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# The degradation of aluminium cathodes by fluoride ion during zinc electrowinning

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The influence of fluoride ions on aluminium cathode surface degradation during zinc electrowinning has been studied. Electrolyte with a composition similar to that employed in plant operations has been used. A direct correlation is shown between the electrolyte fluoride content and the number of deposition cycles possible before zinc removal becomes difficult. The role of initial nucleation and starting electrode morphology is discussed in terms of the degree of adherence observed. Electrochemical tests have also been made on the electrodes at various stages of the process in an attempt to gain a better fundamental understanding of the mechanisms responsible for the adherence. The results indicate that the severity of the adherence is generally determined by the amount of residual zinc remaining on the surface after stripping and the fluoride content of the solution during plating. The contribution of physical surface condition alone seems to be less significant than the chemical conditions imposed during deposition.

## 1. Introduction

During previous studies [1], the intrinsic detrimental effect of excess fluoride on zinc adherence to an aluminium electrode was evaluated. Particular attention was given to the degradation of the aluminium substrate in the presence of fluoride. Electrochemical tests, such as cyclic voltammetry and a.c. impedance measurements, were employed to obtain a better understanding of the zinc adherence mechanism. The results indicated that the mechanism responsible for adherence was mainly due to two factors. Initially, fluoride ion attacks the surface aluminium oxide, exposing metal and allowing direct zinc deposition and metal to metal bonding. In addition, the corrosive attack is non-uniform and the pits which form also provide sites for mechanical keying of the zinc. Cathode preconditioning techniques were also described which modified the fluoride effect and decreased the tendency for zinc sticking.

In a commercial zinc plant, a normal electrolyte is known to contain relatively small amounts of fluoride ion. The actual concentration can change, but is often in the range of 10 to 20 p.p.m. Although this amount of fluoride can cause changes in the electrochemical character of the aluminium electrode, the deposited zinc is still easy to strip after only a few repetitive uses of the electrode. The implication is that the surface aluminium oxide layer is also still stable, showing no noticeable influence of chemical attack by fluoride. However, during zinc electrowinning, some sticking problems occur occasionally during numerous repetitions of the plate/strip cycle, and the adherence is so strong that the deposited zinc must be dissolved by soaking it in acid for relatively long times.

The number of investigations concerned with the effect of fluoride ion on zinc adherence has been limited and directed more toward a quantitative determination of adherence strength [2–4]. The current research extended the general approach used in the previous studies to longer use times in lower fluoride concentrations. Emphasis was then placed on the nature and the degree of degradation of the aluminium substrate and the mechanism responsible for zinc adherence with continued electrode use.

The primary object of this research was to study the effect of cyclic usage of aluminium electrodes in low fluoride solution on zinc adherence. Particular attention was given to the influence of 30 p.p.m. fluoride in the electrolyte and the condition of the aluminium substrate surface after repeated usage in this electrolyte. One major modification employed in this research compared to previous work, was to reuse as-stripped cathodes without any intermediate treatment during cycling. The gradual degradation of the surface could then be monitored and correlated with the onset of adherence.

A morphology study using scanning electron microscopy (SEM) was also employed to examine the cyclically used substrates and the types of nucleation occurring on these substrates. Electrochemical tests such as cyclic voltammetry and a.c. impedance spectroscopy were conducted for the purpose of evaluating the electrochemical modification caused by cyclic usage. Data were compared with those from previous research.

## 2. Experimental details

### 2.1. *Electrolyte*

A neutral zinc sulphate solution was prepared by

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dissolving French Process zinc oxide powder in sulphuric acid to a concentration of 180 g dm$^{-3}$ of zinc. The solution contained 2.91 p.p.m. of lead, 0.5 p.p.m. of cadmium, 0.2 p.p.m. nickel, and traces of some impurities such as arsenic and antimony.

Test solutions were prepared in a 2 dm$^3$ volumetric flask by mixing the proper amount of neutral zinc sulphate solution, deionized water, and reagent grade sulphuric acid to produce a composition of 50 g dm$^{-3}$ zinc and 150 g dm$^{-3}$ sulphuric acid electrolyte.

Stock solution was prepared by dissolving reagent grade sodium fluoride in deionized water to a concentration of 20 g dm$^{-3}$ F$^-$. This solution was then added to the zinc electrolyte to provide the desired fluoride concentration.

### 2.2. *Electrodes*

The starting aluminium cathodes obtained from Big River Zinc Co., Sauget, Illinois, had 4 cm$^2$ of deposit area and were prepared by milling, followed by cloth polishing with 0.05 $\mu$m alumina powder. Subsequently these electrodes were cleaned with distilled water in an ultrasonic bath and then rinsed with deionized water and hot air dried. The electrodes were then used repeatedly for deposition, without any additional treatment to the surface after each deposition/strip cycle.

However, in order to evaluate the effect of additional treatment on adherence, the cyclically used substrates were held in 300 g dm$^{-3}$ sulphuric acid solution, rinsed with deionized water, and then dried with hot air. The cleaned substrates were then electrolysed, and the results were compared to those obtained prior to the acid treatment.

Platinum mesh anodes were used to avoid lead contamination.

### 2.3. *Electrolysis*

Tests were made simultaneously with a number of cells connected in series. A constant temperature water bath maintained the electrolyte at 35 °C. For each cell, one cathode and one anode with 2.5 cm spacing was fixed in a Plexiglass holder which also served as a lid for the 250 cm$^3$ beaker cell. The electrodes were then submerged vertically into the solution and kept 2.5 cm below the solution line.

Unless otherwise specified, electrolyses were carried out in solutions with the composition of 50/150 g dm$^{-3}$ of Zn/H$_2$SO$_4$ and various amounts of fluoride ion at a current density of 50 mA cm$^{-2}$ for 2 h. The range of fluoride content was 0 to 3 g dm$^{-3}$. Current was applied immediately after the as-stripped substrate was submerged into electrolyte to avoid excessive reaction time in the electrolyte. After electrolysis, the cathodes were removed, rinsed with distilled water, and dried with hot air before stripping the zinc.

### 2.4. *Zinc adherence test*

The deposited zinc was stripped manually and the adherence of zinc was categorized qualitatively into three categories. These were identified as: easy to strip (E), difficult to strip (D), and impossible to strip (I). In order to obtain a better understanding of the correlation between zinc adherence and continued cyclic usage, the morphology of the aluminium substrate was examined using the SEM. Short time deposits showing zinc nucleation and growth trends were also made.

### 2.5. *Electrochemical tests*

The aluminium electrodes were also subjected to cyclic voltammetry and a.c. impedance tests after various electrolysis stages. The experiments were carried out in 250 cm$^3$ beaker cells at room temperature, employing an aluminium working electrode (fresh or repeatedly used substrate), platinum mesh counter electrode, and a saturated calomel reference electrode. The test solution was held at ambient temperature and was identical in composition to that used for the deposition electrolyses.

## 3. Results and discussion

### 3.1. *Effect of electrode cycling*

As shown by previous surface examination studies of various electrodes, the surface residual zinc content increased with fluoride concentration [1]. From Fig. 1 it is seen that with repeated usage of an aluminium cathode, the surface zinc remaining increases and the rate is accelerated by fluoride content. The relative zinc content was estimated using EDX analysis. Approximately 10% zinc remains on the stripped surface used in 250 p.p.m. fluoride electrolyte, and this value doubles after two additional cycles on the same substrate (Fig. 1a and b). Nearly 30% zinc remained from 750 p.p.m. F$^-$ solution and almost complete coverage with zinc occurred after two more repetitions (Fig. 1c and d).

When the residual zinc is dissolved considerable pitting and surface roughening becomes evident. It is shown in the figures that the degree of roughening increases with increasing fluoride content (Fig. 2a and b). Also with continued use (two repetitions) the number and depth of the pits increases (Fig. 2c and d). The region between the pits is covered with a uniform distribution of shallow, small pits or depressions. If the zinc is deposited in the pits, mechanical bonding or keying can occur in addition to metallic bonding directly to the aluminium at the nucleation site. The combination results in a high degree of adherence.

Table 1 shows the effect of cycling the aluminium cathode in electrolyte containing different fluoride concentrations. The trend is obvious, as the time required for zinc sticking is directly proportional to fluoride content. If it is assumed that the number of cycles to reach I-type strength is the maximum cycle, the aluminium electrodes should be returned to receive a surface retreatment as this value is approached if sticking is to be avoided in industrial operations.

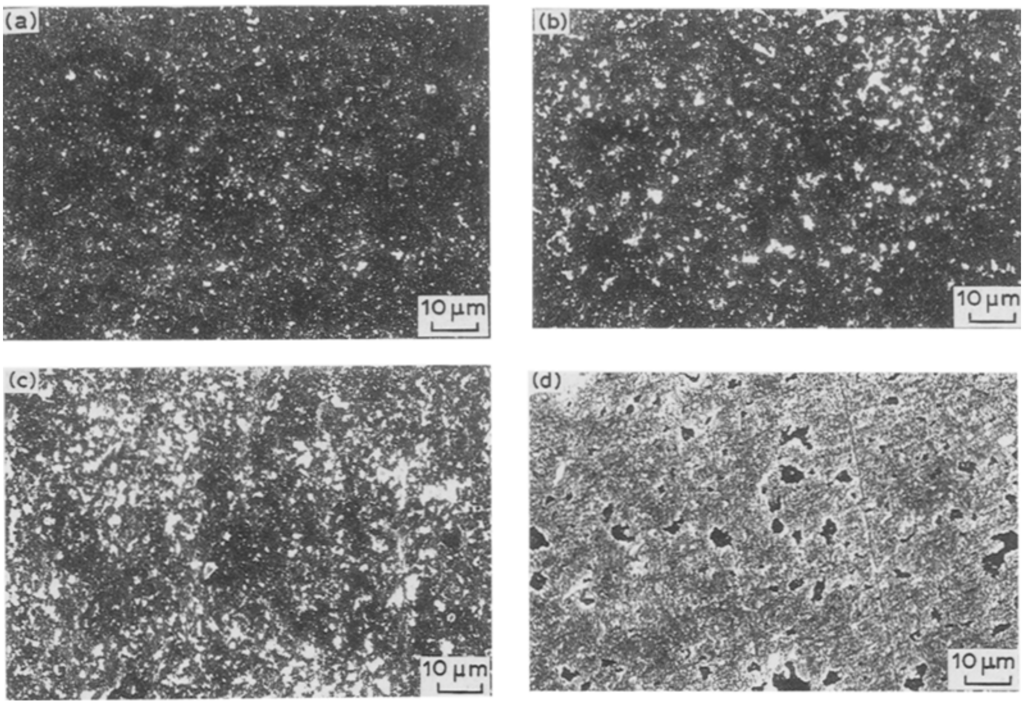

Fig. 1. Surface of aluminium substrate after stripping showing the presence of residual zinc. (a) 1 repetition in 250 p.p.m. $F^-$ solution; (b) 3 repetitions in 250 p.p.m. $F^-$ solution; (c) 1 repetition in 750 p.p.m. $F^-$ solution; and (d) 3 repetitions in 750 p.p.m. $F^-$ solution.

When a logarithmic plot of the number of deposition repetitions before zinc sticking is made against the fluoride content, an approximately linear relationship is obtained as shown in Fig. 3. A linear regression analysis was made and the following relationship between the number of cycles and the fluoride content was obtained for the $50\,g\,dm^{-3}$ Zn and $150\,g\,dm^{-3}$ $H_2SO_4$ electrolyte.

$$\log N = 2.5 - 0.71 \log F \qquad (1)$$

where $N$ is the number of repetitions sticking, and $F$ is the fluoride content in p.p.m. According to this

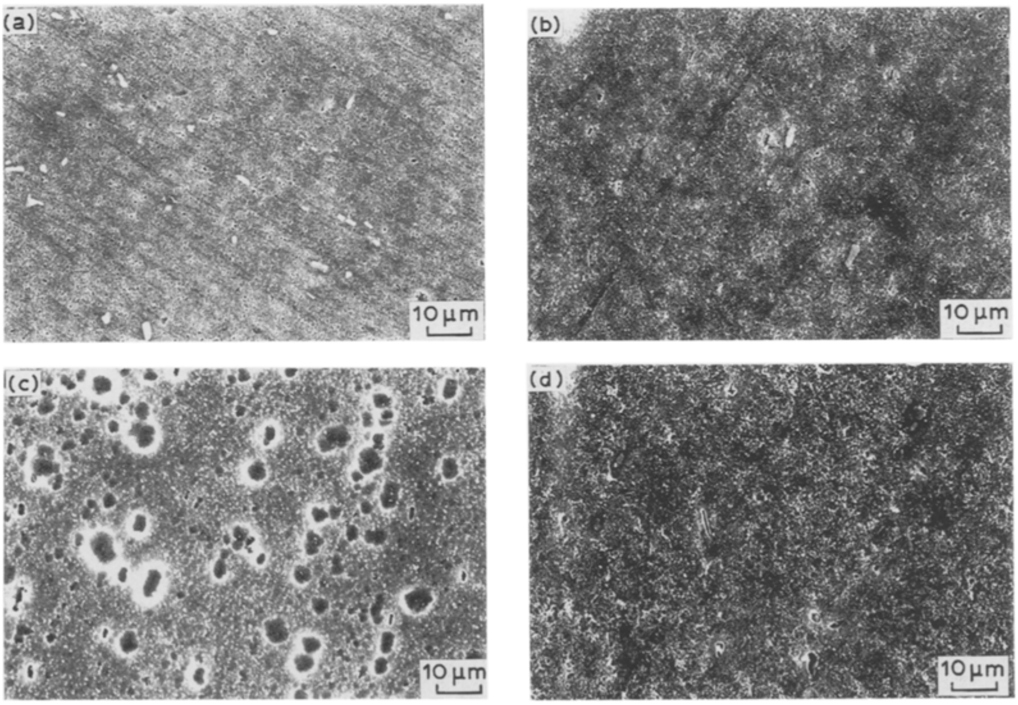

Fig. 2. Aluminium substrate after sulphuric acid cleaning. (a) After 1 repetition in 250 p.p.m. $F^-$ solution; (b) after 1 repetition in 750 p.p.m. $F^-$ solution; (c) after 2 repetitions in 250 p.p.m. $F^-$ solution; and (d) after 2 repetitions in 750 p.p.m. $F^-$ solution.

*Table 1. The effect of repeated cycling of an aluminium substrate in solutions containing various fluoride contents*

| *Cathode* | *Fluoride* | *Repetitions* | *Sticking strength* |
|---|---|---|---|
| 1 | 1.00 g $F^-$ | 1 | D |
| | 1.00 g $F^-$ | 2 | I |
| 2 | 0.75 g $F^-$ | 1 | E |
| | 0.75 g $F^-$ | 2 | D |
| | 0.75 g $F^-$ | 3 | I |
| 3 | 0.50 g $F^-$ | 1 | E |
| | 0.50 g $F^-$ | 3 | D |
| | 0.50 g $F^-$ | 5 | I |
| 4 | 0.25 g $F^-$ | 1 | E |
| | 0.25 g $F^-$ | 5 | D |
| | 0.25 g $F^-$ | 7 | I |
| 5 | 30 p.p.m. $F^-$ | 10 | E |
| | 30 p.p.m. $F^-$ | 20 | D |
| | 30 p.p.m. $F^-$ | 5 | E* |
| | 30 p.p.m. $F^-$ | 10 | D* |

* Additional cycles after dissolving the residual zinc

relationship, the number of repetitive uses of an electrode prior to sticking can be predicted. For example, by extrapolation the curve indicates that an electrode can be cycled about 100 times in 5 p.p.m. $F^-$ solution before adherence problems occur.

The stripped surfaces were examined after each fifth cycle to determine the changes caused by depositing from electrolyte containing 30 p.p.m. fluoride. As shown in Fig. 4, the surface becomes rougher with cyclic usage, but without any residual zinc detected by EDX analyses, until after about 20 cycles. During this time the surface does not show the same severity of deep pits which can be observed when higher fluoride solution is used. But when the substrate has been used more than 20 times, the degree of microroughness developed between deep pits (Fig. 4c and d) becomes more severe than those obtained from high fluoride solution (Fig. 2). The EDX analyses summarized in Table 2 indicate that when the substrate has been pitted to this degree, residual zinc begins to appear. Thus the eventual appearance of residual zinc on the aluminium substrate after stripping seems to be one requisite for the onset of sticking, and is related to the degree of surface attack. Also the residual zinc metal promotes adherence, resulting in rapid transition from D-type to I-type surfaces, as shown in Table 1.

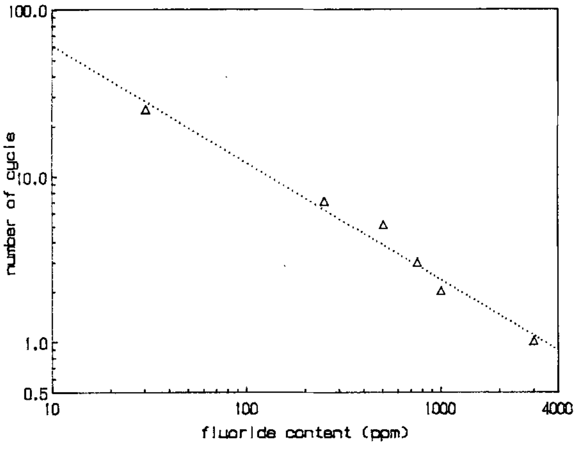

Fig. 3. Number of cyclic usage of aluminium substrate as a function of the fluoride content.

A series of tests were made in which the condition of the initial aluminium substrate and/or the fluoride concentration was changed. Table 1 shows that after complete acid cleaning an aluminium blank which was difficult to strip, the new substrate is now easy to strip even though the surface roughness has not changed appreciably. However, the sticking problem occurs earlier on a rough substrate than a fresh smooth substrate, thus the physical nature of the aluminium can not be completely ignored.

The results suggest that several conditions must be satisfied if sticking is observed in low fluoride solution:

(i) Fluoride ion has to be present in the electrolyte during the initial deposition. There is no "memory effect" with respect to the aluminium cathode, regardless of surface roughness condition.

(ii) A certain degree of corrosion or microroughening has to be initiated for sticking to occur.

(iii) Even though the substrate has been considerably roughened, once it has been treated in sulphuric acid solution, the aluminium oxide layer is at least partially repaired and less sticking is noted. In addition, residual zinc, which may have penetrated the oxide to form a metallic bond, is dissolved in the acid and the sticking problem is eliminated.

### 3.2. *Nucleation tests*

The role of roughness and residual zinc on the stripped aluminium substrate was further studied by applying a cathodic current and observing the nucleation and initial growth. Figure 5 shows the nucleation pattern for 5 s deposits made at the current density of 50 mA cm$^{-2}$ in electrolyte containing 30 p.p.m. fluoride. The nucleation on the smooth substrate (Fig. 5a) is non-uniform and clustered and the size of the deposit particles is relatively large. However, the nucleation rate and surface roughness both increase when the $F^-$ is increased. After continued use of the aluminium, the zinc nucleation is very uniform with a small crystal size (in the range of 0.5 μm, or 5 to 10 times smaller than initial), as seen in Fig. 5c. When such a substrate has been dipped in a sulphuric acid solution and replated (Fig. 5d), a very similar nucleation pattern to that for an electrode used only 10 times (Fig. 5b) emerges.

The importance of the presence of fluoride ion now seems to be clear; but the role of residual surface zinc and roughness in causing sticking must also be considered. Figure 6a shows the nucleation pattern on a substrate which gave an initial high concentration of residual zinc. The surface is almost completely covered after depositing for only 5 s, but no fluoride ion was in the solution. Although the nucleation in $F^-$ free solution is denser than that of 30 p.p.m. $F^-$ solution (Fig. 5c), the stripping of the former is easier

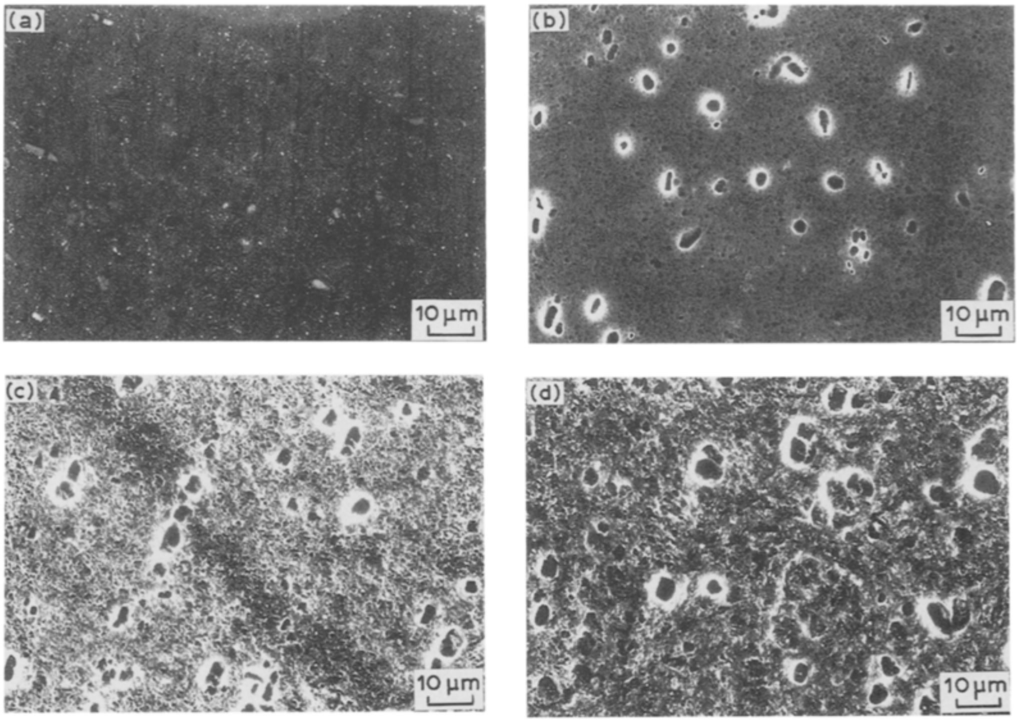

Fig. 4. Aluminium substrate after cyclic usage in 30 p.p.m. $F^-$ solution. (a) The starting substrate; (b) after 10 times cyclic usage; (c) after 20 times usage; and (d) after 24 times cyclic usage.

than that of the latter. Moreover, after repeated use in solution without fluoride (Fig. 6b) progressively less dense nucleation and larger zinc crystals occurs, resulting in easier stripping. Obviously the surface roughness has stayed about the same, but the absence of $F^-$ has decreased the amount of residual zinc remaining on the aluminium.

These nucleation tests are consistent with the previous stripping test observations, indicating that: (i) the rougher the substrate due to cyclic usage in electrolyte containing a constant fluoride concentration, the greater the nucleation rate and zinc adherence; (ii) the nucleation decreases with cyclic usage if $F^-$ is absent, eventually resulting in deposits that are easily stripped, even with a roughened substrate; and (iii) if the substrate has been cleaned in sulphuric acid solution to remove the residual zinc and allow surface aluminium oxide repair, the nucleation pattern changes to one more representative of a fresh, smooth surface, and the sticking problem does not occur.

### 3.3. *Cyclic voltammetry*

The cyclic voltammograms shown in Fig. 7 display the characteristic polarization behaviour for each substrate used during the repeated tests. As the aluminium electrode becomes more prone to sticking, the initial cathodic sweep is depolarized. When the surface is treated in sulphuric acid, allowing the residual zinc to dissolve and the aluminium oxide film to repair, a substantial degree of polarization is observed. Thus, the electrochemical evaluation of the zinc deposition overpotential on aluminium provides a means of indicating the susceptibility to sticking.

### 3.4. *A.c. impedance measurements*

The effect of cyclic usage of a substrate was also studied by using a.c. impedance measurements at open circuit potential in low fluoride containing solution.

Figure 8 shows Nyquist plots obtained with four different substrate conditions in a 30 p.p.m. fluoride containing solution. The charge transfer resistance decreases from 800 to 200 $\Omega\,cm^{-2}$ and finally 40 $\Omega\,cm^{-2}$ as stripping becomes difficult.

On the other hand, the substrate treated in sulphuric acid gives a high charge transfer resistance similar to a fresh substrate. This indicates that no residual zinc remains and the oxide surface is passive to spontaneous attack.

*Table 2. Percent zinc remaining on cycled substrates*

| *Substrate* | *After strip* | *5 s deposit* |
|---|---|---|
| Inert | 0 | – |
| 5 repetitions | 0 | – |
| 10 repetitions | 0 | – |
| 20 repetitions | 1.7 | 7.5 |
| 22 repetitions | 2.0 | 15.0 |
| Dissolved | – | 1.9 |

*Table 3. The open circuit potential of 30 p.p.m. $F^-$ aluminium substrates*

| *Substrate* | *Open circuit potential V/SCE* |
|---|---|
| Inert | −0.42 |
| Easy to strip | −0.75 |
| Hard to strip | −0.98 |
| Dissolved | −0.41 |

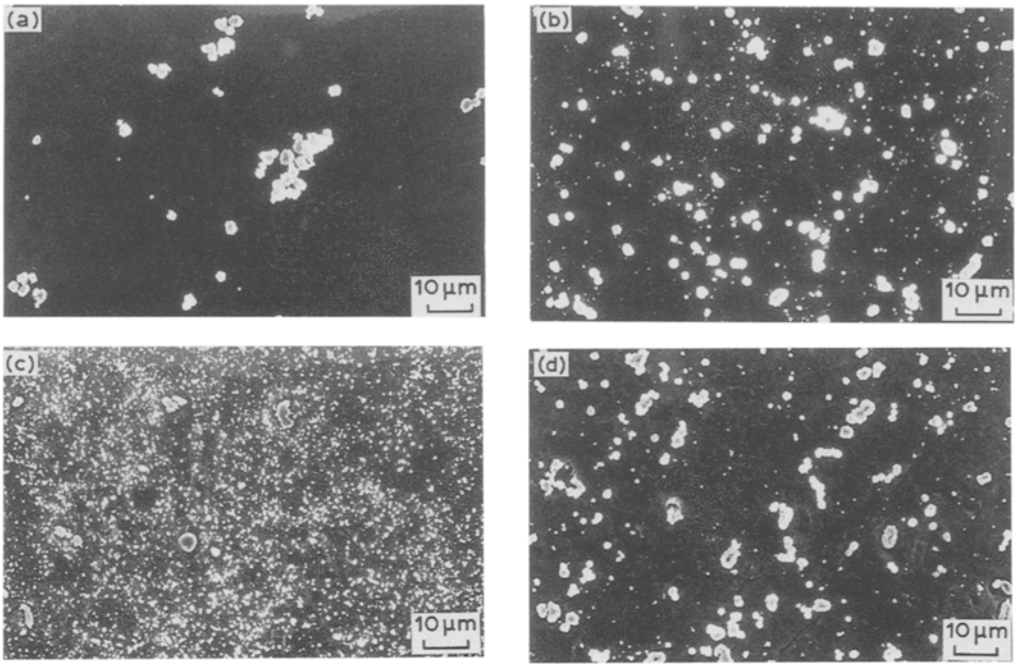

Fig. 5. Initial 5 s deposits at 50 mA cm$^{-2}$ and 35 °C on the cycled substrates in 30 p.p.m. F$^-$ solution. (a) The starting substrate; (b) after 10 repetitions; (c) after 20 repetitions; and (d) first repetition after acid cleaning.

The decrease of charge transfer resistance is also consistent with the open circuit potential (o.c.p.) measurements. The potential becomes more negative (from $-0.42$ to $-0.98$ V/SCE) with cyclic usage and becomes more positive, or reverts back to $-0.42$ V, when the residual zinc is dissolved.

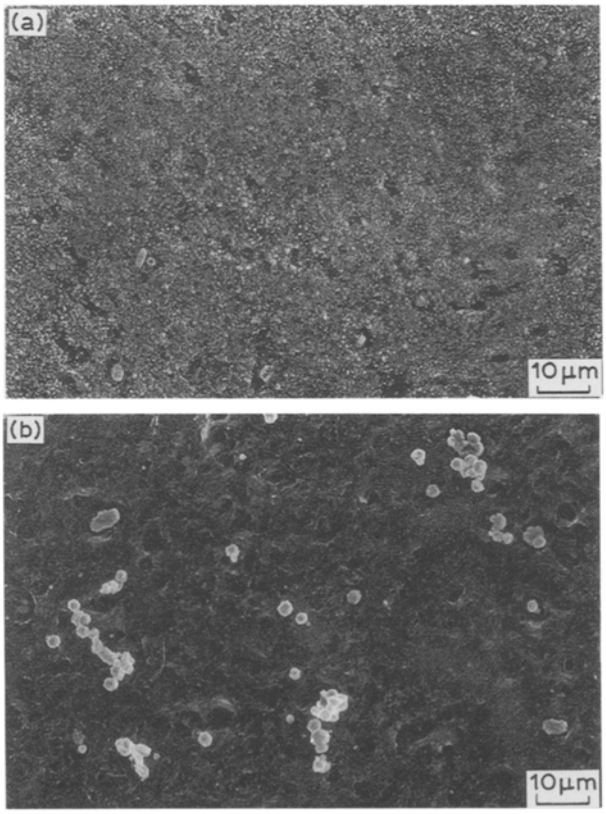

Fig. 6. Initial 5 s deposits at 50 mA cm$^{-2}$ and 35 °C in solution without fluoride. (a) Initial substrate hard to strip; (b) the same substrate of (a) used 5 times in solution without fluoride.

## 4. Conclusions

Repeated usage of stripped aluminium cathodes results in an increase in surface roughness and residual zinc, both of which appear to be directly proportional to fluoride content in solution. For low fluoride concentrations, the residual zinc is not detected until after a certain number of repetitions. When the zinc becomes hard to strip, residual metal can be detected. Thus one characteristic feature of sticking is the presence zinc after stripping.

The substrates exhibiting difficulty in stripping in higher fluoride solution do not show the same difficulty of stripping when they are subsequently used in lower fluoride solution. It appears that fluoride has to be present to cause sticking, regardless of the prior

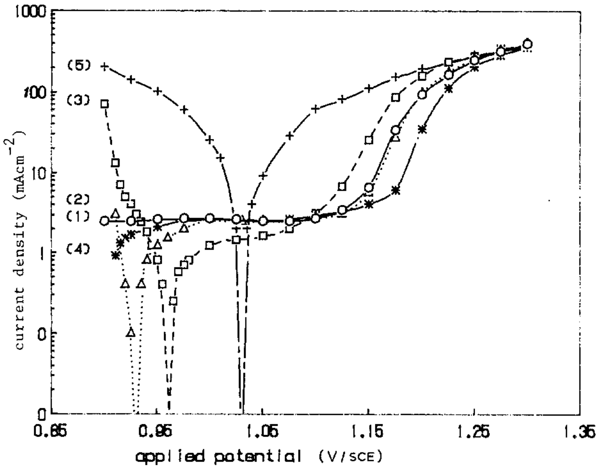

Fig. 7. The cyclic voltammogram of cyclic used substrate in 30 p.p.m. F$^-$ solution. Key: 1 (○) fresh substrate, 2 (△) easy-to-strip, 3 (□) different-to-strip, 4 (∗) dissolved substrate, and 5 (+) reverse scan.

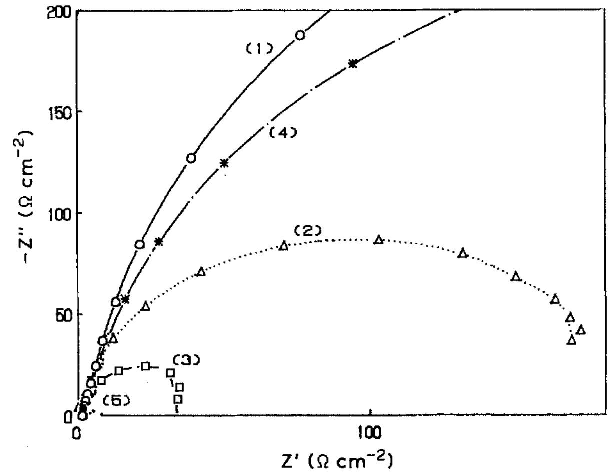

Fig. 8. Complex impedance plant plot (Nyquist plot) for cyclic used substrates in 30 p.p.m. $F^-$ solution. Key: 1 (○) fresh substrate, 2 (△) easy-to-strip, 3 (□) difficult-to-strip, 4 (∗) dissolved substrate, and 5 (◇) zinc.

history of the electrode. Surface pitting and roughness are therefore necessary, but not sufficient to cause sticking, at least using the conditions employed in this research.

The polarization behaviour of a substrate which is difficult to strip is characterized by the presence of an increased anodic region in the front scan and a decreased zinc deposition overpotential, as the degree of difficulty in stripping increases.

The a.c. impedance results clearly show the sensitivity of aluminium substrates to zinc sticking. Such techniques are promising as a means of elucidating the influence of repetition of electrode use in fluoride containing solution. Such tests might also be beneficial in evaluating or screening various aluminium alloys and their surface treatments for tendencies to degradation in fluoride containing electrolytes used in zinc electrowinning.

## Acknowledgement

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