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Electrochemical evaluation of the adherence of zinc to aluminum cathodes

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Abstract

Excess fluoride ions in zinc electrolyte are known to cause problems with the removal of electrowon zinc from aluminum blanks. The mechanisms responsible for this undesirable adherence were studied. Acid zinc sulfate electrolyte similar to that employed in zinc electrowinning was used. Using electrolyte containing various fluoride ion concentrations, the initial nucleation and growth morphology of zinc and the aluminum electrode surface were examined using scanning electron microscopy. Electrochemical tests were also carried out in various solutions to obtain a better understanding of the polarization behavior of the system.

1. Introduction

Proper adherence of deposited zinc to the aluminum blank is critical to electrowinning plant operation. If adherence is poor then deposits may spontaneously drop off, disrupting cell or handling operations. A more common problem is the case in which zinc is difficult or impossible to remove from the aluminum. The “stickers” must be pulled from the normal production cycle and the zinc dissolved in acid in a separate cell.

Recent studies by Kammel *et al.* [1] described the influence of halide ions such as F^- and Cl^- and other metal impurities commonly introduced from leaching of roasted concentrate on zinc deposit adherence. They considered that higher adherence was due to a dominating hexagonal platelet growth parallel to the substrate and weak adherence resulted when more randomly oriented columnar deposits were obtained in the initial nucleation and growth process.

Mackinnon and Brannen [2] showed that the decreased number of nuclei due to large grain size of the starting aluminum cathode had a bearing on the ease of stripping. They also mentioned cathode pretreatment effects, such as soaking in the electrolyte prior to electrolysis, as a means of increasing the number of nuclei, whereas no conditioning resulted in poor adherence.

Another pretreatment method was used by Andrianne *et al.* [3] who confirmed the deleterious influence of fluoride ions on the corrosion of aluminum and the resulting strong adherence of the zinc deposit. They

summarized that fluoride ion attack on the aluminum oxide layer provided deep pits in which two-dimensional growth of zinc parallel to the substrate could occur, acting as anchoring sites for the deposit, resulting in an adherent deposit. Therefore, in order to overcome the problem, brushing the aluminum blank was suggested to eliminate strongly adherent zinc spots remaining on the substrate and to give a uniform starting oxide layer.

Even with these advances in understanding the sticking problem, a fundamental mechanism on the mode of formation of adherent zinc was not clear. Other research has focused on quantifying the adherence strength, which was very helpful. However, there appeared to be a need for additional information on the evaluation of the nature of the aluminum surface leading to adherence with continued cycling during use.

In order to obtain more basic information on the relationship of the fluoride ion to the aluminum condition, a series of tests was designed in which these two parameters were varied. Surface characterization and changes occurring were determined. An investigation was also made on the effect of acid concentration and applied potential. Particular attention was given to determining the degree of spontaneous zinc deposition, or cementation, that could occur. The degree of reactivity observed was then used as an indicator of the aluminum oxide stability.

Other electrochemical tests were employed in this research and included cyclic voltammetry [4, 5] and a.c. impedance measurements [6, 7]. Cyclic voltammograms were used to characterize the effect of fluoride ions on the initial polarization behavior of the aluminum in the various electrolytes and on zinc deposition. A.c. imped-

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ance measurements were carried out to evaluate the electrochemical stability of the aluminum substrate when it was held in solutions containing fluoride ions. Attempts were then made to correlate these data with observations on the adherence tendencies of the zinc deposited from similar electrolytes.

2. Experimental details

2.1. Electrolyte

The electrolyte was prepared by dissolving French zinc oxide in sulfuric acid. The neutral solution ($\text{pH} > 4$) with 180 g l^{-1} of zinc concentration was then diluted with water and sulfuric acid to give an electrolyte composition of $50:150 \text{ g l}^{-1}$, $\text{Zn}:\text{H}_2\text{SO}_4$, respectively. The chemical analysis of the neutral solution showed 2.91 ppm lead, 59 ppb cadmium, 26 ppb nickel, 10 ppb arsenic, and 3 ppb antimony as major impurities.

The NaF solution was prepared by dissolving the pure salt, supplied by Fisher Scientific Company, in demineralized water to give a 20 g l^{-1} concentration.

2.2. Electrodes

Aluminum electrodes, provided by Big River Zinc Co., Sauget, IL, were cut to give a deposit area of 2 cm by 2 cm. Cathodes were prepared by polishing with either 600 grit emery paper or polishing cloth and were then cleaned with water in an ultrasonic bath.

Four different surface preconditioning procedures were used: (1) as polished on 600 grit emery paper (PC), (2) polished and pickled in 3 M sulfuric acid solution for more than 4 h (P'C), (3) polished and aged in a solution with 80 g l^{-1} zinc, 135 g l^{-1} H_2SO_4 , and 4 g l^{-1} F⁻ for more than 4 h (AA), and (4) polished and held in regular electrolyte for 10 min (PH).

Platinum mesh anodes were used to avoid any lead contamination.

2.3. Electrolysis

Each electrolytic cell was composed of one anode and one cathode attached vertically to a Plexiglass lid. The electrode distance was 2.5 cm in the 250 ml beaker cell. To increase the reliability of comparison data of zinc adherence, several cells with various amounts of fluoride and different cathode conditions were run in series. Electrolyses were carried out at a current density of 50 mA cm^{-2} at 35°C for 8 h, using an HP 6248A power supply, unless otherwise noted. After electrolysis, the cathode was quickly removed from the cell, rinsed with distilled water, dried with hot air, and then subjected to the stripping test.

2.4. Examination of deposits

Deposits were manually stripped after electrolysis and the degree of adherence was estimated on a relative basis. Three categories were used to indicate the difficulty of zinc removal: (1) easy to strip (E), (2) difficult to strip (D), and (3) impossible to strip (I).

E-type deposits are easily removed using a low applied force without distorting or damaging the zinc plate. For D-type deposits, a strong force was necessary to strip the deposit, often resulting in some distorting and cracking of the zinc deposit. Type I deposits were so adherent that it was impossible to remove the zinc without physically disrupting the aluminum substrate. Even though the adherence test was very qualitative, differences in bonding were relatively easy to differentiate, and correspond favorably with what is encountered in industrial practice.

In order to compare the degree of adherence with initial surface condition, the nucleation and growth of the zinc deposits on substrates exposed to various fluoride concentrations were also examined by scanning electron microscopy (SEM).

2.5. Zinc cementation test

Very smooth aluminum substrates polished with $0.05 \mu\text{m}$ alumina powder were immersed in zinc electrolyte for short time intervals of 5, 10, 30, and 60 s. Solutions of 50 g l^{-1} zinc content with various amounts of acid and fluoride ion were used. With these conditions zinc spontaneously deposited or cemented onto the aluminum. To test the adherence of cemented zinc, the electrode was quickly transferred to an electrolytic cell containing standard electrolyte with no fluoride, *i.e.* $50:150 \text{ g l}^{-1}$ of $\text{Zn}:\text{H}_2\text{SO}_4$. Electrolysis was continued for 8 h, which gave a deposit sufficiently thick to test for adherence. Micrographs were taken of the cemented zinc and aluminum substrate after the immersion reaction.

2.6. Cyclic voltammetry

Cyclic voltammetry tests were conducted using a Petrolite Potentiodyne Analyzer (model M-4100) to determine the effect of various fluoride contents on polarization behavior. The potential limits for the voltammograms were between -0.9 V and -1.3 V (*vs.* a saturated calomel reference electrode) at a sweep rate of 5 mV s^{-1} . The cell design was the same as described previously, except that the calomel electrode was set between the two electrodes and ambient temperature was used. The working electrodes were prepared by polishing on cloth with $0.05 \mu\text{m}$ alumina powder, rinsing with distilled water in the ultrasonic bath, and then holding in the air for 1 h to obtain a stable oxide layer. A potential sweep was started immediately after placing the working electrode in the electrolyte to avoid any

preconditioning effects in a fluoride-containing electrolyte. The potential scan was started at -0.9 V and driven in a cathodic direction. When it reached the upper limit the direction was shifted in the anodic direction to complete the cycle.

2.7. A.c. impedance

A.c. impedance data were obtained using a Princeton Applied Research Model 378 Electrochemical Impedance System. Smooth aluminum substrates were evaluated at ambient temperature in an electrolyte with various amounts of sulfuric acid and fluoride. The impedance measurements were performed by means of a lock-in amplifier over frequency ranges from 5 Hz to 10^5 Hz at the open-circuit potential. Five points per

decade on a log scale and 5 mV a.c. amplitude were used to generate the impedance plots.

3. Results and discussion

3.1. The effect of fluoride concentration

Using smooth electrodes polished with $0.05\text{ }\mu\text{m}$ alumina powder, the relative adherence of zinc deposit to aluminum due to increasing fluoride concentration was evaluated. The adherence progressed from easy (E) to difficult (D) to impossible (I) types as the fluoride content increased from 0 to 1 to 3 g l^{-1} .

Figure 1 shows the changes in initial nucleation morphology with increasing fluoride content. At very

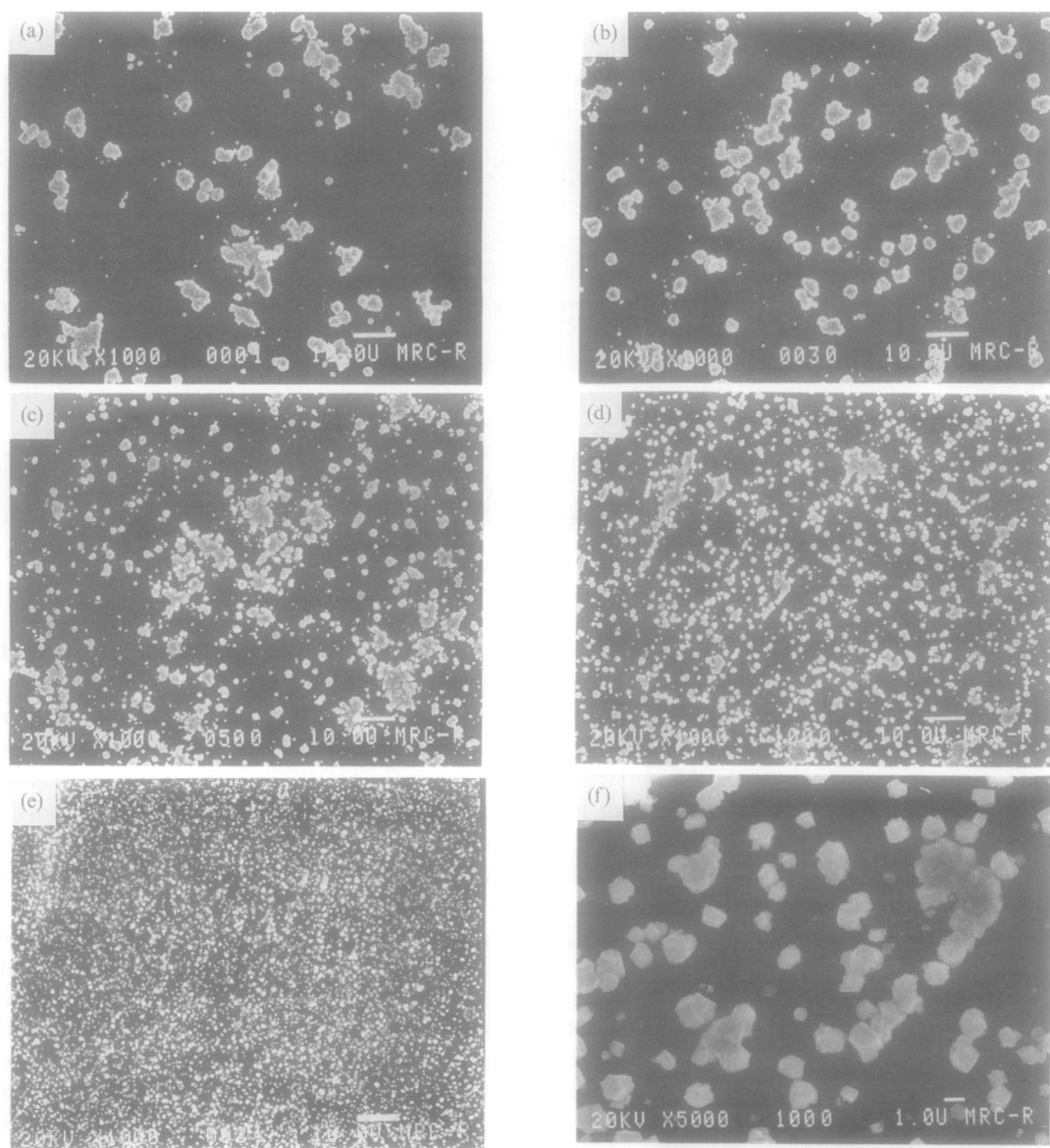


Fig. 1. Initial 10 s deposits on the smooth aluminum substrates at 50 mA cm^{-2} and $35\text{ }^{\circ}\text{C}$ ($1000\times$): (a) in fluoride-free solution, (b) in 30 ppm F^{-} solution, (c) in $0.5\text{ g l}^{-1}\text{ F}^{-}$ solution, (d) in $1\text{ g l}^{-1}\text{ F}^{-}$ solution, (e) for 3 s in $2\text{ g l}^{-1}\text{ F}^{-}$ solution, (f) higher magnification of (d) ($5000\times$).

low fluoride content, *i.e.* zero or 30 ppm F^- (Figs. 1(a) and 1(b)), relatively large nuclei ranging from 5 to 10 μm and low surface coverage occur, with slightly more nuclei when the electrolyte contained fluoride. The growth mode appears to be both outward and lateral, resulting in eventual bridging between zinc particles. The nucleation seems to be progressive, but only a very small number of new nuclei are formed with time, indicating that the growth mode is favored over progressive nucleation.

With higher fluoride content (Figs. 1(c)–1(f)), the nuclei became smaller and the nucleation rate increased dramatically, resulting in more complete coverage of the substrate. The aluminum electrode was nearly 50% covered and the size of nuclei decreased to less than 1 μm . The nuclei are more uniform in size and the bridging or particle agglomeration continued to decrease with increasing fluoride. The morphology reveals that the nucleation was more or less instantaneous, with a very uniform density (Fig. 1(f)).

Figure 2 shows the aluminum substrate, after stripping the zinc, which was used in electrolytes containing various amounts of fluoride. When no difficulty was noted when stripping the 8 h zinc deposit, energy dispersive analyses revealed that the aluminum substrate used in 100 ppm fluoride electrolyte had less than 1% zinc remaining on its surface (Fig. 2(a)). When the fluoride content was increased to 0.5 g l^{-1} , stripping became relatively difficult, and the amount of residual zinc also greatly increased, covering nearly one third of the entire surface area (Fig. 2(b)). The implication was that there would be a relationship between the amount of residual zinc and the adherence. The residual zinc seemed to show evidence of mechanical failure of initial particles which were associated with shallow pits. As seen in Fig. 1, there are smooth blank areas between zinc nuclei that do not show any sign of attack by fluoride ions. Thus, where fluoride attack occurs, pits form and are believed to be the places where the bases of the adherent particles were located.

When the aluminum substrates were immersed in 3 M sulfuric acid solution to remove all surface residual zinc, it is seen in Fig. 3 that only a small number of fine pits are observed on the substrate used five times in 30 ppm fluoride solution (Fig. 3(a)). However, even a 20 s deposit in 3 g l^{-1} fluoride solution caused an I-type adherence. The increasing fluoride not only increased the fine pits but also began to generate a considerable amount of deeper pits (Fig. 3(b)), which were evident only after the aluminum was cleaned in acid. Thus it is felt that the deep pits are the more likely sites for zinc–aluminum adherence.

Based on the microscopic evidence, some explanations for the increased adherence in the presence of fluoride are possible. Generally, the oxide layer on the aluminum

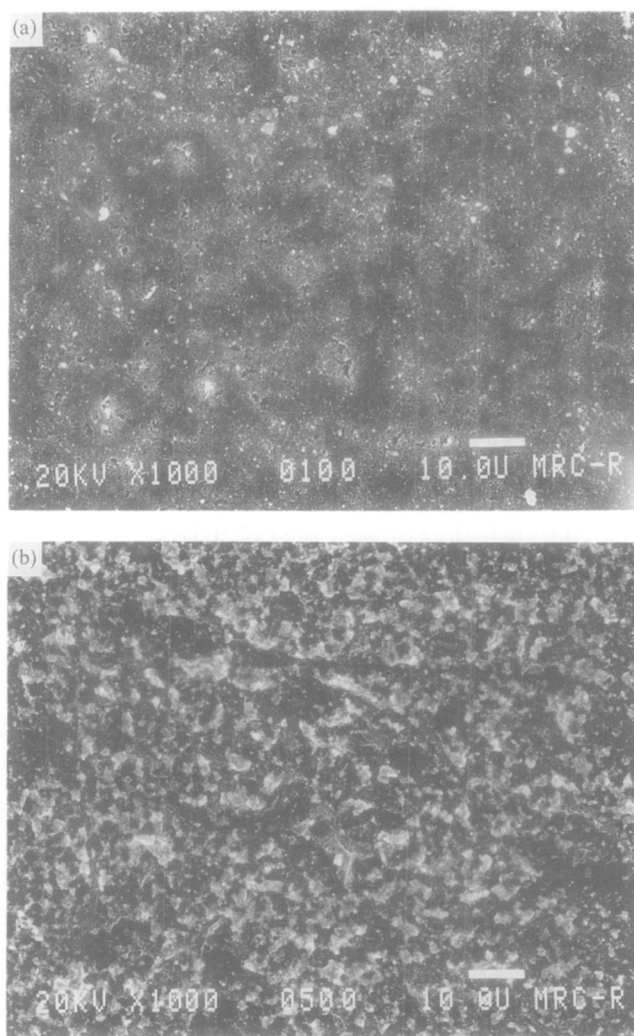


Fig. 2. Stripped aluminum substrate (1000 \times): (a) used in 100 ppm F^- solution, (b) used in 500 ppm F^- solution.

electrode blank is stable in the regular electrolyte and very few sites are provided for zinc nucleation. In fluoride-containing solution, the aluminum oxide layer becomes less stable, possibly exposing the metal substrate and providing more active sites, which results in an increase in nucleation and less growth of the individual zinc crystals. The higher degree of contact and enhanced metallic bonding between the zinc and aluminum lead to more adherent deposits.

With more fluoride in the electrolyte, additional areas on the aluminum substrate are attacked and the rate of reaction increases as well. The zinc now deposits in the deeply recessed areas and provides adherence in two different ways. First the data show that zinc can be cemented onto aluminum, indicating that metal to metal contact is occurring. Simultaneously the aluminum is undergoing non-uniform corrosion with a large amount of hydrogen gas evolution and ultimately pit formation. Zinc can then deposit in the pits and be held in place

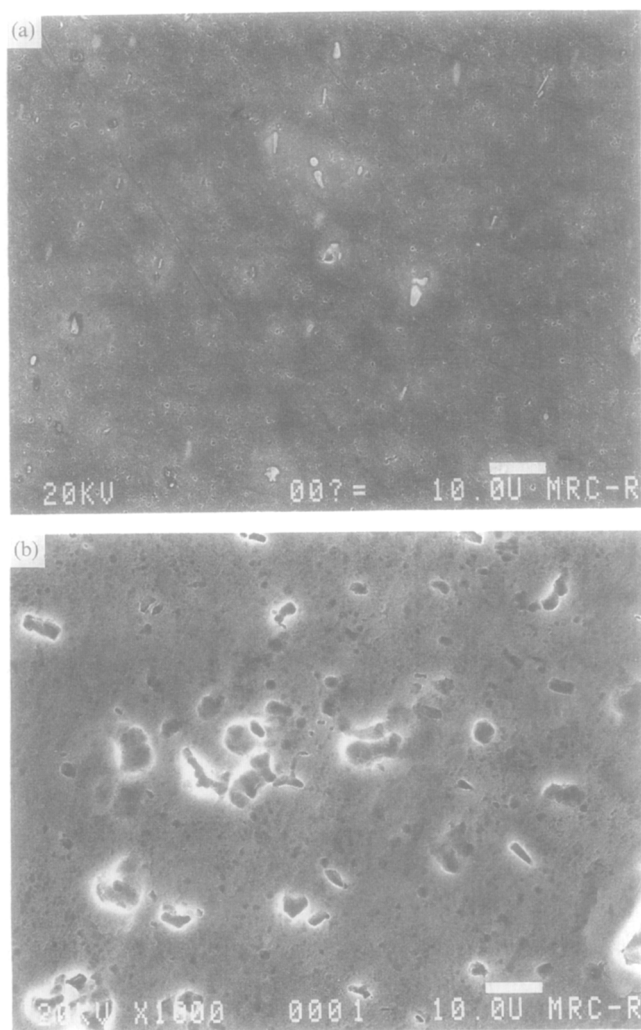


Fig. 3. Dissolved aluminum substrate (1000 \times): (a) used five times in 30 ppm F^- solution, (b) used in 3 g l^{-1} F^- solution.

mechanically. The combination of metallic and mechanical bonding is then dually responsible for the degree of adherence observed. The relative amounts of each type can change with operating parameters and fluoride content, but both appear to play a role in the degree of sticking that is observed.

A simple tape test was also made to check the adherence strength of the zinc nuclei. Adhesive tape was firmly pressed onto the zinc and then detached. When zinc had been deposited for 1 min with 1 g F^- in solution, a substantial amount of zinc still remained on the aluminum substrate after the tape was detached. When no fluoride was present in the electrolyte, almost all the zinc particles were removed by the adhesive tape.

3.2. Zinc cementation test

In order to obtain a better understanding of the effect of fluoride attack, zinc cementation tests were conducted on smooth aluminum substrates in low acid electrolyte,

i.e. 0, 10, and 50 g l^{-1} sulfuric acid, and high fluoride concentrations.

According to previous researches [8, 9], aluminum forms soluble trivalent compounds in hydrofluoric acid with hydrogen evolution being the reduction reaction. It was also shown by Spacht [10] that when aluminum was subjected to the action of hydrofluoric acid, a film protected it for a short while. Not until the film had been completely penetrated did true corrosion occur. The exact nature of the film was not indicated, but it is generally accepted that the halogens can cause extreme localized deterioration of the protective oxide film, allowing the various spontaneous electrochemical reactions to proceed [11].

A similar reaction is likely to occur in the zinc cementation test. With less than 1 g l^{-1} of fluoride ion, no significant zinc could be detected, regardless of acid concentration. When the fluoride content was increased to more than 1 g l^{-1} , a visible amount of zinc was evident within 5 s even at low acid concentrations, and the amount of zinc increased with acid concentration and fluoride content. However, when the sulfuric acid concentration reached 150 g l^{-1} , the cemented zinc dissolved so quickly that no zinc was visible. Instead, fine bubbles evolved continuously from the substrate, indicating that the sequence of aluminum oxide layer disruption, metal aluminum exposure, zinc cementation, and zinc dissolution, was continued. When the electrode is polarized in the cell a similar sequence most probably occurs, but the magnitude and rate of these reactions change with the operating conditions.

After allowing the spontaneous reaction to proceed for 30 s in 50:10 g l^{-1} Zn: H_2SO_4 solution and 3 g l^{-1} fluoride ions, the aluminum substrate was completely covered with cemented zinc. The electrode was removed from the cementation solution and quickly transferred to the electrowinning cell containing electrolyte with a concentration of 50:150 g l^{-1} Zn: H_2SO_4 respectively and no fluoride. Zinc was deposited for 8 h and was very hard to strip, with residual zinc remaining on the aluminum substrate after stripping.

Figure 4 shows the change in morphology of a smooth aluminum substrate after being held in 50:10 g l^{-1} Zn: H_2SO_4 solution with 3 g l^{-1} fluoride for 4 h, and then dissolved in 3 M sulfuric acid solution. The cementation solution caused extensive degradation of the aluminum and zinc completely covered the whole aluminum surface. It is also seen that the aluminum surface was completely roughened and many deep pits could be produced, even without any potential being applied.

Comparison of the adherence and surface morphology of aluminum electrodes resulting from electrolytic and immersion tests provides some supplemental information on the role of the fluoride.

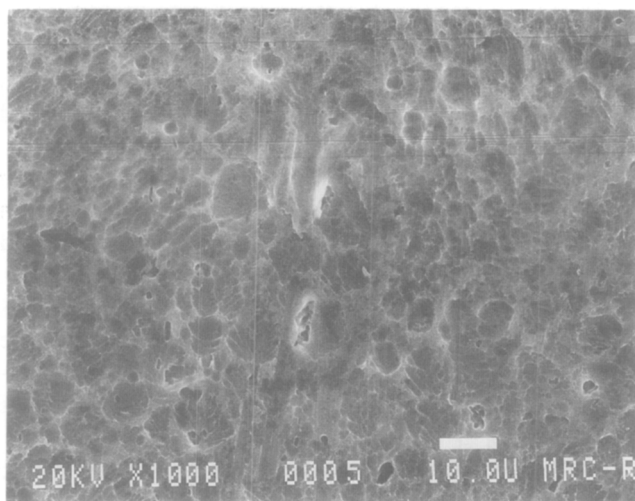


Fig. 4. Aluminum substrate after 4 h in 50:10 g l⁻¹ Zn:H₂SO₄ solution with 3 g l⁻¹ F⁻ and then residual zinc dissolved in sulfuric acid (1000×).

(1) Fluoride ions can attack the aluminum substrate, allowing zinc to be cemented spontaneously.

(2) Sulfuric acid accelerates the rate of attack of the aluminum oxide, but also partially dissolves the zinc deposited during the reaction. The sequence appears to be (a) aluminum oxide layer disruption, (b) metallic aluminum exposure, (c) zinc cementation, followed by (d) zinc dissolution.

(3) Applied cathodic potentials appear to enhance the fluoride attack and adherence by allowing zinc to be deposited electrolytically onto the favorable sites provided by the freshly exposed aluminum. The zinc is now also cathodically protected and is less susceptible to spontaneous redissolution.

3.3. The effect of cathode preconditioning

The effects of four surface preconditioning processes were evaluated with respect to their influence on zinc adherence. The adherence was shown to be minimized when the aluminum received an acid dip (P'C) in 3 M sulfuric acid for 4 h. The relative adherence of the zinc deposit made from 3 g l⁻¹ F⁻ electrolyte increased from easy (E) through to impossible (I) to strip as pickled (P'C) or aged (AA) to held in electrolyte (PH) to polished (PC).

As an indirect measure of the surface condition, a copper decoration method was also used. Samples made using four different types of surface treatment (PC, P'C, AA, and PH) were dipped into a solution containing 90:150 g l⁻¹ Cu:H₂SO₄ for 10 min and then ranked by the amount of copper cemented. Qualitatively, the amount of copper decreased in the order PC > PH > AA > P'C. The relative indication of surface

reactivity was consistent with the zinc adherence strength observed for each surface as mentioned above.

The copper cementation test revealed that a PC treated cathode, showing heavier copper cementation, has numerous active anodic surface sites, whereas the P'C cathode, with considerably less copper present, has a more passive aluminum surface. Assuming the copper cementation process is anodically controlled, the degree of copper reduction would be expected to be an indirect measure of the stability of the aluminum oxide coating. Copper was chosen because, unlike zinc, it was electrochemically stable in the acid solution and did not redissolve.

As indicated, the AA substrate also gives easy stripping, but the mechanism responsible may be somewhat different from that for the P'C substrate. When an AA substrate was used, more than 50% of the back side of the stripped zinc showed bulged or concave areas. This condition was probably caused by the evolving gas generated in the roughened, pitted areas on the aluminum. The bulging diminished as the fluoride content decreased; however, repeated usage of a stripped AA substrate in 1 g l⁻¹ F⁻ electrolyte was eventually impossible to strip, while the acid pickled (P'C) substrate still gave easy stripping.

3.4. Cyclic voltammetry

The polarization behavior of the various systems was evaluated using cyclic voltammetry techniques. The polarization curves generated for a smooth aluminum substrate with various fluoride concentrates are shown in Fig. 5. The surfaces were held in air for 1 h after polishing prior to testing.

The curves in Fig. 5 show that only slight changes are found during the front sweep while the fluoride content stays at a low concentration level (curve 1). With more

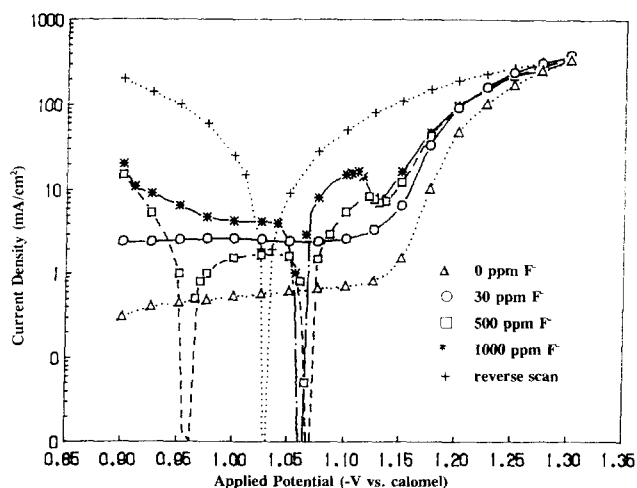


Fig. 5. Cyclic voltammograms of aluminum substrate in an electrolyte containing 50:150 g l⁻¹ Zn:H₂SO₄ and various F⁻ concentrations.

than 500 ppm fluoride (curve 2), the initial starting sweep shows a distinct anodic region. This result correlates well with the earlier results which showed a significant increase in the initial surface nucleation when the fluoride ion content went beyond 500 ppm. The anodic reaction is probably due to fluoride attack of the aluminum oxide, exposing an active aluminum surface to the electrolyte. Once aluminum metal begins to dissolve anodically, zinc and/or hydrogen ions can be reduced. The polarization curve shows net current and, therefore, both active anodic and cathodic reactions can be occurring simultaneously. In this case, the anodic current is dominant on the surface. These curves are quite definitive in illustrating the electrochemical modification caused by the fluoride. As the fluoride content increases, the reactive anodic current increases, meaning that aluminum is dissolving at an increasing rate. The curve eventually exhibits not only high anodic currents, but visually, hydrogen bubbles are in evidence for the localized cathodic reaction. As seen from the zinc cementation test, it can be assumed that zinc also deposits simultaneously, even if it immediately dissolves in the acid. The electrode is at a mixed potential, anodic to the equilibrium zinc potential, but the value approaches the reversible potential (represented by the value of cross-over from anodic to cathodic) as the fluoride content increases. This can also be seen from the shape of the initial cathodic sweep, showing the deposition overpotential to decrease continually with increasing fluoride. At very high fluoride contents, the zinc reduction reaction shows absolutely no nucleation overpotential, indicating that zinc is already present on the surface. Contrast this situation with the curves generated with low fluoride present. The overpotential for zinc deposition is high, giving a hysteresis in the curve; this is the type of polarization behavior expected when nucleation occurs on a truly inert substrate.

The voltammetry results shed considerable light on the electrochemical nature of reactions resulting when the electrolyte contains various amounts of fluoride. The data suggest that the increasing adherence of the zinc is mainly due to the residual surface zinc, deposited either spontaneously or electrolytically on active num sites, establishing a chemical bond between the two metals. If the zinc is not removed, preferential deposition occurs on these sites, which increases the mass of metal which is firmly anchored to the substrate.

3.5. Impedance spectroscopy

Impedance spectroscopy measurements are being used extensively in electrochemical studies, particularly those relating to corrosion. The technique has proven to be particularly valuable by determining an equivalent circuit model for the process [7]. Impedance spectroscopy data were generated in this study, but were used primarily as a qualitative verification for the observations made

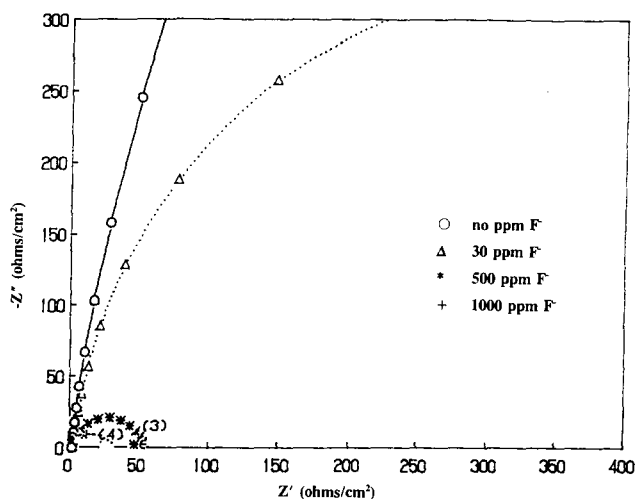


Fig. 6. Complex impedance plane plot for aluminum substrates in 50:150 g l⁻¹ Zn:H₂SO₄ electrolyte and various F⁻ concentrations.

using the other test techniques. As seen in Fig. 6, Nyquist plots from the a.c. impedance tests, obtained from 50:150 g l⁻¹ Zn:H₂SO₄ solutions containing different amounts of fluoride ions on aluminum at its rest potential, are shown. The trend observed for the a.c. impedance experiments is similar to that described previously for the polarization curves. The reactivity increases with fluoride content, causing a significant drop in the observed impedance, which is related to the intersection of the semi-circle on the x-axis. The impedance of the aluminum substrate in solutions without fluoride is so large that measured values in the test range, *i.e.* from 5 Hz to 10⁵ Hz, give a linear plot and thus no apparent intersection. However, with 30 ppm fluoride present, the impedance drops to about 800 Ω cm² and the value continues to decrease substantially with increasing fluoride ion concentration.

Another experiment was conducted to evaluate the combined influence of acid and fluoride on aluminum substrates in a solution containing 50 g l⁻¹ zinc ions as sulfate. For example, with 100 ppm F⁻ in solution, Fig. 7 shows that the impedance is 200 Ω cm² in 150 g l⁻¹ sulfuric acid solution, but is higher in acid-free solution as the linear curve in Fig. 7 implies.

The a.c. impedance tests provide additional qualitative evidence of the effect of fluoride ion on the surface stability of aluminum electrodes and the results correlate well with the tests described previously.

The apparent decrease in measured impedance is also consistent with the open-circuit potential measurements. The potentials of a smooth aluminum substrate were measured in 50:150 g l⁻¹ Zn:H₂SO₄ solutions containing various amounts of fluoride and are summarized in Table 1. As indicated, higher fluoride results in a more negative open-circuit potential, providing the enhanced corrosive environment for the working electrode. During

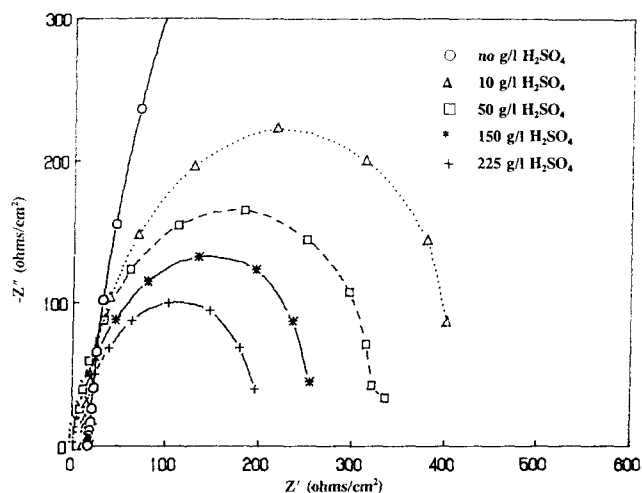


Fig. 7. Complex impedance plane plot for aluminum substrates in 50 g l⁻¹ zinc electrolyte containing 100 ppm F⁻ and various H₂SO₄ concentrations.

TABLE 1. The open-circuit potential between an aluminium substrate and a calomel reference electrode

Substrate	Fluoride content	Open-circuit potential (V)
PC	None	-0.35
PC	100 ppm	-0.65
PC	500 ppm	-0.77
PC	1 g l ⁻¹	-0.98
PC	3 g l ⁻¹	-1.01

PC, smooth substrate polished on cloth with 0.05 µm alumina powder.

the test, hydrogen evolution was more pronounced with more fluoride in solution.

Based on the open-circuit potential data, it appears to be possible that the degree of surface stability of aluminum electrodes can be predicted quantitatively by simple open-circuit potential measurements. Some modifications in interpretation may be necessary for practical applications, however, because of interactive effects caused by other chemical species present in the industrial electrolytes.

4. Conclusions

Based on analysis of the results obtained, the following conclusions can be drawn.

(1) The adherence of zinc to the aluminum blank is directly proportional to the fluoride content of the electrolyte. Fluoride ion attacks the aluminum electrodes to a noticeable degree causing general corrosion and pitting, which in turn generates preferable sites for direct bonding of the zinc to aluminum.

(2) Fluoride attack is enhanced as the acid content

increases. In acid-free solution, fluoride may attack the aluminum substrate, but degradation is not severe.

(3) The types of surface preconditioning used on the aluminum determine the degree of zinc adherence in high fluoride solution. The adherence on preconditioned substrates was decreased in the order polished (PC) > fluoride pickled (PH) > aged (AA) > acid pickled (P'C).

(4) The presence of fluoride is detectable using polarization techniques, and the content or activity can be determined semi-quantitatively by analyzing the nature of the current-overpotential relationship. Solutions high in fluoride concentration show anodic regions during the initial sweep and a decrease in zinc deposition overpotential. As the fluoride content increases, the anodic region increases and the crossover or reversible potential approaches the zinc equilibrium potential.

(5) Impedance spectroscopy is useful in the qualitative evaluation of the stability of the aluminum oxide layer in various acid fluoride solutions. Higher fluoride and acid result in a decrease in the impedance, an indication of the susceptibility of the aluminum substrate to zinc sticking.

(6) The use of open-circuit potential measurements appears to be another promising method both to evaluate the aluminum electrode stability in fluoride solution and to estimate the probability of zinc sticking.

Acknowledgment

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