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The Use of Synthetic Hydrocalcite as a Chloride-Ion Getter for a Barrier Aluminum Anodization Process

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The Use of Synthetic Hydrocalcite as a Chloride-Ion Getter for a Barrier Aluminum Anodization Process

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ABSTRACT

Chloride ion contamination at parts per billion concentrations plaques electrochemists studying barrier anodic aluminum oxide film growth and anodic aluminum oxide capacitor manufacturers. Chloride ion contamination slows film growth and reduces film quality. We have demonstrated that synthetic hydrocalcite substantially reduces the detrimental effects of chloride ion contamination in an aqueous electrolyte commonly used to grow barrier anodic aluminum oxide. We have determined that problems arise if precautions are not taken when using synthetic hydrocalcite as a chloride-ion getter in an aqueous electrolyte. Synthetic hydrocalcite is somewhat hydrophobic. If this powder is added directly to an aqueous electrolyte, some powder disperses; some floats to the top of the bath and forms scum that locally impedes anodic film formation. Commercially available powder contains a wide range of particle sizes including submicrometer-sized particles that can escape through filters into the electrolyte and cause processing problems. These problems can be over come if (1) the getter is placed in filter bags, (2) a piece of filter paper is used to skim trace amounts of getter floating on the top of the bath, (3) dummy runs are performed to scavenge chloride-ion loaded getter micelles dispersed in the bath, and (4) substrates are rinsed with a strong stream of deionized water to remove trace amounts of powder after anodization.

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I. INTRODUCTION

Chloride ions interfere with dielectric grade ("barrier") anodic aluminum oxide film formation.[1] $AlCl_3$ formation competes with anodic Al_2O_3 film formation and detracts from film quality. Aluminum chloride dissociates readily in the electrolyte. There the aluminum ions react with hydroxyl ions and precipitate as a hydrated aluminum oxide powder. Chloride ions return to the anode where they consume more aluminum and cause additional defects. These defects conduct electrical current that would otherwise support anodic film growth. Aberrantly long processing times occur. The relatively high current densities drawn at microscopic defects can result in local heating that causes the defects to grow into visible patches of dielectrically defective film. Some chloride ions may become entrained in the growing coating, where they compromise breakdown strength and cause degradation over long term storage and use as a capacitor.

Because chloride ions recycle during electrolysis, contamination at parts per billion concentrations substantially impedes coating growth. Trace amounts of chloride contamination can originate from a multitude of sources. For example, personnel who sweat, cough, sneeze, do not wear clean gloves and/or surreptitiously snack on salty foods in the processing area can contaminate the bath. Fumes from chloride-containing soldering or casting fluxes used near a barrier anodization facility, can contaminate a process. Chloride ions may be introduced if city water is used to prepare the electrotrolyte or a rinse bath used immediately before electrolysis. A substandard reverse osmosis deionized water system may be a source of chloride ion contamination. Reagent grade salts used to prepare anodization electrolytes may contain sufficient chloride compounds to significantly perturb the anodization process. Hypochlorite-bleached fabrics, lab wipes, towels and ashless cellulosic filter paper are sources of chloride ions.

Recently, it was proposed that synthetic hydrocalcite[2], a porous, zeolite-like powder removes trace amounts of chloride ions from barrier anodic aluminum oxide electrolytes. There is no information in the open literature regarding how to use this material for this purpose. The objectives of the current study are

1. to demonstrate that synthetic hydrocalcite mitigates the effects of chloride ion contamination in an aluminum anodization bath

and 2. to determine how to use this material as part of a practical anodization process.

II. EXPERIMENTAL

A. Substrate Material. We used 0.020-inch thick, cold rolled, 6061-T6 aluminum alloy sheet stock as substrate material. This is a popular aluminum alloy used for a variety of applications at Sandia National Laboratories. Initially, we sheared 2 cm x 4 cm coupons; a 2 cm x 2 cm area was immersed in the electrolyte during electrolysis. Later, we cut 2 cm x 2 cm squares of aluminum alloy with rounded corners and a 0.25 cm wide, 2 cm long tail that extended out of the electrolyte for electrical contact.

We briefly attempted to use 6 cm lengths of 1.6 mm diameter, 99.999 % pure aluminum wire doubled into loops with 0.5 cm inner diameters. A 2-cm loop length was immersed in the electrolyte.

B. Substrate Preparation. We scrubbed the substrates with an abrasive Scotch Brite® cleaning pad loaded with an Alconox® detergent and water, ultrasonically cleaned the substrates in detergent and water, and rinsed the substrates with water. We then used a fairly conventional sequence of etchants and water rinses[3] including

1. **5 wt. % reagent grade NaOH** in deionized water at room temperature for 15 minutes. This etchant was stored in a tightly capped stainless steel container to retard reaction with atmospheric CO_2. A timer was started when we observed bubbles forming over the entire surface of the substrates. We visually checked that a uniform layer of smut (heavy metal 6061 T6 alloying constituents) had formed confirming this etchant was working properly. (No smut formed on the 99.999 % pure aluminum samples.)
2. **City water and deionized water immersion rinse baths.**
3. **50 % nitric acid** and deionized water solution at room temperature for 10 minutes. This etchant was stored in a tightly capped polypropylene bottle.
4. **Deionized water rinse and air dry.**

The substrates were visually inspected to confirm that smut had been removed and there were no stains.

Clean polypropylene or Teflon fixtures were used to handle the substrates during the cleaning procedure. Batches of substrates were cleaned using the above four steps and stored in covered glass containers.

Immediately before electrolysis, a substrate was etched in a solution of 63 gm ammonium bifluoride (NH_4HF_2) per 1 liter reagent nitric acid at room temperature for 10 min. This etchant was stored in a tightly capped polypropylene container. The substrate was rinsed for 5 min in each of two freshly drawn deionized water immersion baths then held under a stream of flowing deionized water before being immersed in the electrolyte.

C. Electrolyte Preparation.

1. Baseline bath. We anodized samples in an extremely dilute solution of reagent grade ammonium tartrate and 16 Megaohm cm deionized water.

Glassware, fixturing and the gloved hands of the operator were copiously rinsed with deionized water before being allowed in the vicinity of the electrolyte and its ingredients. The electrolyte was prepared by first dissolving 1 part $(NH_4)_2C_4H_4O_6$ [formula weight 184.15] to 40 parts by weight deionized water. A hypodermic needle was used to add droplets of this stock to deionized water so the resulting solution had a starting resistivity of 50 to 65 Kohm cm. A resistivity meter indicated when sufficient ammonium tartrate had been added. Typically 5-6 droplets were sufficient to prepare a 450 cc bath.

2. Synthetic hydrocalcite additions. Initially, we added synthetic hydrocalcite to our 450 cc baths by simply stirring in a paste made from 1 gm powder and isopropanol. Later we investigated the effects of possible wetting agents including Triton X100® (a non ionic surfactant), ammonium hydroxide, ethylene glycol, methanol and isopropanol. Eventually, we decided the best way to add synthetic hydrocalcite was to

1. make two tightly woven nylon bags,
2. boil the bags in a succession of deionized water baths for several days (to remove possible hypochlorite bleach residues),
3. load 1 gm dry powder into a bag then tie it shut with nylon line,
4. put this bag and a teflon-coated magnetic stir bar into the second bag and tie the second bag shut with nylon line

and 5. submerse the double bagged powder in 450 cc electrolyte, gently agitate and store for at least 24 hr before commencing electrolysis.

3. Chloride ion additions. Initially, we added no chloride ion contamination and worked with possible trace amounts of chloride inherently in the deionized water and reagent grade ammonium tartrate. Later we intentionally added contamination at the level of 1 chloride ion: 10^{12} water molecules by diluting 1 cc of 35 wt. % (12 mole %) reagent HCl with 100 cc water, then diluting 1 cc of this stock with 100 cc water, diluting 1 cc of this second stock with 100 cc water, and adding 1 cc of the third stock to 2000 cc electrolyte with a resistivity of 62 Kohm cm. The resistivity fell to 55 Kohm cm after the Cl^- addition. We poured 450 cc portions of this contaminated bath into 500 cc beakers and performed differential experiments.

D. Electrolysis. Electrolyte resistivity was measured before commencing electrolysis throughout bath life to confirm it was in the desired working range of 50 to 70 Kohm-cm.

The beaker with the electrolyte was placed in a water bath that provided thermal ballast so the temperature of the electrolyte did not rise more than 3°C above room temperature (19 to 22°C) during anodization. A Teflon-coated magnetic stir bar rotating at 30 to 60 cycles per minute reduced temperature fluctuations within the bath and helped transport ionic species from the diffusion zone to the double layer to replenish species consumed by the growing coatings. In baths containing chloride ion getter, agitation presumably helped circulate chloride ions and getter material to improve the chance of capture.

Eight-cm^2 areas of freshly etched and rinsed 6061-T6 aluminum were immersed in a 450 cc electrolytic bath. The anodically biased aluminum substrate was suspended between two parallel, cathodically-biased, platinized-titanium meshes. The distance between each side of the substrate and the cathodes was 1.5 cm. Anodization was performed at a fixed current density of 1 mA/cm^2 supplied by a Fluke model 3330B "Calibrator" power supply. Current and cell voltage were monitored by two Fluke digital multimeters. When we turned on the power supply, we recorded initial cell voltage and started a timer. Cell voltage was recorded at regular intervals until we either reached a desired forming voltage of 950 V or some aberrant occurrence, such as an observation of visible breakdown patterns, forced us to conclude a run prematurely.

After the completion of a run, the substrate and the cathode mesh were removed from the bath. The anodized substrate was examined visually and under an optical microscope. The cathode mesh was thoroughly rinsed with deionized water and stored in a clean glass container. The filter bags containing chloride getter were never removed from a bath during the life of the bath. The bath was tightly sealed with a piece of aluminum foil during storage. Each bath was reused many times.

III. RESULTS AND DISCUSSION

__A. Overview.__ This study evolved though three phases while we pursued our dual goals:

1. to demonstrate synthetic hydrocalcite could beneficially be used as a chloride getter

and 2. to learn how to solve certain problems associated with its use. First, we observed the performance of the baseline ammonium tartrate plus water bath with no chloride getter and no added chlorine contamination. Second, we explored different methods of adding synthetic hydrocalcite. We operated doctored baths for extended periods to identify problems. We developed approaches to avoid the problems. Third, we added a trace amount of chloride contamination to a large bath. The bath was divided into smaller volumes including one with the chloride getter, one without the chloride getter. We operated both baths over extended periods of time to document the superiority of the gettered bath and to confirm the techniques we had developed to avoid problems associated with using the getter were effective.

The amount of time required for the cell voltage to reach 950 V was observed as a figure of merit. Processing speed is a good indicator of dielectric coating quality. Poor quality coatings have flaws that ohmically consume current that would otherwise support anodic coating growth with an increase in dielectric thickness and an increase in cell voltage required to maintain a fixed current density. We anodized to 950 V rather than the lower forming voltage specified for more practical anodization processes at Sandia on the premise that anything that can go wrong will go wrong when you try to attain a high forming voltage. For example, microscopic flaws present at a cell voltage of 100 to 350 V have a high probability of developing into visible defects at higher voltages. These large defects ohmically consume large amounts of current and greatly prolong processing time.

B. Baseline Studies. During the first phase of this study, we observed the performance of the ammonium tartrate and water electrolyte and reproduced behavior observed during earlier studies:[4]

- The etchants and procedures used to prepare 6061-T6 aluminum alloy substrates are appropriate.

- Only a trace amount of ammonium tartrate is required to prepare a bath with a desirable starting resistivity of 50 to 65 Kohm cm.

- Long processing times are required for a freshly mixed bath (Figure 1 - curve A). As the bath is reused, processing times become shorter (Figure 1 - curve B). When the bath is reused to anodize many samples, resistivity rises, as ions become incorporated in the coatings. As the bath is used and stored, it evaporates. Eventually, the bath must be restored by adding more ammonium tartrate (to lower resistivity) and/or water (to replenish volume). After the bath is restored, slow, erratic processing times and poor quality coatings must again be tolerated while the bath is rebroken-in.

- As compared to a bath that has been used extensively without restoration, during the break-in period, the probability of observing a massively flawed coating is higher (Figure 2).

- This process works well when it is used to anodize 6061-T6 aluminum alloy. In order to avoid experimental uncertainties arising from variations in the concentration, size and type of alloying constituents allowed in this alloy, one might wish to use high purity aluminum substrates for fundamental studies. Unfortunately, when we attempted to use 99.999 % pure aluminum wire loops as substrate material, we had problems. At cell voltages of 325 to 400 V (after processing times of 30 to 40 minutes) the voltage ramp rate became extremely slow and erratic. Numerous narrow, longitudinal defects were visible. When these samples were examined using an optical microscope, it appeared as though strips of the anodic coating with attached underlying aluminum substrate material had peeled off, exposing patches of bare aluminum to the anodization bath and lowering cell voltage. During earlier studies, we experienced similar problems with many mill runs of rolled, high purity aluminum sheet stock. We were not able to circumvent this problem by etching the aluminum for an extended amount of time (>30 min.) in a 5 % sodium hydroxide solution; i.e. this is not a problem associated with damage in the near-surface region as a result of drawing, rolling or handling operations. Perhaps pure aluminum does not have sufficient cohesive strength to withstand high levels of intrinsic stress associated with the formation of a thick barrier anodic coating.

C. Exploration of Processing Alternatives. After observing the performance of a baseline ammonium tartrate plus water bath, we prepared a fresh 450 cc bath with a resistivity of 50 Kohm cm, and added a paste made from 1 gm synthetic hydrocalcite powder and 2 gm isopropanol (to promote wetting). Bath resistivity did not change as a result of this addition. Some powder sank to the bottom. Some went into suspension, especially when the bath was stirred. A trace amount floated to the top of the bath. The first anodization run in a fresh bath with synthetic hydrocalcite was substantially faster than the first anodization run in a fresh bath without synthetic hydrocalcite. (Compare Figure 3 - curve A to Figure 1 - curve A.) The second anodization run in the bath with synthetic hydrocalcite (Figure 3 - curve B) required substantially more time to reach a cell voltage of 950 V. The problem was apparent. Substantial amounts of synthetic hydrocalcite powder had floated to the top of the bath. A thick scum formed that extended the meniscus region on the substrate and impeded transport required for healthy coating growth. The coating in the meniscus region was visibly flawed.

These problems suggested two opportunities for process improvement: (1) Change the shape of the substrate to reduce substrate area in the meniscus region and (2) Constrain the synthetic hydrocalcite powder in a filter bag. Figures 4 and 5 show the results of making these two modifications. Figure 4 shows three voltage ramp rates typical of processes performed in a bath containing no chloride ion getter with 2 cm x 2 cm substrates with a 0.25 wide tail for electrical contact. Figure 5 shows three voltage ramp rates typical of processes performed in a bath containing 1 gm of dry powder in two nylon filter bags with tailed substrates.

Three comments can be made regarding the process modifications. First, the run times for the bath with the chloride getter are shorter than the run times for the bath with no getter. Second, the nylon filter bags are able to keep gross amounts of synthetic hydrocalcite powder from escaping to the surface of the bath, forming a scum and lengthening process times with extended storage and reuse. Third, the average process time is longer here than for similar runs performed with rectangular coupons (compare Figure 4 and Figure 1). The substrates were cut from sheet stock using hand shears then ground to remove a ragged edge along the interior curve leading into the tail. The grinding process left a sharp burr along the edge that was difficult to anodize. The tailed substrates prepared for the remainder of this study were hand-filed to remove the troublesome burr.

After repeatedly observing that processing times for tailed substrates in the bagged chloride getter bath were consistently shorter than processing times for similar substrates in an bath with no chloride getter, we decided to add a trace amount of chloride contamination to learn how much each bath could tolerate. We prepared a stock solution with 1-cc, 12 mole % hydrochloric acid and 100 cc deionized water. One-cc of this dilute HCl stock was added to each 450 cc bath. This level of chloride ion contamination essentially destroyed both baths ability to form barrier anodic coatings. There was no increase in cell voltage above the initial starting voltage of 30 V over extended processing times. We discarded both baths and opened up the double bag containing synthetic hydrocalcite. We observed that, even after being submersed for over five weeks in the electrolyte, the bulk of the powder was dry. Only a small amount of powder in the inner bag had formed a paste that might be expected to capture chloride ions in the bath. This observation led us to be keenly interested in identifying wetting agents.

We mixed and sonicated 0.2 gm synthetic hydrocalcite powder, candidate wetting agents and 5 gm water in test tubes to evaluate (1) how readily the candidate wetting agent caused the powder to disperse in water and (2) how stable the suspensions were. Five candidate wetting agents were evaluated:

1. One drop of a non-ionic surfactant, Triton X100®. This surfactant readily promotes wetting and the formation of a stable dispersion. Unfortunately, this surfactant attaches to particles of synthetic

hydrocalcite and forms micelles with a net electrostatic charge. Baths with synthetic hydrocalcite powder and Triton X100® electrophoretically deposit a thick powder coating on an anode in a few minutes. Little or no anodization occurs.

2. Three grams ammonium hydroxide. No wetting occurs. Dry powder floats on top of this solution.

3. Three grams ethylene glycol. No wetting occurs in this solution. Dry powder floats to the top.

4. One and one-half grams methanol. Wetting occurs. After two days without agitation, the test tube contained a surface layer of foamy paste, some material in suspension and a layer of wet sediment.

5. One and one-half grams isopropanol. These results were similar to those observed for methanol.

Encouraged by these observations, we prepared a 2000 cc bath with a resistivity of 62 Kohm cm. We then added 1 cc of 7 X 10^{13} HCl molecules /cc liquid stock. Resistivity decreased to 55 Kohm cm; 450 cc volumes were poured into three beakers.

Into one beaker, we added a paste prepared from methanol and 1 gm synthetic hydrocalcite powder in double nylon bags. This bath was stored for two days before commencing electrolysis. No escaped powder was visible in the bath. After 30 minutes at a current density of 1 mA/cm^2, the cell voltage had risen to only 64 V. When we stopped the process and removed the anode from the bath, we discovered it was uniformly covered by a transparent, mucous-like gel coating with embedded submillimeter-sized lumps of additional gel-like material that dried, leaving delicate rosettes of white powder. The combination of trace amounts of hydrochloric acid, chloride getter and isopropanol in this aqueous solution appears to lead to the formation of a transparent sol that electrophoretically seals the substrate with a gel coating that blocks the formation of anodic aluminum oxide.

These results discouraged us from trying to use a wetting agent to increase the chloride ion getting efficiency of synthetic hydrocalcite powder.

We used a 450 cc portion of the 2000 cc chloride ion contaminated electrolyte as an experimental control. To another 450 cc portion, we added 1 gm dry synthetic hydrocalcite powder in double nylon bags. The first anodization run with the gettered bath was slow (Figure 6), requiring 39 minutes to reach a cell voltage of 628 V. Problems in the meniscus area (Figure 7) caused us to stop processing at this point. The coating in the meniscus area was flawed and cratered. During electrolysis there was visible arcing in this area. The arcing was sufficiently violent to cause audible whistling. This localized arcing may be a result of small amounts of submicrometer-sized synthetic hydrocalcite powder escaping from the filter bags, capturing chloride ions, and forming agglomerates that stick to the substrate in the meniscus area where agitation is weak. No craters or flaws were visible on submersed areas exposed to strong agitation from the magnetic stirrer. These experiments suggested an additional process refinement. A piece of a porous cellulosic Whatman® filter paper was rinsed in a succession of 80°C deionized water baths for three days to remove trace amounts of chlorides and fluorides characteristically present in "ashless" filter paper. This piece of paper was then jury rigged to form a "wiper" at the surface of the bath to scavenge getter agglomerates that escape from the filter bags and float to the top of the bath. The improvement in processing time obtained by using this wiper was so dramatic (Figure 8 - curve A as compared to Figure 6) that we began the final stage of the study.

D. Process Reproducibility. The final problem we encountered with the bath containing 3.5 X 10^{10} Cl^- ions/cc liquid plus synthetic hydrocalcite was that, if the bath had not been used for two or more days, during the first run of the day, the process would readily reach a cell voltage of 770 to 800 V in 30 to 40 minutes, then problems occurred. A few small dark spots, visible to a careful observer, appeared on submersed substrate surfaces and rapidly (in 1 to 2 minutes) grew into large pepper-sized grains. Cell voltage decreased catastrophically by 50 to 100 V while these spots grew. Under an optical microscope, these millimeter-sized grains typically have a raised and cratered rosette structure (Figure 9) somewhat different from the trailing strings of craters typical of a freshly mixed bath with no synthetic hydrocalcite and no added Cl^- contamination (Figure 2). After this first-run-of-the-day the chloride contaminated, chloride getter bath performed well. These results suggest that, during extended storage, particles of synthetic hydrocalcite escape from the filter bags into the bath, capture chloride ions and form large, charged micelles that, at sufficiently high voltages, contact the surface of the substrate and cause macroscopic damage. These micelles adhere to the substrate and are removed from the bath when the first-run-of the day is concluded. After the first-run-of-the-day, the chloride ion contaminated, chloride-gettered bath performs well (Figure 8 -curves B,C and D). Processing times to 950 V are rapid and reproducible. Flawless coatings form.

This behavior can be compared to the control bath with the same amount of added chloride contamination and no synthetic hydrocalcite (Figure 9). Processing times to 950 V for the control bath are more than twice as long as processing times for the chloride gettered bath. At this level of chloride ion contamination, there was no steady decrease in processing time with continued use. The coatings produced by this bath were not visibly flawed. The defects that robbed current from anodic film growth and extended processing time were microscopic. As in earlier chloride ion contamination studies[1], there was frequently a characteristic slowing or reversal in the voltage ramp rate that occurred over a period of a few minutes when the cell voltage reached 650 or 750 V.

IV. SUMMARY AND CONCLUSIONS

Chloride ion contamination in barrier anodic aluminum oxide electrolytes can cause extended processing times, erratic behavior and flawed dielectric coatings. Synthetic hydrocalcite is a promising chloride ion getter that can be added to aqueous ammonium tartrate solutions used to form barrier anodic aluminum oxide coatings. Problems can arise if certain precautions are not followed when synthetic hydrocalcite powder is used for this application. The powder must be kept from dispersing freely in the electrolyte, especially if there are substantial amounts of chloride contamination in the bath. The amount of synthetic hydrocalcite dispersed in an anodization bath can be reduced and the effects of dispersed synthetic hydrocalcite can be minimized by

1. loading the dry powder into filter bags,
2. skimming the surface of the bath with a porous filter
3. performing dummy runs after the bath has been stored for a day or

more without use.

and 4. carefully rinsing anodized piece-parts under a strong steam of deionized water.

Precautions 1 and 2 are suitable for lab bench experiments. A pressurized in-line filter may be more appropriate for a large, dedicated anodization facility.

V. UNRESOLVED ISSUES AND SUGGESTIONS FOR FUTURE STUDIES.

Processing time is an readily recorded figure of merit for judging an anodization process, but the dielectric properties of aged-in anodic coatings produced by chloride contaminated baths with and without synthetic hydrocalcite should be evaluated. In view of the reported relationship between entrained chloride contamination and shelf-life failures, an accelerated aging study would be appropriate.

It is desirable to do more work with different levels of chloride contamination to learn what concentration range can be accommodated by the synthetic hydrocalcite.

If resources permit, it would be enlightening to do fundamental analysis and try to map the distribution of chlorine and microstructural deformations on the "first-run-of-the-day" samples with gross macroscopic flaws produced by baths with added chloride ion contamination and synthetic hydrocalcite.

FOOTNOTES

1. D. J. Sharp and J. K. G. Panitz, Journal of the Electrochemical Society, 127, 6 (June, 1980) 1412.

2. Cat. No. DHT-4A from Mitsui and Co., 200 Park Av., New York, NY 10166; (212) 878-4000.

3. Janda K. G. Panitz and Donald J. Sharp, "Characterization of a Procedure for Preparing 6061 Aluminum Alloy for Barrier Anodization", Sandia Report SAND82-1524. UC-25, (Oct. 1982).

4. Janda K. G. Panitz, Donald J. Sharp, F. Edward Martinez, Raymond M. Merrill and Kenneth J. Ward. "Barrier Anodic Coatings Formed on 6061-T6

Aluminum Alloy in Electrolytes Containing Different Ethanol to Water Ratios", Sandia Report SAND86-2822. UC-25, (Dec. 1988).

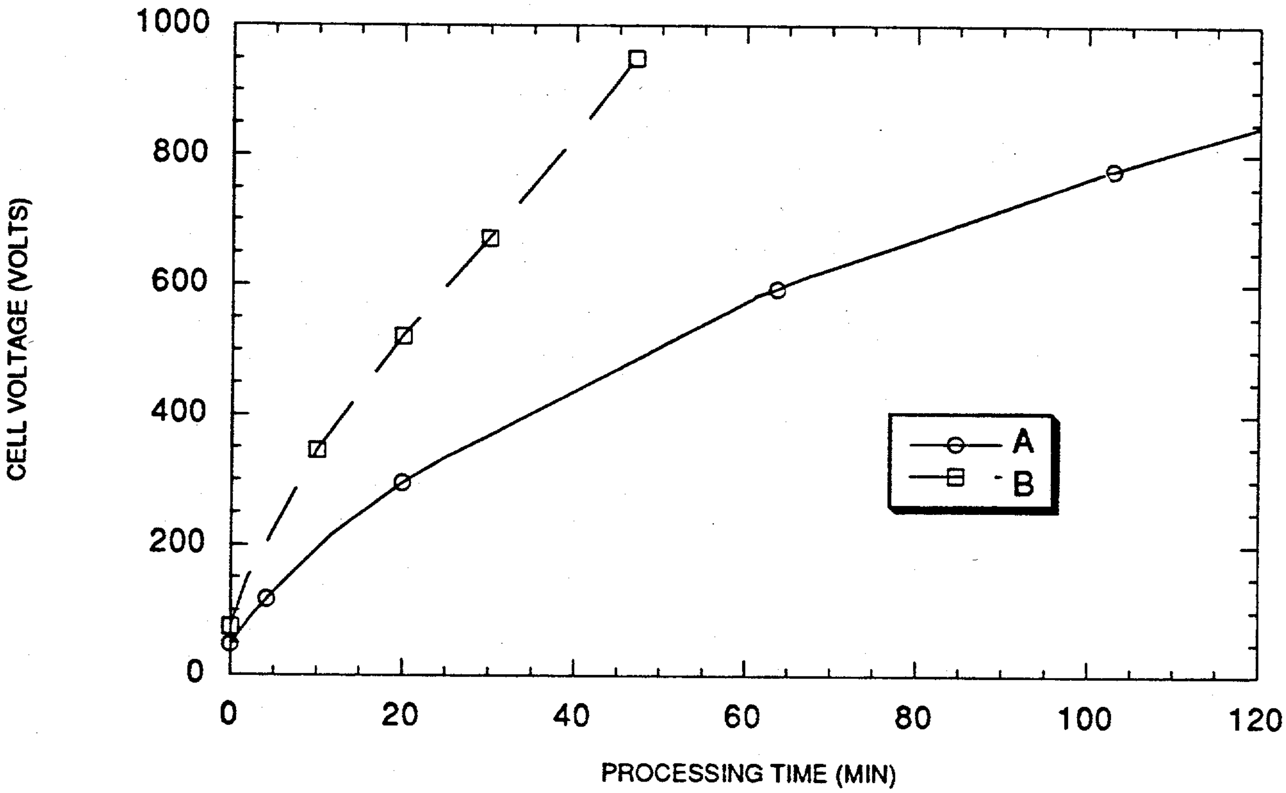

Figure 1 Representative processing times for a solution of ammonium tartrate and water with 6061-T6 aluminum alloy coupons. Curve A. First run and curve B fourth run in this bath. As the bath is reused, voltage rise times become faster until a steady state value averaging around 950 V/30 minutes is achieved.

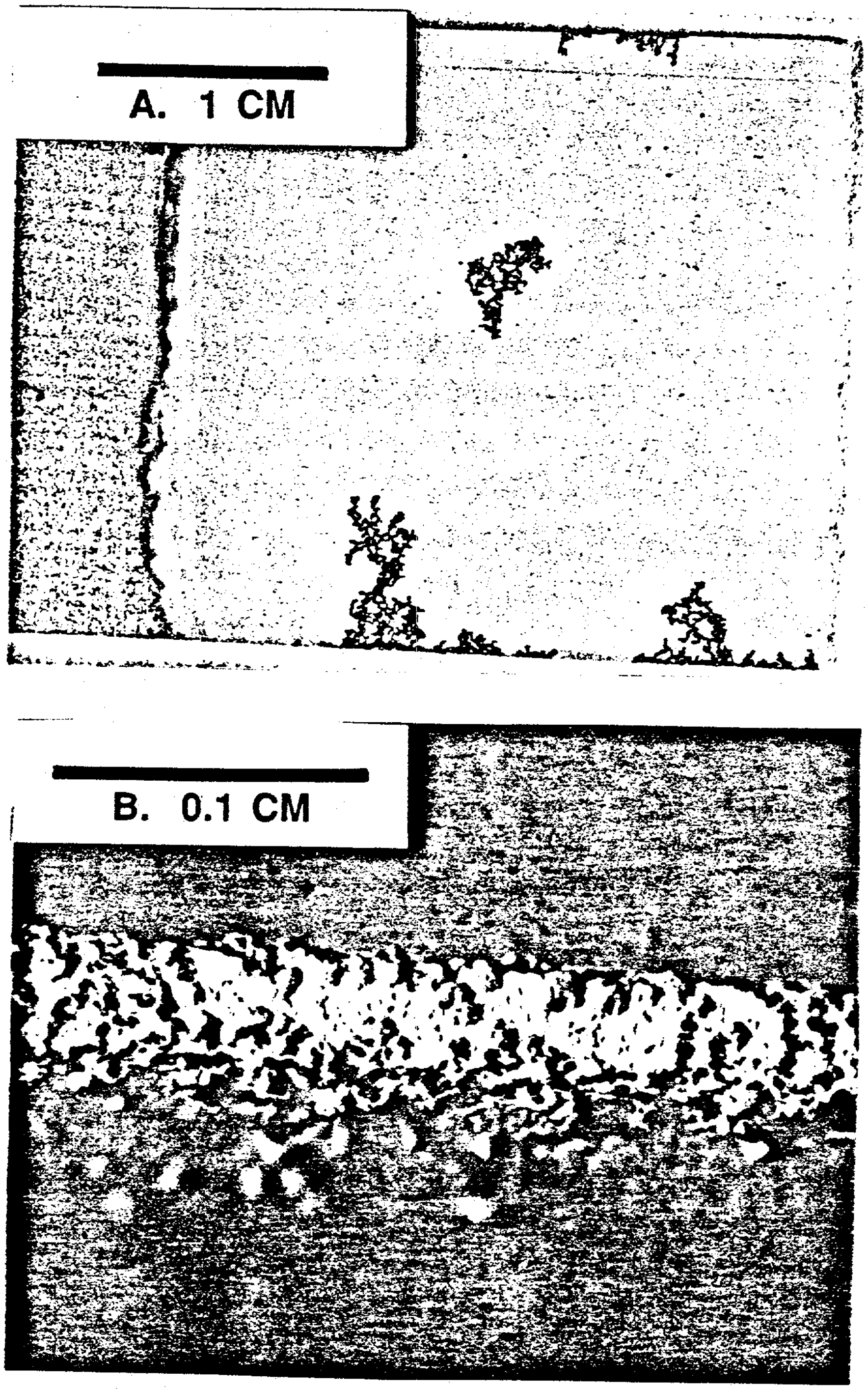

Figure 2. A massively flawed coating formed in freshly mixed electrolyte. A. Surface. B. Area along an edge at one of the three sites where macroscopic trails of defects appear to have originated from a high electric field site at an exterior corner. As a bath is reused, the probability of forming a massively flawed coating decreases.

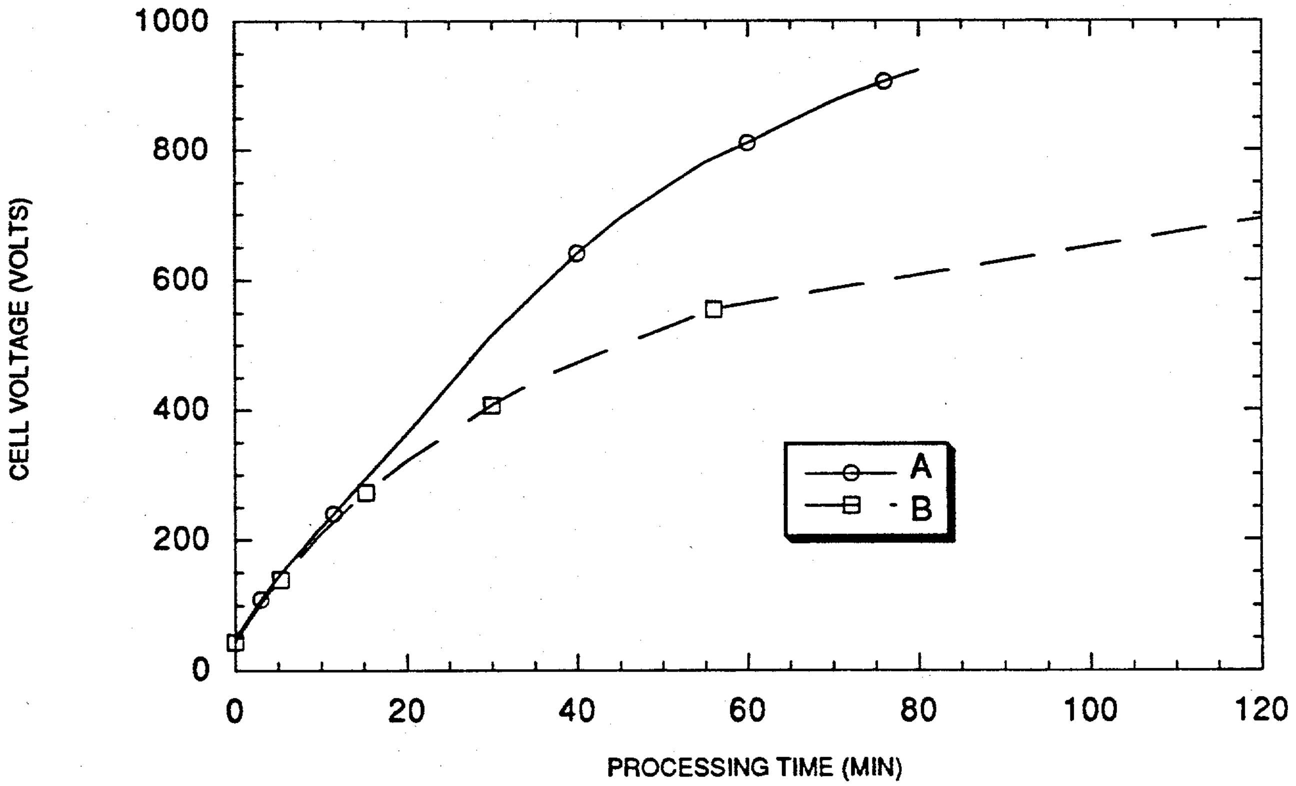

Figure 3. Representative processing times for a bath containing synthetic hydrocalcite. Here a powder plus isopropanol paste was prepared and stirred directly into a freshly mixed bath; rectangular coupons were used as substrates. Curve A. First run. This is a relatively short processing time for a freshly mixed bath. Curve B. Second run - problems! The powder has formed a thick scum on the surface of the bath.

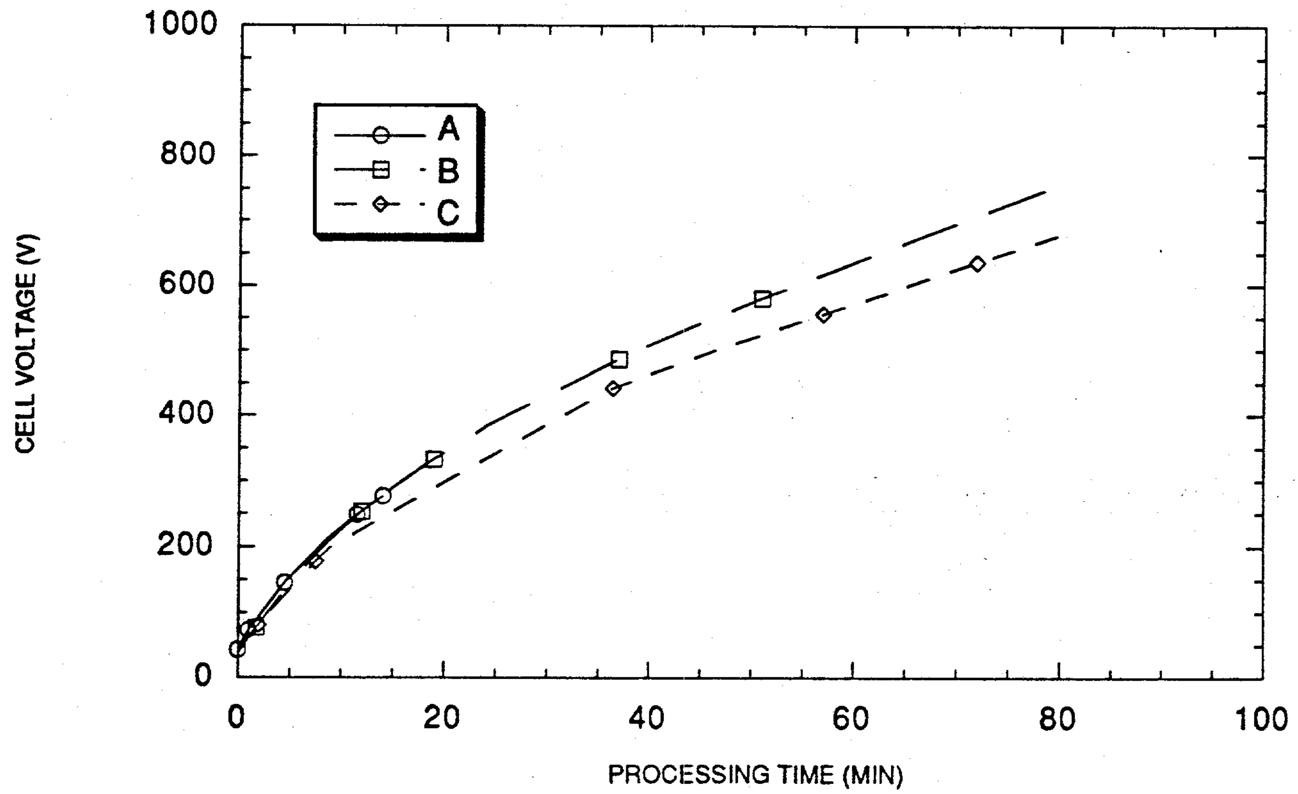

Figure 4. Processing times for the second series of experiments in a control bath with no synthetic hydrocalcite. Substrates with unfiled edges and tails that extended out of the electrolyte were used. Processing times were long, in part, because of metal burrs on the unfiled substrate edges. Curve A. First run. Curve B. Second run. Curve C. Third run.

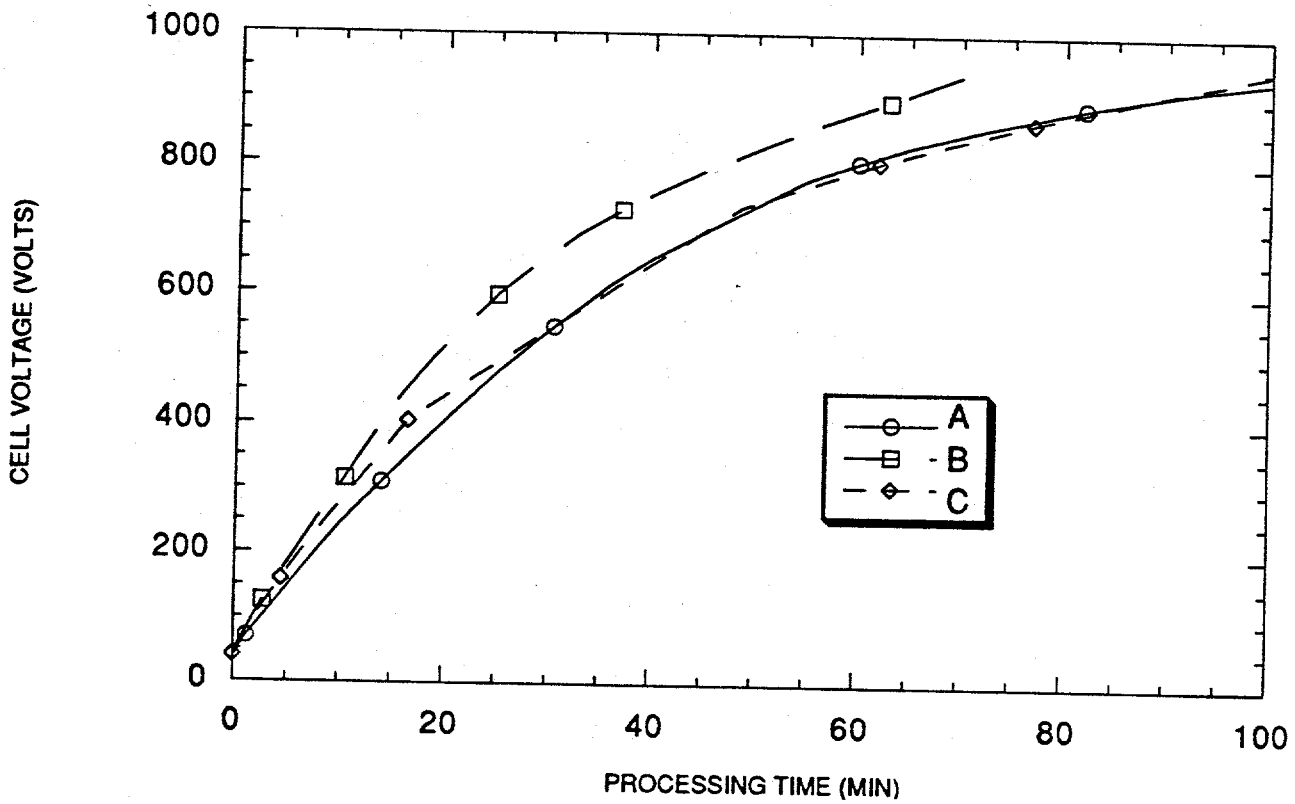

Figure 5. Processing times for the second series of experiments in a bath with synthetic hydrocalcite powder in double nylon filter bags. Here substrates with unfiled edges and tails that extended out of the electrolyte were used. These processing times when compared to those shown in the preceding figure, show that shorter processing times consistently occur when the bagged chloride getter is added to the bath. Curve A. First run. Curve B. Second run. Curve C. Third run.

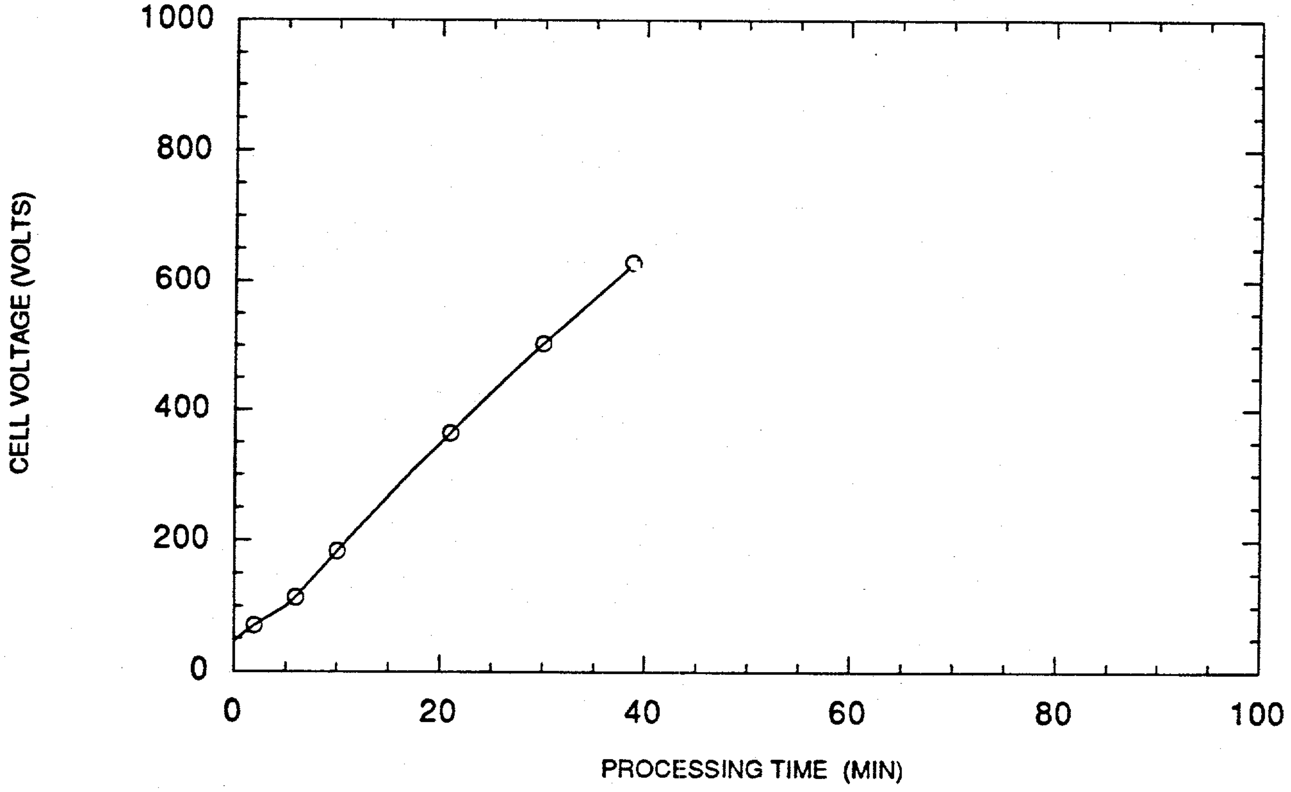

Figure 6. Aberrantly long processing time associated with the sample with the flawed meniscus region. These samples were anodized as part of the third series of experiments using filed substrates in a bath with trace added chloride contamination, and bagged synthetic hydrocalcite (A micrograph of this sample is shown in Figure 7 - view A). At 688 V the problems in the meniscus area were obvious and the run was terminated.

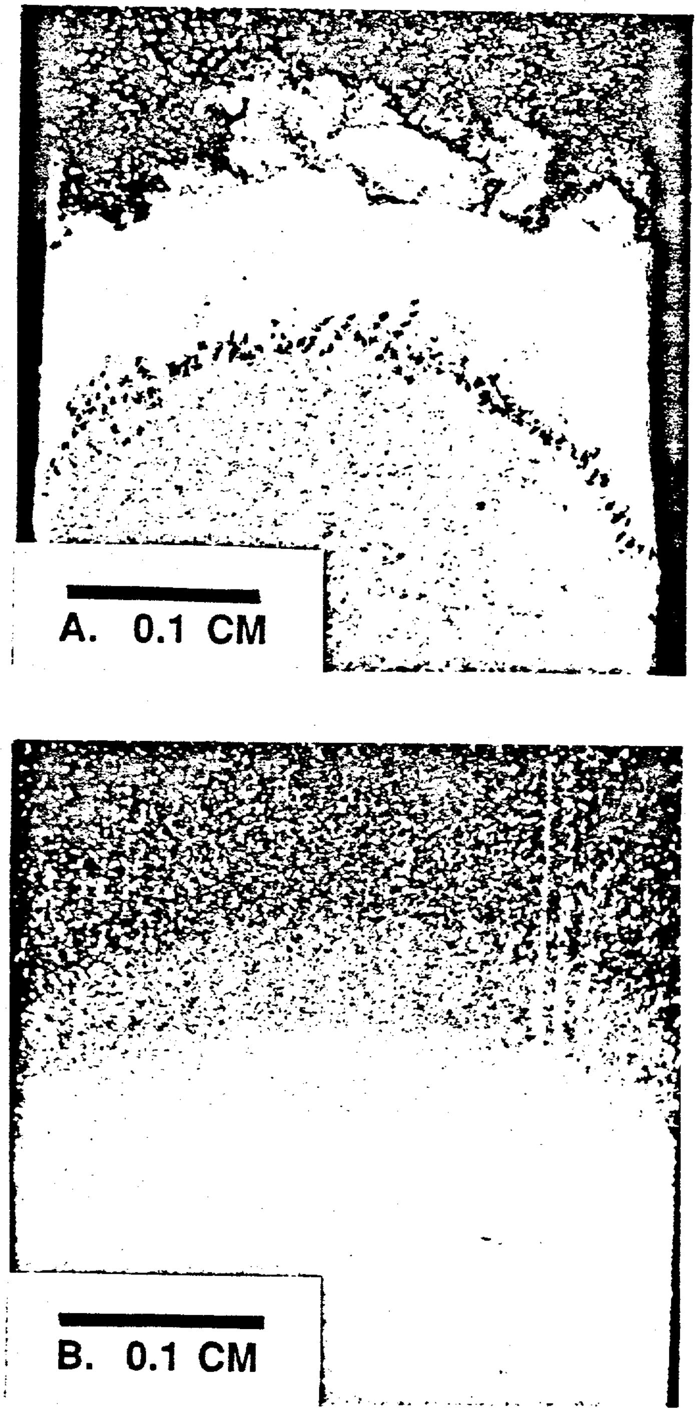

Figure 7. A micrograph showing the meniscus region on two anodized samples. . A. Flawed coating formed in a bath without a filter paper "wiper" to scavenge micelles of synthetic hydrocalcite and chloride ions floating on the surface of the bath. B. Good quality coating formed in the same bath after wiper installation.

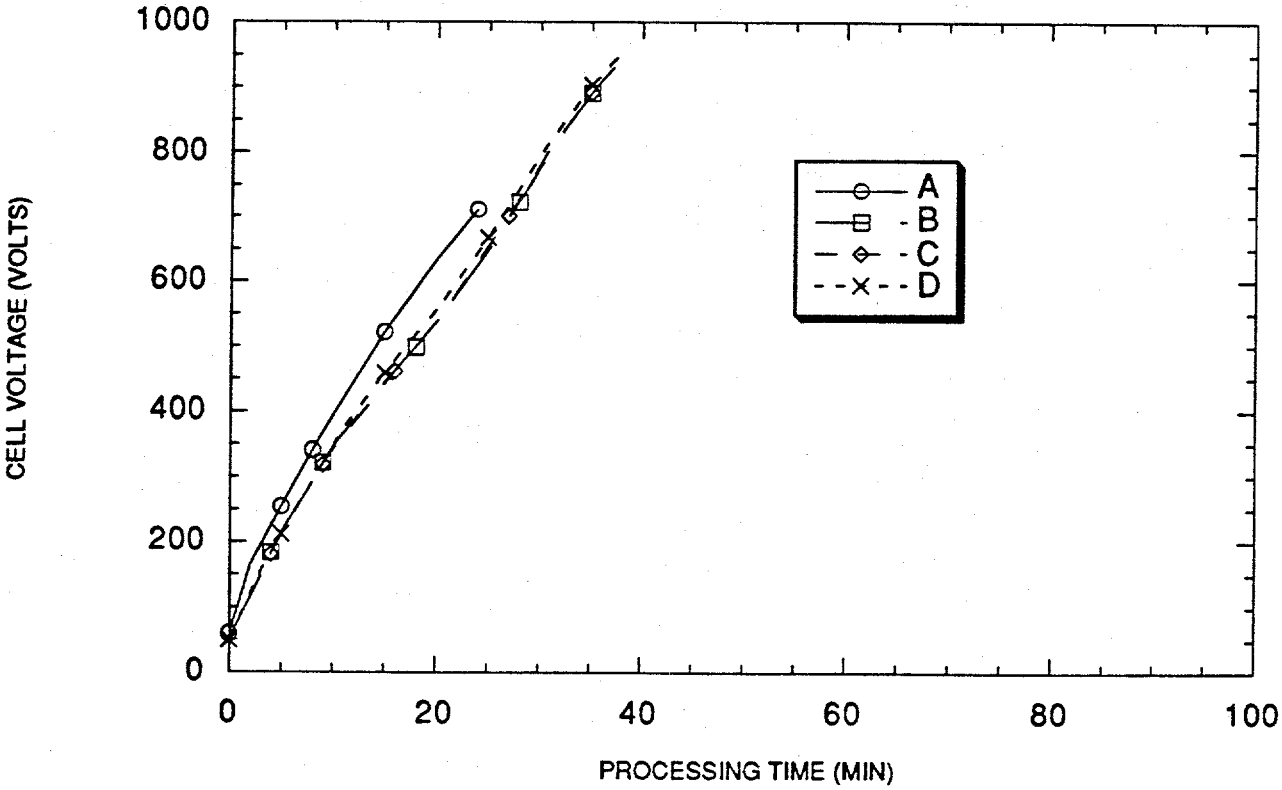

Figure 8. Run times for the third series of experiments in a bath with a trace of HCl, bagged Cl- getter and a surface wiper (filed substrates). Curve A. First run of the day. The cell voltage rose rapidly to 725 V in 30 .5 minutes then black defects appeared, and the cell voltage fell to 695 V in 1 min. The run was then terminated. Curves B. C. and D. Subsequent anodization runs produced good quality coatings at 950 V in a short amount of time.

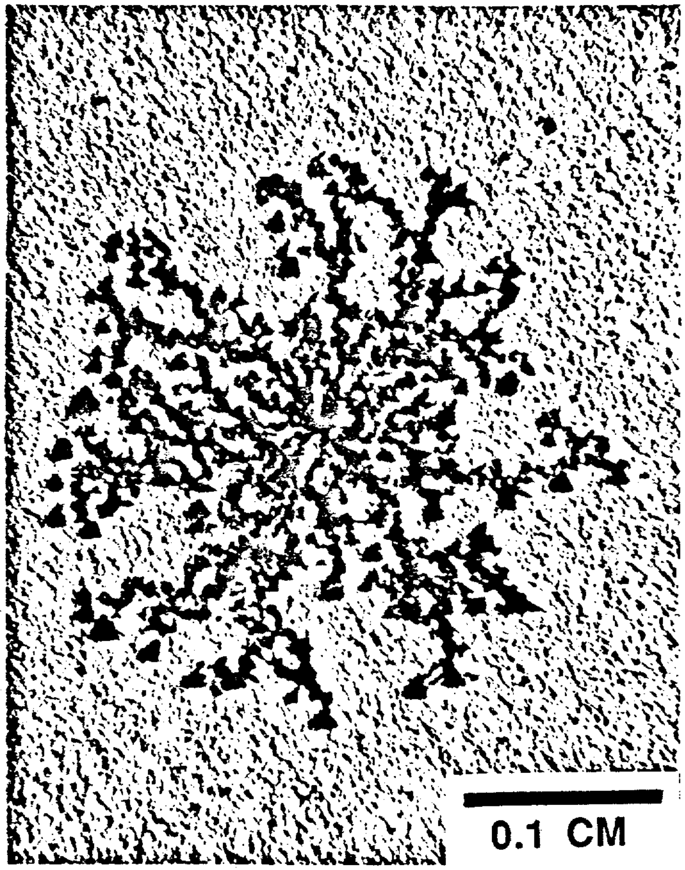

Figure 9. Micrograph showing a rosette-like defect on the first-run-of-the-day sample logged by Figure 8 - curve A.

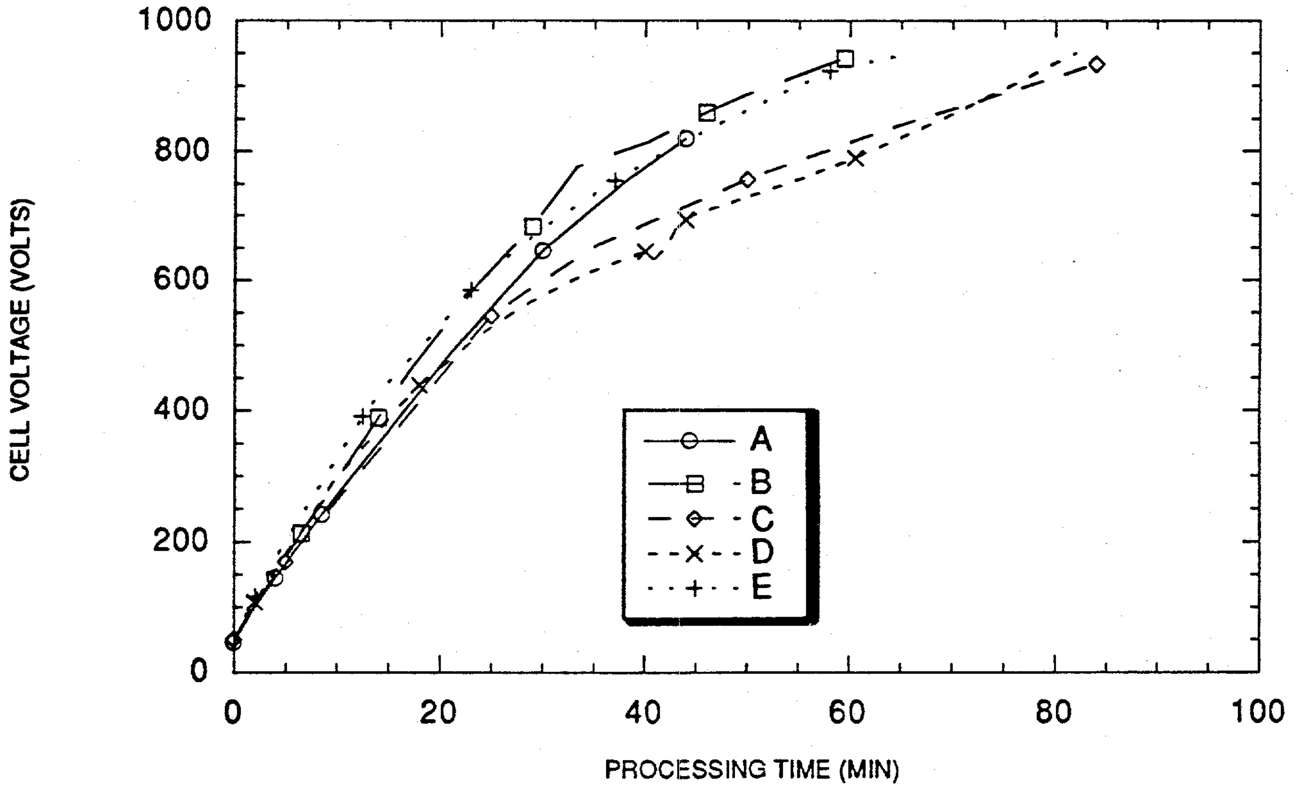

Figure 10. Run times for the third series of experiments in a control bath with HCl and no Cl- getter (filed substrates). Curve A. First run Curve B. Second run Curve C. Third run. Curve D. Fourth run. and Curve E. Fifth run. Processing times with this amount of Cl- contamination are slow and not improving. These process times can be compared with the relatively rapid processing times illustrated in Figure 8, curves B, C, and D for the gettered bath.

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