

Anodic Oxide Film Formation Relating Mechanism to Composition and Structure

By

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Abstract: In-depth studies of aluminum anodic film microstructures have enabled insights regarding the thermodynamics of film formation. Chemical analysis via high-intensity infrared spectroscopy and X-ray photoelectron spectroscopy shows a compositional gradient that can be related to the reactivity of the film microstructure. Understanding of the structure-chemistry relationships can enable manipulation of the anodizing process such that the film microstructure is modified to yield specific engineering properties.

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Introduction

Under typical atmospheric conditions, a native oxide or passive film naturally forms on aluminum. The native oxide layer is nonuniform, thin and noncoherent. Nevertheless, the native oxide film imparts a certain level of corrosion protection, provided the environment contains no unusual contaminants. Exfoliation, the formation of a network of oxide flakes or “leaves” on the aluminum surface is an example of how corrosion of the surface can be changed through the introduction of sulfur to the environment. In fact, removing sulfur from the atmosphere can control the exfoliation of aluminum [1-3].

Anodizing can be viewed as the deliberate, controlled corrosion of the aluminum surface in sulfuric acid to yield a uniform, continuous protective oxide film. Its unique columnar structure has been extensively studied, yet the mechanism of anodic oxidation of aluminum is still not fully established. This paper discusses a mechanism for film formation based in the results of comprehensive microstructural and chemical studies of conventional and modified Type II and Type III anodic films.

The results of these studies show the anodic film exhibits a microstructural and compositional gradient. Through scientific characterization of the various film features, and a clear understanding of the anodizing process parameters utilized to yield the various films, an understanding of the structure-chemistry relationships can enable manipulation of the anodizing process such that the film microstructure can be modified to yield specific engineering properties.

Review of the General Mechanism

It is well documented that the nature of the anodizing process is based upon the electrochemical principle that when a current is passed through an electrolyte in which an aluminum anode is employed, the anion migrates to the anode. The anion is then discharged with a loss of one or more electrons. In an aqueous solution, the anion consists in part of oxygen, which is adsorbed by the aluminum surface. As adsorption via chemisorption proceeds, the surface is reconstructed, forming a contiguous

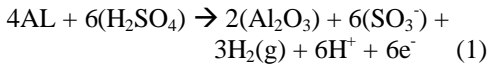
film aluminum oxide as Al_2O_3 . The resultant oxide is slightly soluble in the electrolyte. The slightly soluble characteristic of the film causes localized dissolution of the forming film. Pores are thus formed in the film, which are wide enough to allow continuous access of the current via the electrolyte to the metal.

Anodic film growth continues and is gradually retarded as the film grows thicker and the electrical resistance increases. When the rate of film growth has decreased until it is equal to the rate of dissolution of the film in the electrolyte, the film thickness remains constant.

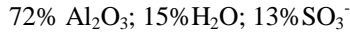
The resultant film has been presented as dual phase aluminum oxide. The structure (as presented) consists of a thin, nonporous inner oxide layer adjacent to the substrate metal (also called the barrier layer) and a thick porous outer oxide layer. The continuing anodization reaction takes place from the aluminum substrate surface, i.e. from the aluminum-barrier layer interface. The film effectively grows from within; therefore, the adsorption/surface reconstruction reaction occurs continually throughout the process, consuming the aluminum substrate. However, the outer part of the film is in contact with the electrolyte for the full anodizing time, and this interface develops into the second, outer phase. If the anodizing conditions favor film dissolution, this phase is porous Al_2O_3 . The outer porous oxide has a columnar cell structure [4-6].

Figures 1a and 1b illustrate accepted schematics of the anodic film structure and the constituents thereof. Figure 1a is representative of the microstructural concept derived from metallographic and some Scanning Electron Microscopic (SEM) investigation. The anodic film is presented as a close-packed network of hexagonal straws growing from a thin continuous (barrier) layer. Figure 1b is representative of a more current microstructural concept derived from Transmission Electron Microscopic (TEM) investigation. The anodic film is presented as a close-packed network of interconnected hexagonal columns with rounded bottoms. The intersection of the rounded bottoms that form a two-dimensional field of loops has been referred to as the barrier layer, as has the substrate region directly beneath the loops.

The chemical reaction, which takes place at the surface of the aluminum anode, can be written as follows:



Wenick, Pinner and Sheasby [7] report the anodic film composition as:



The sulfite content of the normal anodic coating produced for a sulfuric acid electrolyte is between 13% and 17% but is higher at lower temperatures of operation and increases with current density. The constituents of the film composition can be accounted for as follows: the outer porous film is composed of partially hydrated alumina ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), and sulfite ion (SO_3^-), which is discharged at the base of the pores of the columnar structure of the outer film. The barrier layer is reportedly comprised of alumina as Al_2O_3 .

Consideration of the electrochemical value for the half-cell reaction of aluminum coupled with the above information enabled the hypothesis that the porous structure would be reactive with additives that could possibly simultaneously oxidize during anodization. An entire body of research has stemmed from this hypothesis that has resulted in a new patented process for finishing aluminum that yields a composite anodic film. Additional offspring of this research are the following insights regarding film formation, that is, nucleation and growth of the anodic film.

Scientific Characterization

Transmission Electron Microscopy

Ultramicrotome sections of conventionally processed and unsealed Type II and Type III anodized films were further prepared for Transmission Electron Microscopy (TEM) by way of Precision Ion Processing (PIPs). The films were imaged and analyzed by way of TEM with Electron Energy Loss Spectroscopy (EELS).

Images of the Type II and Type III films were consistent with the representation presented as 1b. See figure nos. 2 and 3. The Type II

films were comprised of several close-packed hexagonal columns with rounded bottoms. The column walls were very thin and the pore diameters very small. The Type III films were comprised of fewer columns with rounded bottoms. The column walls appeared appreciably thicker and the pore diameters larger than a Type II anodic film.

An additional feature not satisfactorily described in the reviewed literature was observed and appeared to be a boundary line between the columns. The boundary lines exhibited unidirectional porosity and appeared to "knit" the individual columns together. These came to be called "knit lines" in our research and their location and appearance were key in developing the theory of film formation presented in this paper.

Chemical analysis via EELS and imaging by way of diffraction contrast show conclusively that the film is comprised primarily of disordered hydrated aluminum oxide, i.e. aluminum hydroxide. The anodic films, regardless of Type, are amorphous and do not exhibit any diffraction contrast necessary to identify the oxide phase as corundum, α alumina, Al_2O_3 . Furthermore, related research has disclosed the only crystalline anodic films are those formed by way of spark anodization, where the crystalline phase of alumina formed through the process was determined to be γ alumina [8].

TEM and Scanning Tunneling Transmission Electron Microscopic (STEM) imaging proceeded on a variety of modified Type II and Type III microstructures. Samples of 1) Passive post treatments (PTFE/FEP dip and spray coatings after anodizing) 2) chemically active post treatments (nickel acetate sealing) and 3) codeposition of an electroactive additive during anodizing (patented composite anodizing process) were studied.

Examination of the anodic film microstructures prepared with passive post treatments exhibited no microstructural change. No evidence of polymer intrusion was noted within the columnar structure. This is an important point to remember because vendors of polymer post treatments will often tout their coatings as capable of intruding the anodic microstructure. With anodic film pore sizes ranging from 4 to 15 nanometers and the minimum size of available colloidal PTFE

particles at 10 nanometers, it is feasible one could introduce PTFE to the structure. However, because of entropic forces between particles, agglomeration of colloidal PTFE particles in solution cannot be avoided. Therefore, inert post treatments, i.e. PTFE/FEP supplementary finishes are isolated to the surface of the anodic film and never incorporated within the columnar structure. Treatments such as these have a useful life limited to the effective thickness of the supplementary coating. See figure no. 4.

Examination of chemically active sealed anodic films determined evidence of microstructural modification within the first 100 to 400 nanometers of the surface. The anodic film surface microstructure was changed from its regular columnar structure to one finer and more random-appearing, with remnants of the columnar structure. Energy Dispersive X-ray Spectrographic (EDS) analysis determined chemical modification of the structure as well. Nickel was detected in line profile analysis via EDS throughout the thickness of the region of microstructural modification. See figure nos. 5 and 6.

Imaging and analysis of the composite anodic film revealed distinct differences in the film microstructures produced by conventional anodization, modified through post treatment and modified during anodization. The typical columnar structure associated with conventional and hard anodizing (Type II and III respectively) is modified throughout the composite anodic film. Instead of long, straight columns, the composite film exhibits a more cellular structure so that, although still following a columnar pattern, the individual "cells" create a self-sealed structure. It was found that by allowing the composite anodization process progress beyond the conventional anodizing time of one (1) hour, that the film surface microstructure became more random, somewhat similar but not as fine as the post treated/active sealed microstructures. See figure nos. 7 and 8.

High Intensity Infrared (FT-IR) Spectrographic Analysis

TEM sections of a Type II unsealed anodic film and a composite film were analyzed by way of high intensity Fourier Transform Infrared Spectrographic analysis. The energy source for the instrument was hooked up to a synchrotron

light source. The resolution of the instrument was 4 – 5 μ .

Sections of each coating were analyzed using a 4 μ X 30 μ aperture. Data was collected from the aluminum-anodic film interface (bottom), the film center and the top. The films measured 20-25 μ thick.

The trends in the infrared data collected from the bottom of the films to the top strongly suggest a shift in the formation and amount of active hydroxide and sulfate groups. The Al-O feature at approximately 750 cm^{-1} dominates, but shifts upward in the spectra as the sulfate peaks at 1000 to 1100 cm^{-1} become larger and more defined. With the development of the sulfate absorption, hydroxide absorption becomes pronounced. This actually makes sense, as the surface of the anodic film regardless of Type or formulation, should exhibit more hydration.

The composite coating exhibited evidence of inclusion of the electroactive modifier with absorption in the higher IR. The spectral shifts toward the higher IR were noted from the substrate, where the inorganic absorbances were most pronounced to the middle and finally the surface portions where absorption of both OH^{-1} and carbon-based inorganic salts were detected within the composite film. See figure nos. 9 and 10.

A hot water sealed Type III coating was processed within argon plasma. With increased exposure time within the plasma, a residue developed on the surface of the coating. Infrared analysis of the residue determined absorption characteristics for hydrated aluminum sulfate and/or aluminite: $\text{Al}_2(\text{SO}_4) \bullet 18\text{H}_2\text{O}$ and/or $\text{Al}_2(\text{SO}_4)(\text{OH})_4 \bullet 7\text{H}_2\text{O}$.

These results indicate consideration should be given to the stability of the oxide phases from the column wall to the pore center as well as from the substrate interface to the film surface. The portions of the film that remain in contact with the electrolyte, in addition to hydration, will also adsorb active counterion species from the electrolyte, forming a compositional and therefore reactivity gradient across the porous structure.

X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) studies were performed on Type II and on two (2) groups of composite anodized samples (similar to the group 3 samples analyzed by way of TEM). The composite samples were exposed to different anodizing times. One group of samples was representative of the typical exposure time of 60 minutes and the other group was representative of an extended exposure time. The samples were anodized and mechanically removed to sealed containers to prevent surface contamination through handling or by ambient air. This insured the analysis results would reflect the actual anodized surface composition from a depth of 0 to 30 Angstroms.

The Type II and composite samples anodized for the typical exposure time exhibited the presence of sulfur as sulfate. Additional oxygen and aluminum was also detected. The high-level binding energy component for oxygen corresponded to H_2O and OH , which supported the infrared data. The aluminum detected in the film surface of these samples was not metallic in nature; the low binding energy component was typical for disordered aluminum oxide. The composite sample did show chemical inclusion of the electroactive modifier. Saturated and π - conjugated carbons were noted with distinct linkages to the disordered (hydr)oxide structure as HO-C=O , O-C=O and C-OH .

XPS analysis of the extended exposure samples determined strikingly different surface constituents. More of the electroactive additive was detected in the surface of these samples. No sulfur was determined. Evidence of metallic aluminum, aluminum as Al_2O_3 , and copper, as Cu_2O was also identified. The results were important because they indicated these species were actually deposited from the electrolyte and not a function of the anodization of the substrate.

Discussion

Intensive microstructural and chemical analyses of several types of anodized aluminum coatings were performed. The results provide increased insight regarding the mechanism for anodic film formation as well as its resultant chemistry.

Surface Reconstruction

A comprehensive thermodynamic treatment of chemisorption, which precedes surface oxidation, is presented in Murr [9]. It is important to note that the resultant "infant" oxide layer begins at nucleation sites that may have a preference for certain crystallographic surface orientations as well as surface structural features such as dislocations, steps, or ledges. Temperature impacts nucleation such that fewer preferential sites will form at lower temperatures. On the molecular level, it has been shown that grain boundaries, inclusions and other forms of surface contamination will also impact the initiation of the oxidation reaction [10].

Film Growth

Without the imposition of an external electrostatic potential, the initial oxide layer would grow in excess of a monolayer to an equilibrium thickness we refer to as "native oxide" or a passive layer. Regardless, film growth requires diffusion of either the oxygen or the metal through the forming layer, or both. Because the anodization reaction is one of simultaneous substrate consumption with film growth, we must consider the nature of the oxide network formed to understand how the passive layer can be developed to form the ordered microstructures familiarly recognized as Type II and Type III anodic coatings.

As nucleation proceeds on the substrate surface, a certain amount of lateral film growth occurs as the forming layer exceeds monolayer thickness. Preferential nuclei, formed at sites on the substrate surface where the energy required for chemisorption was lowest, will continue to grow and develop as long as there is available free aluminum to oxidize, and the thermodynamic work function of the metal is such that the oxidation reaction is favorable. Work function can be defined as the difference in energy between the electrostatic potential outside the forming oxide layer and the electrochemical potential of the anode. Under atmospheric conditions, the oxidation reaction will cease as the passive layer exhibits continuity, causing the work function of the aluminum to reach equilibrium (equal zero).

With a deliberate increase in work function, such as through the introduction of a chemical contaminant to the atmosphere (as in corrosion) or through the imposition of an external current bias (as in anodizing) and/or a change in

temperature (as in corrosion or anodizing), the passive network continues to grow. The infant nuclei become a network of hydrated, charged flakes that impinge on one another. As the reaction kinetics continue to favor the initial oxidation sites, exfoliation of the aluminum surface will proceed in a contaminated atmosphere. In anodizing, the impinging flakes repel one another and grow outward from the substrate surface, forming the distinct columnar structure that is so well recognized in the metal finishing industry. See figure no. 11.

The “Ion Pump”

The feature critical to the forming anodic film is its central pore. As the base network of oxide flakes impinge on one another and grow outward, field effects created on the inside surface of the flakes also repel such that the erect nature of the network is maintained from the inside out. The pore wall becomes a dynamic surface as the oxidation reaction continues. As the electrolyte enters the porous structure, the anion, which is in part oxygen reacts with the film and hydrogen ions as H^+ as well as hydrogen gas are ejected from the primary reaction sites and so consumption of the aluminum continues.

As the pore wall is negatively charged, it becomes an additional surface for chemisorption of various electrolyte species. A certain amount of reductive dissolution of the film occurs to maintain film formation through electrolyte access at the pores and adsorption of sulfate, chromate or other network modifiers follows.

The reactivity of the pore wall determines the film thickness. As adsorption of less reactive species occur on the pore wall, the field effects diminish and the columnar structure can no longer be maintained. At this point, the work function of the anode approaches zero. When this occurs, the oxidation reaction no longer dominates and deposition of electroactive components within the electrolyte can occur. QED the deposition of copper within the surface of the extended exposure samples determined through XPS analysis.

Reactivity of the pore wall also can explain sealing phenomena. A reactive seal will complex with available adsorbed species from the electrolyte or otherwise active OH^- ligands in

the disordered aluminum oxide structure. As these reactions proceed, a certain level of film dissolution occurs from the inside out. Depending upon the robustness of the structure, the column walls may become thinner and collapse, forming the random surface structures of modified Type II and Type III anodic films. Therefore, the inert, stable nature of adsorbed complexes on the inside surfaces of the pores disables the “ion pump”.

The Formation of Knitlines

Consideration must also be given to the column walls. 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, as in the pores, which can disturb the formation of the final aluminum oxide species. Therefore, the integrity of the finished film often is based on the integrity of the knitlines.

What About the Barrier Layer?

At no time during the course of this research was a film feature that resembled a continuous, contiguous layer beneath the forming oxide coating identified. It became obvious as data collection and analysis continued that what has been referred to as the barrier layer was the intersection of rounded bases of the individual columns. As each base is encompassed by a knitline, one can understand the important role the knitline boundaries play.

Clearly the anodic film is a microstructural network of individual columns. The concept of a barrier layer was developed from data limited by the technology of laboratory equipment in the past and fostered out of respect for our mentors. It is by no means out of disrespect that we report there is really no barrier layer; simply, it appears to be the result of the extensive analysis of anodic films produced both in the laboratory and in production environments.

Summary

Through extensive analysis of anodic oxide films produced through a variety of parameters commonly utilized to form Type II, and Type III

coatings on aluminum, the following conclusions can be drawn regarding the mechanism for film formation.

- 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.
- The columnar structure of the anodic film is the result of lateral film growth and impingement of “infant oxide” flakes on one another. The repulsive forces of the similarly charged flakes foster outward growth.
- Pores are also formed through repulsive field effects on the “inside” surfaces of the flakes, as they grow outward from the substrate.
- The rate of substrate oxidation initially exceeds the rate of adsorption of electrolyte network modifiers on the inside surface of the pores.
- A critical time, t_c , exists where substrate oxidation ceases to be the dominant reaction and the work function of the reaction becomes zero.
- Film modification is facilitated by reactive species in the electrolyte that adsorb on the pore walls as the work function approaches zero.
- There is no barrier layer.
- The integrity of intercolumn knitlines governs the integrity of the anodic film in service.

Conclusion

Through comprehensive scientific characterization of the anodic film microstructure and its chemical constituents, a correlation to engineering characteristics important to the application and service life in various industries can be drawn. Extensive engineering tests documenting corrosion and wear resistance, hardness, fracture toughness, fatigue strength, dye ability, color fastness and adhesion of subsequent laminate or lacquer

finishes comparing conventional and modified anodized films have also been carried out. By understanding the age-old process of anodizing aluminum first determined by Faraday himself, new and improved, truly different anodic films can be introduced to a market complacent with mature designs.

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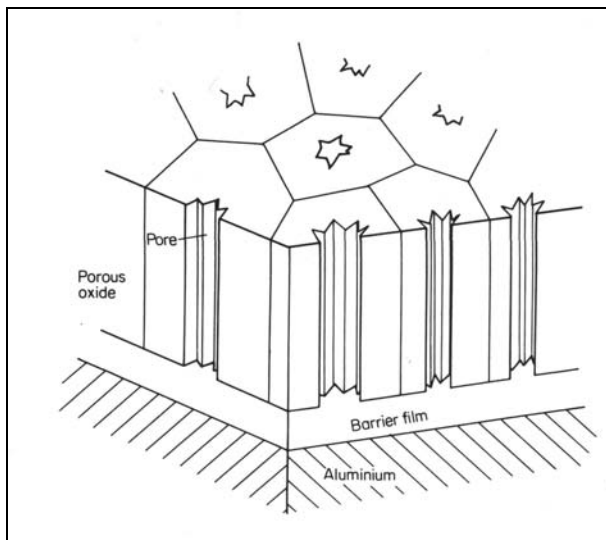


Figure 1a: Schematic of traditional anodic film concept.

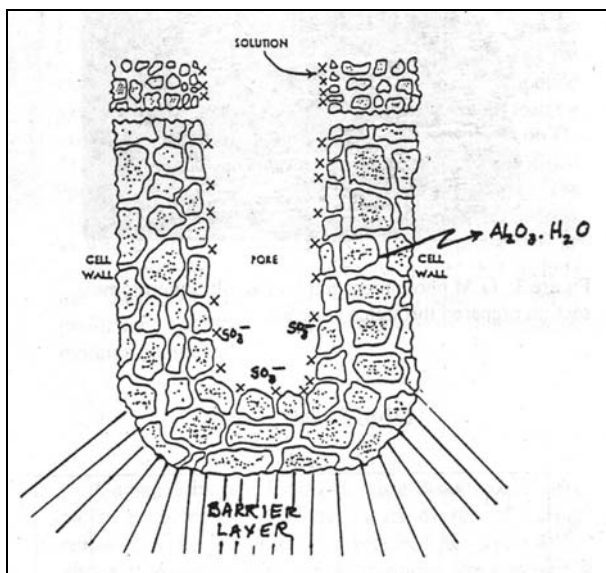


Figure 1b: More current schematic of a single pore of an anodic film.

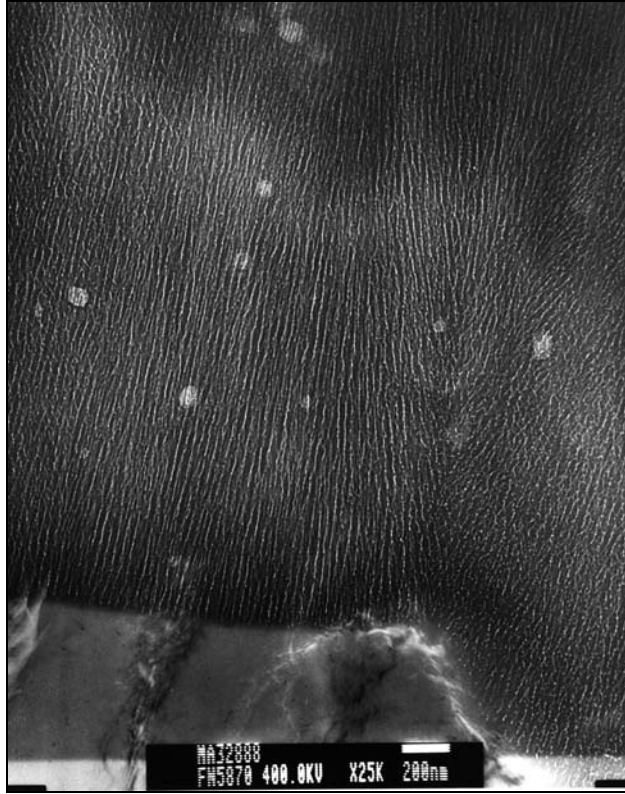


Figure 2: Representative TEM photomicrograph of a Type II anodized film X25,000.

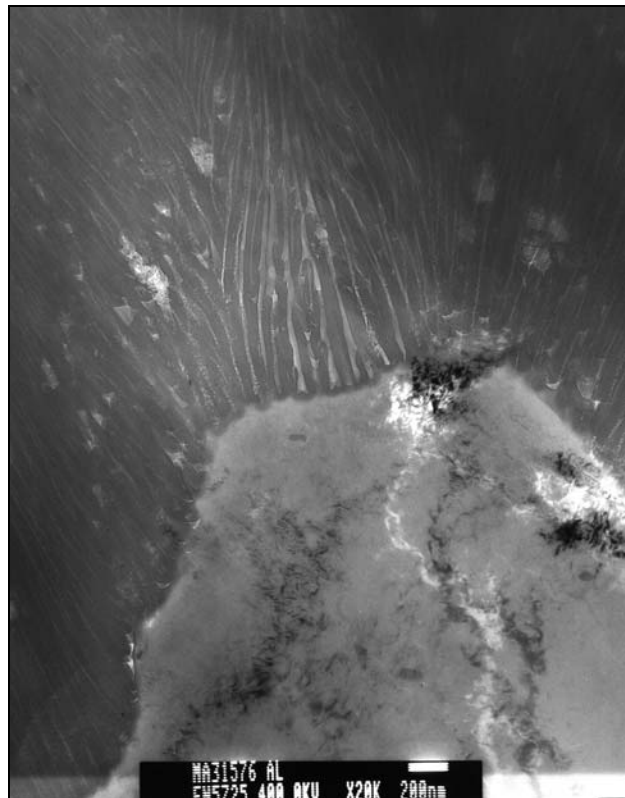


Figure 3: Representative TEM photomicrograph of a Type III anodized film X20,000.

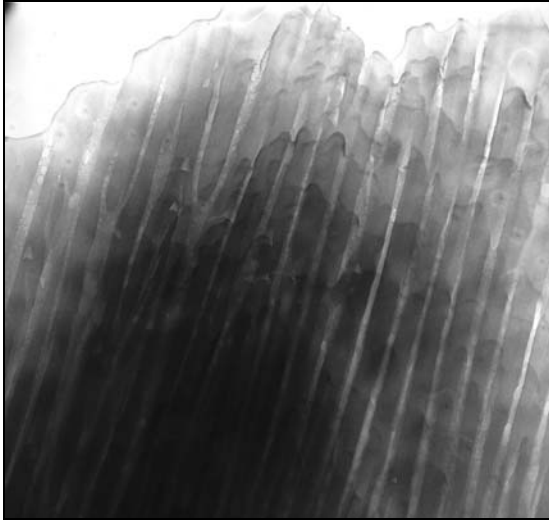


Figure 4: Top surface of PTFE post treated Type III film. Note no structural modification at the surface and no polymer intrusion to the porous structure.

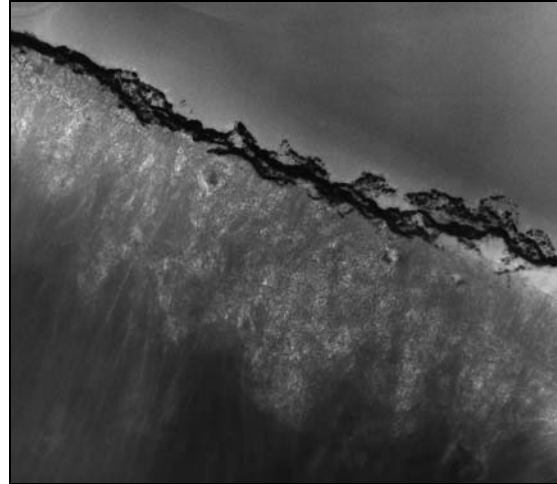


Figure 5: Top surface of nickel sealed Type III film. Note surface structure modification due to the reaction between the nickel acetate seal and the anodic film.

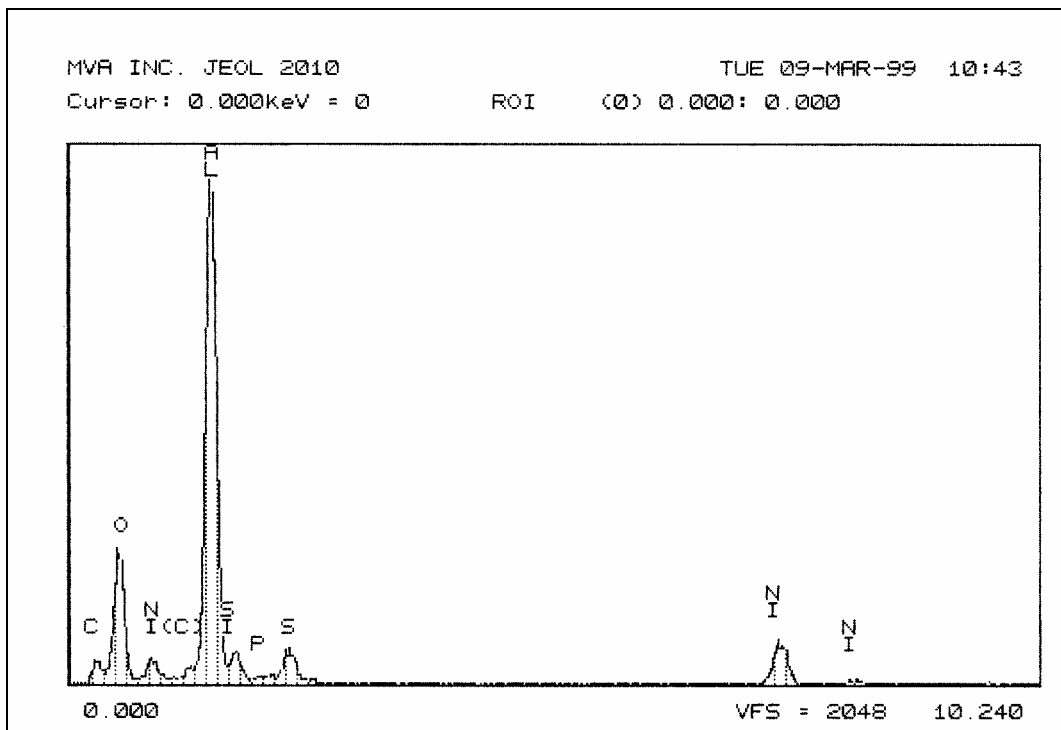


Figure 6: EDS spectrum of nickel sealed Type III film.



Figure 7: Representative TEM photomicrograph of the modified structure of a composite anodized film. Note the cellular, rather than directly columnar structure.

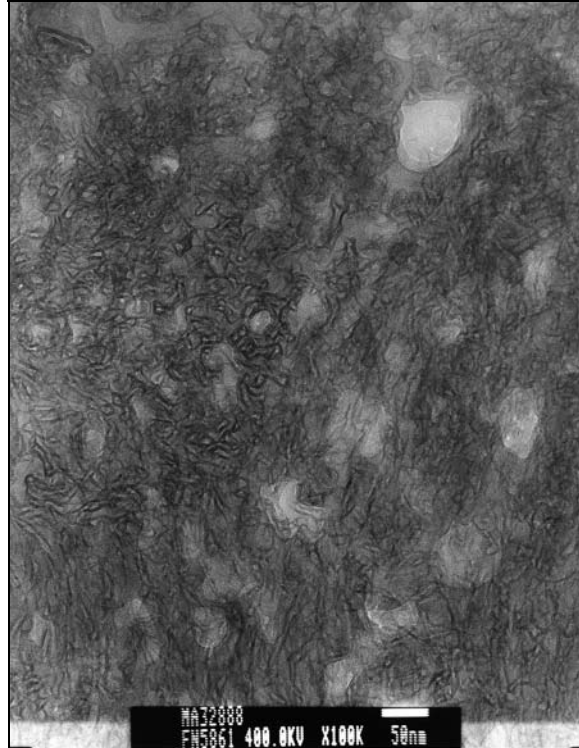


Figure 8: Highly modified surface structure of the composite anodic film is randomly oriented. Note however, the fragments of the columns interspersed throughout the structure.

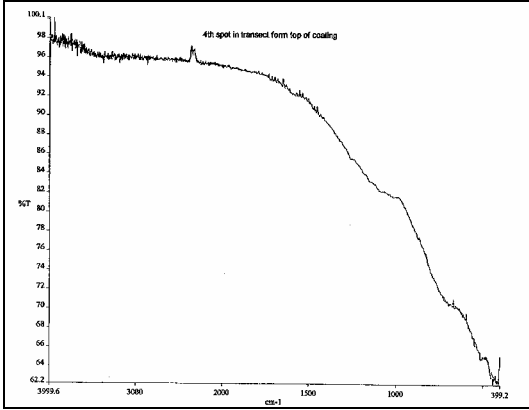


Figure 9: IR spectrum of composite anodic film adjacent to the aluminum substrate is identical to a conventionally anodized Type II film. The low end absorbance is typical for inorganic species.

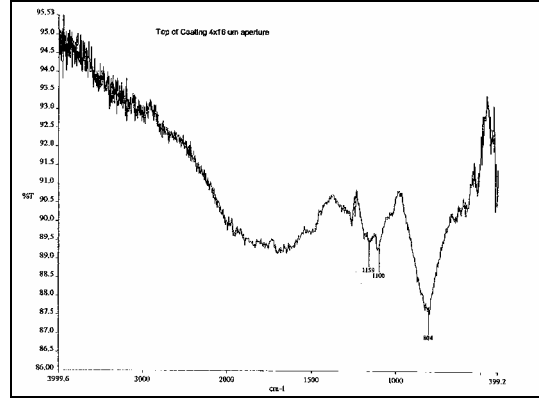


Figure 10: IR spectrum of modified composite film exhibits a shift in the inorganic spectrum toward the more chemically reactive species of sulfate and hydroxide. Some organic absorbances are also present indicative of additive inclusion.

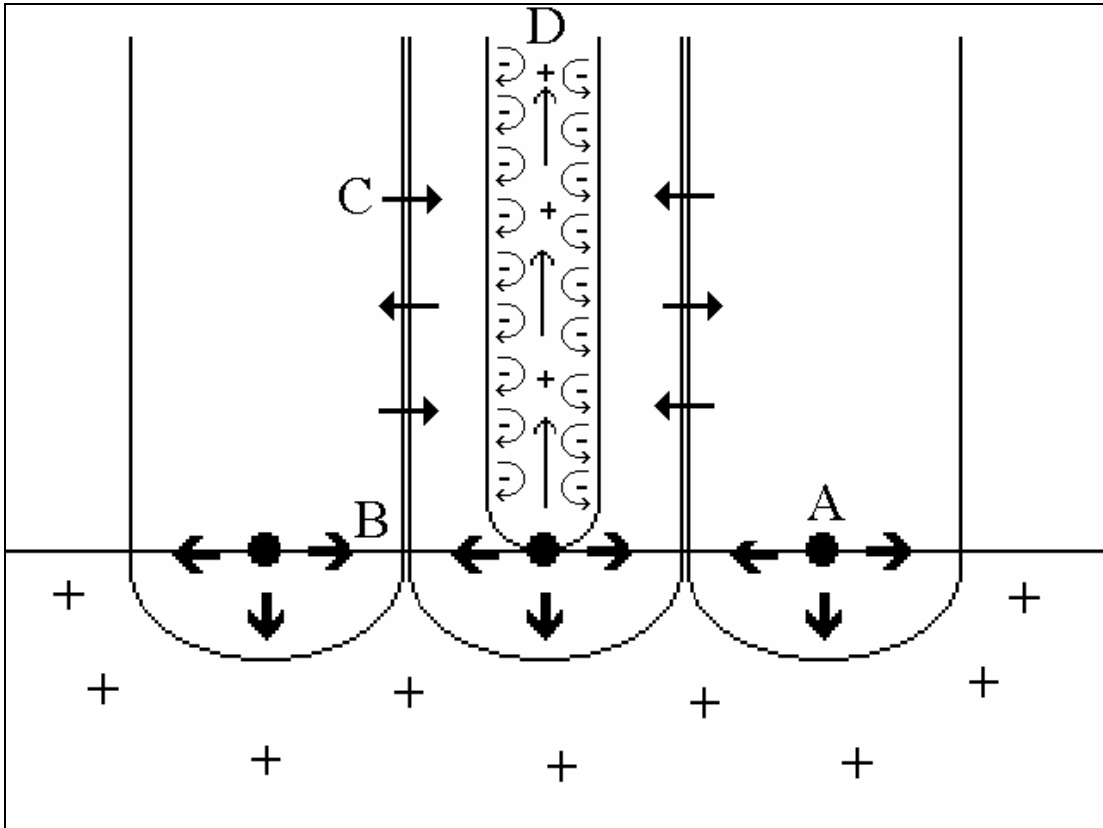


Figure 11: "Constraint" concept of film formation. A: Preferential nuclei form base of pore. B: Repulsive forces between similarly charged oxide "flakes" foster outward growth. C: Mass transport and diffusion across column walls form knitlines. D: Repulsive forces within pore maintains the erect nature of the column and dynamic flow of the electrolyte.