Challenges in Anodic Oxide Finishing Arising
From Different Substrate Manufacturing Processes

By: Dr. Jude Mary Runge
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Abstract: This paper describes, through case study and scientific theory, the impact of various microstructures; cast, wrought and sintered, on the anodizing process. Problems are identified and explained; and solutions are proposed. Armed with this awareness, the surface finisher can more actively participate in root-cause failure investigations that may manifest themselves as anodizing problems, but are actually substrate related.

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Introduction: The surface quality of the substrate is a chief concern for every metal finishing process. Cleanliness of the surface is of paramount concern regardless if the process is placing a label, painting, electroplating or anodizing. Adhesion of the finish, and all defects associated with the lack thereof, such as blisters, delamination, cracks, etc., can in one way or another be related to surface quality. Therefore, all surface finishing operation begins with a cleaning step.

Of the processes considered, anodizing is the most dissimilar because, unlike adhesives, paints or electrodeposits, that is exactly what anodizing is not, a deposit. Instead of placing or depositing a layer on the substrate, in anodizing, a nanoscale network of self assembling corrosion cells are nucleated and grown from the aluminium substrate surface. But the process does not end at the substrate surface; experience and analysis have shown the anodizing process *consumes* the aluminum such that approximately half of the finish thickness was at one time substrate. Therefore, while the anodizer must be aware of substrate surface quality, he/she must also be aware of the underlying substrate microstructure in order to understand finish process limitations and defects that may manifest themselves as finishing problems that are actually substrate related.

This paper describes, through case study and scientific theory, the impact of various microstructures; cast, wrought and sintered, on the anodizing process. Problems are identified and explained; and solutions are proposed. Armed with this awareness, the surface finisher can more actively participate in root-cause failure investigations and adjust the anodizing process to appropriately deal with variations in substrate microstructure.

Scientific Background: Through the course of our work beginning in the late 1990's and continuing through 2001 at the University of Illinois at Chicago, Saporito Finishing in Cicero, Illinois and Bodycote Surface Engineering in Kaufbeuren, Germany [1 – 3], and continuing work today at CompCote International, Inc., we have learned much about the anodic oxide finish as it applies to various anodization processes, parameters and electrolytes. As a result, we developed new insight regarding porous oxide formation which presents solid corrosion theory as the source for the self-assembling nanoscale structure of the anodic finish.

Atomic Force Microscopy (AFM)

Preparation and characterization of porous oxide anodized finishes on aluminum by Wang et al at the Argonne National Laboratory in Argonne, Illinois, USA [4] confirmed the porous oxide finishes were nanoscale. Although the purpose of the research performed was to utilize the finish as a template for nanoscale wires and tubes for electrical, magnetic and photonic applications, their work also documented clearly the nature of the porous oxide finish as a self-assembling array of individual columns.

Atomic Force Microscopy (AFM) techniques clearly document the anodic porous oxide finish as consisting of several columns per grain aluminum, self-assembled in

an array not unlike a simple bubble array, hence the hexagonal arrangement. One of the samples, a coupon manufactured from 1100 aluminum alloy, was anodized at 0^oC for 3 hours at a DC voltage of 30 V in oxalic acid. The unit column per grain density of this sample, for an average substrate grain size of 2.5 microns, averaged 200 columns per grain. The pore diameter for this sample was 40 nanometers and the pore to pore central distances measured 100 nanometers.

In general, for all samples anodized, the column sizes and spacing varied, depending upon the current density and electrolyte utilized. They ranged in size for pore to pore distance from 51 nanometers for lower current density finishes to 100 nanometers for higher current density finishes. See figure nos. 1 and 2.
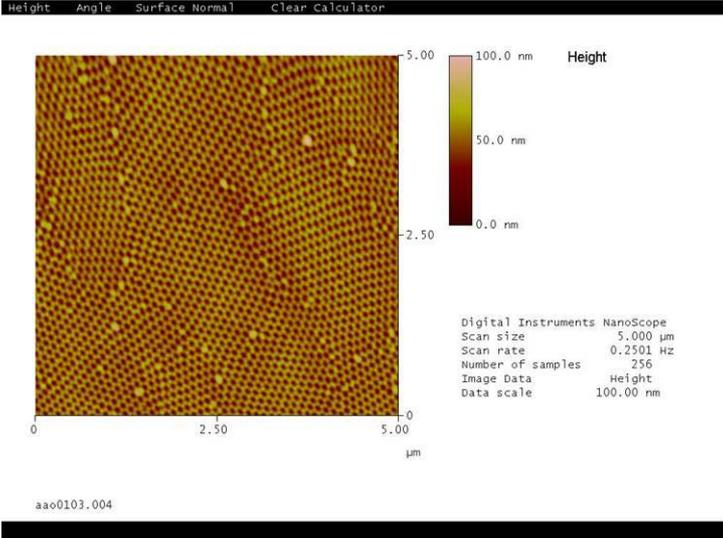

Figure No. 1: AFM image of the top of an anodic oxide finish shows several columns per substrate grain arranged in a hexagonal close-packed nanoscale structural order.
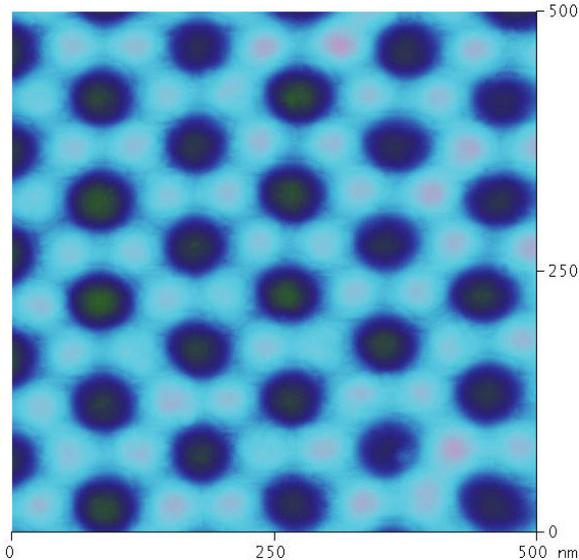

Figure no. 2: AFM image of the aluminum substrate after the anodic oxide was chemically removed shows the arrangement of the oxide on the substrate. Each pore center is represented by a dark spot. The column walls are represented by the hexagonal arrangement of the light blue spots. The pink spots are centers of impingement between column walls.

Images of the underside of the porous oxide finish show conclusively that each column base is rounded at the bottom and that the interstitial spaces are regular but can vary. This result indicates structural order of the anodic finish can be disrupted at the finish – substrate interface due to substrate defects that intersect the surface. The image shows that disruption of the structure occurs between columns of the anodic oxide and clearly documents the importance the substrate quality has on the finish quality. In addition these images clearly show no evidence of a continuous underlying barrier layer, but show each column is part of a nanoscale finish network. See figure no. 3.
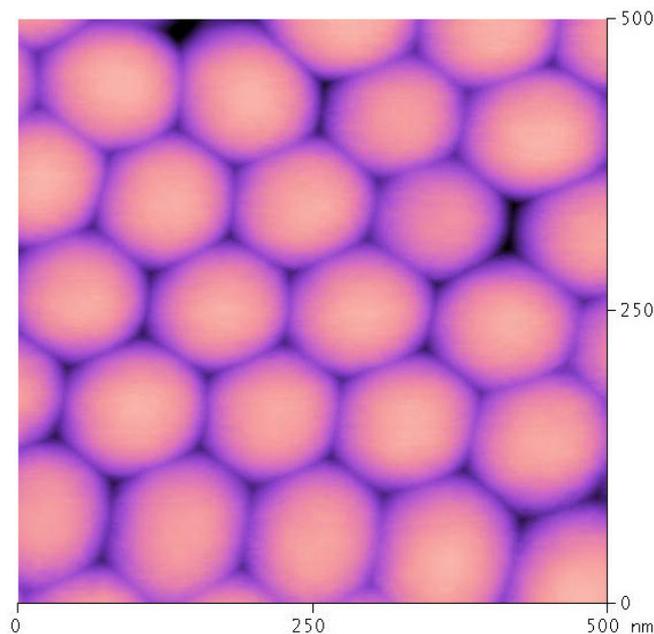

Figure No. 3: AFM image of the underside of the anodic oxide finish after removal from the aluminum substrate. Note the simple hexagonal arrangement of each rounded column bottom. Also note the variations in the interstitial spacing. Each column measures approximately 100 nm from edge to edge.

Upon consideration of the 1100 alloy used for this research, its composition (99% pure aluminum) and wrought microstructure, the impact of atomic level defects on the anodic oxide finish was clearly documented. Virtually all crystalline materials contain atomic level defects such as dislocations, vacancies, steps, etc. as the result of solidification (as in castings), plastic deformation (as in wrought material) and lattice mismatch (as in sintered material). Defects even at this level disrupt the surface reconstruction process that precedes finish growth during anodizing.

Transmission Electron Microscopy (TEM)

Ultramicrotome sections of conventionally processed and unsealed Type II (commercial anodized) and Type III (hard anodized) 6061 T6 wrought aluminum alloy substrates were prepared parallel to the direction of finish growth. The sections were further prepared for TEM by way of Precision Ion Processing (PIPs). The anodic finishes were imaged and analyzed by way of TEM with Electron Energy Loss Spectroscopy (EELS).

Images of the Type II and Type III anodized finishes disclosed they were comprised of several close-packed unidirectional columns with closed, rounded bottoms. The number of columns, pore diameter and column wall thickness was consistent for each finish type but varied with process type. The Type II finish was comprised of many fine columns, each with a uniformly small pore diameter. The pore diameter

measured approximately 5 - 10 nanometers and the column walls approximately 10 - 15 nanometers thick. (Approximately 25 nanometer pore center to pore center distances.) See figure no. 4.

The Type III finish exhibited fewer columns with wider pore diameters and thicker column walls. The pore diameter measured approximately 30 nanometers and the column walls approximately 25 nanometers thick. (Approximately 80 nanometer pore to pore distances.) A feature more easily discernible on the Type III finish was that of a distinct boundary line between each column. The boundary lines exhibited the same unidirectional character as the central pore and appeared to "knit" the individual columns together. These features were also well documented in the AFM images and came to be called "knit lines" in our research. See figure no. 5.

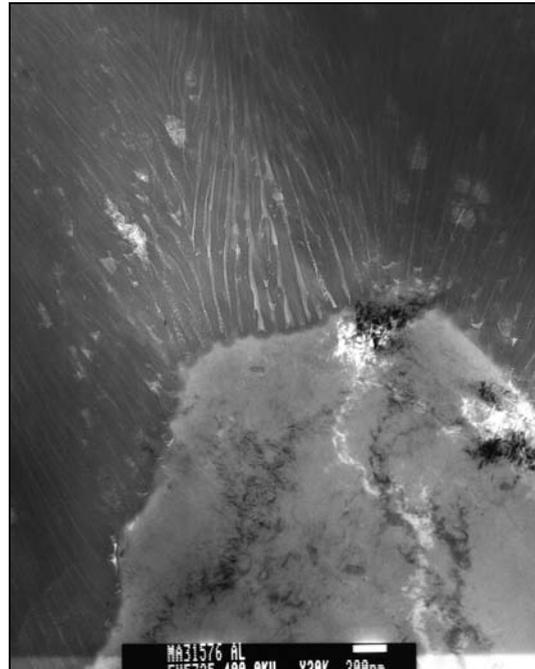Figure No. 4: Representative TEM micrograph of a Type II anodic oxide finish.

Figure No. 5: Representative TEM micrograph of a Type III anodic oxide finish.

Chemical analysis via EELS and imaging by way of diffraction contrast showed conclusively that the finish is comprised primarily of amorphous, disordered, hydrated aluminum oxide, that is, aluminum hydroxide. No other metal oxides were identified within the finish that would indicate that alloy additions such as copper or silicon participate to become part of the anodic oxide finish. The anodic finish, regardless of type, is amorphous and doesn't exhibit diffraction contrast necessary to identify the oxide phase as corundum, α alumina, Al_2O_3.

TEM also disclosed that while the anodized finish exhibited an ordered appearance, interfacial disorder was observed at the substrate in areas where the anodic oxide intersected grain boundaries, dislocations and inclusions. Disorder was identified as the apparent increase in column bases in the interfacial defect areas, increased outgassing (entrapped gas bubbles within the finish) and deviation from the perpendicular orientation of the finish to the substrate. Recovery of the finish growth was noted as additional growth fronts were observed below the disordered areas. See figure nos. 6a and 6b.
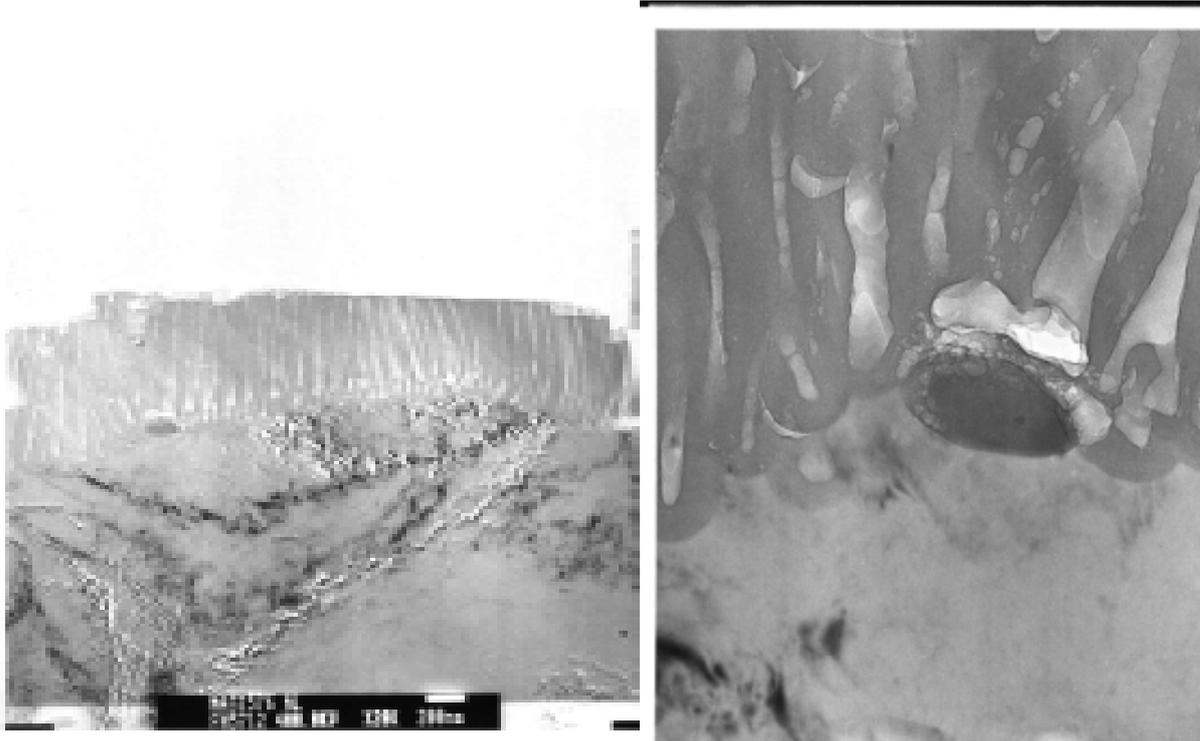
Figure 6a: X15,000 Documentary TEM micrograph of a Type III anodized aluminum substrate. Note the presence of circular inclusions (iron-chromium) which were taken up into the Type III columnar structure during anodization. Atomic level defects such as grain boundaries and dislocations in the aluminum substrate also affect the finish structure at the finish-substrate interface. Figure 6b: X100,000 Higher magnification TEM micrograph of the iron-chrome inclusion at the substrate – finish interface. Outgassing at inert inclusions can cause blistering in the finish.

Through examination and analysis of more complex wrought alloys with the TEM, it became clear that in segregated alloy solutions with inert inclusions, corrosion (anodization of the aluminum substrate) will proceed about and even around the inclusions, lifting them into the anodic oxide finish as it grows out from the substrate. The impact of inert or insoluble defects such as inclusions, grain boundaries and atomic level sinks on the finish is in the spacing of the oxide nuclei during surface reconstruction. This disruption in order can lead to irregular growth and irregular intercolumn spacing. However, as the surface is consumed and a more ordered surface is presented for oxidation, the finish recovers its ordered structure as growth takes place. This is also documented in figure 6.

Metallographic Examination

Cross sections from anodized die castings and sintered components were metallographically prepared and examined with a metallurgical microscope and Scanning Electron Microscope (SEM) because of defects identified as reduced finish thickness, cracks, and localized discoloration in the anodic oxide [5, 6]. The defects were erroneously associated with the anodizing process and could be tied directly to the microstructure of the substrates by virtue of this analysis. Chemical analysis of the discoloration on the anodic oxide finish as well as of the substrate was performed by Energy Dispersive X-ray Spectrographic Analysis (EDS).

Small anodized die castings exhibited variations in the thickness of the anodized finish, with some components being unacceptably thin. Metallographic examination disclosed the ADC 6 alloy, a high strength low alloy composition that is typically easier to anodize, displayed a highly segregated microstructure. The script phase, $(Fe,Mn)_3SiAl_2$, intersected the surface and did not anodize at the same rate as the aluminum rich portions of the substrate. In areas where the script phase was more pronounced, the reduced thickness was also more pronounced.

The substrate microstructure was homogenized through a heat treatment process called Hot Isostatic Pressing or HIP. The HIP process re-solution treated the cast microstructure, providing a more homogeneous surface for anodizing, and as an added plus, consolidated the microstructure to remove porosity throughout the casting. See figures 7a and 7b.
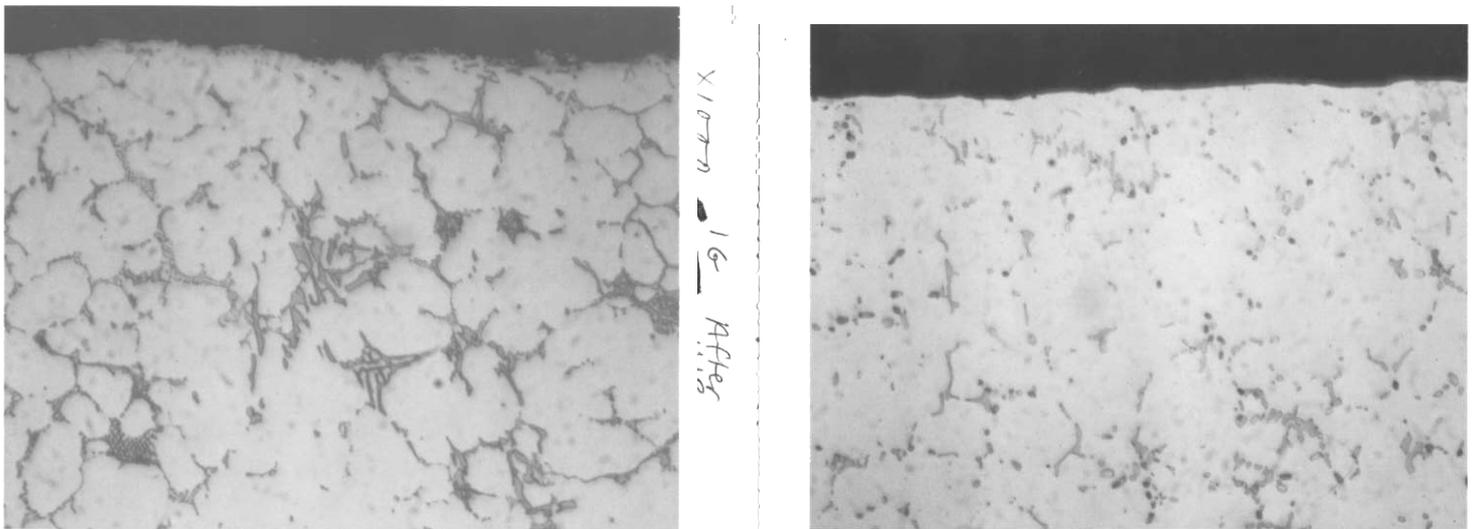

Figure 7a and 7b: X 1000, microstructural detail developed with Keller's reagent. Note the distinct change in microstructure by the reduction in the silicon-rich script portion of the microstructure due to the HIP process. By re-solution treating the ADC 6 alloy, the surface anodized more uniformly.

Rotors manufactured from sintered aluminum alloy powder exhibited discontinuities and discoloration in the anodized finish. Examination and analysis disclosed the components were highly segregated such that a bulk alloy chemistry that was specified as a maximum 14% Silicon, locally exhibited concentrations as high as 27%. When these areas of high Silicon concentration intersected the surface, not only was the anodic oxide thickness significantly reduced, but dark-appearing discoloration was deposited around the silicon inclusions on the surface of the finish. EDS analysis determined the discoloration was comprised of metallic copper.

SEM and metallographic examination of the rotors enabled documentation of the high level of segregation in the sintered substrates, and lead to a re-evaluation of the sinter process parameters, such as alloy powder mixing prior to molding and the time and temperature of the sinter process. The high level of segregation was clearly not an anodizing problem and could not be related to the finishing process. See figures 8a and 8b.
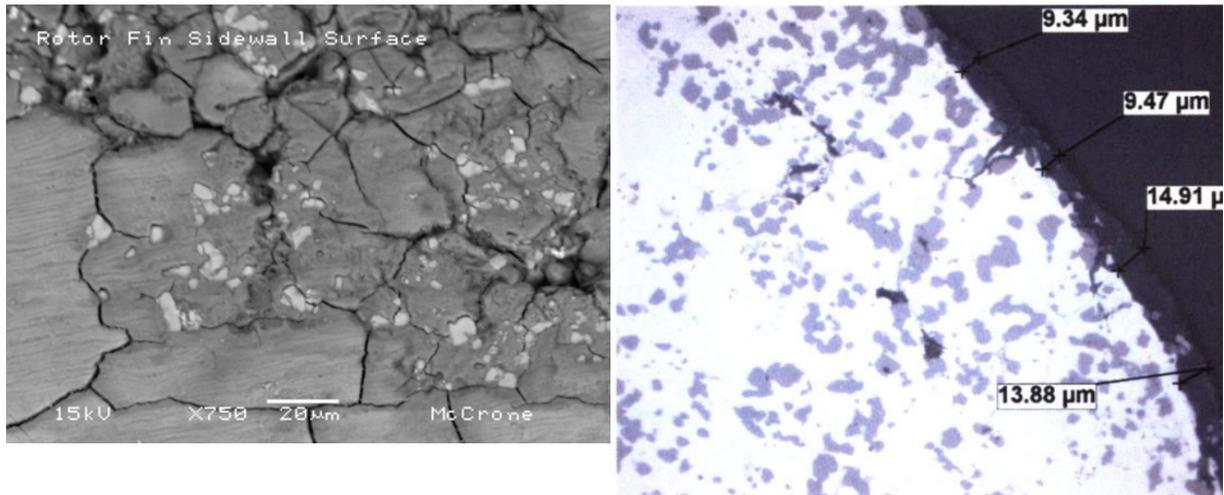
Figure 8a (left): SEM photomicrograph documenting the silicon inclusions within the anodized finish. Note the dark gray discoloration (copper) on the light gray finish surface (anodic aluminum oxide) in the region of each white-appearing inclusion (silicon). Figure 8b (right): Metallurgical cross section of the rotor determined a high level of segregation throughout the sintered component. In one piece, the Si concentration could range from 16% to 27% in different areas. Wherever a silicon-rich area intersected the surface, a reduction in finish thickness and/or crack would result.

As documented in the wrought specimens analyzed with the TEM, inert inclusions will not participate in the anodic oxide finish reaction and will be taken up into the finish, creating local discontinuities in the nanoscale finish order. In addition, copper in solution will be dissolved in the anodizing electrolyte, and as a positive counterion, will redeposit on the component surface in areas where the oxidation kinetics are retarded due to the inert, high resistance of the inclusions. Therefore, the copper redeposited on the anodized rotor surface.

Discussion: Intensive microstructural and chemical analyses of anodized aluminum finishes on various types of substrates (wrought, cast and sintered) were performed. The results provide increased insight regarding the mechanism for anodic film formation as well as its resultant chemistry. The analysis results consistently show that variations in the substrate microstructure, dependent upon the manufacturing process for each component, impart distinct structural changes to the anodic oxide finish that are predictable but not easy to control, and that the structure of the anodic oxide is of a nanometer scale.

By virtue of these changes and the predictable manner in which they occur, new insight regarding the relationship between the substrate microstructure and the anodic oxide and how the surface is reconstructed was achieved. This work clearly defines the anodic oxide finish as a self-assembling network of individual nanoscale corrosion cells and explains how various oxide microstructural characteristics are achieved through initial surface reconstruction (corrosion of the substrate surface). In keeping with corrosion theory, variations in chemical potential in the first few microns of the substrate surface significantly impact the corrosion (anodizing) kinetics which in turn, govern finish uniformity and continuity.

Surface Reconstruction

A comprehensive thermodynamic treatment of chemisorption, which precedes surface oxidation, is presented in Murr [7]. It is important to note that the oxidative process of exfoliation on passive metals such as aluminum, will take place only in protonic acids which oxidize; for example in sulfuric acid, chromic acid, oxalic acid,

phosphoric acid, etc. Other acids will tend to corrode by other mechanisms, such as pitting. It is also important to note that throughout the anodization of aluminum and aluminum substrates, we are creating the thermodynamic conditions to <u>only</u> make *hydrated aluminum oxide*, therefore alloy additions and other contaminants retard the reaction kinetics.

The "infant" anodic oxide finish begins as corrosion nucleation points over the entire substrate surface. On ideal surfaces, without alloy additions, atomic level defects or other surface contamination, nucleation will be ordered and the number of nuclei will be governed by the temperature of the anodization process; that is, lower temperature processes will exhibit fewer nuclei than higher temperature processes. As the exfoliation corrosion process continues to favor aluminum oxidation, the nuclei will grow outward, while consuming the substrate, to form a contiguous passive layer comprised of many ordered oxide flakes. The initial reconstructed ideal surface will have the appearance of a hexagonal bubble layer.

However, in industry we rarely encounter an ideal substrate. Nucleation sites will exhibit preferences for the more ideal such as certain crystallographic surface orientations, and other atomic level defects may impede nucleation, such as vacancies, dislocations, steps or ledges. Grain boundaries which can function as sinks for atomic level defects can also impede nucleation. Alloy additions which may be inert to the anodization process can retard oxidation kinetics uniformly, as when copper dissolves into the electrolyte while the aluminum oxidizes, or nonuniformly, as when inert inclusions such as silicides or insoluble alloy additions, such as lead, segregate and intersect the substrate surface. Our TEM analysis results clearly document such substrate – finish interactions, see figure nos. 4 and 5.

An explanation for the significant impact that alloy chemistry and microstructure variation has on the aluminum anodizing process is that in all types of aluminum anodization, the thermodynamics of the process seek to oxidize free aluminum. In alloy solutions, the kinetics will be retarded as the available aluminum is oxidized. The surface will be reconstructed, but more slowly than with a pure aluminum substrate. Depending upon the size and extent of the substrate crystal defect, the corrosion reaction at the substrate will nucleate and renucleate as long as there are aluminum atoms available to oxidize. Therefore defect pockets of dislocations or vacancies will exhibit multiple nucleation points. Solute atoms within the aluminum lattice structure, such as copper, will be dissolved into the electrolyte as aluminum oxidation proceeds, and may redeposit onto the finish when oxidation kinetics no longer dominate the anodization reaction.

In segregated alloy solutions with inert inclusions, corrosion will proceed about and even around the inclusions, lifting them into the anodic oxide finish as it grows out from the substrate. The impact of inert or insoluble defects such as inclusions, grain boundaries and atomic level sinks on the finish is in the spacing of the nuclei. This disruption in order can lead to irregular growth and irregular intercolumn spacing. However, as the surface is consumed and a more ordered surface is presented for oxidation, the finish recovers as growth takes place. See figure no. 6.

Chemical Potential

The surface portion of the anodization reaction can be modeled electrochemically by the Tafel equation [8, 9].

$$\eta = \beta a \log \frac{ia}{io} + \frac{2.3RT}{ZF} \log \left(1 - \frac{ia}{io}\right) \qquad (1)$$

Where η = free energy of oxidation, ia = anodic current density,

io = exchange current density, βa = resistance determined by

$$= ZFK \exp\left[\frac{E^*}{kT}\right] \quad \text{the properties of the substrate.}$$

The βa term represents not only the alloy chemistry; it also reflects the manufacturing conditions of the component. Alloy additions, the solubility of the alloy additions, heat treatment and mechanical processing can serve to change the local surface resistance and therefore the electrochemical potential for the anodizing reaction. Variations in the electrochemical potential are the reason for the variations in the oxidation kinetics on segregated surfaces and therefore the basis for thickness variations for a given processing time.

It is important to realize the impact alloy additions that are soluble in the anodizing electrolyte have on the substrate and therefore the anodic oxide. Upon dissolution, alloy additions that are soluble in the electrolyte leave behind a continuous, albeit rather spongy aluminum matrix which is easily anodized. In contrast, an inert alloy addition such as lead, or stable inclusions such hypereutectic silicon based inclusions documented in figure 8, or the iron-chromium inclusions documented in figure 6, lead to an increase in activity about the inclusion as the anodizing reaction proceeds around the area of the inert defect. This increase in activity increases the local resistance and can cause a corresponding reduction in finish thickness as well as the redeposition of dissolved electrolyte-soluble M^+ counterions.

Inert alloy additions and stable inclusions can sometimes be dislodged through pulse anodizing which can in turn reduce the propensity for increased local resistance and therefore avoid the redeposition of soluble counterions. In keeping with this line of electrochemical processing, the surface of the substrates can sometimes be rid of the inert alloy additions and inclusions through reverse cleaning or pulse electrocleaning followed by standard surface processing such as desmutting before anodizing.

Conclusion: Differences in alloy chemistry as well as the manufacturing process for an aluminum substrate impact how the anodic oxide finish will nucleate and grow. The nucleation process is directly related to how the surface reconstruction proceeds during the initial oxidation phase. Atomic level defects such as dislocations and vacancies impact surface reconstruction as well as interfacial defects such as grain boundaries and phase boundaries. Chemical potential differences affect the anodizing kinetics; alloy additions soluble in the aluminum matrix as well as insoluble alloy additions or inclusions are examples of phenomena that impact the chemical potential.

The level of microstructural homogeneity imparted to components manufactured in various ways will impact the defect population and the variation of chemical potential across the component surface. It is critical to know and understand the component history should anodizing problems arise to connect manufacturing variations to variations in the finish function or appearance. Such understanding enables the appropriate adjustments to the anodizing process or to the component manufacturing or handling and accordingly, they can be targeted for corrective action.

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