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

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Chloride ion contamination at parts per billion concentrations slows barrier anodic aluminum oxide film growth rate and detracts from film quality. It has been determined that synthetic hydrotalcite can be used to substantially reduce the detrimental effects of chloride ion contamination in an aqueous-based electrolyte used to grow barrier anodic aluminum oxide. Precautions must be taken so that this material does not come into contact with the aluminum substrate during anodization.

It is well established that chloride ions interfere with dielectric grade ("barrier") anodic aluminum oxide film formation.¹ During electrolysis, AlCl₃ formation competes with anodic Al₂O₃ film formation and detracts from film quality. Aluminum chloride hydrolyzes readily in electrolytes having a pH of approximately 7. It may be speculated that neutral, out-diffusing aluminum chloride molecules react with available hydroxyl ions at the anodic oxide surface and precipitate as hydrated aluminum oxide. Negatively charged chloride ions are released and return to the anode where they consume or undermine more aluminum and leave more pores or defective oxide film. These defects conduct electric current that would otherwise support anodic film growth. Aberrantly long processing times occur. Relatively high current densities drawn at microscopic defects can result in local heating that causes defects to grow into visible patches of dielectrically defective film. Some chloride ions undoubtedly become entrained in the film, where they compromise breakdown strength and lead to degradation over long-term operation as a capacitor dielectric.

It is thought that chloride ions recycle as a result of the above process. This may partially explain why chloride contamination at parts per billion concentrations substantially impedes coating growth and compromises dielectric quality. Trace amounts of chloride contamination can originate from a multitude of sources including careless operators, fumes from chloride-containing soldering or casting fluxes used near an anodization facility, city water or a substandard reverse osmosis deionization system, hypochlorite-bleached fabrics, lab wipes, towels, ashless cellulosic filter paper, etc.

Synthetic hydrotalcite,² a porous, zeolite-like powder, removes chloride ions from thermoplastics, such as polyvinyl chloride. This suggests its use for purifying aluminum barrier anodization baths. There is no information in the open literature regarding the use of synthetic hydrotalcite for this purpose. The objectives of our study were (1) to demonstrate that synthetic hydrotalcite mitigates the effects of chloride ion contamination in an aluminum anodization bath and (2) to optimize the use of this material as part of a practical anodization process.

Experimental Procedure

Cold-rolled, 6061-T6 aluminum alloy sheet stock was used as substrate material in the form of 2×4 cm coupons; a 2×3 2 cm area was immersed in the electrolyte during electrolysis. Later, $2 \times 2 \text{ cm}$ squares of aluminum alloy with rounded corners and a 0.25-cm-wide, 2-cm-long tail that extended out of the electrolyte formed the electrical contacts.

The substrates were scrubbed with an abrasive cleaning pad, wetted with a solution of detergent and water, ultrasonically cleaned in a solution of detergent and water, and rinsed with water. A standard etching sequence was used for preparing the 6061 aluminum alloy for anodization.³ This included (1) 5 wt. percent reagent grade NaOH in deionized water at room temperature for 15 min, (2) two immersion rinse baths, (3) 50-percent nitric acid and deionized water solution at room temperature for 10 min and (4) immediately before anodization, a solution of 63 g ammonium bifluoride (NH₄HF₂) per 1 liter reagent nitric acid at room temperature for 10 min, followed by immersion and spray rinses. Samples were anodized in very dilute, 50 to 70 Kohm-cm solutions of reagent grade ammonium tartrate and 18 Megohm-cm deionized water.

Initially, synthetic hydrotalcite was added to selected baths by stirring in a paste made from powder and isopropanol (to promote wetting and dispersal). Later, a tightly woven nylon filter bag (with an average mesh size less than 5 micrometers) was filled with synthetic hydrotalcite and a magnetic stir bar, then submerged in the electrolyte for at least 24 hr before commencing anodization.

No chloride contamination was added initially; the experiments were conducted with existing trace amounts of chloride inherent in the deionized water and reagent grade ammonium tartrate. Later, contamination was added at the level of one chloride ion per 10^{12} water molecules by diluting 1 cc of 35 wt percent (12 mole percent) reagent HCl with 100 cc water, then diluting 1 cc of this stock with 100 cc water, diluting 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. This contaminated bath was subdivided for differential experiments.

Electrolyte resistivity was measured before commencing electrolysis throughout bath life to confirm that 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 that 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 min reduced temperature fluctuations within the bath and circulated ionic species to the double layer to replenish species consumed by the growing coatings. In baths containing chloride ions to the getter material to improve capture efficacy.

An anodically biased aluminum substrate was suspended between two parallel, cathodically-biased, platinized-titanium meshes, spaced 1.5 cm from each side. Anodization was performed at a fixed current density of 1 mA/cm². Cell current and voltage were monitored by two digital multimeters. Initial cell voltage was recorded, then recorded at regular intervals until reaching either a desired forming potential of 950 V, or aberrant occurrences, such as gross breakdown patterns, that forced premature conclusion of a run. A number of anodization baths was prepared to complete these experiments. Each bath was reused many times.



Fig. 1—Representative processing times for a solution of ammonium tartrate and water with 6061-T6 aluminum alloy coupons: Curve A, first run; curve B, fourth run in this bath.





Fig. 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.



Fig. 3—Representative processing times for a bath containing synthetic hydrotalcite. 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 in a relatively short processing time for a freshly mixed bath; curve B, second run, where the powder has formed a thick scum on the surface of the bath.

Results and Discussion

Overview

This study evolved through three phases. First, the performance of the baseline ammonium tartrate plus water bath was observed with no chloride getter and no added chlorine contamination. Second, different methods of adding synthetic hydrotalcite were explored. Gettered baths were operated for extended periods to identify problems and to develop approaches to avoid them. Third, a trace amount of chloride contamination was added to a large bath. The bath was divided into smaller volumes, including one with the chloride getter and one without. Both baths were operated over extended periods of time to document the superiority of the gettered bath and to confirm that the techniques 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 used as a figure of merit. Processing speed is a good indicator of dielectric coating quality. Poor quality coatings have flaws that consume current that would otherwise support anodic coating growth. The relatively high potential of 950 V was employed to increase the sensitivity of the experiments. Microscopic flaws present at a cell voltage of 100 to 350 V have a greater probability of developing into visible defects at higher voltages. These large defects consume large amounts of current and greatly prolong processing time.

Baseline Studies

During the first phase of this study, the baseline performance of the ammonium tartrate and water electrolyte was observed.⁴ Figure 1 shows typical run times which become shorter and approach a reproducible value as the bath is reused. Figure 2 shows flaws that frequently form on substrates anodized in freshly prepared baths.

After observing the performance of a baseline aqueous ammonium tartrate bath, a new 450 cc, 50 Kohm-cm bath was prepared and stirred in a paste with 1 g synthetic hydrotalcite powder and 2 g isopropanol. 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 agitated. A trace amount floated to the top of the bath. The first anodization run in a fresh bath with synthetic hydrotalcite was substantially faster than the first run in a fresh bath without synthetic hydrotalcite. (Compare Fig. 3, curve A, to Fig. 1, curve A.) The second anodization run in the bath with



Fig. 4—Processing times for the second series of experiments in a control bath with no synthetic hydrotalcite. Substrates with non-filed edges and tails extended out of the electrolyte. Processing times were long, in part, because of metal burrs on the non-filed substrate edges. Curve A, first run; curve B, second run; curve C, third run.



Fig. 5—Processing times for the second series of experiments in a bath with synthetic hydrotalcite powder in a nylon filter bag. Substrates with non-filed edges and tails extended out of the electrolyte. Shorter processing times are shown to occur consistently when the bagged chloride getter is added to the bath. Curve A, first run; curve B, second run; curve C, third run.



Fig. 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 hydrotalcite (A micrograph of this sample is shown in Fig. 6 - view A). At 688 V, the problems in the meniscus area were obvious and the run was terminated.

synthetic hydrotalcite (Fig. 3, curve B) required substantially more time to reach a cell voltage of 950 V. The problem was apparent: Substantial amounts of synthetic hydrotalcite powder had floated to the top of the bath. A thick paste formed that extended the meniscus region on the substrate and impeded acceptable coating growth. The coating in the meniscus region was visibly flawed.



Fig. 7—Micrograph showing the meniscus region on two anodized samples: A, flawed coating formed in a bath without a filter paper skimming the surface; B, good quality coating formed in the same bath after wiper installation.

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) restrain the synthetic hydrotalcite 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 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 g of dry powder in a nylon filter bag and using 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 bag was able to keep gross amounts of synthetic hydrotalcite powder from escaping to the surface of the bath, forming a surface suspension and lengthening process times as the bath was stored and reused. Third, the



Fig. 8—Run times for the third series of experiments in a bath with a trace of HCl, bagged chloride getter and a surface skimmer (filed substrates). Curve A, first run-of-the-day. Cell voltage rose rapidly to 725 V in 30.5 min, 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 show subsequent anodization runs produced good quality coatings at 950 V in a short time.



Fig. 9—Micrograph showing a rosette-like defect on the first-run-of-theday sample logged in Fig. 8, curve A.

average process time is longer here than for similar runs performed with rectangular coupons (compare Fig. 4 and Fig. 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 observing that (1) processing time was typically shortened by adding synthetic hydrotalcite to an anodization bath, and (2) freely dispersed synthetic hydrotalcite caused problems, a large bath was prepared and intentionally contaminated with hydrochloric acid at a concentration of one chloride ion to 10¹² water molecules. Two 450-cc portions were decanted. One HCl-contaminated portion was used as-



Fig. 10—Run times for the third series of experiments in a control bath with HCl and no chloride getter (filed substrates). Curves A-E represent the first five runs. Processing times with this amount of Cl⁻ contamination are long without improvement. These process times can be compared with the relatively short processing times illustrated in Fig. 8, curves B, C, and D for the gettered bath.

prepared. A nylon bag with 1 g synthetic hydrotalcite powder was added to the other portion. The first anodization run with the gettered bath was slow (Fig. 6), requiring 39 min to reach a cell voltage of 628 V. The appearance of flaws and craters in the meniscus area (Fig. 7), accompanied by visible arcing and audible whistling, caused us to stop processing at this point. We consider this localized arcing a result of small amounts of submicrometer-sized synthetic hydrotalcite powder escaping through the nylon filter, capturing chloride ions, and forming positively charged micelles that agglomerate on the substrate in the meniscus area where the electric field is high and agitation is weak. No craters or flaws were visible on submerged areas exposed to strong agitation from the magnetic stirrer. These experiments suggested an additional process refinement. A piece of a porous cellulosic #42 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. The paper was positioned to skim the surface of the bath and scavenge getter agglomerates that escaped from the filter bag and floated to the top of the bath. The improvement in processing time obtained by using this wiper was sufficiently dramatic (Fig. 8, curve A, compared to Fig. 6) that we proceeded to the final stage of the study.

Process Reproducibility

The final problem encountered with the HCl-contaminated bath with synthetic hydrotalcite occurred after storage. If the bath was used after being stored for two or more days, the cell voltage would readily rise to 770 to 800 V in 30 to 40 min. Then, a few barely visible dark spots appeared on submerged substrate surfaces and rapidly (in 1 to 2 min) grew into halfmm-dia. grains. Cell voltage decreased catastrophically by 50 to 100 V as the spots grew. Under an optical microscope, the spots appeared as raised and cratered rosettes (Fig. 9). The chloride-contaminated, chloride-gettered bath performed well after an initial run following extended storage. These results suggest that, during extended storage, particles of synthetic hydrotalcite escape through the filter, capture chloride ions and form large, charged micelles that, at sufficiently strong fields, migrate to the surface of the substrate and initiate damage. These micelles seem to 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 was completed, processing times to 950 V were rapid and reproducible (Fig. 8, curves B, C and D). Coatings formed that appeared to be flawless.

This behavior can be compared to the control bath with the same amount of added chloride contamination and no synthetic hydrotalcite (Fig. 10). 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 exhibited 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 as the cell voltage approached 650 to 750 V.

Summary and Conclusions

Chloride ion contamination in barrier anodic aluminum oxide electrolytes can cause extended processing times, erratic behavior and flawed dielectric coatings. Synthetic hydrotalcite is a promising, practical and convenient chloride ion getter that can be added to aqueous ammonium tartrate solutions used to form barrier anodic aluminum oxide coatings. Difficulties arise if the powder is allowed to disperse freely in the electrolyte, especially if there are substantial amounts of chloride contamination in the bath.

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