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Effect of Thiourea on the Electrical Breakdown of Aluminium

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Para estudar a influência da tiouréia durante a anodização de alumínio super-puro em pentaborato de amônio, fez-se SEM de alta resolução de superfícies anodizadas de alumínio e TEM de filmes dissolvidos. A adição de tiouréia no eletrólito aumentou o potencial de ruptura em 25 V, diminuindo apreciavelmente a densidade populacional dos eventos de ruptura. Esse efeito parece estar associado a uma redução na densidade populacional das falhas. Estudos voltamétricos suplementares, em Al (99,99 m%), Cu (99,99 m%) e Al3,5 m%Cu, sugerem que tal redução está relacionada à adsorção local da tiouréia nas respectivas superfícies.

High resolution SEM of anodized aluminium surfaces and TEM of stripped films were employed to study the influence of thiourea during the anodizing of superpure aluminium in ammonium pentaborate. The addition of thiourea into the electrolyte increased the breakdown voltage by 25 V, notably decreasing the population density of the breakdown events. This effect seems to be associated with a reduction in the flaw population density. Supplementary voltammetric studies on Al (99.99 wt%), Cu (99.99 wt%) and Al-3.5 wt% Cu, suggest that such a reduction is related to local adsorption of thiourea at the respective surfaces.

Keywords: *thiourea, electrical breakdown, aluminium*

Introduction

Several mechanisms have been proposed to explain the electrical breakdown during aluminium anodizing. They include electronic impact ionization and avalanching[1-5], local heating due to the conduction through electrolyte-filled microfissures in the anodic film[6], and local crystallization in the anodic film[7,8]. Further, the development of crystalline material and the initiation and propagation of breakdown have been related to processes developed in the vicinity of flaws, which are associated with the presence of impurities in the metal substrate[9,10].

Regarding the interplay between flaws in the metal substrate and the development of breakdown, this work studies the influence of complexing agents with copper. Thus, the effect of thiourea during barrier type film growth on aluminium is reported.

Experimental

In the preparation of the electrodes, Al 99.99% and Al-3.5% Cu sheets were employed, with the latter being heat-treated at 808 K for 48 h and quenched in oil. The aluminium electrodes were prepared in two different ways depending on the particular experiment; they were either electropolished at 20 V for 5 min in a 20% v/v perchloric

acid-ethanol solution, or etched in 5% NaOH for 3 min at room temperature. The Al-Cu alloy samples were electropolished following the procedure described above, but after electropolishing the samples were immersed in 50% nitric acid for 40 s. After the respective surface treatment the samples were rinsed thoroughly in distilled water. Anodizing was carried out at a constant current density of 5 mA/cm^2 in 0.1 M ammonium pentaborate solution, in both the absence and presence of the additive, at 293 K up to different final voltages. The anodized specimens were examined in an ISI DS 130 scanning electron microscope and the stripped films in a Philips E400 transmission electron microscope.

Results and Discussion

The voltage-time behavior of Fig. 1 showed that from the start of anodizing up to 320 V, the voltage rises at similar rates of 135 V/min in the absence and presence of thiourea. Sparking over the surface was evident in both solutions, from 320 V, indicating dielectric breakdown. However, differences were observed on approaching the breakdown voltage. For anodizing in the presence of the additive, a breakdown voltage 25 V higher than for anodizing in the absence of thiourea was observed. For longer anodizing times, beyond 5 min, the voltages tended to overlap increasing at similar rates with time. This may be associated with the decomposition of thiourea at the film-solution interface, and/or with the retarded effect of the temperature rise in the resistivity of the electrolyte[1].

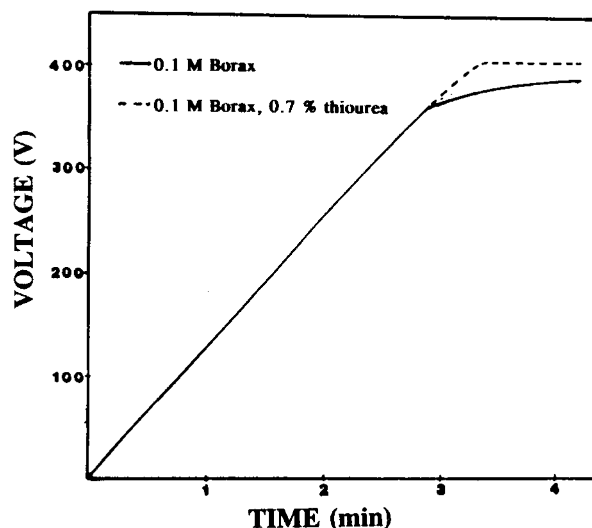

Figure 1. Variation of voltage with time for electropolished superpure aluminium anodizing at 5 mA/cm^2. a) 0.1 M ammonium pentaborate; b) 0.1 M ammonium pentaborate + 0.7 % thiourea.

Figure 2 shows the aluminium samples after anodizing for 270 s in the absence and presence of thiourea. On specimens anodized in the presence of the additive (Fig. 2b), a lower population density of breakdown events is observed. Thus, the differences observed in the voltage-time behavior are associated with different final surface morphologies. Further, since both surfaces show breakdown events, the change in the V/t slope could be related to a critical population density of breakdown events in the anodic film.

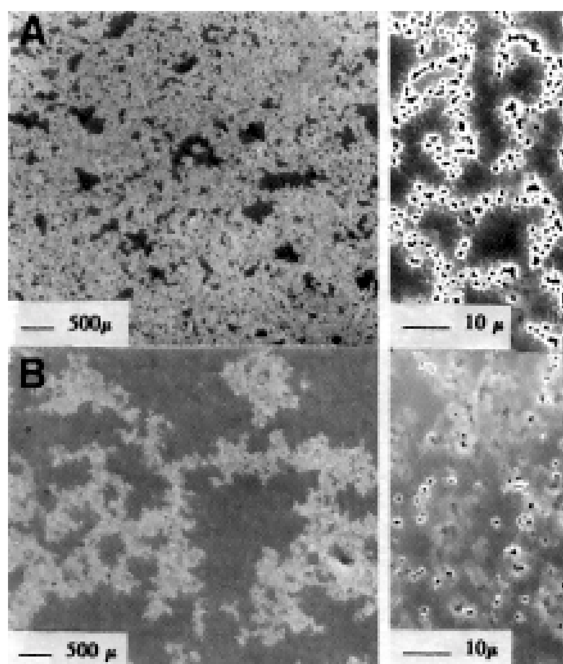

Figure 2. Scanning electron micrographs showing the surface morphology of electropolished superpure aluminium after anodizing for 270 s at 5mA/cm^2 in the absence and presence of thiourea. (a) 0.1 M ammonium pentaborate; (b) 0.1 M ammonium pentaborate + 0.7 % thiourea.

It is well known that films formed on electropolished superpure aluminium present a very low population density of flaws, which are not easily revealed by TEM of stripped films[12]. Thus, to study the interplay between flaws and the initiation and propagation of breakdown events, the morphology of anodic films formed on etched Al (99.99%), in the absence and presence of thiourea, was examined. Further, to elucidate the possible relation between the effect of thiourea and particular flaws associated with copper impurities in the metal substrate, the morphology of films formed on Al-3.5 wt% Cu, in the absence and presence of the additive was also studied. The flawed appearance of films formed on Al-Cu alloy associated with the presence of copper sites has been previously reported[11].

The stripped films formed to 30 V on etched superpure aluminium (Fig. 3), show local light spots with diameters up to 500 Å associated with the presence of flaws in the film. Flaws appear at film regions growing above metal ridges separated by troughs in the metal substrate (marked X), suggesting a local segregation of impurities such as copper and iron as a result of etching. For films formed in the absence and presence of thiourea, flaw population

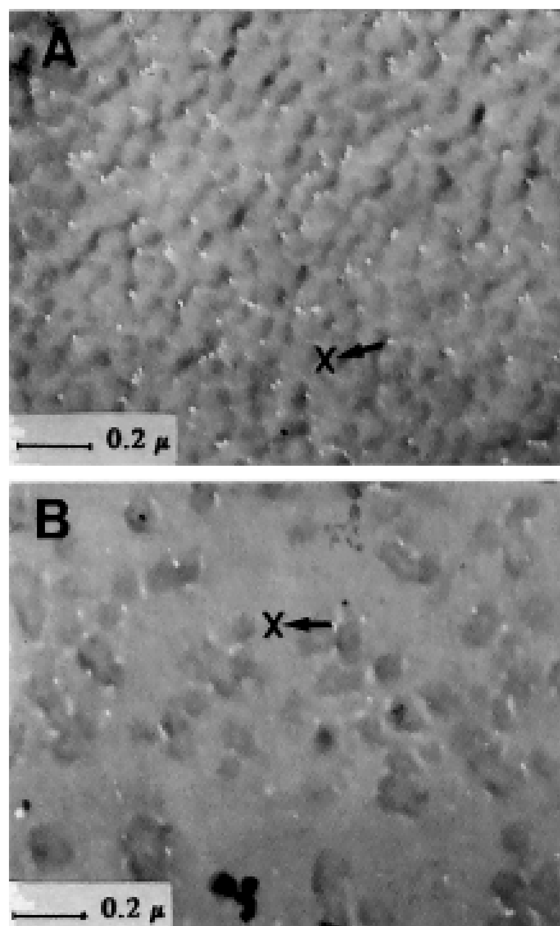

Figure 3. Transmission electron micrographs showing stripped films formed on etched aluminium at 5 mA/cm^2 to 30 V, in the absence and presence of thiourea. (a) 0.1 M ammonium pentaborate; (b) 0.1 M ammonium pentaborate + 0.7% thiourea.

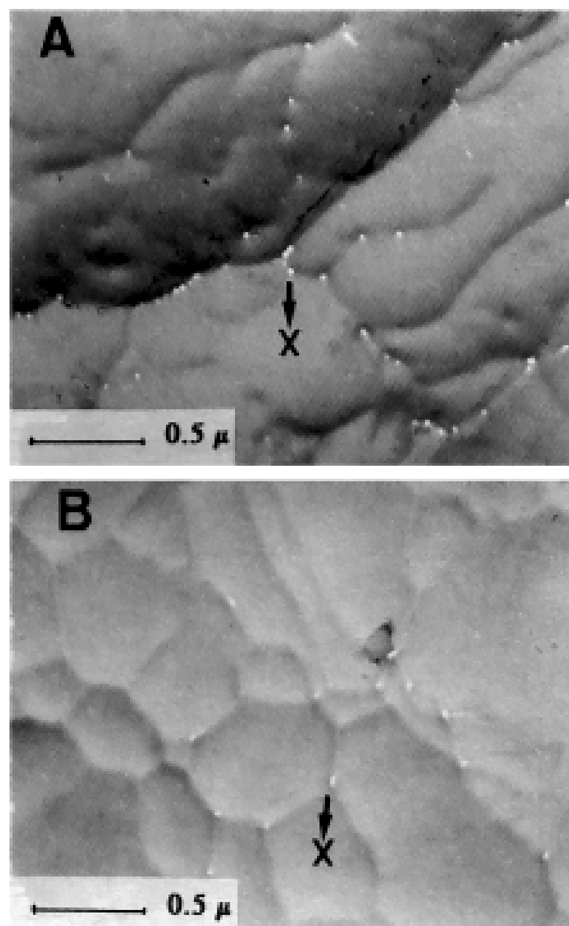

Figure 4. Transmission electron micrographs showing stripped films formed on the Al-Cu alloy at 5 mA/cm^2 to 20 V in the absence and presence of thiourea. (a) 0.1 M ammonium pentaborate; (b) 0.1 M ammonium pentaborate + 0.7% thiourea.

densities of $10x10^{11}$ and $5x10^{11}$ m^{-2} were estimated. Thus, the addition of thiourea decreases the flaw population density in the film by a factor of two.

For films formed up to 20 V on electropolished Al-3.5 wt% Cu in the absence and presence of the additive (Fig. 4), flaws appear in film regions growing above metal ridges of cells in the metal substrate (marked X). It is in these regions where, during the surface treatment, most of the impurity segregation occurs[12]. Despite the differences in oxide morphology between films formed on etched superpure aluminium and electropolished Al-Cu alloy, the presence of thiourea also decreases the flaw population density by a factor of two. In addition, as a result of the decrease in the flaw population density and hence, a more uniform current distribution during film growth, the film formed on Al-Cu in the presence of thiourea appears more uniform compared to that formed in its absence.

In order to understand the effect of the additive during aluminium anodizing, voltammetric studies on Al (99.99%), Al-3.5% Cu and Cu (99.99%) in 0.1 M borax, in the absence and presence of thiourea, were carried out. Figure 5 (solid line) shows a typical voltammogram for a copper electrode in borax solution. Two relatively sharp anodic peaks at approximately -0.18 and 0.05 V, corresponding to Cu(I) and Cu(II) oxide formation[15], are observed, which are followed by a region of passivity up to the potential for oxygen evolution. In the potential range 0.9 to 1.6 V a broad peak appears. This is attributed to oxygen evolution, which is visually observed. During the cathodic scan, a current peak at 0.8 V is observed, which has been related to Cu(III) oxide reduction[15], and/or to reactions involving soluble compounds[16]. Approaching the cathodic limit, two current peaks appear close together, which have been associated with Cu(I) and Cu(II) oxide reduction[15].

The CV curves on Al and Al-Cu in borax solution are presented in Fig. 6 (solid line). Because of the noble charateristic of copper and, the possible behavior of the alloying element during the air-formed oxide growth, the corrosion potential for the Al-Cu alloy was about 400 mV more anodic than for Al[17]. Because of this, and possible variation in the thickness and composition of the air-formed

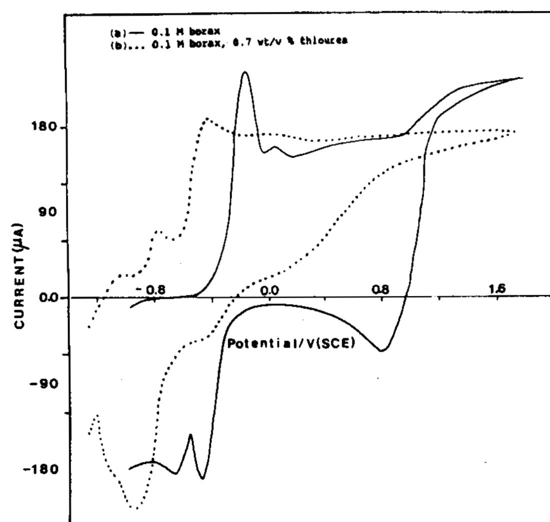

Figure 5. Potentiodynamic polarization curves at 200 mV/s showing the electrochemical behaviour of the copper electrode in borax solution, in the absence and presence of thiourea.

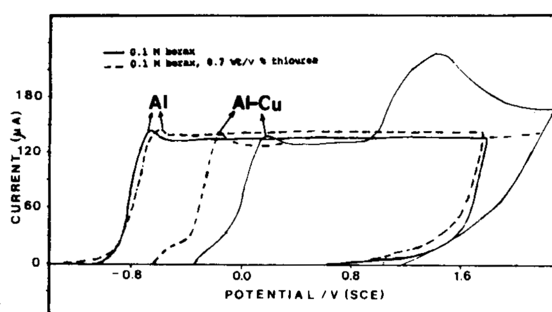

Figure 6. Potentiodynamic polarization curves at 200 mV/s showing the electrochemical behavior of Al and Al-Cu electrodes in borax solution, in the absence and presence of thiourea.

oxide, the starting potential for alloy oxidation is observed at a value 800 mV more anodic than for Al. Despite the difference in the initial potentials, the anodic response of both materials is discussed.

The CV curve for Al in borax solution revealed a current peak associated with aluminium oxidation, followed by a passive region. For the alloy, previous to the current associated with aluminium oxidation and the passivity region, a small current shoulder, commencing at -0.18 V, is evident. This is apparently associated with Cu(I) oxide formation, since such a peak appears at a potential similar to that on the copper electrode (Fig. 5, solid line). The current peak related to Cu(II) oxide formation is masked by the current peak related to aluminium oxidation. These results are in good agreement with similar studies reported by Strehblow and Doherty[18]. Approaching 0.9 V, a broad peak associated with oxygen evolution is observed. Since on Al-Cu and copper electrodes, oxygen evolution occurs in the same potential range, such a reaction apparently takes place at copper sites in the alloy material.

The CV curves for copper and the Al-Cu alloy (Figs. 5 and 6, dashed lines) clearly illustrate the effect of the additive in the voltammetric features. In both cases, the corrosion potential, which was measured after a stable potential was reached (approximately 2 h), was displaced by 200 mV to a more cathodic potential. Further, after one potential cycle, the natural color of copper and the alloy is altered by the formation of an insoluble compound. It is apparent that because of this insoluble compound, oxygen evolution, which is observed in the absence of thiourea between 0.8-1.6 V, is inhibited. In addition, on copper, a small current peak at approximately -0.8 V, suggest that some adsorbed species are oxidized during the anodic scan. The results are in good agreement with the voltammetric studies of copper electrodes in acid medium containing thiourea[13,14]. These studies[13,14] suggest the formation of a complex Cu-thiourea that remains strongly adsorbed on the copper surface. However, it is likely that in relatively alkaline solutions such a complex polymerizes, becoming insoluble in nitric acid.

In the case of the voltammetric response of superpure aluminium, the shape of the CV curve does not change significantly in the presence of thiourea. However, the corrosion potential is also displaced by 200 mV in the cathodic direction. This is interesting, since the corrosion potential of aluminium is very sensitive to impurities such as copper sites at the surface. Thus, it is apparent that the displacement of the corrosion potential is associated with adsorption of the additive at copper sites on the aluminium surface.

In conclusion, the effect of thiourea in increasing the electric breakdown voltage of electropolished and etched aluminium is associated with a decrease in the population density of active flaws in the film material. Such a decrease seems to be related to adsorption of thiourea at flaws, possibly associated with impurities such as copper. During anodizing, the adsorbed thiourea prevents the passage of high local current through flaws, thus allowing alumina film growth to bridge over and to encroach beneath the flaws, and thus isolating them from the aluminium surface and hindering the access of the electrolyte. This finding supports the earlier work of Yahalom and Hoar[7] and Shimizu *et al.*[10], who proposed that the Joule heating effect in the vicinity of flaws is associated with the development of breakdown.

Acknowledgments

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