the oxide and, therefore, using higher voltages was considered to be impractical. Analysis for iron in these films indicated its absence, both on the top surface and at various depths. XPS and Auger techniques were totally coincident in this respect. This absence of iron, even from the top surface, is surprising since it was expected that some solution would be entrapped within the pores. Furthermore, as no particularly stringent method of cleaning was used, for example ultrasonic agitation, the species present in the anodizing bath should remain to some extent absorbed on the outermost surface, hence being available for detection by sensitive surface analysis techniques like XPS and Auger spectroscopy. Only one specimen showed some iron on the outer surface ($\sim$0.3 at. %) but after removing 12 nm of oxide the Auger iron signal had dropped to zero. This observation is more likely to correspond to inadequate cleaning than to incorporation of iron into the oxide.

3.4. *Transmission electron microscopy*

Tentative attempts to study the pores on the anodized

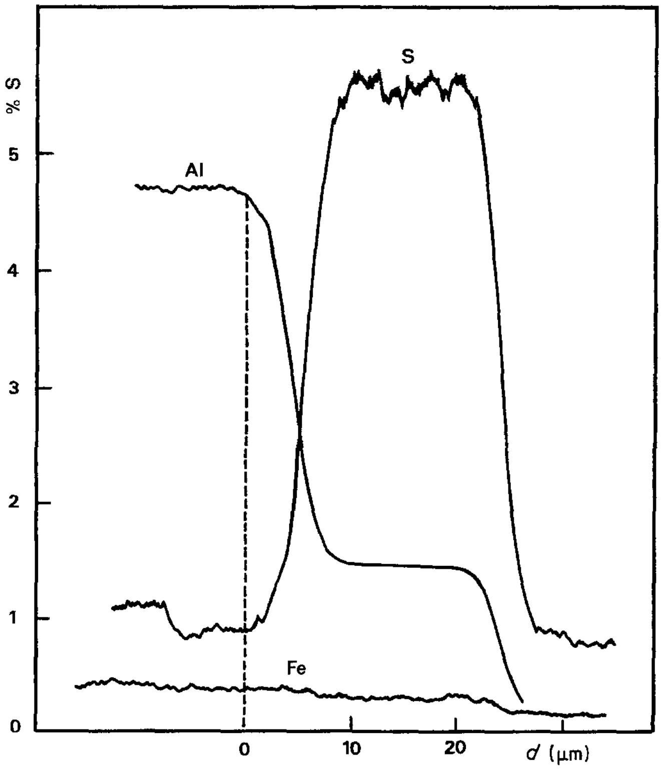

Fig. 9. Sulphur, aluminium and iron distribution across a film produced in modified solution (10 g l Fe^{3+}) at 20 V during 30 min. EPMA results.

samples using the scanning mode of the microscope failed due to the very small dimensions of the pores. A micrograph of a carbon replica can be seen in Fig. 12 The pore diameter was ~30 nm and no significant changes occurred with the variation of the experimental conditions, namely ferric ion concentration, voltage and time. For the limited depths examined no change in the pore diameter occurred, as shown in Fig. 13. Characteristic ridges were observed on many of the films produced in modified solutions at 30 V (see Fig. 13); while this can be characteristic of surface growth processes no definite origin has been found.

4. General discussion

One of the objectives of this work was the determination of the patterns of sulphur distribution through the anodic film. For thicknesses greater than ca 10 μm the distribution was practically uniform, the amounts of sulphur varying very little. For thinner films a constant sulphur region could not be found and the existence of a maximum (Fig. 8b) probably reflects the proximity of the two film interfaces rather than a genuinely different distribution. The maximum sulphur content of these films was approximately the same as that of the thicker ones, i.e. of the order of 5–6 wt %. No direct relationship seems to exist between the sulphur content and the anodizing conditions. It is somewhat surprising that voltage, time and composition of the anodizing solution do not appear to have any significant effect on the amount of sulphur and that its value is similar to those reported for d.c. films [7, 13]. Available data does not provide a satisfactory explanation for this phenomenon. The possibility of the anodizing solution being trapped inside the pores would seem to be the most likely interpretation if it is assumed that the pore size and distribution are independent of the anodizing conditions. Although this assumption is confirmed by the TEM observations the absence of iron at any distance from the oxide surface may invalidate the argument.

The other objective of this work was to determine the nature of the species responsible for the yellow colouration of the aluminium anodized in unmodified

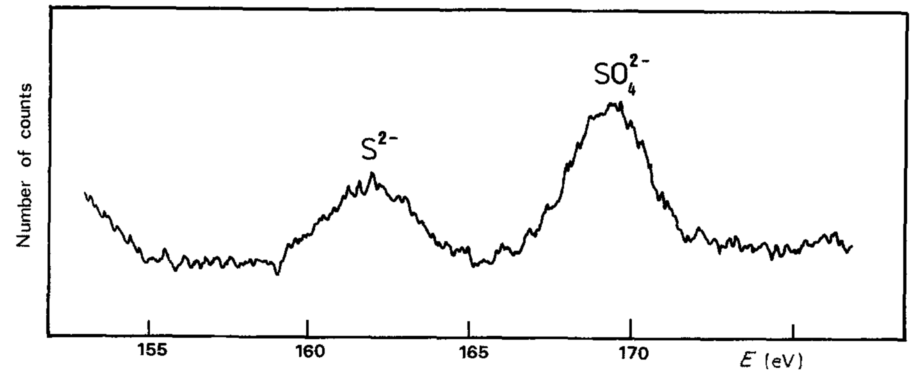

Fig. 10. XPS spectrum obtained for a film produced in an unmodified solution at 25 V for 30 min showing that sulphur is present in the form of sulphide and sulphate only.

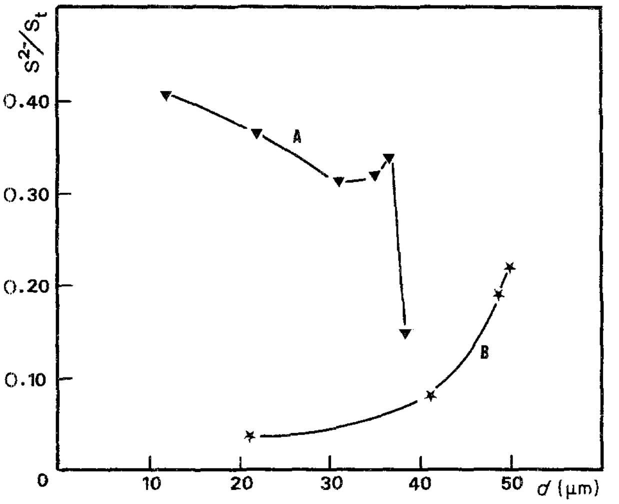

Fig. 11. Variation of the ratio of sulphide to (sulphate plus sulphide) concentration with distance to the aluminium–oxide interface for (A) a slightly yellow specimen (25 V, 30 min, live terminal); (B) a non-yellow specimen (40 V, 15 min, live terminal). Unmodified solution. XPS results.

Table 3. Comparison between the EPMA and XPS results

Anodizing conditions	*wt % S*	
	EPMA	*XPS*
Unmodified solution, 40 V, 15 min, live terminal	5.0	4.7
Unmodified solution, 40 V, 15 min, neutral terminal	6.4	6.8
$10\,g\,l^{-1}$ Fe^{3+}, 30 V, 5 min	6.1	7.2

solution. During the experimental programme it was found that at high voltages the specimens connected to the neutral terminal systematically showed a stronger yellow colour than those on the live line. Subsequent work has shown that it is possible to invert this tendency in the initial stages of the anodizing process, for example by acting on the rate of voltage increase [14]. In both types of specimen, however, sulphide species were detected by XPS and their amount increased as the colour intensity became greater. For modified solutions all sulphur was in the form of sulphate. Since these specimens were always light grey, as in normal d.c. processes, the colouration must be due to the presence of sulphide. It is suggested that Al_2S_3, which is yellow, is the contaminant and that it can be either inside the pores or in the surrounding hydrated aluminium oxide. Other species which might result from the breakdown of sulphate ions have not been identified. In strongly acid solutions H_2S is stable, whereas elemental S, SO_3^{2-} and $S_2O_3^{2-}$ and other sulphur-containing species have limited thermodynamic stability [15]. This suggests that the rise in pH, due to hydrolysis of the Al^{3+} cations [16] and to the reduction of H^+ species during the cathodic half-cycle is not sufficient to change the conditions for sulphide formation, which would occur according to

$$2Al^{3+} + 3H_2S \longrightarrow Al_2S_3 + 6H^+$$

The release of protons in this reaction tends to counterbalance their consumption in the other two reactions.

The ease with which sulphide forms on the neutral specimen must be related to the electrode potential obtained during cathodic half-cycles which, in turn, is a function of the polarization current. This implies that if the live specimen is being anodized faster, as indicated by the oscilloscope current traces, the cathodic polarization currents on the neutral specimen are higher and, hence, the tendency for the reduction of sulphate to sulphide is also higher than on the live electrode.

The formation of sulphide had a strong inhibiting effect on the oxide growth, as clearly shown by the much smaller thicknesses obtained on the neutral specimens. A possible explanation lies in the partial obstruction of the pores which would lead to a hindrance to the migration of the species in solution.

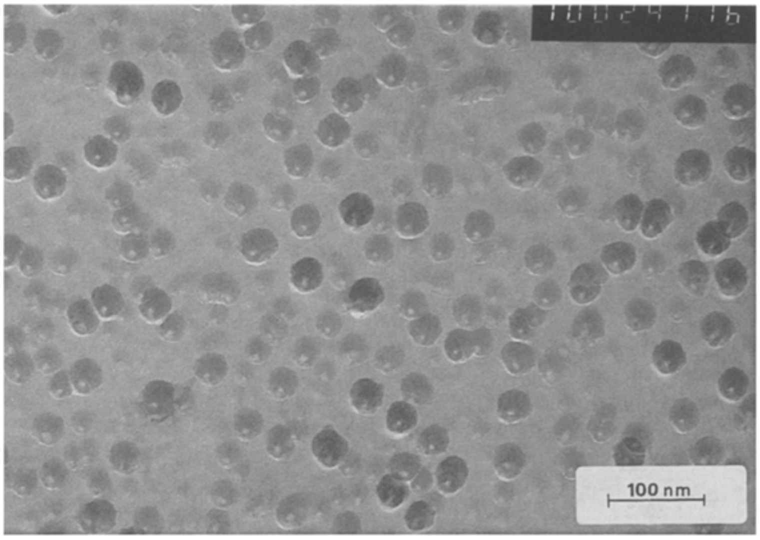

Fig. 12. TEM photograph of a carbon replica obtained on an oxide grown in $10\,g\,l^{-1}$ Fe^{3+} solution at 30 V for 5 min. The pore size is approximately constant and of the order of 30 nm.

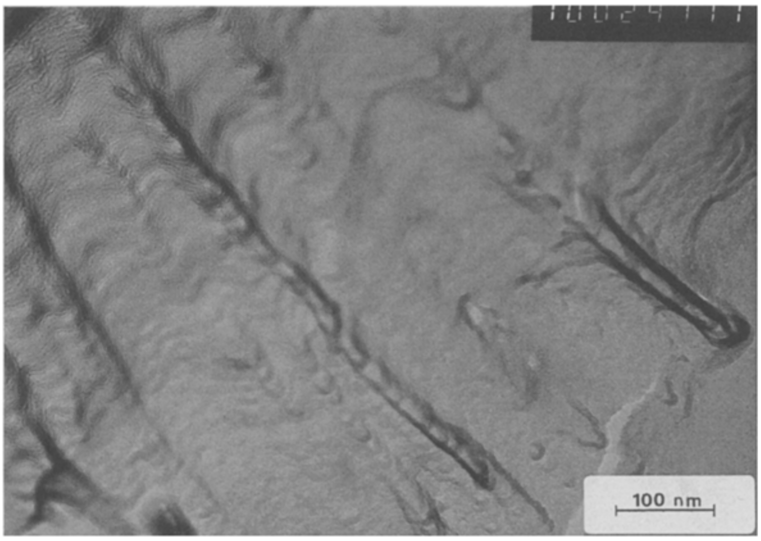

Fig. 13. TEM photograph of a carbon replica of the side of a crack located near the surface, showing that the pore diameter does not change significantly through the topmost part of the film. $10\,\mathrm{g\,l^{-1}}$ Fe^{3+} solution, 30 V, 5 min.

The higher solubility of aluminium sulphate ensures that the pores do not become blocked by a precipitate, enabling continued film growth to take place.

Although a difference in sulphide content may explain why the kinetics for aluminium oxidation is different on both electrodes a change in anodizing efficiency is the most probable explanation. It seems clear, however, that once established this tendency is maintained for long periods of time until the resistance of the thicker film becomes so large that formation of hydrated alumina is easier in the sulphide-rich oxide film.

This work also aimed at determining the extent of incorporation of solution modifiers in the oxide. For the salt chosen – ferric sulphate – no incorporation occurred and contamination at the outermost surface was negligible.

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