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Anodizing
Technical research study

Basic Anodizing reaction

When aluminum is polarized as the anode, the basic oxidation reaction that occurs at the interface with the electrolyte can be summarized as follows:

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$$

$$4Al + 6(H_2SO_4) \rightarrow 2(Al_2O_3) + 6(SO_3^-) + 3(H_2)g + 6H^+ + 6e^-$$

The aqueous sulfuric acid electrolyte is hydrolyzed to enable oxidation of the aluminum, while sulfite ions and hydrogen gas are produced at the interface by way of simultaneous oxidation of the aluminum and electrolysis of the electrolyte. Because the primary reaction produces exclusively aluminum oxide, adsorbate from the electrolyte counterion is incorporated into the portion of the oxide, which is in contact with the electrolyte, and is significant enough to be detected when the anodic oxide is analyzed by way of Energy Dispersive Spectroscopy (EDS). Wernick, Pinner, and Sheasby publish the approximate composition of the total anodic oxide layer as 72% Al2O3; 15% H2O, and 13% SO3

Oxide to substrate ratio

The oxide thickness accounts for corrosion of the substrate by the anodizing process; however, there are specific trends for particular anodizing processes that enable general characterization of the characteristics of the anodic oxide. For example,

For anodic oxide grown under Type II or technical anodizing conditions, (20–22 °C and a current density of 0.8 A/dm2 < ia < 1.8 A/dm2), a process typically run in a sulfuric acid electrolyte with wrought substrates with a corresponding alloy loading ≤ 8%, approximately 60% of the AAO total thickness is accounted for by substrate consumption; the remaining 40% of the oxide extends beyond the substrate surface.

For oxides grown under Type III, or hard anodizing conditions (0–5 °C and a current density of 2.0 A/dm2 < ia < 3.5 A/dm2), which is a process that typically employs more highly alloyed substrates such as wrought aluminum super alloys and castings with alloy loading exceeding 12%, in a sulfuric acid electrolyte, approximately 50% of the AAO thickness is accounted for by substrate consumption and the balance extends beyond the surface

Type II or Technical Anodizing

- By far, most anodizing is processed in sulfuric acid electrolytes. The fine, highly ordered, unidirectional, nanoscale porous columnar microstructure of the Type II finish explains why it can be utilized for decorative applications. Type II anodizing is referred to as technical anodizing, “clear coat,” decorative anodizing and/or mild anodizing. This is because the process is usually operated at “room temperature,” from 20 to 25 °C, and depending on the alloy, other process parameters employ a range of lower sulfuric acid concentrations as compared to other anodizing processes, from 120 to 275 g/L (grams per liter). Lower current densities are used to develop a Type II finish, usually 1.0–1.5 A/dm2. The anodic oxide yielded by these processes is used primarily for corrosion protection and decoration, and they offer a modicum of abrasion resistance. The anodic oxide processed under these conditions is optically transparent, and the quality of the aluminum microstructure can be developed by the anodizing process, and observed through the oxide after anodizing. Because the oxide is transparent, the structure is dyeable and can be screen- printed to yield a wide range of colors and patterns. Thicknesses of 8–20 µm are usually specified, depending upon the substrate alloy. These finishes are typically sealed to enhance corrosion resistance and to prevent dye from bleeding out of the porous AAO structure. Type II anodizing has a niche in the metal finishing industry for finishes with outstanding clarity and color on aluminum and its alloys

Type II or Technical Anodizing

- The structure of a decorative (Type II) anodic oxide is highly ordered, comprising fine columnar cells with rounded bottoms. The cellular network is oriented by and grows perpendicular to the substrate, and each cell has a central pore that is parallel to the oxide growth direction. Because of the lower density of the total oxide in comparison with the aluminum substrate, for an anodic oxide of total thickness x, approximately 60% is into the metal, and 40% exceeds the former surface of the substrate.

Surface defects

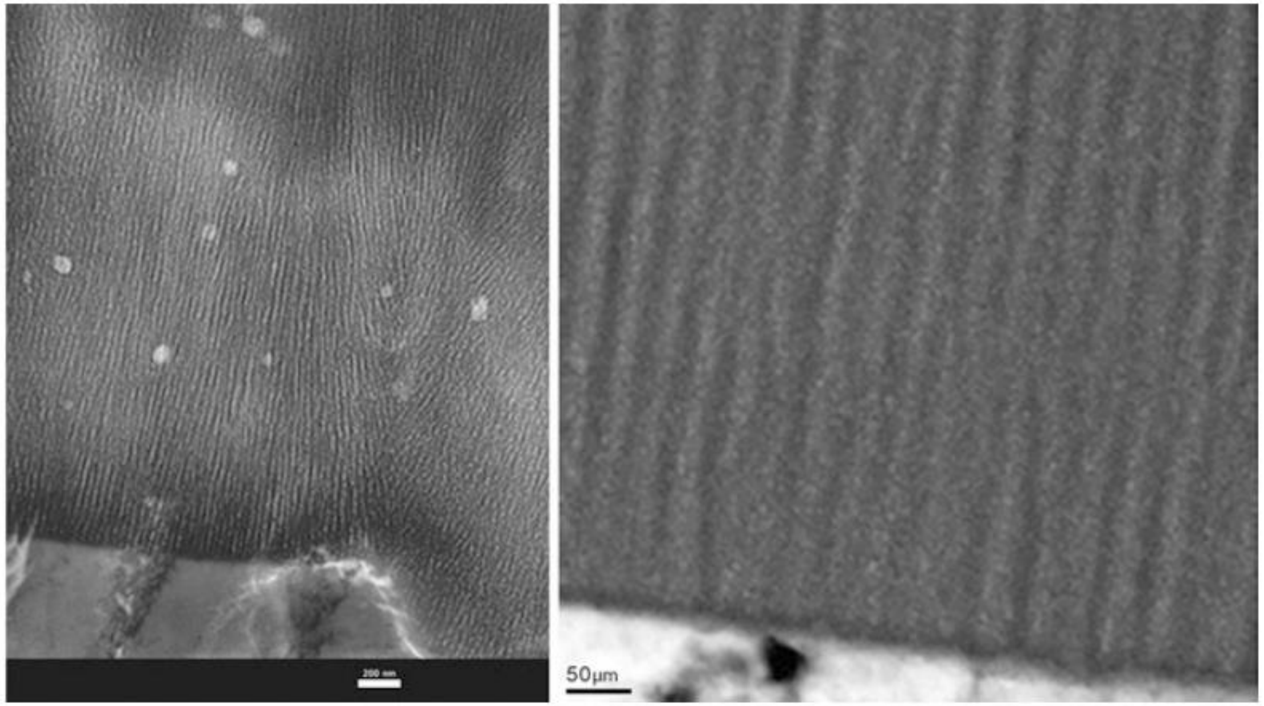

Fig. 3.12 TEM images of a decorative technical anodic oxide (AAO) grown on aluminum alloy 6061 T6. In the image on the left, the columnar structure exhibits changes in the growth pattern, corresponding to the near-surface microstructural features of the substrate aluminum. The column walls and central pores are uniform and fine. The pore diameters measure 10–13 nm and the column walls measure ~6 nm. The pore-to-pore center distances measure approximately 25 nm. Process parameters were sulfuric acid electrolyte = 120 g/L, current density = 1.2 A/dm^2, temperature = 20 °C [19]

Fine bubbles are concentrated within the central pore, and larger bubbles occur randomly, throughout the structure, mostly when complex alloys are anodized, and are a product of the hydrogen evolved when the advancing oxide growth front encounters a defect. These characteristics of anodic oxide growth are found in all types of anodizing processes that produce a cellular structure

Flash Anodizing

A technique called “flash anodizing,” based on the process for Type II anodizing, yields thin AAO finishes that measure only several nanometers thick [20]. It is produced at a current density that is rather high in comparison with other Type II processes (about 1.8–2.0 A/dm2), and the exposure time is less than a minute. The AAO produced by way of flash anodizing develops a uniform and continuous porous oxide from sulfuric, oxalic, or phosphoric acid electrolytes, and is used as a stable and robust interface to enhance bonding. Because it is an integral oxide, it eliminates the concern for filiform corrosion and it doesn’t chip or peel like deposited layer. Thin oxides are also the most transparent and are used as the finish for aluminum alloy coil product that will be used as reflectors for overhead lighting and in several automotive, aerospace, and aircraft applications.

Type III or Hard Anodizing

Hard or Type III anodic oxides are thick, hard finishes that are used in applications that require wear resistance. They are typically carried out in sulfuric acid electrolytes, but other electrolytes including phosphoric acid, oxalic acid, and acid mixtures can be used. Electrolyte concentrations up to 350 g/L sulfuric acid are used industrially. The structure of a hard anodic oxide exhibits thicker cell walls and wider pores.

Thicknesses of 25–50 µm are typically specified, but finish thicknesses as high as 125 µm are reported when rework has been done to restore component dimensions. To grow such a thick oxide, current densities can be markedly higher than those used.

In order to produce a thicker, harder oxide, the anodizing bath temperature is typically lowered to range from about 0 to 10 °C and agitation by way of the introduction of air or bath recirculation is incorporated to the bath to keep the electrolyte temperature down, keep the work cool, and limit the amount of oxide dissolution.

Type III or Hard Anodizing

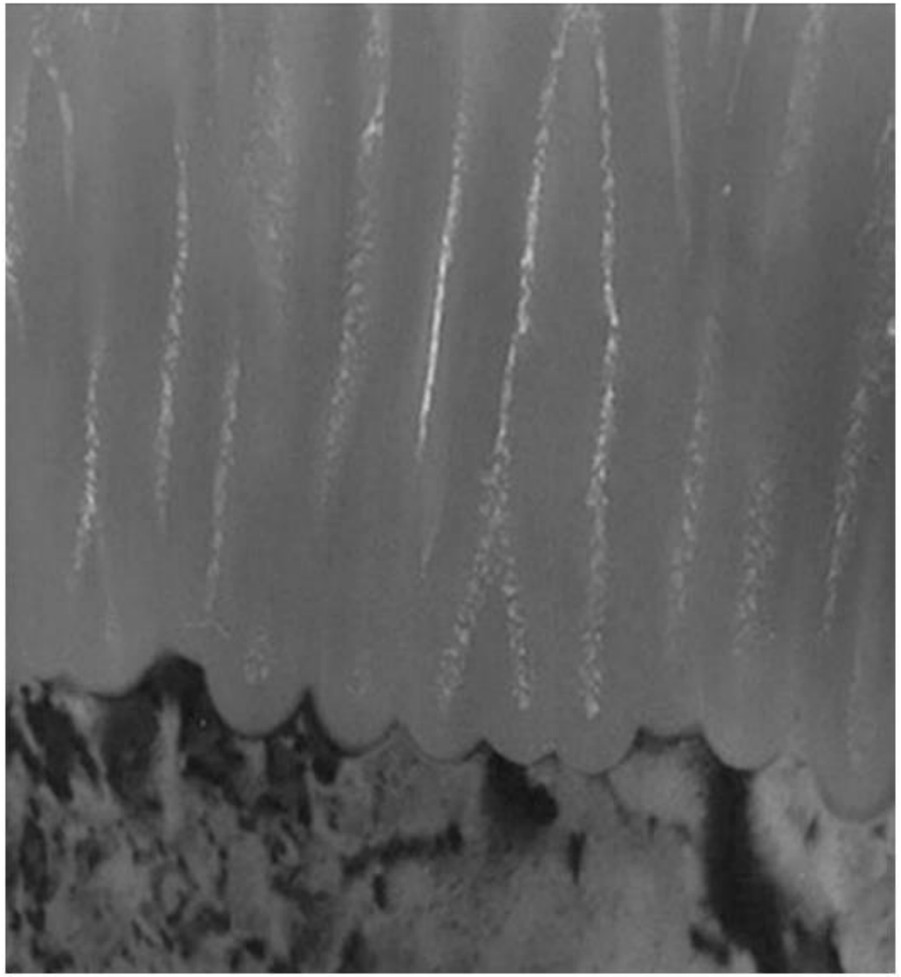

Fig. 3.16 TEM image of a representative structure of Hard (Type III) AAO, grown on aluminum alloy 6061 T6 and anodized in a sulfuric acid electrolyte. Process parameters alone yielded differences in the AAO structure than a Type II anodic oxide. The cell dimensions for the Type III oxide (right) measure 30 nm (pore diameters) and the column walls measure 15 nm. The pore-to-pore center distances measure approximately 90 nm. Electrolyte concentration = 220 g/L, current density = 2.2 A/dm^2, temperature = 0 °C [19]

Type III or Hard Anodizing

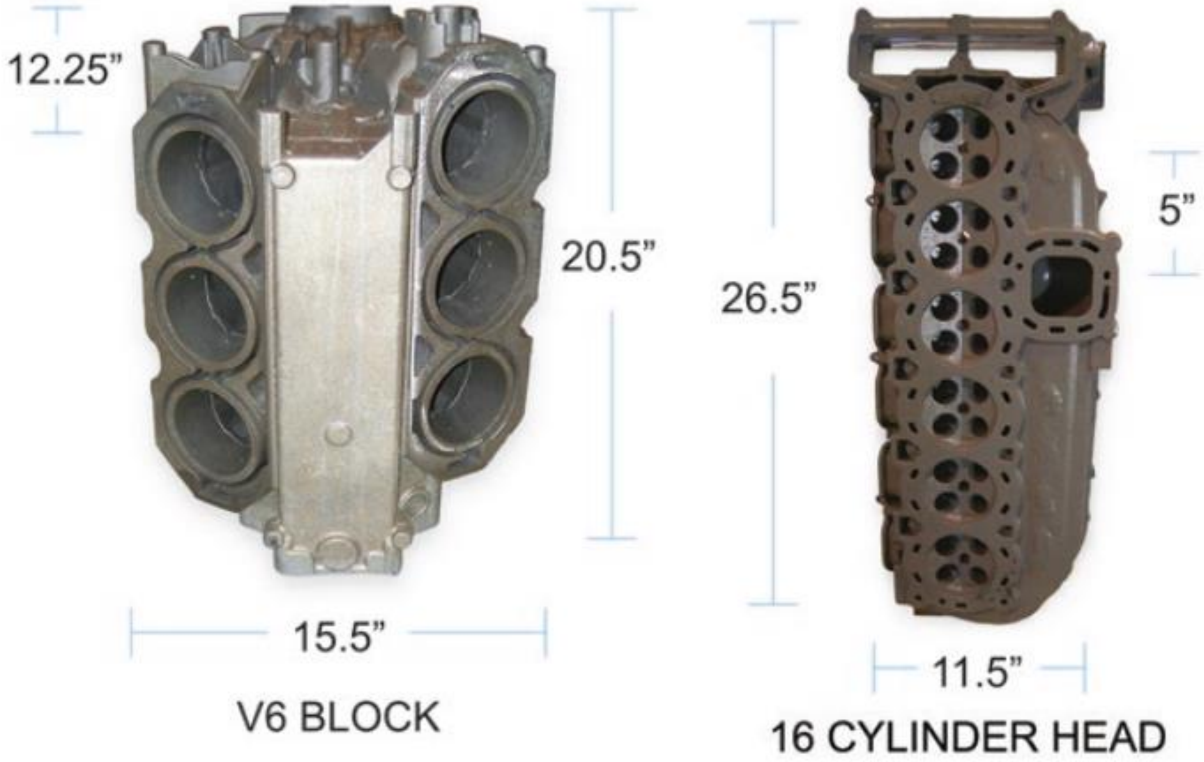

Fig. 3.17 Example of as-cast engine parts, alloy A356 before (left) and after anodizing (right) using hard anodizing or Type III process parameters. The oxide finish thickness measured about 20–25 μm. Note the brown-gray appearance of the anodized finish due to inherent coloring by alloying elements in the cast alloy [21]

Type III or Hard Anodizing

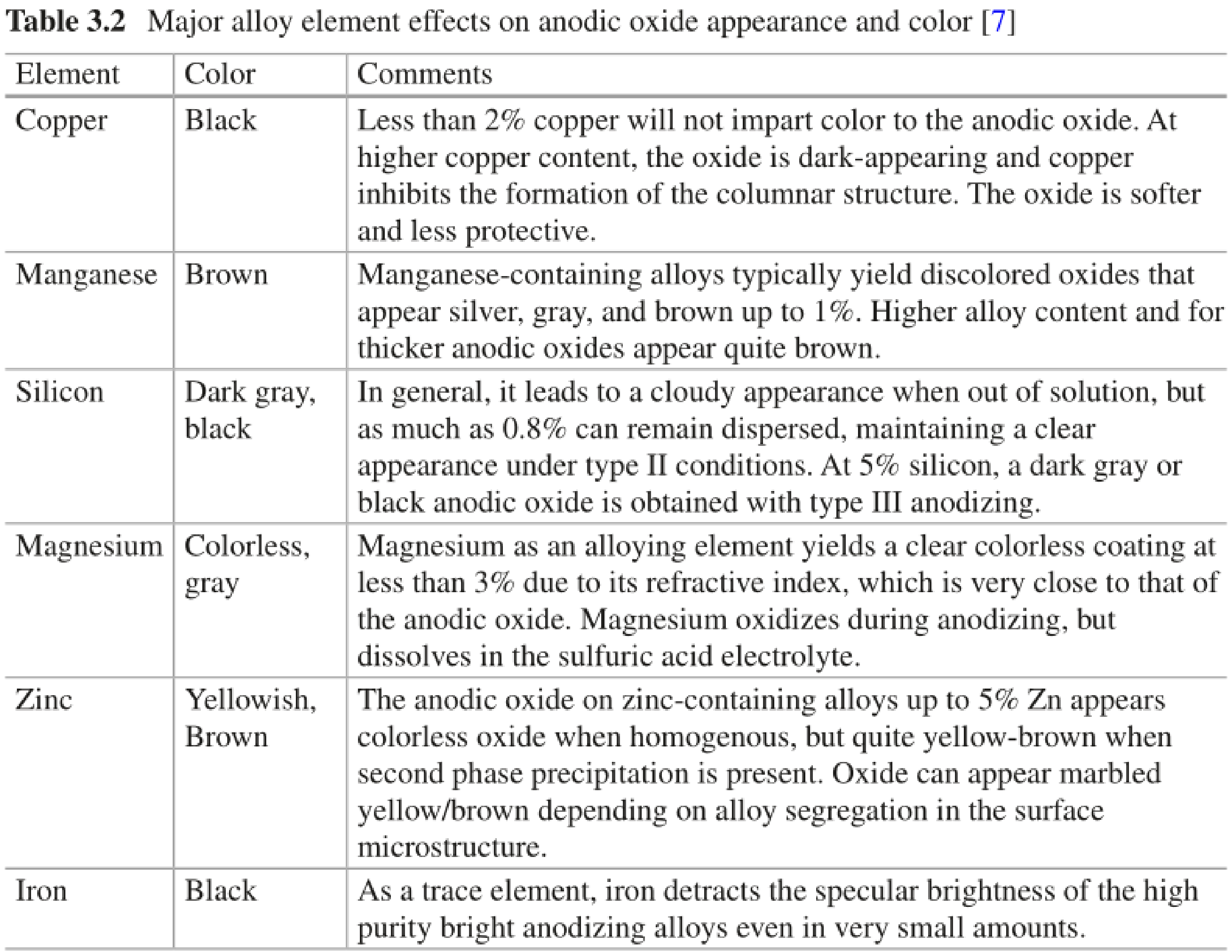

Table 3.2 Major alloy element effects on anodic oxide appearance and color [7]

Element	Color	Comments
Copper	Black	Less than 2% copper will not impart color to the anodic oxide. At higher copper content, the oxide is dark-appearing and copper inhibits the formation of the columnar structure. The oxide is softer and less protective.
Manganese	Brown	Manganese-containing alloys typically yield discolored oxides that appear silver, gray, and brown up to 1%. Higher alloy content and for thicker anodic oxides appear quite brown.
Silicon	Dark gray, black	In general, it leads to a cloudy appearance when out of solution, but as much as 0.8% can remain dispersed, maintaining a clear appearance under type II conditions. At 5% silicon, a dark gray or black anodic oxide is obtained with type III anodizing.
Magnesium	Colorless, gray	Magnesium as an alloying element yields a clear colorless coating at less than 3% due to its refractive index, which is very close to that of the anodic oxide. Magnesium oxidizes during anodizing, but dissolves in the sulfuric acid electrolyte.
Zinc	Yellowish, Brown	The anodic oxide on zinc-containing alloys up to 5% Zn appears colorless oxide when homogenous, but quite yellow-brown when second phase precipitation is present. Oxide can appear marbled yellow/brown depending on alloy segregation in the surface microstructure.
Iron	Black	As a trace element, iron detracts the specular brightness of the high purity bright anodizing alloys even in very small amounts.

Type III or Hard Anodizing

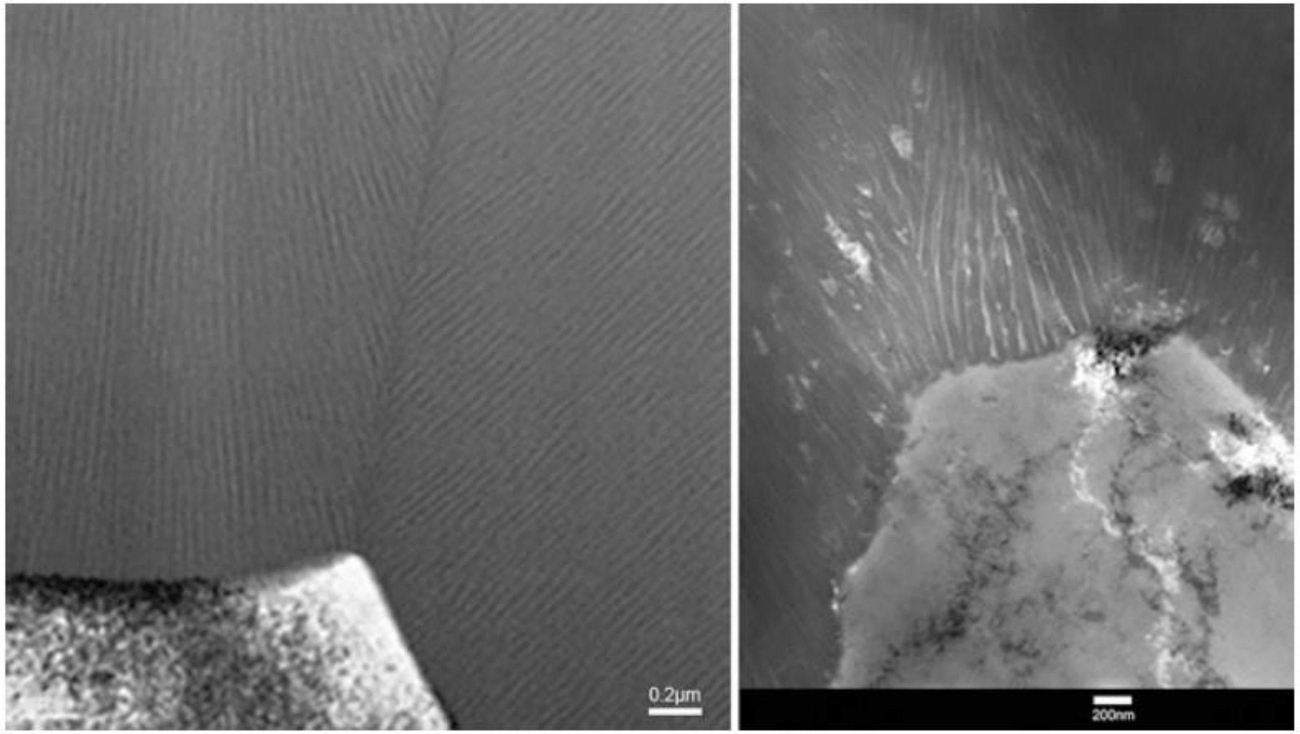

Fig. 3.18 (left) TEM image of a decorative anodic oxide (Type II) as it proceeds along a change in surface orientation. Note the oxide columns have grown perpendicular to the substrate surface, and as the oxide consumed the substrate, a seam was created in the AAO structure that knits the two oxide growth fronts together. (Right) The columnar structure of this Type III oxide exhibits changes in the growth pattern corresponding to the microstructure of the substrate aluminum. Structural deviations can be related to microstructural features in the substrate metal: surface texture, grain boundaries, and tangles of dislocations produce columnar bifurcations, voids, and the detachment of columns from the substrate [19]

Type III or Hard Anodizing

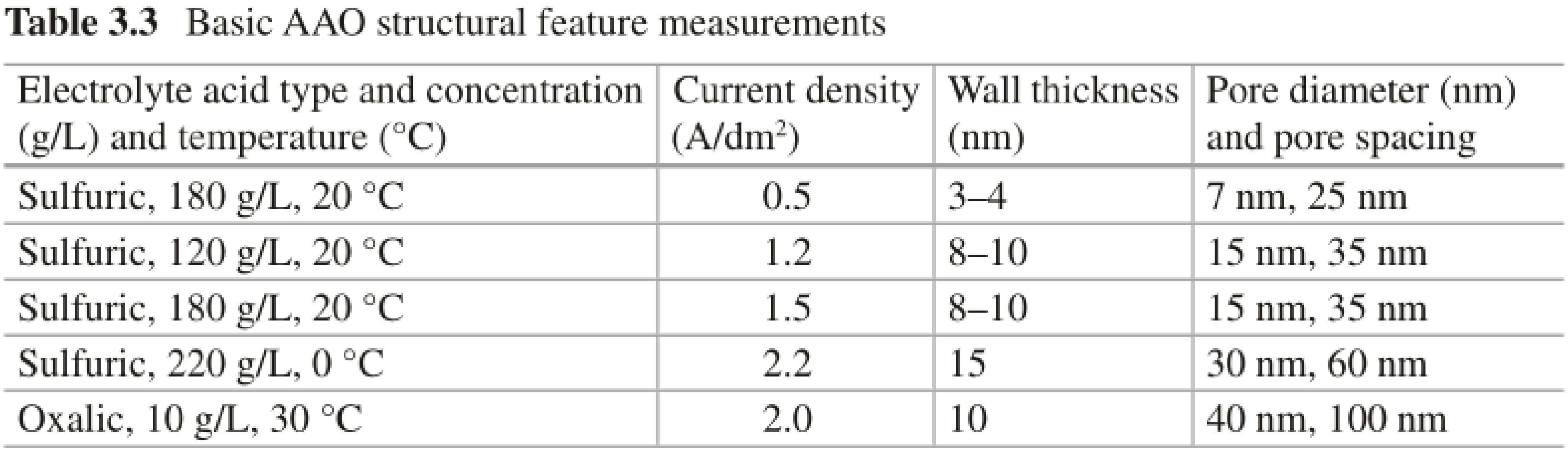

Table 3.3 Basic AAO structural feature measurements

Electrolyte acid type and concentration (g/L) and temperature (°C)	Current density (A/dm^2)	Wall thickness (nm)	Pore diameter (nm) and pore spacing
Sulfuric, 180 g/L, 20 °C	0.5	3–4	7 nm, 25 nm
Sulfuric, 120 g/L, 20 °C	1.2	8–10	15 nm, 35 nm
Sulfuric, 180 g/L, 20 °C	1.5	8–10	15 nm, 35 nm
Sulfuric, 220 g/L, 0 °C	2.2	15	30 nm, 60 nm
Oxalic, 10 g/L, 30 °C	2.0	10	40 nm, 100 nm

Phosphoric acid anodizing

Phosphoric acid anodizing is used as a pretreatment for structural adhesive bond- ing in high-humidity environments for the aerospace and aircraft industries. This process was developed by Boeing and is carried out in a 10–12% by weight phosphoric acid electrolyte at 10–15 V. The adhesive bonds achieved with the phosphoric acid

AAO have greater durability under adverse conditions than bonds formed with oxides from chromic acid or sulfuric acid electrolytes. Anodic oxides formed in phosphoric acid electrolytes at higher current densities (formation voltages), up to 195 V and lower temperatures (as cold as −5 °C) are utilized for templates for nano-patterning, such as wires, dots, and foils for sensor applications. Because of the scale of the oxide dimensions achieved under hard anodizing conditions, less complex alloys with a high level of metallurgical cleanliness are hard anodized in phosphoric acid electro- lytes to yield a relatively coarse anodic oxide structure with regular spacing and pore size. These oxides are used as templates for the manufacture of nanoscale wires, or for other applications that require a regular, highly ordered nanostructure. Table 3.4 presents a summary of various electrolytes, including phosphoric acid, oxalic acid, and a variety of organic acids that can be used to produce template-quality AAO, suit- able for uniform nanoscale devices

Type III or Hard Anodizing

Table 3.4 Major electrolyte formulations used to produce porous oxides on aluminum substrates [22]

Main acid used in electrolyte	Molecular formulas	Concentration (M)	Pore size range (nm)
Acetic	CH_3CO_2H	1.0	Not specified
Citric	$HO_2CCH_2(OH)(CO_2H)CH_2CO_2H$	0.1–1.0	90–250
Chromic	H_2CrO_4	0.3–0.44	17–100
Glycolic	$CH_2(OH)CO_2H$	1.3	35
Malic	$HO_2CH_2CH(OH)CO_2H$	0.15–0.3	Not specified
Malonic	$CH_2(CO_2H)_2$	0.1–5.0	Not specified
Oxalic	$C_2H_2O_4$	0.2–0.5	20–80
Phosphoric	H_3PO_4	0.04–1.1	30–235
Sulfuric	H_2SO_4	0.18–2.5	12–100
Tartaric	$HO_2CCH(OH)CH(OH)CO_2H$	0.1–3.0	Not specified

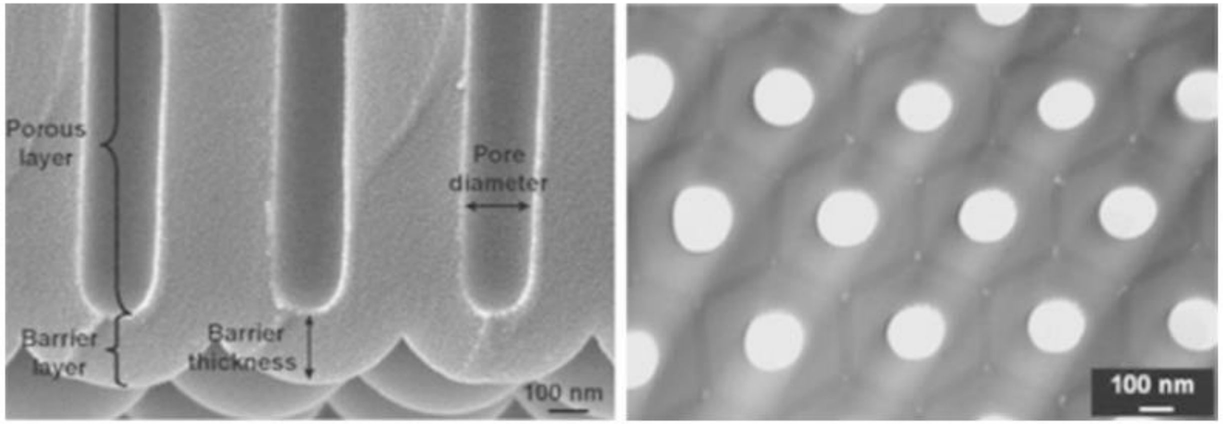

Fig. 3.20 Field emission SEM images of AAO produced in an 8% phosphoric acid electrolyte at −1.5 °C, 185 V for 4 h. The image on the left is a longitudinal cross section of the oxide after the aluminum substrate was etched away. The image on the right is a transverse section through the oxide, showing the distinct honeycomb structure so well recognized as AAO. Note the uniformity of the pore diameter and the dimensions of the "barrier layer" and cell walls [23]

Post-anodizing Processes: Dyeing and Sealing

During anodizing, the electrolyte contacts the porous structure, while the anion, which is in part oxygen, reacts with aluminum ions diffusing through the finish at the pore surface. Anion species (OH−, SO3 −, CrO3−, etc.) are adsorbed on the pore walls, facilitating conduction and maintaining the net negative charge of the anodic oxide and the erect nature of each column. These adsorbed anions also provide individual reaction sites for the growing finish, sustaining the ion exchange system known as the “ion pump,” which maintains the erect nature of the columns comprising the AAO structure. Even as finished, the porous structure of the AAO remains ionic, which lends itself to processing after anodizing such as dyeing, sealing, or bonding with supplementary coatings that may be inorganic or organic

Post-anodizing Processes: Dyeing and Sealing

The ionic nature of the surface of the anodic oxide enables continued reaction with other species in aqueous solution. Some reactions are due to physisorption, and the bond forces are weak, with no chemical bonds forming. These reactions can be reversed with rinsing. Other reactions are due to chemisorption and surface chemical compounds form with the available ligands on the pore surface. The polar surface alone drives hydroxyl-reactions that naturally occur at the pore surface, and are the basis for dyeing and sealing reactions. Spaces in structure accommodate ionic movement, restricting dye reactions, which are on the molecular level, to within the pore or at the finish surface. In other words, AAO does not behave as a sponge. Quite the opposite, based upon the chemical principle of "like dissolves like," hydrous solutions tend todissolve hydrated structures, if only limited to the surface. This is also the primary reaction for sealing. Temperature, of course, affects the extent of the reductive dissolution reaction, with higher temperatures dilating the structure at a minimum, increasing the surface activity and encouraging more diffusion of the reductant molecules to the anodic oxide surface, promoting both dyeing and sealing reactions.

Post-anodizing Processes: Dyeing and Sealing

There are a variety of inner pore surface complexes that are available on the surface of the pore onto which bonding can occur [41]. Some of the complexes are monodentate (A monodentate ligand is a ligand that uses only one pair of electrons to bond to the central metal atom or ion) and some are bidentate. These are potential sites for the absorption of metal ions in the electrolyte, which have diffused through the oxide from the alloy during anodizing or may be contamination from some other part of the anodizing circuit. Adsorption of metallic ions on the AAO sometimes causes inherent discoloration of the oxide. The rest of the bonding sites on the oxide can be more complex: mononuclear, binuclear, and combinations such as bidentate mononuclear. The distinctions are based upon the fundamental nature of the AAO, its semiconductor structure and surface chemistry that it develops through constant contact with the electrolyte

Post-anodizing Processes: Dyeing and Sealing

The adsorption of other anions, such as borates, phosphates, bicarbonates, sulfates, fluorides, and anionic colorants, can occur using the inner pore surface complexes of AAO as adsorbents because these compounds have physicochemical properties that are similar to those of the ions of aluminite (hydrous aluminum sulfate) and any aluminate that can form with the electrolyte. Therefore, the various bonding sites on the surfaces of the pores in the AAO drive the different types of reactions that occur post anodizing such as dyeing and sealing. Phosphate, sulfate, and silicate anions from the electrolyte or cleaners or even rinse water can react at the surface blocking sites for dye and seal complexes. It is therefore necessary to maintain the anodizing process to limit drag-out from other steps, and to keep rinses
clear and flowing

Dyeing

Aluminum and aluminum alloy substrates selected for clarity and color tend to exhibit the most homogeneous substrates. Because they have limited compositions, most wrought alloys are limited to less than 8% total alloy additions, and consequently, there is less precipitation. Deformation parameters and aging to a T6 temper typically produce a moderately fine grain size (60–100 µm) that yields a uniform chemical potential across the surface, see Chap. 4. The homogeneity of the substrate, especially as it intersects the surface, produces the most uniform and continuous AAO, with optimal clarity and a fine, dense AAO microstructure. The oxides with the most clarity tend to have wider pores and thinner column walls (ramp from low to relatively higher current densities) and are processed according to Type II anodizing parameters: 18–22 °C, at 1–1.2 A/dm2. To optimize clarity, the total oxide thickness should be as thin as possible for the design application. It must be kept in mind that thin oxides tend to be iridescent when grown on polished substrates, and must be thick enough to hold enough dye for the color intended. AAO grown under technical anodizing parameters (Type II) presents a highly oriented transparent structure for post-anodizing processes such as dyeing and sealing. By increasing the surface area of the pore, by increasing thickness and/or pore diameter, color can be optimized. Dye molecules can be large, and the size of the pore in the AAO can restrict the ingress of large molecules. Dyeing is an equilibrium process, and the movement of dye molecules into the AAO structure is driven by three concentration gradients between the dye solution and the oxide: (1) the concentration of the dye itself; (2) pH, the dye is a slightly acidic solution and the base of the pore in the AAO is rather basic; (3) temperature, dyeing is a warm process, the AAO is typically rather cool coming out of its final rinse. For all of these reasons, anodizing parameters must be considered that would maximize pore diameter, without developing a thick columnar structure. This would typically mean anodizing at a higher current density relative to normal Type II parameters. Color requires a fine structure with thin walls and a relatively large pore, similar to the transparent finish. Clear finishes are typically thin, about 3–5 µm. A good darkappearing black-dyed AAO requires greater thickness, experience indicates that a minimum 12 µm thick; best 20–25 µm thick oxide yields the best looking blackdyed component. To achieve a stable color, the oxide requires at least 8 µm

Dyeing

Fig. 3.28 Anodized bicycle headset components. The anodic oxide measured on the clear sample is 2.14 μm, and on the red sample, 11.11 μm. Note the distinctness of image (the reflection of the photographer in the surface of the part) is higher for the part with the thinner oxide. The AAO must be of a thickness to maintain color through dyeing; the thicker oxide yields a beautiful, stable red color [44]

Anodizing

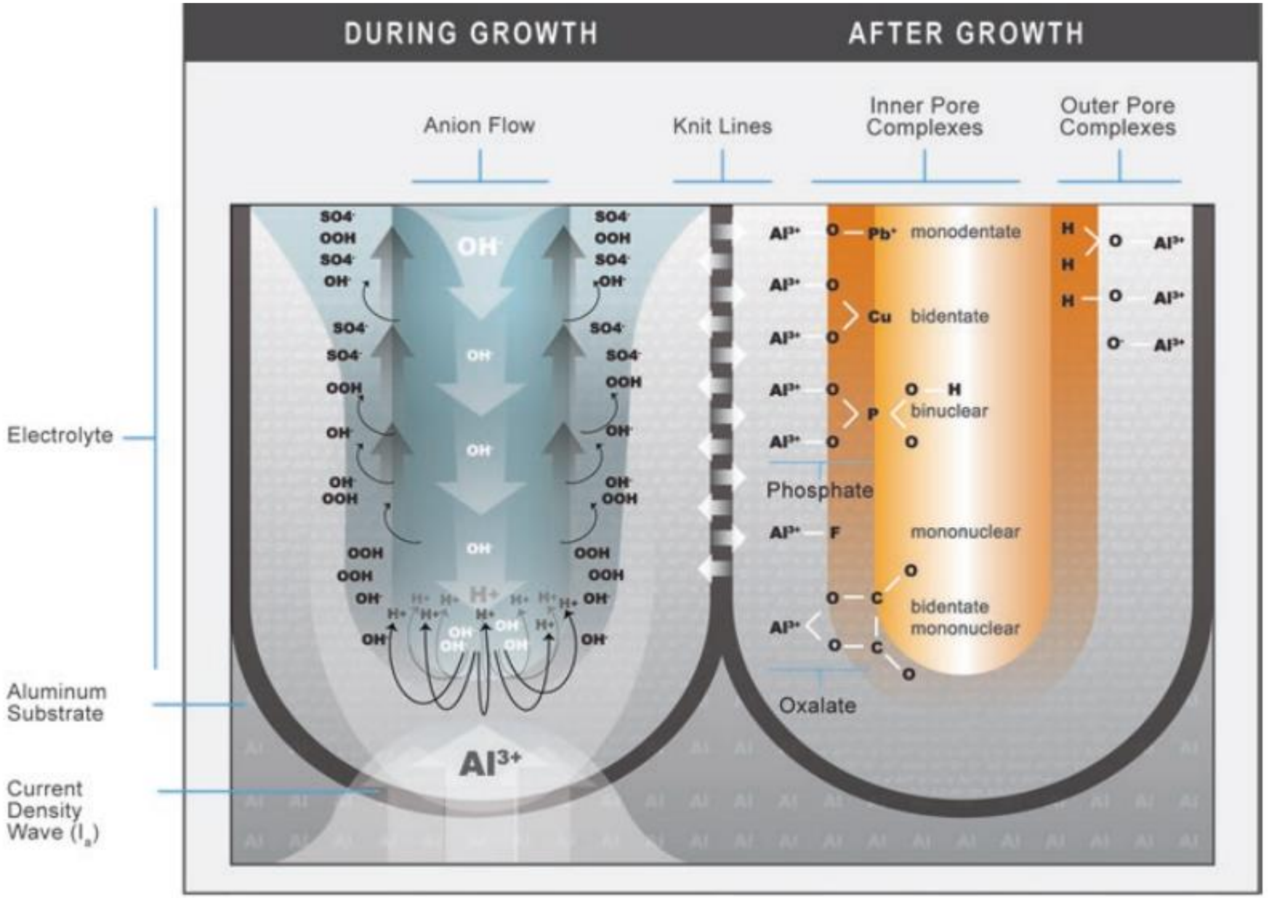

Fig. 3.27 Schematic for the development of the ionic nature of the inside surface of the pore. Following anodizing, the ionic sites remain, providing bonding sites for dyeing and adhesives, as well as a reactive surface for sealing

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Sealing

Sealing, the final step of the anodizing process, is performed to stabilize the AAO structure by reacting all residual ionic sites. Sealing does much more than “plug the pores” of the AAO; sealing is the actual reductive dissolution of the oxide structure. Hydrothermal and precipitation sealing processes react to dissolve the AAO structure at the surfaces that have been in contact with the electrolyte, including all possible open avenues of ingress from the top surface of the AAO, such as the top surface and the inside surfaces of the pores. This reaction effectively changes the AAO structure at the surface, where it will be in contact with the application environment during service. The seal chemistry, whether hot water, nickel acetate, or nickel fluoride, creates reaction products that remain adsorbed at the oxide surface, or precipitated throughout the seal, increasing the corrosion resistance of the anodic oxide.

Sealing

Aluminum oxide is amphoteric, that is, it dissolves in both bases and acids. This is clearly illustrated in the Pourbaix diagram for aluminum in which the stability for alumina under equilibrium conditions is shown to be over a pH range from about 4 to about 8 [5]. See Sect. 5.3.1. Conversion of the amorphous AAO surface structure to micro-crystalline pseudo-Boehmite is facilitated by "aging" the structure in a hot water solution (95–100 °C) at pH values between 5 and 7.4 [45]. A fundamental chemical principle: "the addition of a salt of a weak acid to water makes a basic solution," is the premise for the sealing reaction. Sealing baths are typically mildly acidic solutions (pH = 5.5–6.0), but are operated at higher temperatures, over 95 °C. When AAO is reacted with a weak alkaline solution, it forms micro-crystalline pseudo boehmite and hydroxyaluminate ions as a product of the reductive dissolution reaction presented below:

$$\mathrm{Al_2O_3 + H_2O \rightarrow 2AlO(OH)}$$

Hydroxyaluminate, AlO4 −, is the fundamental, nonstoichiometric oxide that comprises the passive layer, and forms initially during anodizing, ripening to develop more stoichiometric AAO close to the aluminum substrate as the oxide grows. Sealing is a reverse of this reaction: by continuing to expose the AAO to a mildly basic sealing solution close to the boiling point of water, the reaction proceeds toward dissolution by way of reduction from anodic alumina to pseudo boehmite (reaction 3.1), also forming aluminum hydroxide and hydroxyaluminate ions. Temperature and time enhances the reaction, catalyzing it and promoting dissolution of the AAO structure to the point of collapse at the oxide surface. The randomized and skewed structure together with various hydrated aluminum oxide compounds completely seals the bulk of the AAO from the external environment

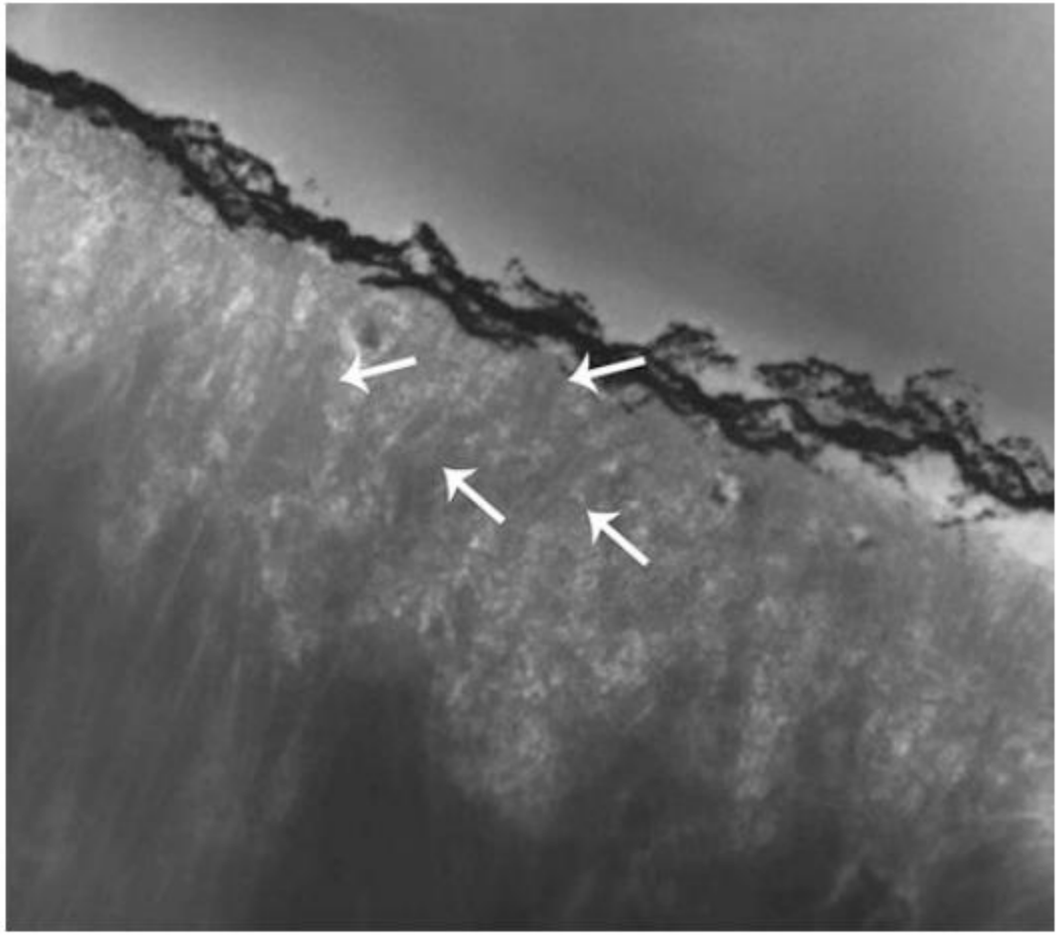
Sealing

Because the structure of the AAO is collapsed by the sealing reaction, when the AAO is dyed, sometimes dye can bleed from the AAO during sealing. In the mid 1930s the first patents were filed for precipitation seals, in which additions of a metal salt were made to the sealing bath to prevent the extraction of dye from the oxide structure during sealing. The most common metal salt used for precipitation seals is nickel acetate

The reactions that occur during nickel acetate sealing can be considered to occur as follows [46]. With conventional nickel acetate sealing, the solution is again that of a salt of a weak acid, and the addition of a salt of a weak acid to water makes a basic solution. So, if nickel acetate is considered, Ni2+ ions with CH3COOH will be in solution

$$Ni^{2+} + CH_3COOH \leftrightarrow Ni^{2+} + CH_3COO^- + H^+$$

Fig. 3.29 TEM image of a nickel acetate sealed Type III (hard) anodized oxide. The black layer is a layer of sputter-deposited gold, placed to maintain the surface during sample preparation. The blue arrows indicate representative fragments of residual, undissolved AAO columns retained in the seal area, which has been randomized and skewed by the dissolution process of sealing



In solution, the acetate dissociates and the solution creeps basic. This is why additions of acetic acid are made to keep pH within the proper range for operation.

$$Ni^{2+} + CH_3COO^- + H_2O \rightarrow Ni^{2+} + CH_3COOH + OH^- \tag{3.7}$$

When the Ni^{2+} ions are in the presence of OH^- ions, insoluble $Ni(OH)_2$ forms and precipitates out of solution, onto the collapsing structure surfaces, increasing the passivity of the porous structure.

$$Ni^{2+} + OH^- \rightarrow Ni(OH)_2\,(ppt) \tag{3.8}$$

There are a variety of seal formulations that incorporate other metal salts, developed to avoid possible environmental issues with nickel.

Cold seals, based upon nickel fluoride chemistries, can be developed at rather low temperatures (30 °C). Because the temperature of the reaction is low, these seals tend to be shallower than hydrothermal seals. Brace [3] provides a rather comprehensive description of different seal chemistries and processes, as well as the associated reactions and process recommendations.

Anodizing process efficiency

- Anodizing process efficiency can be calculated by measuring the actual oxide coating
- weight for a specific anode, and dividing it by the theoretical weight of the oxide as Al2O3.
- Such calculations show the impact of alloy of process efficiency, with more complex alloys, such as 2014 and 2024 exhibiting coating efficiencies of ~80% and alloy 6063 exhibiting a coating efficiency of ~100%

Pilling–Bedworth ratio (PBR)

$$\text{PBR} = \frac{V_{\text{oxide}}}{V_{\text{metal}}} = \frac{M_{\text{oxide}} * \rho_{\text{metal}}}{n * M_{\text{metal}} * \rho_{\text{oxide}}}$$