

## **Anodic Oxide Finishes: Relating Engineering Performance To Microstructure and Hardness**

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Comparative testing of typical sulfuric acid anodic oxide finishes: Type I, Type II, and Type III and composite anodic finishes by way of conventional Taber Abrasion, Pin-Disk Friction and Microhardness Testing, as well as unconventional Torque and Charpy Impact Testing have brought to light the importance of the engineering property of fracture toughness. Test performance differences and comparative microstructural analysis suggest enhanced wear may indeed be a function of higher toughness rather than hardness. Increased cohesive strength within the microstructure of the anodic finish established through modifications to the anodizing process appears to yield lower friction and reduced wear in even dissimilar wear couples.

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## Introduction

Anodic finishes are utilized in various industries to impart protection, durability and decoration to aluminum substrates. In the case of durability, the focus of the finishing industry has been to provide anodic films with high hardness, to minimize finish weight loss through abrasion and wear.

In high wear applications, the finish of choice is typically the Type III or hard-anodized film. Without modification, this finish is not considered decorative, although it can be dyed to yield dark colors. The typical microhardness measured for a Type III finish ranges from the high 300's to about 600 Vickers Hardness Numbers (HV). Most often the finish is expected to withstand shear forces as in piston applications where an aluminum piston is the active wear component within a cylinder. Resistance to impact forces is also of concern.

The other typical anodic finishes; produced in a chromic acid electrolyte (Type I) and conventional sulfuric acid (Type II) anodic oxides are utilized mainly for corrosion resistance and their capability to be decorated through screen printing and dyeing. Type I finishes in particular must not impact the fatigue resistance of the substrate as this finish is utilized primarily in the aircraft industry. The durability of Type I and Type II finishes hinges most on impact and scratch resistance.

Supplementary tribological coatings based on Teflon® as colloidal suspensions of PTFE and TFE are often employed to reduce the coefficient of friction between wear surfaces including an anodic finish. It is well documented that even with coatings that tout the ability to intrude the porous anodic structure, that surface entropy between colloidal particles as well as between the edge of a pore and the particles, prohibit intrusion of the supplementary coating into the anodic finish. [1, 2] These coatings therefore have a useful life limited to the time required to wear the supplementary finish away. The bulk of the interfacial wear

therefore occurs between the anodic finish and the opposing wear surface.

Extensive comparative mechanical testing of various types of anodic finishes has aided in the understanding of the microscopic aspects of finish wear. Finishes made via typical Type I, II and III anodization processes were made and compared to those processed similarly but with an addition of an electroactive polymer to the electrolyte.

## Scientific Background

One must consider the typical wear mode for the anodic oxide in order to truly evaluate the mechanisms for tribology and wear. Typically, the finish is loaded in shear as well as in compression. The load will be translated to the finish surface, across and along the column walls of the anodic oxide microstructure. The shear stress produces angular displacement within the finish, and recovery of the structure depends upon its inherent mechanical properties and the continuity of the microstructure. See figure no. 1.

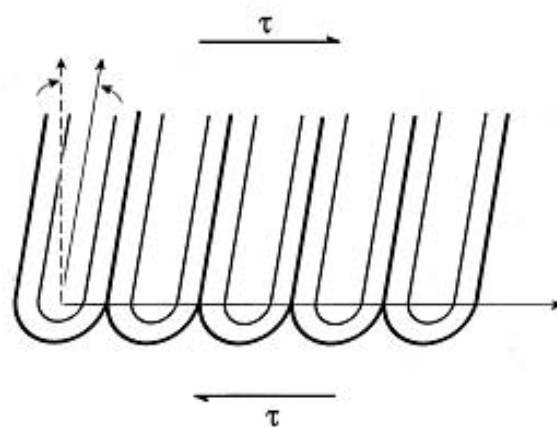


Figure No. 1: Schematic of the columnar structure of the anodic finish under applied shear force,  $\tau$ . Angle represents displacement of structure through elastic deformation.

It is important to remember while considering the wear mechanisms that regardless of the type of finish, anodic films are amorphous and do not exhibit diffraction contrast necessary to identify the oxide phase as corundum,  $\alpha$  alumina,  $\text{Al}_2\text{O}_3$ . Chemical analysis by way of electron energy loss spectroscopy (EELS) shows conclusively that the film is comprised primarily of

disordered hydrated aluminum oxide, i.e. aluminum hydroxide [3]. Therefore, Type I, II and III anodic oxide finishes are all comprised of the same material.

Material failure due to excessive elastic deformation is controlled by the modulus of elasticity, a material property, and not by the strength of the material. Little metallurgical control can be exercised over the elastic modulus. Therefore, the most effective way to increase the stiffness of a component is to change its shape and/or increase the dimensions of its cross section. [4] Because the anodic finishes, regardless of type, are chemically the same, the modulus of elasticity for the various types is also the same. Finish resistance to shear forces in wear is therefore partially governed by the robustness of the structure, in other words, by the thickness of the column walls. Clearly it follows that a Type III finish would exhibit superior wear resistance to Types I and II anodic oxide finishes.

Other microstructural features that impact the durability of the anodic finish are interfacial and substrate defects such as burrs and laps on the macroscopic level, and, on the microscopic level, grain boundaries and inclusions. At the atomic level, defects such as vacancies and dislocations can “pile up” leading to discontinuities in the anodic finish. [5] See figure no. 2.

*Figure No. 2: Crystallographic defects impact the way the anodic oxide finish nucleates and grows.*

As the anodic oxide fails in shear it chips and spalls, the finish breaks apart. Surface discontinuities on the anodic finish offer crack

initiation sites. As tiny pieces of the finish are cracked from the anodic oxide and incorporated into the wear debris, the film wears rapidly. Oxide chards exacerbate wear at edges and asperities within the microstructure.

Cohesive strength, the ability of a material to “hold together” seems to greatly enhance the mechanical properties of a material in shear. Increased cohesion increases the ductility of the microstructure and therefore its resistance to fracture, making the material more “fracture tough”. For a material to have high strength and high toughness, other material conditions, such as hardness are often compromised. This is sometimes counterintuitive as one imagines that harder means stronger. However, harder can also mean brittle with low cohesive strength.

It is clear that hardness and toughness impact the wear resistance of the anodic oxide finish. The following analysis characterizes the anodic oxide in terms of engineering performance and microstructure. By defining the role each material condition plays, engineering decisions that clarify the boundaries between application and process are enabled.

## **Experimental Procedure**

All comparative testing was performed following standard test procedures for anodic finishes for aluminum and aluminum alloys per MIL A 8625 F. Where other standard test procedures were followed, they are designated in the specific test sections.

### *Charpy Impact Testing*

Charpy test pieces were precision machined in accordance with ASTM E23. Two groups were prepared for comparison; the first group was conventionally anodized (Type II) for comparison to specimens anodized with the modified electrolyte following Type II process parameters (composite finish). The second group was hard anodized (Type III) for comparison to specimens anodized with the modified electrolyte following Type III process parameters (hard version of the composite finish). The samples were finished to comparable thicknesses. Test pieces were cryogenically frozen and fractured using a Charpy Impact testing device.

The resultant fractured surfaces were then examined using a scanning electron microscope (SEM).

Imaging within the SEM determined distinct fracture surface morphological differences. The Type II and Type III fracture surfaces exhibited characteristics typical for brittle fast fracture with no evidence of ductile tearing. The Type III films exhibited a shattered appearance; in fact, the finish appeared fragmented in areas. Areas where the Type III finish remained coherent exhibited a single plane fracture and true cleavage. See figure no. 3.

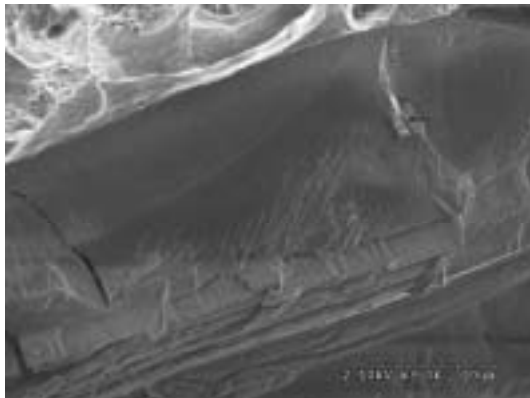


Figure No. 3: Brittle fracture surface of Type III finished charpy impact sample.

The composite films held together through cryogenic impact. No evidence of shattering was observed. The fracture surfaces from both versions of the composite finish exhibited evidence of tearing across and between the columns within the finish microstructure, a feature typical for a ductile fracture. The distinct difference in the fracture surface indicates the composite finish is more fracture tough. See figure no. 4.

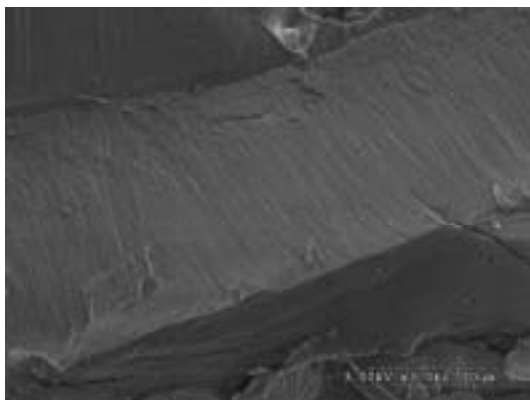


Figure No. 4: Ductile fracture surface of the hard version of the composite finished charpy impact sample.

### *Microhardness Testing*

Sections of Type II and Type III anodic finishes on 6061 aluminum substrates as well as various composite anodic finishes on 6061 aluminum substrates were metallographically prepared per ASTM E8. The sections were examined and tested at 400X with a calibrated Buehler microhardness tester equipped with a Vickers diamond pyramid indenter and a 100 g load.

Examinations of the cross sections revealed the as-polished structure of all finishes exhibited the unidirectional columnar structure typical for an anodized oxide finish on an aluminum substrate. Microhardness values ranged from 300 to 325 HV for the Type II and composite finishes processed with Type II parameters. Microhardness values ranged from 360 to 440 HV for the Type III and composite finishes processed with Type III parameters.

### *Abrasion Resistance*

Three samples of conventionally anodized finish (Type II), three samples of hard-anodized finish (Type III), and three samples of anodized composite finish were provided on 4 X 4 inch aluminum 6061 T6 square coupons.

The coupons were not dyed or sealed, desiccated for 24 hours and weighed to the nearest tenth of a milligram on a calibrated Ohaus Explorer analytical balance. 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 coupons.

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

Poor performance of the Type II finish through abrasive testing created a problem for producing a meaningful yet comparable wear index. The finish produced at the production thickness of 5  $\mu\text{m}$  (.0002 inches) could not endure a 10,000-cycle test without wearing into the aluminum substrate. To properly correlate coupon revolutions to the weight loss of the finish only, the number of cycles was reduced to 500, thereby establishing a connection between finish weight loss and total revolutions.

Concerns regarding the abrasion test performance of conventional Type II coupons carried over to the composite anodized sample coupons finished with Type II parameters. The polymer-metal oxide composite was tested to 3,000 cycles. Upon realizing that the wear did not proceed into the aluminum substrate, testing continued at 3,000 cycles to maintain consistency within its own test group.

**Table I**

Finish	Thickness ( $\mu\text{m}$ )	Wear Index (mg/1000 cycles)
Conventional Anodizing (Type II)	5.0 (.0002 in)	6.70
Hard-Anodized (Type III)	37.5 (.0015 in)	1.56
Composite Finish (~ Type II)	20.0 (.0008 in)	1.85
Composite Finish (~Type III)	37.5 (.0015 in)	1.01

Coupons finished with the composite finish with Type III processing parameters were run for a total of 10,000 cycles. These samples consistently exhibited the lowest wear index.

Comparative abrasion resistance was also performed on coupons anodized with a Type I (chromic acid) finish and coupons anodized with the composite finish to the same 2  $\mu\text{m}$  thickness. The testing was based in ASTM B571, "Adhesion of Metal Coatings to Metal Substrates", paragraph 4, "Burnishing Test". The qualitative results indicated the composite finish exhibited increased

abrasion resistance as the Type I film was easily scratched, exposing the aluminum substrate, while the composite finish was not scratched with the same tool. [6]

### Friction Testing

It is important to realize that interfacial friction values are determined per material system. Comparison can only be made between wear couples when a value for the coefficient of friction,  $\mu$ , has been established for a material system control. In the case of determining the coefficient of friction for a coating, it is imperative that one realizes the value for  $\mu$  does not depend only on the coating; there are also substrate considerations. In determining what finish performs best it is necessary to evaluate precision within a specific material system and to compare that precision as well as the values for the coefficient of friction between the different finish groups.

For the following tests, the parameters were varied thusly. For the Pin-Disk Tests, weight loss and  $\mu$  values were determined and compared with abrading pairs in which the same finishes were wearing against one another under the same external test conditions. For the Torque Tests,  $\mu$  values were determined individually for different finishes under the same test conditions and then compared.

### Pin-Disk Testing

Tribological characteristics of Type II, Type III and corresponding composite anodic finished aluminum samples were determined by way of Pin-Disk abrasive wear/friction testing. The samples were tested under standard laboratory conditions at 23°C, 50% relative humidity throughout.

The pin tip radius was precision machined to 40  $\mu\text{m}$ . The test plates were 10  $\text{cm}^2$  sheet samples machined from 6061 T6 aluminum alloy. Four sets of the two sample groups (the pins and the "disks" were finished as described above. The Type II and composite samples were finished to a thickness of 20  $\mu\text{m}$ ; the Type III and hard composite samples were finished to a thickness of 40 $\mu\text{m}$ . The test program was set up such that the pin-disk sample pairs were finished identically.

The test apparatus was set up such that a finished pin rotated at a rate of 0.3 meters/sec for 1

hour against a finished plate. A normal force of 5 Newtons was applied. Mass loss of the pin and the disk were determined with an analytical balance. The depth of the wear track was measured with a laser profilometer. Coefficient of friction values were calculated by dividing the normal force by the frictional force.

Upon comparison of the weight loss data for the pin-disk test to the Taber Abrasion weight loss data, corresponding results were noted. That is, the Type II finish exhibited the greatest weight loss. The composite finish performed significantly better than Type II films. Type III and hard composite finishes exhibited the lowest weight loss. Additional testing consistently showed the hard composite finish exhibited the lowest weight loss with corresponding shallower wear tracks. See figure 5.

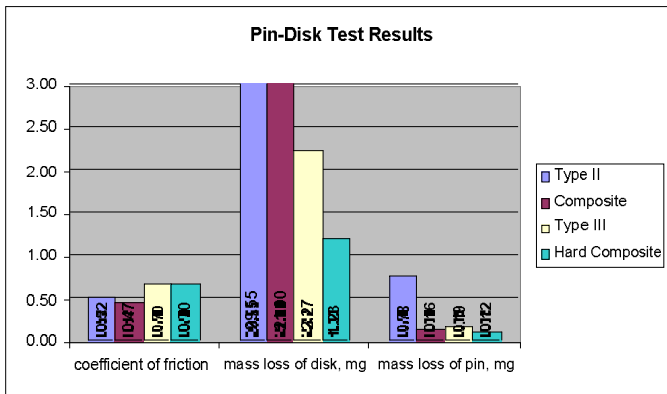


Figure No. 5: Pin-Disk Test Results. Note the range in mass loss values for the finished disk samples.

The coefficient of friction for pin-disk pairs finished the same was determined to be consistent within sample groups. The Type II samples exhibited an average  $\mu$  value of 0.52; for the composite finish samples, an average  $\mu$  value of 0.47 was determined. Type III and hard composite finishes were determined to have approximately the same value for  $\mu$  values, 0.70. [7]

### Torque Testing

Torque testing was performed per the German Industrial Specification DIN 946 "Determination of Coefficient of Friction of Bolts and Nuts under Specified Conditions" in order to determine and compare the coefficient of friction of various types of finishes on aluminum fasteners.

The applied load utilized to insert a fastener depends upon the coefficient of friction within the threads. This applied load ultimately governs the integrity of the bolt-nut joint. An over-torque condition damages the actual components through galling of the threads and by possibly exceeding the yield strength of the base material of the bolt. Under-torque conditions lead to fatigue problems within the joint. Therefore, with the assurance of reliable wear characteristics of a given finish, one will reduce the likelihood of galling within the joint and help to achieve a precision load for a given torque.

Comparative testing with threaded aluminum fasteners was performed. Alloys tested were aluminum alloy 7075 and 7278; finishes tested were the anodic composite finish, standard sulfuric acid anodizing (Type II) and yellow dichromate conversion coating. The average finish thickness for the anodized coatings was 15 micrometers. Steel nuts (alloy 34CrMo4), were utilized as test mates. Three possible lubricants were used on the nuts: MoS<sub>2</sub>, cetyl alcohol, or lanolin. Each bolt was tightened to a fixed load, removed and retightened ten (10) times. Load versus thread torque was charted. The coefficient of friction in the threads was determined as the slope of each charted excursion. Precision could be directly observed on the curves; overlapping data indicated an absence of finish galling for the applied load.

The load-torque curves for the fasteners finished with the yellow dichromate conversion coating exhibited increased thread torque values for each tightening. This suggested the finish galled with each insertion. The load-torque curves for fasteners finished with the standard anodized finish also exhibited increasing thread torque values, but to a lesser degree. The composite finish yielded precise load torque curves, with the slope (coefficient of friction at the threads) decreasing slightly with each tightening.

Direct comparison of change in friction values between Type II anodized threaded fasteners and composite anodized fasteners with a MoS<sub>2</sub> lubricant on the steel nut determined  $\Delta\mu_{\text{type II}} = 0.08$  with  $\mu$  values increasing with each load excursion and  $\Delta\mu_{\text{composite}} = 0.04$  with  $\mu$  values decreasing with each load excursion. These results indicate the composite finish exhibits antigalling characteristics

superior to the other finishes tested. See figure no. 6. [8]

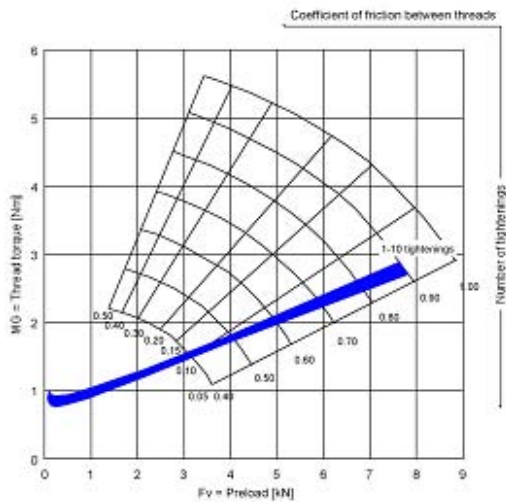


Figure No. 6: Torque test data for composite finished aluminum fastener, MoS<sub>2</sub> lubricant and steel bolt. The data band represents all ten load excursions. The data overlap indicates the finish exhibits good antigalling properties.

## Discussion

Continuing research and analysis regarding the nature of engineering property changes of anodic oxide finishes on aluminum through electrolyte modification and modifications of the external electrical input to the anodizing process has yielded much information. These modifications impart distinct microstructural changes to the anodic oxide as compared to the microstructures of anodic oxides formed through traditional processing. See figure no. 7.

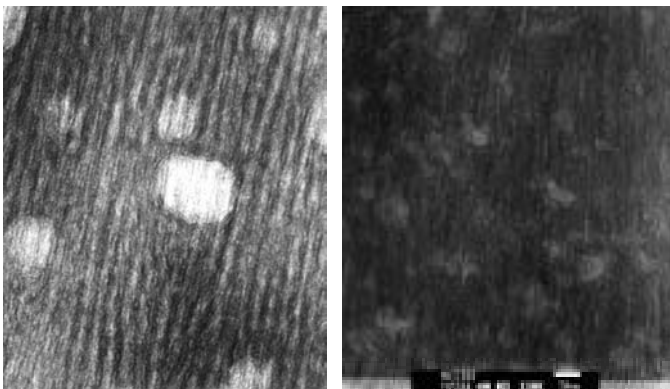


Figure No. 7: (left) Type II microstructure. (right) composite microstructure. Note how the unidirectional columns of the Type II structure (left) have become more skewed and random with the change in electrolyte, yielding the composite structure on the right.

By virtue of these changes and the predictable manner with which they can be achieved, the Constraint Concept of Film Formation was proposed. This theory explains how various oxide microstructural characteristics are achieved through electric field effects, as well as diffusion and mass transport that occur within the anodic oxide during anodizing, and how they change through modifications to the process. [9]

The kinetics of anodic oxide film formation are governed by 1) the thermodynamics at the surface and 2) diffusion and mass transfer across the oxide layer as it forms. [10] The columnar structure of the anodic film is the result of lateral film growth following surface reconstruction during early stages of the oxide growth process. As the “infant oxide” flakes impinge on one another, the repulsive forces of the similarly charged oxide flakes foster outward growth of the finish. Pores are also formed through repulsive field effects on the “inside” surface of the flakes.

As the oxide flakes impinge and grow outward, it is apparent that diffusion occurs across the column wall “knitting” the structure together. The stability and robustness of the final structure appear to hinge on this portion of the film formation. This is because there is no dynamic flux or ion flow that can disturb the formation of the final aluminum oxide species as in the pores. Therefore, the mechanical and chemical integrity of the finished film often is based on the integrity of the knitlines.

The integrity of the intercolumn knitline appears to play a significant role in the mechanical durability of the Type III finish. Particularly broad knitlines appear to degrade the wear resistance of the anodic finish i.e. finishes that exhibit this characteristic tend to chip and spall in shear. Broad knitlines tend to be most pronounced in Type III finishes that are processed at high current density without regard to internal resistance heating. The cohesive quality of a Type III finish processed as such is apparently low. See figure 8.

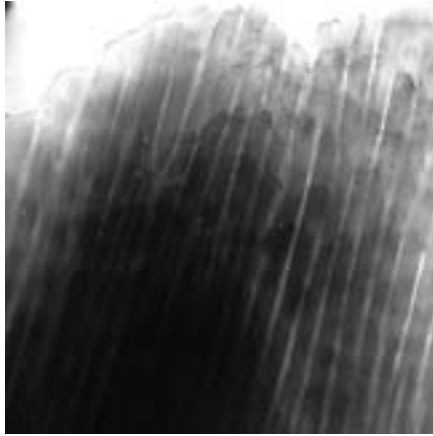


Figure No. 8: Top surface of Type III finish after exposure to shear forces. Note the structure has chipped off across the tops of the columns.

The knitlines were minimized through the addition of electroactive polymer to the anodizing electrolyte. This addition randomized the typically columnar microstructure, virtually eliminated the knitline as a feature and produced a consistently smoother surface finish. Although not as structurally robust as a conventional Type III finish, the composite finish appeared to withstand elastic deformation in shear far better than Type I and II finishes and as good or better than a Type III finish. The hard composite finish performed only slightly better than the Type III finish.

These results indicate that in specifying finishes for high wear applications normally relegated to Type III finishes, serious consideration can be given to the composite finish. Should actual application tests determine the composite finish performs comparably to Type III, added benefits can be derived in the form of energy savings, as the formation current density is lower and the process temperature is ambient for the composite finish.

Test performance differences and comparative microstructural analysis suggest enhanced wear resistance, higher impact strength and lower friction may be a function of enhancing the cohesive strength and therefore higher fracture toughness of the anodic finish produced with the modified electrolyte. Through understanding the anodizing process, a basis for microstructure-mechanical property relationships can be developed to enable manipulation of the process such that the film microstructure can be modified to yield specific engineering properties.

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