Improving Engineering Properties of Anodic Films Through Microstructural Modification

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Extensive studies on a new electrolyte formulation for aluminum anodizing have given tremendous insight as to the changes in the resultant anodic film microstructure. The impact of these changes on the engineering properties of corrosion and abrasion resistance, surface roughness, color fastness, fatigue strength, and fracture toughness has also been studied. A description of the engineering test program, presentation of the data and results will be discussed emphasizing the practical and efficient nature of the new coating as well as how this simple yet elegant modification has optimized the standard anodic film.

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Introduction

The anodizing of aluminum has always been a sturdy fixture in the mind of the light metals industry. By capturing the essence of the natural phenomena of oxide film formation in a production environment, the anodization process has become synonymous with protection and durability.

Through its three most widely used variations (Types I, II, and III), aluminum anodizing allows for corrosion and abrasion resistance, dyeability, fracture toughness, and fatigue strength in a wide variety of applications. The aluminum industry has grown complacent with the ability of these finishes to work in specific applications and the technology has become stagnant.

Active research into the ability of forming polymer-metal oxide composites through a variation of the anodizing process has led to fresh ideas regarding anodizing. This new outlook has produced numerous areas for further research, as well as a new coating that attacks the status quo of the anodized film's expected engineering properties. The various properties of the anodic polymer-metal oxide composite film were tested and compared to the three major standard variations of aluminum anodizing.

Experimental Procedure and Results

All comparison testing was done using the standard test procedures for anodic films, mostly taken from MIL A 8625 F and related materials regarding anodized films on aluminum and aluminum alloy substrates.

Abrasion Resistance

The determination of abrasion resistance was based in MIL A 8625F. Three samples of conventionally anodized film (Type II), three samples of hardcoat film (Type III), and three samples of the anodized polymer-metal oxide composite film were anodized on 4 X 4 inch Aluminum 6061 T6 panels.

The panels were anodized, not dyed or sealed, then desiccated and weighed on an Ohaus Explorer analytical balance to the nearest tenth of a milligram. Using a Taber Model 5130 Digital Abraser, the panels were individually turned on a vertical axis while in contact with two rotating CS-17 abrading wheels. The wheels, each under 1000 gram loads, were resurfaced before and in-between tests using S-11 abrasive disks to ensure a consistent abrasive surface in contact with the test panels.

The panels were run for a total of 10,000 cycles (revolutions) as abrading media and abraded coating were removed by vacuum. After the completion of all cycles, excess media and coating were removed by brush and the samples were desiccated and weighed once again. By subtracted the final weight of the panels from the original and divided by the cycles, overall coating weight loss was expressed as an abrasion index, weight loss per 1000 cycles. Results of the testing are summarized in Table I.

The poor performance of the conventionally anodized film (Type II) created a problem for producing a meaningful yet comparable wear index. The films produced at the production thickness of 5 µm (.0002 inches) could not endure a 10,000 cycle test without wearing into and beginning to remove the base material, therefore losing accuracy in determining the weight loss of the coating only. To properly correlate panel revolutions to the weight loss of the coating only, the number of cycles was reduced to 500, thereby establishing a connection between coating weight loss and total revolutions.

With worries about the performance of the thinner conventionally anodized (Type II) panels, the lower thickness of the polymer-metal oxide composite was thought to pose a problem. The polymer-metal oxide composite was tested at 3,000 cycles, and when its was realized this was no problem, the testing simply continued at this number of cycles to maintain consistency within its own test group.

Table I.

Coating	Thickness (µm)	Wear Index (mg/1000 cycles)
Conventional Anodizing (Type II)	**5.0** *(.0002 in)*	**6.70**
Hardcoat Anodizing (Type III)	**37.5** *(.0015 in)*	**1.56**
Polymer-metal oxide	**20.0** *(.0008 in)*	**1.85**

Corrosion Resistance

To best compare the corrosion resistance of the composite film to the standard variations of anodization, multiple tests were designed to exploit the obvious differences between films under similar conditions.

A group of 6061 T6 test panels representing the monthly corrosion testing required for conventional anodizing (Type II) were anodized to a thickness of 7.5 to 12.5 µm (.0003 to .0005 inches), dyed black, and nickel acetate sealed. Another set of test panels, anodized to thicknesses ranging from 2.5 to 30 µm (.0001 to .0012 inches) with a polymer-metal oxide composite were left undyed and unsealed. Both groups were monitored according to ASTM B 117 in a salt spray chamber until pitting was noticed.

The salt spray chamber produces a salt-fog with a fixed pH between 6.5 and 7.2 and a specific gravity of 1.0255 and 1.0400 grams. The fog flow rate is between 1 to 2 milliliters per hour and the temperature inside the chamber is maintained at 33.3 to 36.1 degrees Celsius.

After 450 hours of exposure, the conventionally anodized panels exhibited small pits and were removed from the machine. After 1000 hours, the anodized composite exhibited no signs of pitting corrosion, but started to show the first signs of a general corrosion, hazing the face of the part. Parts were pulled from the machine before pitting was evidenced to allow for machine maintenance.

A second corrosion test compared the relatively thin chromic acid anodized (Type I) panels at thicknesses of 1.5µm (.00006 inches) to anodized polymer-metal oxide composite panels at the same thickness. Both groups of samples were sealed but left undyed. The difference between the two anodized coatings was noticed at 288 hours when the chromic acid anodized panels exhibited breakdown, whereas the composite anodized panels remained intact.

A modification on this comparison tested the two films, chromic acid anodized (Type I) and the anodized polymer-metal oxide, both dyed and sealed, similar to the monthly corrosion test for chromic acid anodized panels that requires a passing test of 336 hours. After 504 hours, the anodized polymer-metal oxide panels exhibited no corrosion while the chromic acid anodized (Type I) panels exhibited white streaks. See Figures 1 and 2.

Surface Roughness

Panels with identical surface roughness were anodized both conventionally (Type II) and with the composite finish. Interference microscopy, which provides three-dimensional mapping and average roughness of surfaces by way of vertical non-contact scanning white light interferometry, was performed on both panels.

The average roughness for the surface of the panel anodized with the polymer-metal composite was 733 nm (28.86 microinches), as opposed to the average roughness for the conventionally anodized panel, 1007 nm (39.65 microinches).

Color Fastness

Accelerated weathering tests were performed according to MIL A 8625 F modifications to ASTM G 23 by the South Florida Test Service. Panels were anodized both conventionally (Type II) and with the composite finish, both dyed black and sealed. Specific panel color, quantifying both the hues and brightness, was determined with a Hunterlab Ultrascan spectrocolorimeter. The panels were then exposed to 200 hours of radiation using an Atlas FDA-R Single Enclosed Carbon Arc Fade-Ometer. Differences in color were then quantified by the spectrocolorimeter, outlining the color change over time.

The reported summation of all color and brightness changes for the anodized polymer-metal oxide composite finish, the coefficient value E*, was 0.42, one third of the change exhibited by the 1.45 E* value for the conventionally anodized (Type II) panel.

Fatigue Strength

Reverse bending fatigue test bars were precision machined per ISO 1143-1975 (E). The test bars were machined from one rod each of Aluminum alloy 2024 T4 and 7075 T6. Five samples were left raw, six were anodized in the gage (test) area with a chromic acid anodized finish to a thickness of 1.5 to 2 µm (.00006 to

.00008 inches), and six were anodized with the same thickness of the composite finish.

The endurance limit for each alloy group was established through reverse bending fatigue testing of the unfinished test bars for N=107 – 108, at a frequency of 1,000 to 9,000 cycles per minute. The finished bars for each alloy group were tested following the same profile.

Complete results were not available at the time of publication for this article but preliminary results indicate greater fatigue strength for the composite finish as compared to chromic acid anodic coatings, and in some cases, improvements over unfinished samples. More complete data will be presented orally at Sur/Fin 2000 in Chicago.

Fracture Toughness

Charpy test pieces were precision machined according to ASTM E 23, conventionally anodized (Type II) and anodized with the anodic polymer-metal oxide composite to a thickness of 20 µm (.0008 inches). Test pieces were cryogenically frozen and fractured using a Charpy impact testing device. The resultant fracture surface was then examined using a scanning electron microscope.

High magnification comparison imaging of the fracture surfaces within a JEOL 8620 Scanning Electron Microscope revealed distinct morphological differences. The Type II fracture surface exhibited characteristics typical for brittle fast fracture with no evidence of ductile tearing. The composite film fracture surface exhibited evidence of tearing and micropore coalescence features typical for a ductile fracture. The difference in the fracture surfaces indicates the polymer-metal oxide composite film is more fracture tough.

Discussion

The polymer-metal oxide composite consistently shows improved engineering properties over the three standard variations of aluminum anodizing. By highlighting the vast engineering improvements made by the simple composite coating, it becomes apparent that the performance of the basic aluminum oxide film is optimized.

Using a transmission electron microscope at high magnifications, differences in the film microstructures start to clarify the differing performances. The typical columnar structure associated with conventional and hardcoat anodizing (Types II and III, respectively) is modified in the polymer-metal oxide composite. Instead of long, straight columns, the composite film exhibits a more cellular structure so that, although still following the columnar lanes, the individual 'cells' create a more tortuous path to the base material, therefore increasing the resistance to corrosion. Also, this more randomized structure leads to a more compliant film, ductile and more fracture tough. See Figures 3-6.

With its lack of long vertical columns, the composite film meets horizontal abrasion with a less opposed surface, differing from the traditional 'bigger is better' thicker pore walls of a hardcoat anodized (Type III) film. By manipulating the shape of the structure, the size of the pores becomes less important.

Conclusion

By modifying the standard three aluminum anodizing processes and therefore the resultant films, an improved coating was achieved, breaking new ground in engineering capabilities and applications for anodic films. Active research into the basic science of these accepted technologies results in a broader platform from which to base further research.

From a closer look at coatings that have become common-place in the industry, new ideas and directions can be imagined, pushing the status-quo beyond previous expectations. The new composite finish enables product differentiation in a market stagnant with mature designs.

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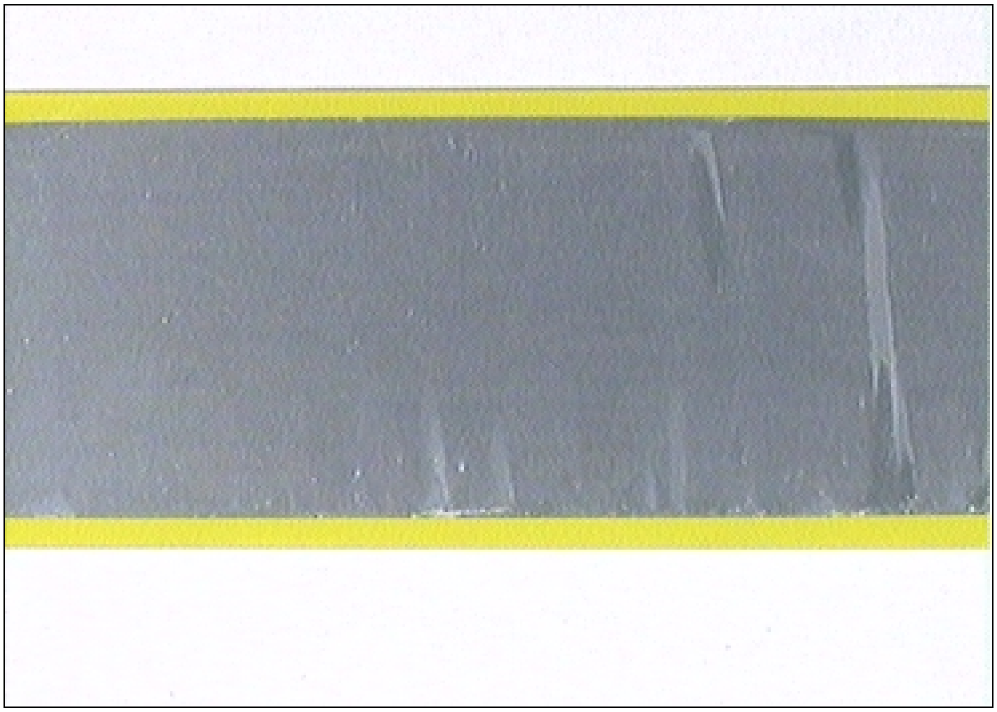

Figure 1. Composite Film

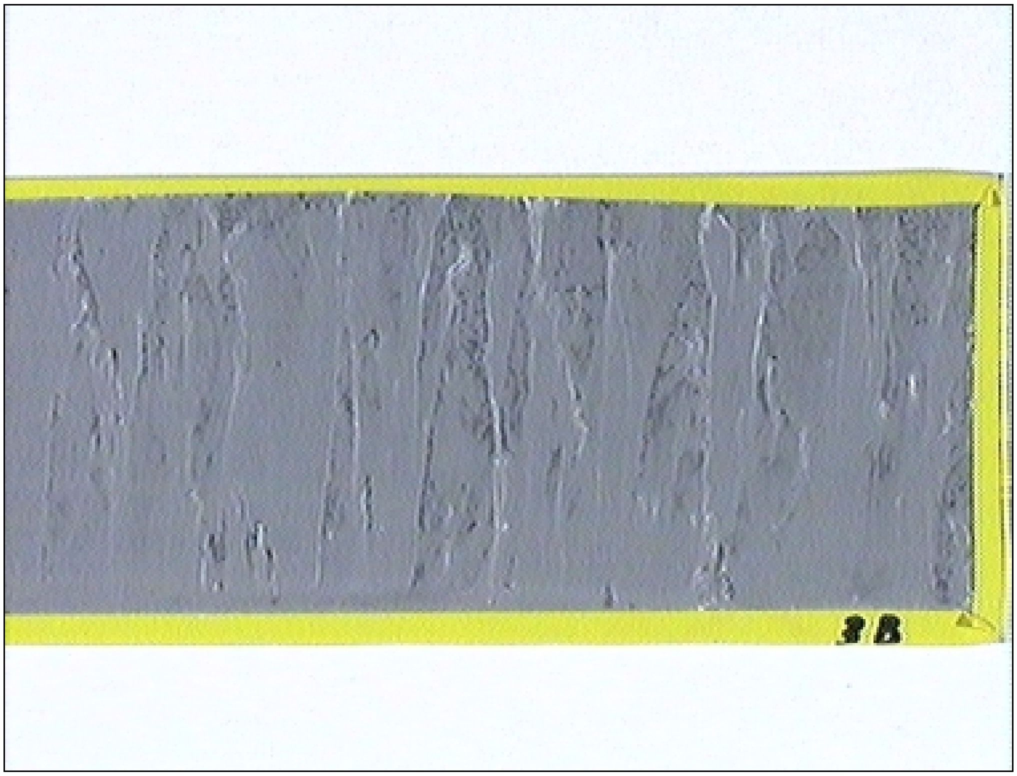

Figure 2. Chromic Acid Anodized

Figure 3. Composite film

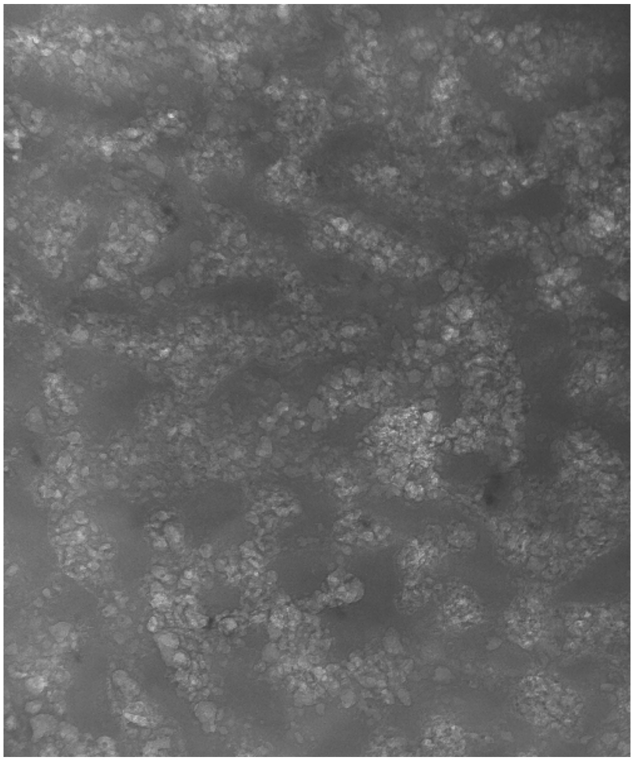

Figure 4. Chromic acid (Type I)

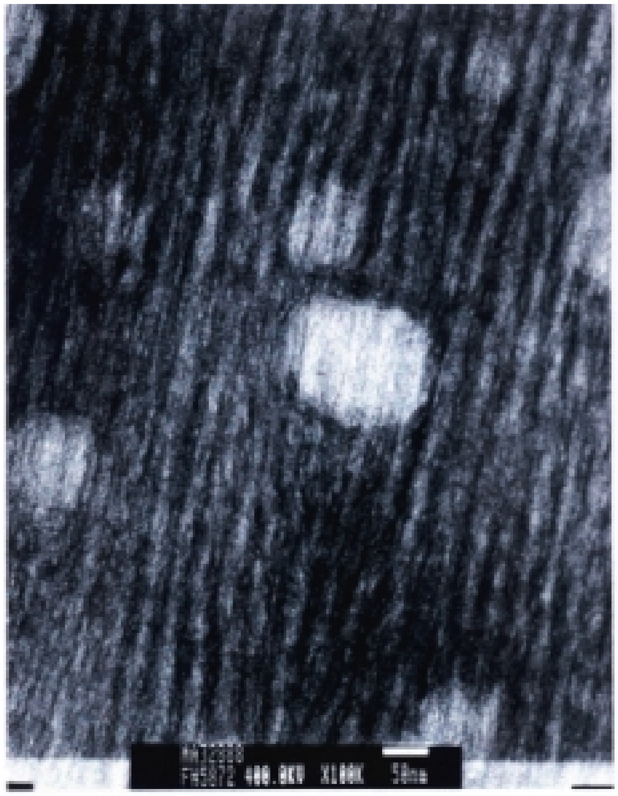

Figure 5. Conventional Anodizing

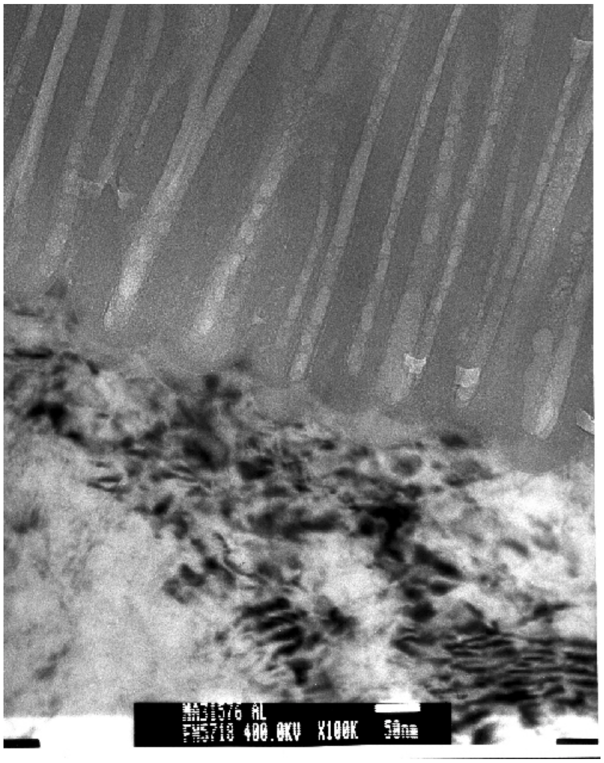

Figure 6. Hardcoat Anodizing