Toughness: The Key to Improved Anodic Oxide Finish Performance

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Comparative testing of typical sulfuric acid anodic oxide finishes to a novel composite anodic finish 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 indicate enhanced wear resistance is a function of higher toughness rather than hardness. Increased cohesive strength and reduced surface roughness of the composite finish due to modifications to the finish microstructure resulted in lower friction and reduced wear in even dissimilar wear couples. The results indicate the importance of understanding the anodizing process and the synergy between process, microstructure and engineering properties to bring innovation and improvement to our mature industry.

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Introduction

Anodic finishes are used 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 high 300 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 is also of concern.

The other typical anodic finishes; Type I, produced in a chromic acid electrolyte and Type II, produced in sulfuric acid are used mainly for corrosion resistance and their ability 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 used primarily in the aircraft industry. The durability of Type I and Type II finishes depends most on impact and scratch resistance.

Finishers often use supplementary tribological coatings based on Teflon® as colloidal suspensions of PTFE and TFE to reduce the coefficient of friction between wear surfaces including an anodic finish. It is well documented that even with such coatings, that surface entropy between colloidal particles and between the edge of a pore and the particles prohibit intrusion of the supplementary coating into the anodic finish. [1, 2] Thus the useful life of the supplementary coating is limited to the time required to wear it away. Most 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 with those processed similarly but with the 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, and 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 1).

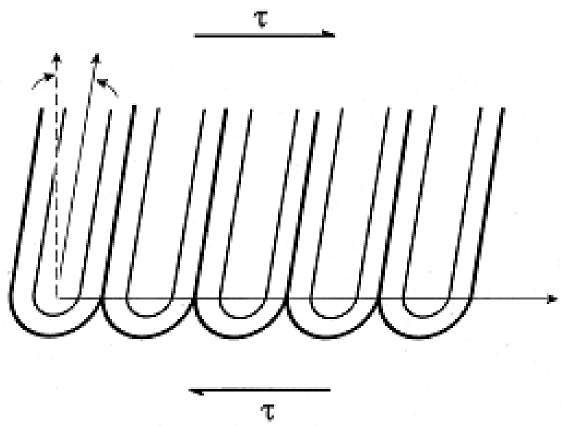

Figure 1: Schematic of the columnar structure of the anodic finish under applied shear force (τ). The angle represents displacement of the structure through elastic deformation.

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 the diffraction contrast necessary to identify the oxide phase as corundum, (α alumina, Al_2O_3). Chemical analysis by electron energy loss spectroscopy (EELS) shows conclusively that the film is composed primarily of disordered hydrated aluminum oxide, i.e. aluminum hydroxide [3]. Therefore, Type I, II and III anodic oxide finishes are all composed of the same material.

Material failure due to excessive elastic deformation is controlled by the modulus of elasticity, and not by the strength of the material. Since the elastic modulus is a material property, little metallurgical control can be exercised over it. 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 elastic modulus 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 grain boundaries and inclusions on the microscopic level. At the atomic level, defects such as vacancies and dislocations can “pile up”, leading to discontinuities in the anodic finish [5] (see Figure 2).

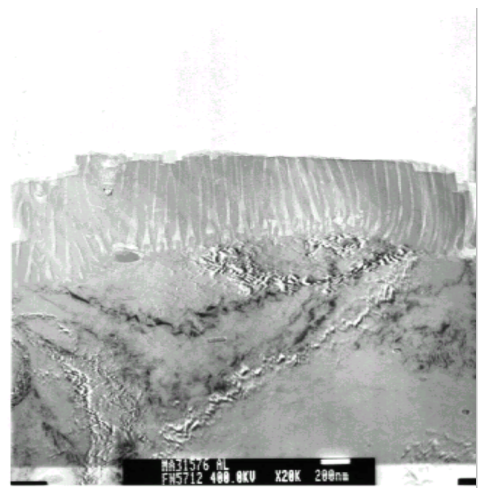

Figure 2: Microstructural and crystallographic defects impact the way the anodic oxide finish nucleates and grows.

As the anodic oxide fails in shear it chips and spalls, and 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 more brittle with lower 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 Procedures

Except as designated, comparative testing was performed following standard test procedures for anodic finishes for aluminum and aluminum alloys per MIL A 8625 F.

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 with specimens anodized with the modified electrolyte, following Type II process parameters (composite finish). The second group was hard anodized (Type III) for comparison with 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).

SEM imaging determined distinct differences in fracture surface morphology. 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 3).

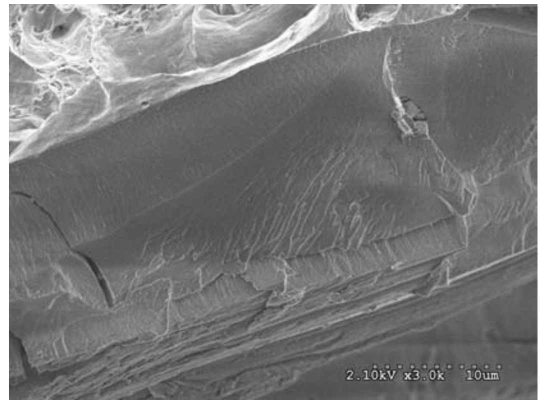

Figure No. 3: Brittle fracture surface of Type III finished charpy impact sample.

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 4).

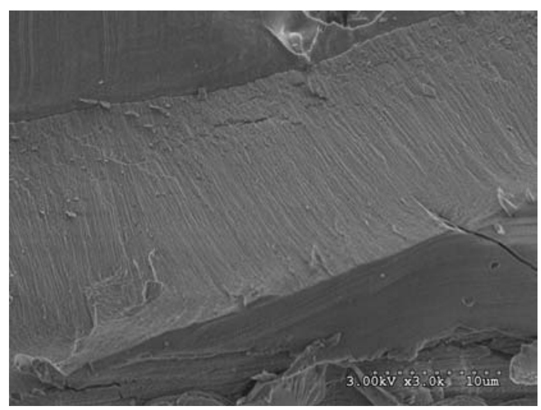

Figure No. 4: Ductile fracture surface of the hard version of the composite finished Charpy Impact sample.

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 that 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; they were 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 1,000 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 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 1,000 cycles. Results of the testing are summarized in Table I.

Poor performance of the Type II finish through abrasive testing created a problem in producing a meaningful yet comparable wear index. The finish produced at the production thickness of 5 µm (.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. The wear did not proceed into the aluminum substrate, and so testing was continued at 3,000 cycles to maintain consistency within the Type II test group.

Table I Taber Abrasion Test Results

Finish	Thickness (µm)	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 µm thickness. The testing was based on

ASTM B571, “Adhesion of Metal Coatings to Metal Substrates”, paragraph 4, “Burnishing Test”. The qualitative results indicated that the composite finish exhibited increased abrasion resistance; 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 be made between wear couples only when a value for the coefficient of friction, μ, 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 also realizes the value for μ 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 as follows. For the pin-disk tests, weight loss and μ 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, μ 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^{o}C and 50% relative humidity throughout.

The pin tip radius was precision machined to 40 mm. The test plates were 10 cm X 10 cm 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 μm; the Type III and hard composite samples were finished to a thickness of 40 μm. 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 m/s for 1 hr 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.

A comparison of the weight loss data for the pin-disk test and the Taber Abrasion weight loss data revealed corresponding results -- that is, the Type II finish exhibited the greatest weight loss. The composite finish performed significantly better than the Type II films. Type III and hard composite finishes exhibited the lowest weight loss. Additional testing consistently showed that the hard composite finish exhibited the lowest weight loss with corresponding shallower wear tracks (see Figure 5).

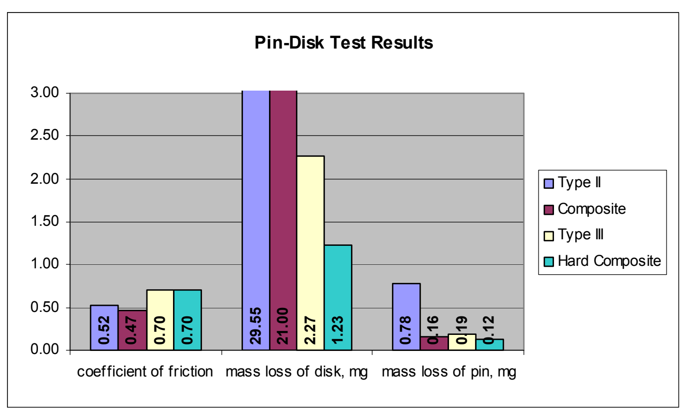

Figure 5: Pin-Disk Test Results. Note the range in mass loss values for the finished disk samples and correspondence to the Taber Abrasion data, especially for the mass loss of the pin.

The coefficient of friction for pin-disk pairs with the same finish was consistent within sample groups. The Type II samples exhibited an average μ value of 0.52; for the composite finish samples, an average μ value of 0.47 was determined. Type III and hard composite finishes were determined to have approximately the same μ value, 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 components by galling of the threads and may exceed the yield strength of the bolt base material. Under-torque conditions lead to fatigue problems within the joint. Therefore, the assurance of reliable wear characteristics of a given finish will reduce the likelihood of galling within the joint and help 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 μm. Steel nuts (alloy 34CrMo4), were used as test mates. One of three lubricants was used on the nuts: MoS_2, 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 that 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.

A direct comparison of the change in friction values of Type II anodized threaded fasteners and composite anodized fasteners with a MoS_2 lubricant on the steel nut showed that $\Delta\mu_{type\ II} = 0.08$ with μ values increasing with each load excursion, and $\Delta\mu_{composite} = 0.04$ with μ values decreasing with each load excursion. These results indicate that the composite finish exhibits antigalling characteristics superior to the other finishes tested (see Figure 6) [8].

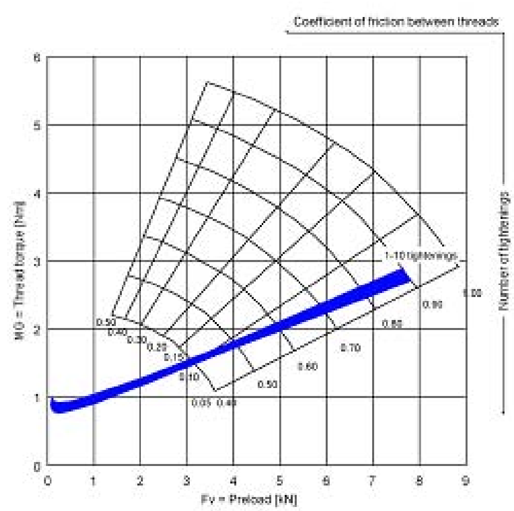

Figure No. 6: Torque test data for composite finished aluminum fastener, MoS_2 lubricant and steel bolt. The data band represents all ten load excursions. The data overlap indicates the finish exhibits good antigalling properties.

Discussion

Much information has been yielded by the 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. These modifications impart distinct microstructural changes to the anodic oxide compared with the microstructures of anodic oxides formed through traditional processing (see Figure 7).

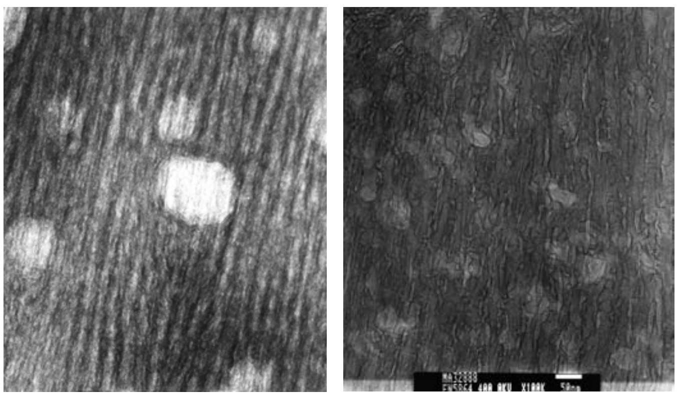

Figure No. 7: Type II microstructure (left) composite microstructure (right). Note how the unidirectional columns of the Type II structure (left) have become more skewed and random with the change in electrolyte, yielding the composite structure on the right.

By virtue of these changes and the predictable manner in which they can be achieved, the Constraint Concept of Porous Oxide Finish Formation was developed. 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 finish 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 finish is the result of lateral growth of oxide nuclei 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 depend on this stage 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 (see Figure 8).

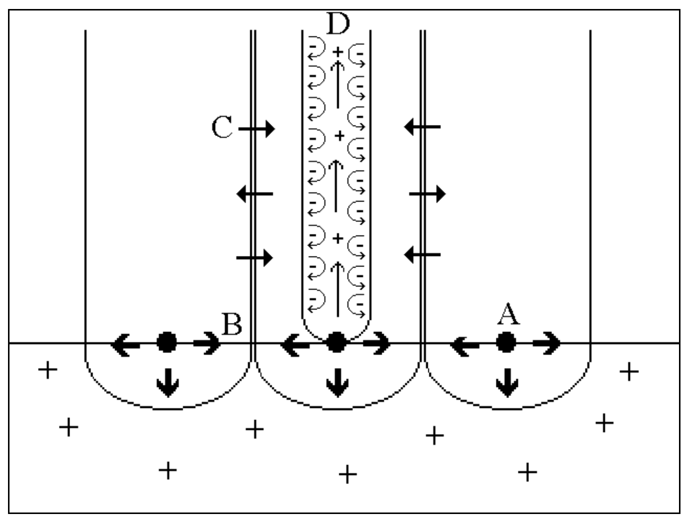

Figure No. 8: Schematic of the anodic oxide finish formation based in the Constraint Theory of Porous Oxide Finish Formation. The theory is based on the concept that each column is a nanoscale corrosion cell.

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 9).

The knitlines were minimized by 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 as or better than a Type III finish. The hard composite finish performed only slightly better than the Type III finish.

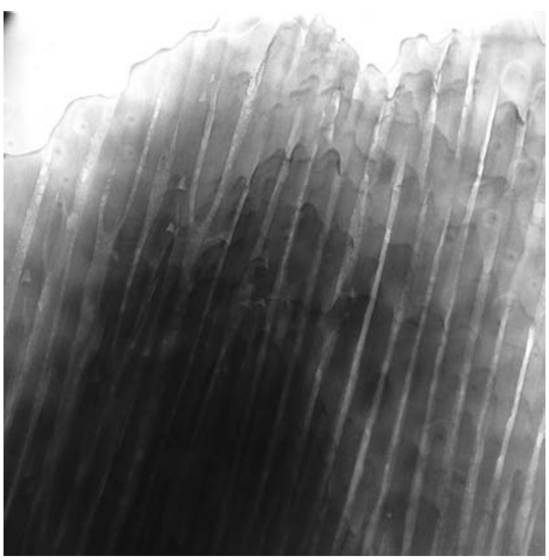

Figure No. 9: Top surface of Type III finish after exposure to shear forces. Note the structure has chipped off across the tops of the columns.

These results indicate that in specifying finishes for high wear applications normally relegated to Type III finishes, serious consideration can be given to finishes that are not considered hard, but exhibit the necessary robustness for the application. In our study, such an alternative was found in 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 that enhanced wear resistance, higher impact strength and lower friction may be a function of enhanced cohesive strength and therefore higher fracture toughness of the anodic finish produced with the modified electrolyte. Understanding the anodizing process permits the development of a basis for microstructure-mechanical property relationships. This enables manipulation of the process such that the film microstructure can be modified to yield specific engineering properties.

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