JOURNAL OF APPLIED ELECTROCHEMISTRY **16** (1986) 127–133

Aluminium cathode effects in zinc electrowinning from industrial acid sulphate electrolyte

D. J. MACKINNON, J. M. BRANNEN

Metallurgical Chemistry Section, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, 555 Booth Street, Ottawa, Ontario K1A 0G1, Canada

Received 25 February 1985

The effects of aluminum cathode grain size and surface conditioning treatments on zinc electrodeposition from purified industrial acid sulphate electrolyte were investigated. The Al cathode grain size had no effect on the long-time (15–60 min) deposit characteristics although deposits obtained using large-grain Al cathodes were often easier to strip. A study of the initial zinc nucleation (5–80 s) showed that fine-grain Al cathodes had more zinc nucleation sites than large-grain cathodes. The influence of cathode preconditioning and glue on the initial zinc nucleation were also determined.

1. Introduction

The control of cathode growth while maintaining high current efficiency remains a major problem in the electrowinning of zinc. Part of the difficulty may be attributed to determining the properties which constitute a properly balanced electrolyte. Recent studies [1–3] involving the voltammetric evaluation of zinc electrolytes showed promising advances in this area. Further, correlations of deposit morphology data with current efficiency results can provide an insight into the definition of the desirable deposit structure characteristics and how they may be obtained. Deposit morphology and current efficiency seem to be intimately related [4] so that proper control of cathode growth can yield periods of high current efficiency (> 90%) for extended electrolysis times (> 24 h).

An area which has received little attention with respect to the control of cathode growth is the role of the aluminum starting sheet. This area is worthy of study not only because the initial deposit morphology has a bearing on the overall deposit structure, but also because the problems of 'stickers' and deposit roughness appear to be related to the initial nucleation of zinc. The results of previous work [4] indicate that significant changes in deposit morphology and orientation can occur in the first few hours of electrolysis with a stable structure growing after this time. In the present work, the effect of aluminum cathodes of various grain sizes on the zinc deposit morphology for electrolysis times ranging from several seconds to 1 h is reported.

2. Experimental procedure

2.1. *Materials and apparatus*

The electrolyte was prepared from hot neutral zinc clarifier overflow purified with zinc dust obtained from Cominco Ltd., Trail, British Columbia. The average analysis was (in mg l^{-1}): Zn, 150 000; $MgSO_4$, 38 000; Mn, 1600; Cd, 0.2; Sb, 0.02; Co, 0.3; Ge, 0.01; Ni, 0.1; Cu, 0.1; Fe, 0.9; Pb, 0.2; Cl, 80.0; F, 3.0. Cell solutions were prepared by adding H_2SO_4 and redistilled water to the electrolyte to give final concentrations of 65 g l^{-1} Zn and 200 g l^{-1} H_2SO_4. Animal glue was added as a concentrated solution.

The electrolysis cell consisted of a 1-litre beaker fitted with a Lucite cover which had slots cut in it to mount the electrodes. A three-electrode assembly consisting of a central aluminum cathode and two Pt anodes was used. Platinum anodes were used to eliminate the Pb

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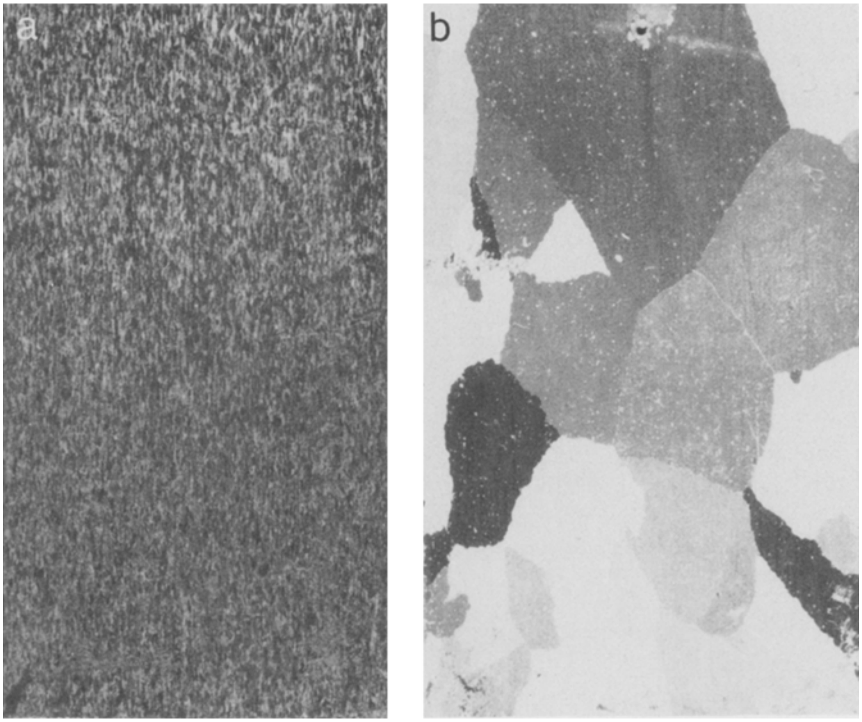


Fig. 1. Photographs of commercial purity Al cathodes with surfaces etched to reveal the grain size. (a) Fine grain size; (b) large grain size. × 2.

effects on the zinc deposits that can result from using conventional Pb–Ag anodes [5].

The cathodes were fabricated from commercial purity Al (99.6%) obtained from Cominco. Cathodes of varying grain size were produced from this material by the strain anneal method as follows: Al sheet (0.3 cm thick) was cold rolled to 0.2 cm in one pass and then annealed for 30 min at 550° C and quenched in cold water. This treatment had previously been shown to give a fine grain size. Specimens about 5 cm × 35 cm were then strained 2% in tension using punch marks and calipers. The aluminum was then annealed for 30 min at 600° C and cold water quenched. Photographs of typical cathodes showing the extremes in Al grain size are presented in Fig. 1.

The cathodes used in the experiments designed to examine initial zinc nucleation measured 2.5 cm × 2.5 cm.as this was the maximum size which could be accommodated in the SEM specimen chamber. Thus, the large-grain Al cathodes consisted of a single crystal only. The cathodes were mounted in a specially designed Plexiglas holder such that only one side of the cathode was exposed to the electrolyte; zinc was therefore deposited on only one side of the cathode so that the deposit-free side could be mounted directly onto the SEM specimen stub. The exposed cathode area was 3.6 cm^2. Electrical contact to the cathode was made via a length of commercial Al which was kept isolated from the electrolyte. The types of cathode used together with their pretreatment conditions are listed in Table. 1. The cathodes used in the longer-time electrolyses (15–60 min) measured 15.2 × 3.2 × 0.3 or 0.2 cm thick and were mounted in the cell such that the total deposit area was 25.8 cm^2. Prior to use for the first time, all cathodes were etched for 10 min at room temperature in a solution consisting of 3 parts HNO_3 and 1 part HF.

2.2. *Electrolysis*

For the initial nucleation studies, zinc deposits were electrowon at current densities ranging from 22 to 215 mA cm^{-2} for deposition times of 2–300 s using the various cathode types listed

Table 1. Types of cathode used and their preparation

Cathode	*Surface treatment*	*Preconditioning*
Type 1		
A. Large-grain Al	10-s etch* to reveal grain	—
B. Large-grain Al	Degreased with acetone	—
C. Large-grain Al	10-s etch to reveal grain	24-h soak in electrolyte
D. Large-grain Al	10-s etch to reveal grain	72-h soak in electrolyte
Type 2		
A. Commercial Al (fine grain)	10-s etch to reveal grain	—
B. Commercial Al (fine grain)	Degreased with acetone	—

* 3 parts HNO_3 + 1 part HF.

in Table 1. Deposits were also obtained using the large-grain Al specimens in electrolytes containing 15, 30 and 45 $mg\,l^{-1}$ glue to determine the effects of glue additions on the early stages of zinc deposition. After the specified deposition time, the cathodes were removed from the holder, washed, dried and mounted on the SEM specimen stubs.

In the longer-time experiments (15–60 min), fresh electrolyte was used only at the beginning of each series of runs, i.e. when a cathode was used for the first time. During a series, the zinc removed by electrodeposition after each run was replaced by adding the appropriate amount of neutral clarifier overflow. The amount of zinc removed from solution during each run was determined by accurately weighing the stripped deposit. Sections of each deposit were examined in the SEM to determine their morphology in relation to the Al grain size and current density.

3. Results and discussion

3.1. *Long-time deposit characteristics*

The 'long-time' deposits obtained on the large-grain Al cathodes were wet-backs (i.e. the backsides of the deposits were covered with a thin film of electrolyte) and in many instances the deposits bulged out from the surface of the Al cathode. At the highest current densities, i.e. 161 and 215 $mA\,cm^{-2}$, the 60-min deposits were quite rough except for the deposits formed on the cathodes composed of large grains (Fig. 1b). In addition, the deposits formed on the large Al grains were generally easier to strip than those formed on the cathodes composed of fine grains.

Sections of the deposits obtained from the various cathodes were examined in the SEM. For the large-grain Al cathodes, sections of the deposits from individual grains were examined by this technique. The results revealed that the size of the zinc platelets and their orientations were essentially the same for each cathode, irrespective of the Al grain size. A typical deposit morphology is shown in the SEM photomicrograph, Fig. 2. The deposit morphology is seen to consist of sharply defined hexagonal zinc platelets aligned at intermediate angles (30–60°) to the Al cathode. The preferred orientation is predominantly [1 1 2] [1 1 4] [1 0 2] relative to the ASTM standard for zinc powder. These deposit characteristics are typical of zinc electrowon from highly purified zinc electrolyte [2].

Fig. 2. SEM photomicrograph showing the typical zinc deposit morphology. × 700.

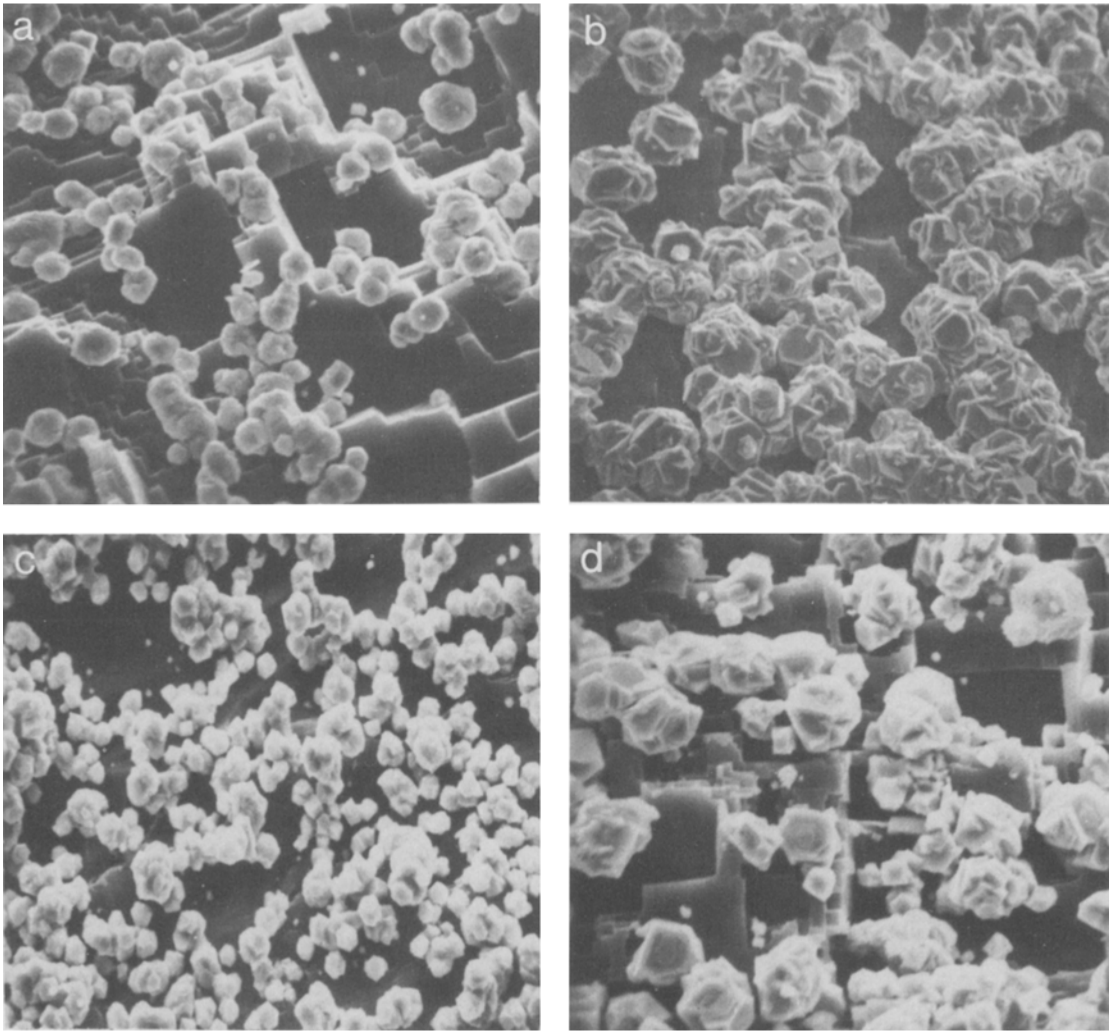


Fig. 3. SEM photomicrographs showing the initial zinc nucleation on various etched Al cathodes as a function of current density and deposition time. (a) $215\,\mathrm{mA\,cm^{-2}}$; 5 s; large-grain Al. (b) $215\,\mathrm{mA\,cm^{-2}}$; 15 s; large-grain Al. (c) $215\,\mathrm{mA\,cm^{-2}}$; 5 s; fine-grain Al. (d) $54\,\mathrm{mA\,cm^{-2}}$; 80 s; large-grain Al. × 1400.

3.2. *Initial zinc nucleation*

To obtain more information on the type of zinc deposits formed on the large-grain Al cathodes and also to investigate more fully the lack of influence of Al grain size on the zinc deposit morphology, the initial zinc nucleation was studied for a variety of experimental conditions.

The initial tests were carried out using the large-grain Al specimens in addition-free electrolyte. A SEM photomicrograph of a 5-s zinc deposit electrowon at $215\,\mathrm{mA\,cm^{-2}}$ on a type 1A cathode (see Table 1) is shown in Fig. 3a. In addition to detailing the initial zinc deposit characteristics, the photomicrograph also reveals the surface detail of the large-grain Al cathode. As indicated by Fig. 3a, the Al surface (single crystal) is extremely rough and consists of an irregular series of steps. The zinc deposits initially as isolated clusters with nucleation generally occurring on the high edge (ridge) of a step site. Subsequent deposition occurs on the initial zinc nuclei and eventually results in a network of zinc clusters joining one edge site to another on the surface of the Al grain. This type of growth eventually results in the formation of zinc deposits which have large portions of their backsides not in contact with the Al cathode surface and thus accounts for the wet-backed and bulging long-time deposits obtained on the large-grain Al cathodes.

The subsequent growth and detail of the zinc clusters is clearly indicated in the SEM photomicrograph of a 15-s deposit obtained at 215 mA cm^{-2} (type 1A cathode) (Fig. 3b). The clusters are essentially spherical in shape and are composed of small hexagonal zinc platelets randomly oriented to one another. The formation of new nuclei on the surface of the clusters is clearly indicated in the photomicrograph (Fig. 3b).

A SEM photomicrograph of a 5-s deposit electrowon at 215 mA cm^{-2} on a fine-grain Al cathode (Type 2A, Table 1) is shown in Fig. 3c. In this case there is a more complete coverage of the surface by the deposited zinc (cf. Fig. 3a), that indicates the presence of more nucleation sites. This growth pattern explains the lack of 'wet-backed' deposits obtained for the fine-grain Al cathodes. Otherwise, the initial growth pattern of the zinc deposit is the same as that observed for the large-grain Al cathodes.

Initial zinc deposits were also electrowon at lower current densities, e.g. 54 and 22 mA cm^{-2}. The SEM photomicrograph of an 80-s deposit electrowon at 54 mA cm^{-2} (Type IA cathode) (Fig. 3d) indicates essentially the same growth pattern observed for the 15-s deposit electrowon at 215 mA cm^{-2} (cf. Fig. 3b).

3.3. *Unetched surfaces*

For comparative purposes, initial zinc deposits were obtained using unetched cathodes (see Table 1). Fig. 4 shows an SEM photomicrograph of a 10-s deposit electrowon at 215 mA cm^{-2} on a section of unetched commercial Al, Type 2B. As was the case for the etched surface (see Fig. 3a), the initial growth of zinc occurs in clusters. A comparison of Figs 3a and 4 indicates that the surface of the etched Al is covered more completely with zinc than is the unetched surface, despite the fact that the deposition time for the etched sample was one half that of the unetched surface. The initial deposits obtained on the unetched surface were poorly adherent and care had to be taken not to dislodge the deposit during the washing stage.

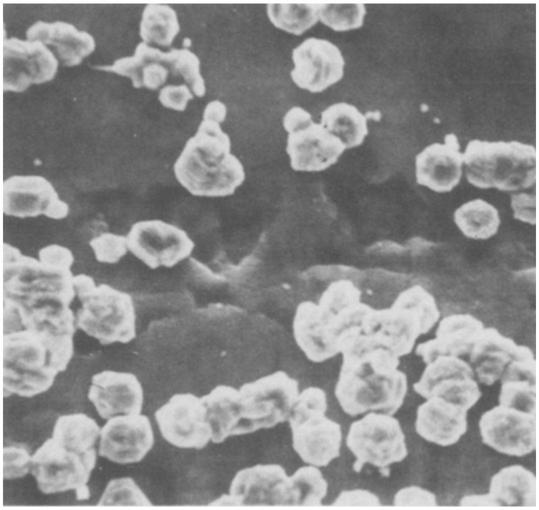
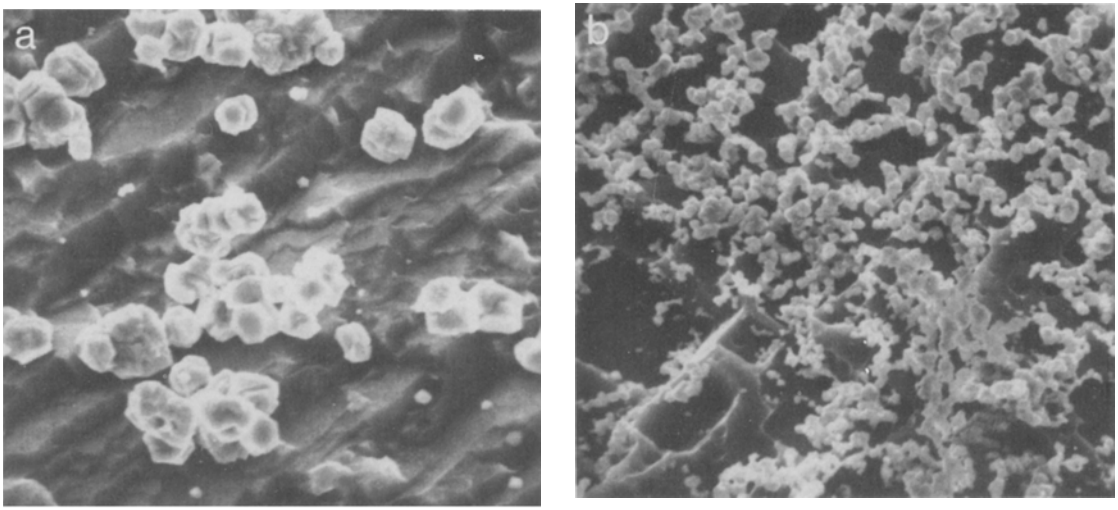


Fig. 4. SEM photomicrograph showing the initial zinc nucleation on an unetched Al cathode (215 mA cm^{-2}, 10 s). × 1400.

3.4. *Cathode surface conditioning*

Initial zinc deposits were obtained on large-grain Al cathodes which had been presoaked in the electrolyte for times of 0, 24 and 72 h. The effect of this cathode pretreatment on the initial zinc nucleation is shown in Fig. 5a–c. The 24 h conditioning resulted in a substantial increase in the number of zinc nuclei formed compared to the unconditioned cathode (cf. Fig. 5a, 5b). This resulted in a more complete coverage of the cathode surface by the deposited zinc. The 72 h conditioning, however, had a detrimental effect on the initial zinc nucleation, as indicated by Fig. 5c. The number of zinc clusters was considerably reduced (less than for the unconditioned surface, cf. Fig. 5a), but the zinc platelets were similar in size to those formed on the unconditioned surface. The striking feature to note from Fig. 5c is that soaking the Al cathode in the electrolyte for 72 h resulted in a severely pitted surface.

A possible explanation for the increased number of zinc nuclei formed on the 24-h conditioned cathodes is that the treatment results in the formation of a surface coating (oxide) which 'blocks' the few highly active low-energy



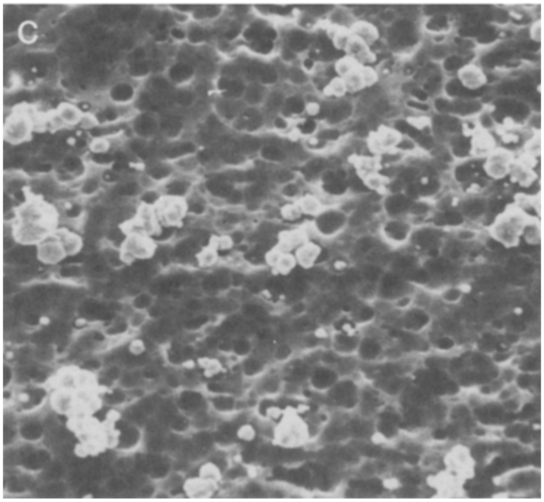


Fig. 5. SEM photomicrographs showing the effect of cathode pretreatment on the initial zinc nucleation. Cathode: large-grain Al (etched), deposited at $108\,\mathrm{mA\,cm^{-2}}$ for 10 s. (a) No soak; × 1400. (b) 24-h soak; × 1400. (c) 72-h soak; × 700.

nucleating sites usually present. The increased zinc nucleation leads to the formation of a more uniform, non-lacy zinc deposit and also reduces the tendency for 'wet-backs' to occur.

3.5. *Initial zinc nucleation in the presence of glue*

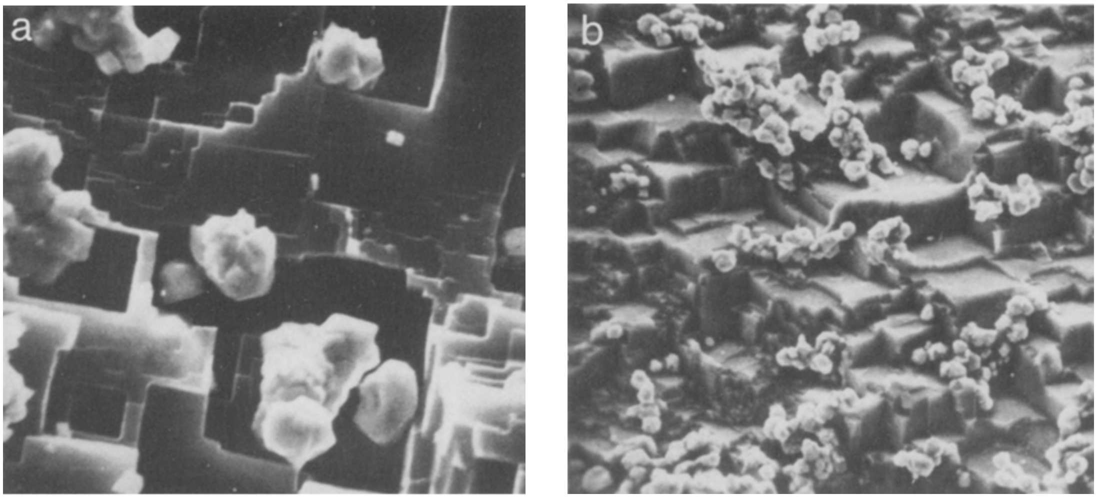
Glue is usually added to the electrolyte in regulated amounts to control the growth characteristics of the zinc deposits. In the presence of glue, the zinc platelets become oriented perpendicular to the surface of the Al cathode [4]. In the presence of glue the outer face of the deposit becomes quite smooth because all of the platelet edges grow at a similar rate.

In the present study, a series of tests was carried out to examine the effect of glue additions to the electrolyte on the initial zinc nucleation. The zinc deposits were obtained on large-grain Al cathodes (etched to reveal the grain; Type 1A) for various current densities and deposition times from electrolytes containing 15, 30 and $45\,\mathrm{mg\,l^{-1}}$ glue. The results are presented in Fig. 6a–c. In the presence of higher concentrations of glue there is a tendency for the zinc clusters to nucleate in the surface depressions rather than on the high edge sites. Subsequent zinc deposition occurs on the initial zinc nuclei and the clusters tend to grow upwards, out of the surface depressions. The tendency for zinc nucleation to occur in surface depressions could lead to the formation of 'stickers' (deposits difficult to strip) during prolonged electrolysis.

4. Conclusions

The grain size of the Al cathode had no significant effect on the structural characteristics of 'long-time' zinc deposits. However, deposits obtained using large-grain Al cathodes were often 'wet-backs' and tended to bulge out from the surface of the Al cathode.

The study of the initial nucleation of zinc on



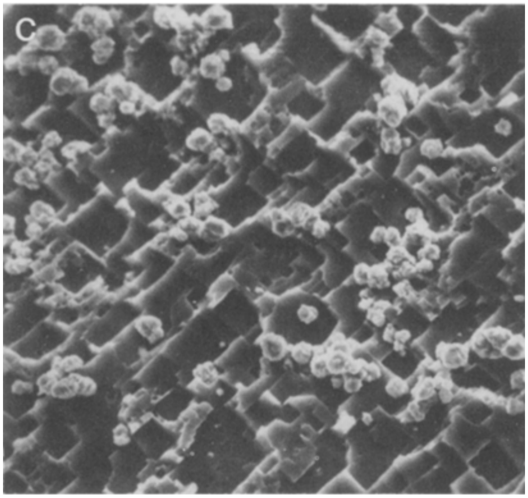


Fig. 6. SEM photomicrographs showing the effect of glue on the initial zinc nucleation of large-grain etched Al cathodes. (a) $22\,\mathrm{mA\,cm^{-2}}$; 50 s; $15\,\mathrm{mg\,l^{-1}}$ glue; × 3500. (b) $215\,\mathrm{mA\,cm^{-2}}$; 5 s; $30\,\mathrm{mg\,l^{-1}}$ glue; × 700. (c) $108\,\mathrm{mA\,cm^{-2}}$; 10 s; $45\,\mathrm{mg\,l^{-1}}$ glue; × 700.

various types of Al cathode indicated that the etched surfaces of both the large and fine grain Al are very similar and this explains why the zinc platelets were of comparable size for both types of cathode. The initial growth mode of the zinc deposits on the large-grain Al cathodes also explains the formation of the bulging long-time deposits obtained on this type of substrate.

The type of cathode surface pretreatment had a significant effect on the initial zinc nucleation. Soaking the cathodes for 24-h periods in the electrolyte prior to zinc depositon resulted in a substantial increase in the number of zinc nuclei and a more complete surface coverage. The same treatment carried out for 72 h, however, had a detrimental effect on the initial zinc nucleation that was probably related to the severe pitting of the Al surface that resulted from this treatment. When the surface of the Al cathode was not conditioned in any way, including etching, the initial zinc deposit was poorly adherent.

The presence of glue in the electrolyte resulted in a tendency for the initial formation of zinc clusters to occur in the surface depressions on the cathode.

Acknowledgement

Thanks are due to Cominco Ltd for supplying the electrolyte and commercial Al sheet.

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