Anodic Coating Formation on Aluminum without a "Barrier Layer"

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Editor's Note: *This paper is a timely and useful critique of anodic film formation. It is most welcome as it challenges conventional thought. This is the first of two papers dealing with the mechanism of Al anodization. The second, in which Dr. Brace proposes an alternative theory of film formation, will be published in the first half of 2010.*

This paper has been written after an involvement of the author in the anodizing industry for over 50 years. With it comes a feeling of disappointment at the continued acceptance of the "barrier layer" theory which, as a personal judgment, at the anodizing shop floor level has been found to be inadequate and misleading. At the academic level, contributions seem to have become of increasing intellectual sophistication but of increasingly limited help to the production anodizer. Whilst the "barrier layer" has been researched to the n^{th} degree, only limited attention has been given to factors affecting film quality. There is no explanation offered as to why, under controlled constant conditions, the anodic film can change from a homogeneous film to a degraded one that "chalks" badly on exposure when the thickness exceeds 20 μm.

Another problem has been the academic obsession with 99.99% purity aluminum. The author is unaware of any papers on the morphology of coatings produced on the main materials anodized by industry, *e.g.*, 1050, 5050 and 6063. These alloys behave differently from 99.99% in anodizing, so it is highly probable this will affect the morphology and properties of the coatings produced.

The development of industrial processes

The production of an anodic oxide film on aluminum was established in a patent by Pollok[1] in 1896. The coating produced was what became known as a "barrier layer" coating. Subsequently, the process was used in the production of electrolytic condensers. Plants were set up in the 1920s to serve the infant electronics industry.

The introduction of processes producing relatively thick, porous anodic films on aluminum also began in the 1920s, with the publication of a series of patents. The first of these was developed at the National Physical Laboratory in England.[2] It covered the use of a chromic acid electrolyte in a cell in which aluminum was the anode and direct current was used. It has remained in use for many years for the protection of aircraft and defense components.

This was followed in 1927 by a patent granted to a firm of consultant chemists in England[3] for the use of a sulfuric acid electrolyte within a stated range of conditions. This patent was later acquired by the Aluminum Company of America who licensed it as the "Alumilite"™ process for use by customers and others, including companies in overseas countries. However, in 1937 a patent was granted in the United Kingdom[4] for a process in which the sulfuric acid concentration and operating conditions were confined to a limited range. Despite a legal challenge, the validity of this later patent was upheld and both processes were subsequently widely employed in industry. The use of sulfuric acid as an anodizing electrolyte accounts for the overwhelming majority of the industrial anodizing carried out at the present day.

The use of oxalic acid as an anodizing electrolyte was developed and patented in Japan[5] in 1924. It was not used outside Japan until the mid-1930s, when the process was licensed to Siemens and Halske AG in Germany, who were particularly interested in its possible use for electrical insulation. The process was widely used for several years by companies in Germany where its applications included aircraft parts, architectural components and a variety of engineering applications. However, the economic advantages of the sulfuric acid process saw its use overtake that of the oxalic process by around 1940.

In the late 1930s, the use of phosphoric acid electrolytes for the electropolishing of aluminum was patented.[6] This was followed in the late 1940s by formulations based on this acid but modified to give chemical polishing.[7] Details of these processes and patents have been summarized and the processes described by Brace.[8] Phosphoric acid as an electrolyte to produce an anodic coating applied as a pretreatment of aluminum before electroplating was patented by Siemens and Halske in 1936.[9] Subsequently, phosphoric acid electrolytes were developed for specialized product applications, *e.g.*, lithographic plates,[10,11] adhesive bonding[12] and micro-filtration.[13]

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In the period 1960-80, a number of electrolytes were patented which were known as "self-color" processes. These gave a range of bronze shades and were widely used on buildings. The first process was known as "Kalcolor"™.[4] Others were subsequently developed and have been reviewed in Sheasby and Pinner.[15] They were based on organic acid electrolytes using around 50 to 100 g/L with $\approx$20 g/L of sulfuric acid added. A rise in electricity prices and the development of post-anodizing electrolytic coloring brought about a cessation in their use.

Understanding the anodizing process

With the increasing industrial use of these processes, investigations began into the formation and structure of anodic coatings. As early as 1932, Setoh and Miyata[16] proposed that a barrier film was formed, allowing the nascent oxygen evolved from the electrolyte to act continuously to form oxide and a porous structure by anion attack. They envisaged oxygen as being locked in the pores. In 1934, Wernick[17] suggested that initially the coating was a peptized gel and offered a mechanism by which it was transformed into a porous coating. Later, Rummel[18] envisaged a porous structure with the composition of the film exhibiting increasing hydration towards the surface. These and other early growth models are reviewed in Sheasby and Pinner.[15]

At the industrial level, Siemens and Halske AG conducted detailed research on anodic coatings during the 1930s. They had the advantage of having oxalic acid anodizing facilities as well as being the principal sub-licensee of the Alcoa Alumilite™ (sulfuric acid) anodizing process for the whole of Germany. In 1938, a monograph written by Dr. A. Jenny of that company was published and later an English translation followed in 1940.[19] The book contained much detail on the chemistry of aluminum, as well as the results of investigations into the production and properties of coatings obtained from the oxalic and sulfuric acid processes.

In 1948, Schenk[20] published a comprehensive volume on anodizing, but, in contrast to Jenny, much of the text was concerned with aluminum and its alloys and their manufactured forms. However, it covered in detail the production and properties of coatings and the process technology in use at that time. Of course, there is data common to both books.

The "Barrier Layer" theory

A basic problem facing early investigators was that although there was evidence of a porous structure, resolution of the detail of coating structure was beyond the range of the optical microscope. It was only when the electron microscope became available in the late 1940s that it became possible to measure the size of the cells and pores in anodic coatings. This led to the pioneering work carried out in the Aluminum Company of America's Research Laboratories, where measurements were made of the cell and pore diameters of anodic coatings prepared in chromic, oxalic, phosphoric and sulfuric acid electrolytes, using up to 140 V. These values were recorded and subsequently published.[21,22]

The photomicrographs reproduced in the original paper were obtained using a plastic replica technique. These showed a cell base pattern consisting of a series of polygons, predominately hexagons (Fig. 1) but also a number of pentagons. The paper does not detail how the cell base dimensions were measured and whether the five-sided cells were included, or the measurement method.

On the basis of their measurements, the authors constructed a model of an ideal hexagonal anodic cell with a central pore. The authors then proceeded to develop what became known as the "barrier layer" theory to explain the formation and growth of this porous anodic cell structure in oxide-solvent electrolytes. They offer the following mechanism for the formation of porous anodic coatings:

"A barrier layer of oxide starts to form in the usual manner, but as soon as any oxide is formed, solvent action by the electrolyte also starts, which tends to reduce the thickness of the barrier layer. From observations of the voltage and current excursions which occur at the start of coating formation, these processes tend to reach a balance within a relatively short time, after which coating formation proceeds at a uniform rate."

The essential concept of the authors was that of a uniform anodic coating made up of hexagonal cells consisting of a barrier layer and a central pore, as shown in Fig. 2. It is this model that has been widely accepted by most investigators. Even so, since 1953, there have been numerous papers published based on this model, which has increased knowledge of the morphology of anodic coatings. On the other hand, there have been papers published since

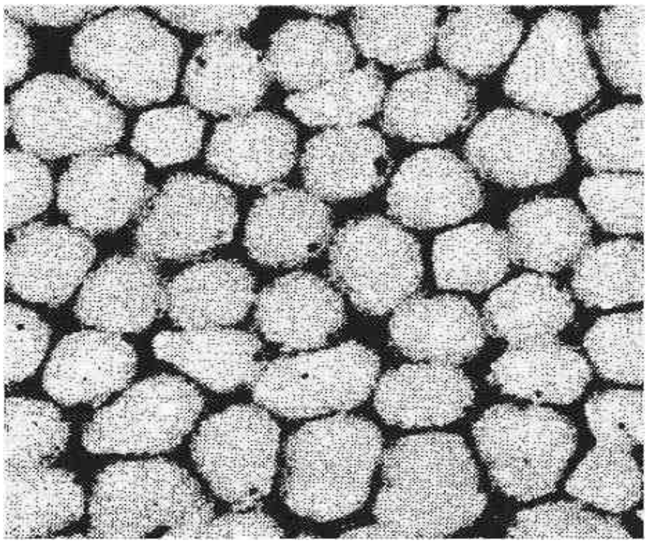

Figure 1—*Photomicrograph of an 80-volt H_3PO_4 coating.*

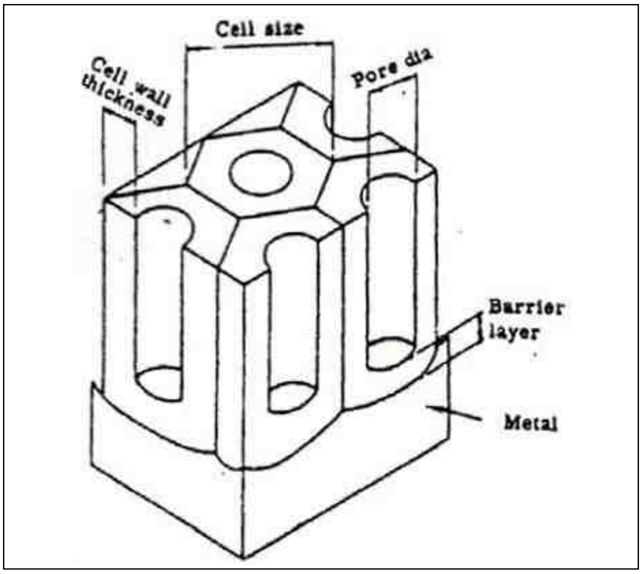

Figure 2—*Model of anodic cell structure.*

the late 1950s whose findings seem to be at variance with one or more aspects of the "barrier layer" theory. So far, researchers have offered minor variations on the basic theory but no one has provided a coherent inclusive alternative.

In the following text it is argued that, not only are there deficiencies in the "barrier layer" theory, but there is already in existence literature which gives new insights into the formation and growth of anodic oxide cells and seem to provide a skeleton on which to construct a new model for the process.

A reappraisal of the Barrier Layer theory

It is necessary to commence with an evaluation of the deficiencies of the "barrier layer" theory accumulated over a number of years.

The effect of the "Barrier Layer" on corrosion resistance

In the early 1990s, producers of equipment for etching semiconductors were faced with an unacceptable level of equipment failures in service. This was due to breakdown of the DEF-MIL8625 -Type 3 anodic coating, which had a critical function in providing corrosion resistance preventing electrical insulation breakdown in the etching equipment.

Anodizers in Silicon Valley had read the Keller, Hunter and Robinson paper[21] on the "barrier layer" theory. This stated: "For resistance to corrosion, pore and cell size and, particularly, the thickness of the barrier at the pore bases, are particularly important. If the thickness of the barrier is increased by increasing the forming voltage, more time is required for the corroding media to dissolve through this portion of the coating." (*op. cit* p. 419).

For nearly 18 months, this problem cost the industry hundreds of thousands of dollars. Anodizers tried increasing the "barrier layer" thickness, with and without electrolyte additives, but failed to obtain the desired improvement in performance. What had been overlooked was that a 50-volt coating has a thickness of 50 × 8.0 Å/volt = 400 Å. Increasing the voltage to 100 volts increases the "barrier layer" thickness to 800 Å. The thickness of a Type 3 coating is 50,000 Å, so this increase has an insignificant effect on corrosion resistance. This demonstrates that incorrect theory can have adverse economic consequences when applied in industry.

Misconceptions on the nature of the barrier layer

The foregoing led to a reappraisal of the "barrier layer" theory. Examination of the literature failed to provide any evidence of a "barrier" function other than the assumption of the authors that it was a barrier to oxide dissolution by the electrolyte.

Figure 3 shows the basic ionic movements taking place in the initial "barrier layer," but its composition is not uniform. It ranges from a film at the metal/oxide interface deficient in oxygen while at the electrolyte/oxide interface, there is an excess of oxygen over that required to form Al_2O_3. It also envisages that sulfate ions are built into the anodic coating, as shown by Brace and Baker[23] using radioactive tracer techniques.

Sato and Kaminga[24] have applied to aluminum a model developed by Sasaki (ref. not given) to explain the mechanism of anodizing tantalum. In summary, they state "...in other words, the inner layer of 20 to 50 Å in contact with the metal phase consists of n-type oxides of excess metal ions, ... the middle layer consists of a genuine semiconducting oxide with stoichiometric composition which grows in thickness, and the outer layer of 20 to 50 Å of p-type oxides. ... The existence of excess Al^{+3} ions or deficient oxygen ions in the "barrier layer" during formation of the film has been experimentally verified. The outer p-type oxide is also formed by protons that penetrate from the electrolyte." Sato and Kaminga further develop this model in stating..."In other words, the part in contact with the substrate metal is an n-type semiconductor with excess metal ions or deficient oxygen ions; the surface of the film is a p-type semiconductor consisting of deficient metal ions, excess oxygen ions or protons that have penetrated from the electrolyte, therefore the diode functions as an n-p junction or an n-p-n junction."

Omissions from the "barrier layer" theory

This theory is essentially one of film formation in which the atoms of a perfectly uniform metal are converted into anodic oxide. To the practical anodizer this is a basic omission, since most anodizing problems are related to imperfections in the metal surface and variability in the material composition and structure.

Effect of material composition

For many years it has been evident to anodizers that different materials often require different anodizing conditions. This is considered in detail elsewhere.[25] However, the metal composition affects growth dynamics and film properties. So it is reasonable to look to theory for an explanation. The potential needed to maintain a given current density varies with composition and the anodic film can differ on different grains. Anodizers wish to understand why, but the "barrier layer" theory offers no help.

Effect of material lattice structure

One of the early problems experienced by anodizers was the production of a streaky appearance after anodizing. Investigations showed that this was due to the effects of anisotropy.[26-28] Aluminum has a face-centered cubic lattice, so that some planes are more densely packed than others. This results in a slightly thicker anodic coating on the more densely packed planes, which gives the visual effect of the finish appearing streaky. The "barrier layer" theory assumes a uniform material forming a uniform coating. The producers of aluminum have had no help from the "barrier layer" theory in explaining this behavior. This meant that they had to develop fabrication practices on an *ad hoc* basis to enable streak-free material to be supplied.

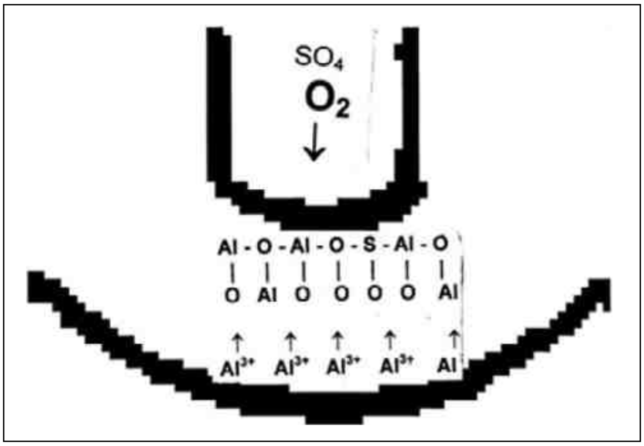

Figure 3—*Portrayal of the ionic movements involved in coating formation.*

Misconceptions in the measurement of "Barrier Layer" thickness

The method developed to measure "barrier layer" thickness[22] compares the resistance of a "barrier" coating produced in a boric acid electrolyte with that of the coating being investigated. What has been overlooked is that there are increasing amounts of electrolyte anion incorporated into the coating as anodizing takes place. The amounts incorporated increase in the order:

$$CrO_3 \rightarrow H_3PO_4 \rightarrow H_2(COOH)_2 \rightarrow H_2SO_4.$$

The incorporation of these anions reduces coating resistance, so the values are false.

Comments

The above analysis reveals what appears, from a practical anodizing viewpoint, to be serious deficiencies in the existing theory. Searching and reading the literature suggested that the academic community does not consider the above omissions to be significant. The visible fact of the irregular morphology of the polygonal cells has not been explained, although it can be argued that this feature does not support the formation model.

Present theory and published data leads anodizers to assume that the cell and pore sizes are uniform and voltage determined. It was decided to analyze existing data on coating morphology to evaluate what were the essential features of anodic coatings.

Features of cell morphology

Reference to Fig. 2 (a coating formed in sulfuric acid electrolyte) shows the following features which are common to all anodic cells:

- All cells are irregular polygons, with hexagons predominating.
- Pentagons and other shapes are also present.
- There also appears to be wide variability between cells.

It also seemed appropriate to check if these features were found for anodic cells formed in an oxalic acid electrolyte. Work by Bailey and Wood[29] reported the results of cell size and pore diameter measurements of anodic coatings produced in 0.25M oxalic acid, mainly at 50 mA/cm² and 25°C. They reported the following results for 120 V coatings:

• Cell size - mean value:	8,230 Å
• Pore diameter - mean value:	3,220 Å
• Cell size range:	4,100 - 12,600 Å
• Pore diameter range:	1,900 - 6,300 Å.

Much of the study was concerned with the development of pore widening during anodizing. The authors regard the variability as related to anodizing conditions, but with the variability at approximately ±50%, it seems surprising that this was not investigated further. It seemed appropriate to attempt to measure actual cell sizes and record their variability.

Because cells are irregular polygons, it was decided that measurement of the area of each cell would provide a useful check on cell size variation. To this end the photomicrograph shown in Fig. 4 was scanned from Bailey and Wood's paper and processed to improve image quality. The area of each cell was measured by counting the number of squares contained in each cell plus an allowance for incomplete squares. The results were then analyzed statistically. The following were the results:

• Average area of each cell	40.6 squares
• The cell width = 1.0746 × √area	6.85 squares
• One square	38 nm
• Cell width	261 nm (2,610 Å)
• Size variability (STD)	11.2 (± 27%)
• Number of cells measured	35

The degree of variability seems high for a simple anodizing process. Anodizers regularly produce films with no more than a ±10% variability. The limited number of cells measured makes it difficult to draw firm conclusions but the variability calls for an explanation.

Variability of pore diameters

Csokan[30] has observed variation in pore diameters over the surface of hard anodized coatings but gives no details. However, he states that he shares with other investigators the opinion that "... the size and distribution of the pores may in some cases be quasi-homogeneous and in other cases very irregular and lacking any order." These observations seemed to indicate the need for further investigation of the origins of pore size variability.

O'Sullivan and Wood[31] measured the diameter of pores in anodic coatings produced in a 1.6M sulfuric acid electrolyte under five sets of anodizing conditions and the surface diameter of 400 pores per set were measured and plotted as graphs in the original paper. These were photocopied and enlarged and the graph of the 15-min coating replotted at 10 Å intervals (Fig. 5). This is a large enough population to give highly significant results statistically. The values read off from the distribution curve were analyzed statistically and the results were the following:

• Mean pore diameter	140 Å
• Standard deviation	30.3 (± 21.6%)
• Number of measurements	400

It is relevant to note that the authors were apparently only concerned with establishing whether pore widening occurred. However, they state: "There is no evidence of major pore widening. It seems reasonable to conclude that the graphs represent actual pore sizes." There is no comment on the extent of the spread of values measured or the possible causes of the variability.

An explanation of this fact is probably that, as-produced, anodic coatings are usually under compression. This is because, according to Schenk,[20] there is room, on average, for only two out of every three aluminum atoms to be converted into anodic oxide.

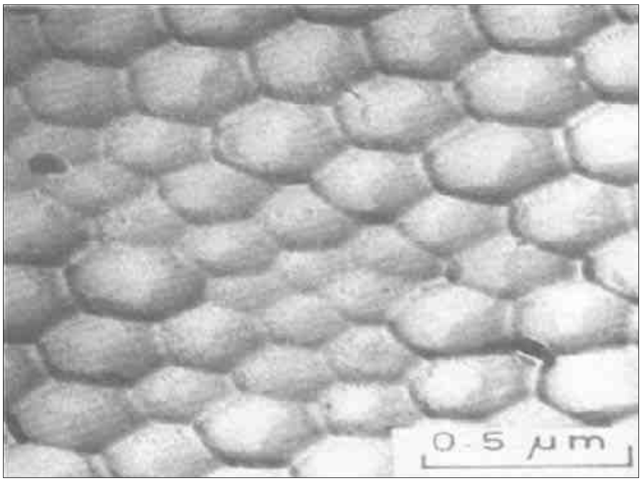

Figure 4—*Photomicrograph of the cell base pattern of a film formed for 70 min at 25 mA/cm² to 120 V in 0.25M oxalic acid at 15°C.*

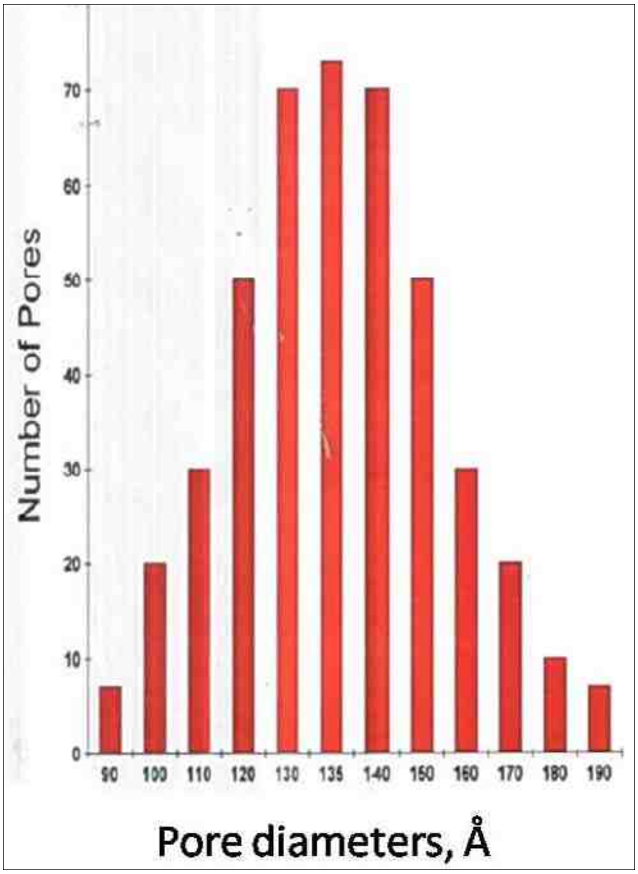

Figure 5—*Distribution curve of pore diameters for a 15-min coating produced in a 1.5M H_2SO_4 electrolyte at 20°C at 25 mA/cm^2 (Based on data published by Wood and O'Sullivan.[30]).*

If one accepts that in a population of 400 cells there will be some which have a low level of lattice defects, against these has to be set, at least, an equal possibility of having a high defect structure. It seems probable that where there is a low level of defects, aluminum atoms will find space in which the conversion to oxide exceeds the ratio of two atoms of aluminum combining with three atoms of oxygen. Complementing this, in the high vacancy areas, there will not be enough atoms to fill the available space.

It has also to be appreciated that the KH&R model is misleading. Many anodizers assume that the pores extend continuously from the "barrier layer" to the surface. Using the Stereoscan™ microscope, Arrowsmith[32] showed that although the cells and pores grew normal to the metal surface, the variations in surface contour of semi-fabricated products and engineering components, even in a thin coating, pores did not extend continuously to the surface. Instead there was a complex maze involving pore branching and termination.

Are there any anodic coatings without pores?

It has been generally accepted that coatings produced for electrolytic condensers are "barrier layer" coatings but this overlooks the paper published by Franklin[33] who demonstrated the presence of pores in a boric acid anodic (barrier) coating, as shown in Fig. 6. Franklin concludes "...the same fundamental growth mechanism is operative for barrier layers as for porous anodic coatings."

The surface chemistry of aluminum

In retrospect, it seems surprising that the authors of the "barrier layer" theory should have ignored the literature on the surface chemistry of aluminum that already existed in the early 1950s. It seems logical to assess whether the mechanism of anodic film formation proposed by KH&R was compatible with that of other surface films formed on aluminum. Some relevant examples of surface reactions on aluminum known in the early 1950s are summarized in the following paragraphs.

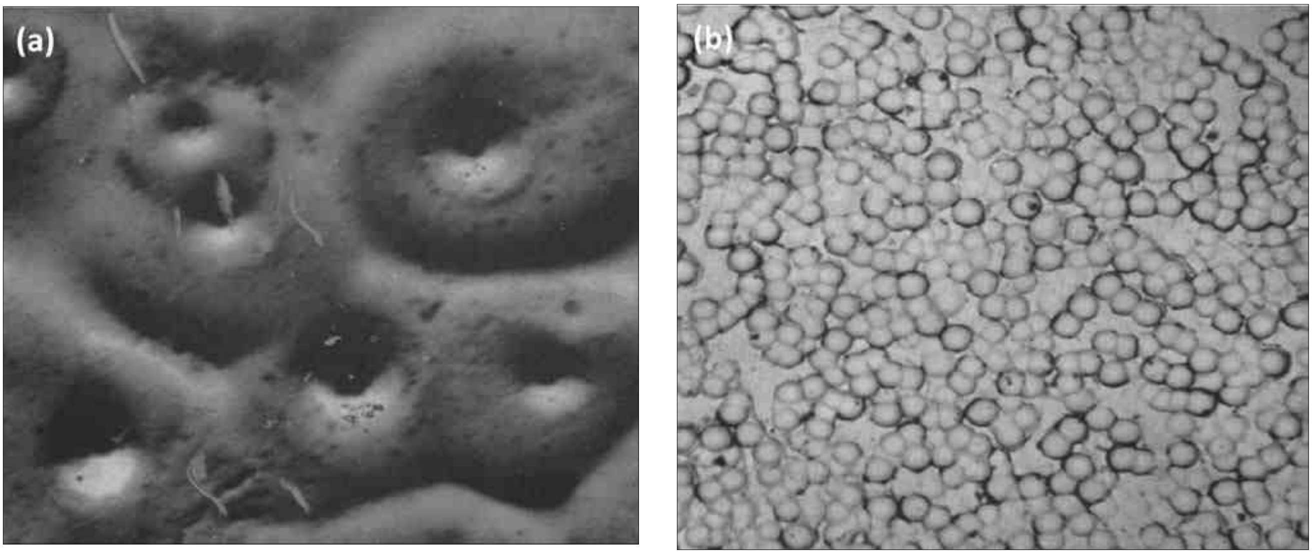

Figure 6—*(Left) Pores in a barrier coating formed at 525 V in a 4.5% boric acid electrolyte; (Right) Cell base structure produced at 500 V in a boric acid-borax electrolyte.*

High temperature oxidation

Studies in the aluminum industry of the formation of the oxide film on aluminum had established that oxidation did not occur uniformly but started at a series of apparently random nuclei which progressively covered the surface.

It had also been established that the oxide film on aluminum-magnesium alloys contained five to ten times more magnesium oxide at the air interface as compared with the metal/oxide interface. According to Short,[34] this behavior extends to extruded 6063 alloy (and presumably to other 6000 series alloys).

The formation of oxide nuclei was later confirmed by Murr,[35] who investigated the oxidation characteristics of a number of metals, including aluminum. He states that "… oxidation begins at nuclei which may have a preference for certain crystallographic orientations, as well as surface structural features such as dislocations, steps or ledges."

Atmospheric corrosion

In atmospheric corrosion testing it had been established that the formation of corrosion centers developed with a similar nucleation mechanism to that found in thermal oxidation.

Marine corrosion

It had also been established that the high magnesium oxide content of the outer surface film enhanced corrosion resistance in marine environments due the enhanced resistance to corrosion conveyed by the presence of MgO in alkaline pH. It had also been established that there was a similar pattern of development of corrosion centers in aqueous conditions to those found in thermal oxidation. In marine corrosion generally it has been found that corrosion nuclei developed at random centers associated with structural features.

Rinse water corrosion

The greater use of anodized aluminum in the 1960-80 period led to the observation that rinse water corrosion in anodizing plants developed with the same nuclear pitting formation as had been seen in other corrosion environments.[36]

Anodic oxidation

Work carried out in the 1980s showed that the magnesium oxide gradient resulting from high temperature oxidation was reproduced in the 5000 series alloys when anodized and resulted in lower hardness values. The minimum acceptance values in BS5599 "Hard Anodic Oxidation Coatings" were lowered in recognition of this behavior.

Observations on the initial growth of anodic films

Starting in the late 1950s, investigators were questioning the validity of the KH&R model, particularly the primary film formation. Representative of these are the papers by Bogoyavlenski,[37] Csokan,[38] Franck,[39] Ginsberg[40] and Kaden.[41] They have noted that coatings appeared to be forming initially at high energy points such as structural defects. This led to an extensive series of investigations by Csokan which continued into the 1970s.[30]

In his first investigation, Csokan[38] linked a cine-camera with an electron microscope to study initial anodic formation in a 1% sulfuric acid electrolyte under hard anodizing conditions. This demonstrated that film growth commenced with a nucleation process. He observed that anodic coating formation took place at a series of initial active nuclei and then spread to other secondary centers until the entire surface was covered (Fig. 7).

The foregoing observations appear to suggest that the formation of such active primary nuclei were probably related to the defect structures referred to the above. To counter suggestions that these observations were due to the low conductivity of the electrolyte, he subsequently extended his work over the range of 1 - 20 vol% concentration.[30] This work firmly established that the nucleation process occurred in a similar way to that reported previously. Clusters of oxide nuclei grew at high energy points and their spread depended on the electrolyte concentration and anodizing voltage. Subsequently, the work was extended to cover the main electrolytes in industrial use.[30] For all of these the basic nucleation process was similar with only minor variations.

In the period 1960-80, there were a number of proprietary processes for the production of "self-colored" anodic coatings (mainly bronze shades). These were organic carboxylic or sulfonic acids with 20-50 g/L sulfuric acid added to obtain uniform coverage. Szontagh[42] investigated film formation using a proprietary process. He found that growth started as clusters at separate nucleation centers and spread to cover the whole surface.

It is relevant to mention that Csokan regarded his observations as a modification of the "barrier layer" theory, but the earlier evidence in this paper on the surface chemistry of aluminum are considered to show that growth of films from nuclei are the normal surface chemistry mode of initiation of film growth rather than the formation of a continuous film.

Ideas on the mechanism of initial nucleation and growth

In his first paper, Csokan referred to Franck[39] who had stated that the growth of an oxide film always began at points of high energy, *i.e.*, at "nuclei" and not uniformly over the surface. Csokan further developed this model and observed that: "The initial film forming process always takes place on a heterogeneous structure. The conditions for film growth are more favorable at the edges of the nuclei and the rate of growth at these points is much higher than the rate of growth normal to the surface. This results in lens-shaped isolated nuclei which grow together within a short period of time. The primary film formed in this way then covers the whole surface and further growth is solely vertical. After this time, film growth takes the form a stationary basis film and further growth is solely vertical."[30] His work continued into the 1970s and covered the whole range of electrolytes and conditions in current industrial use.

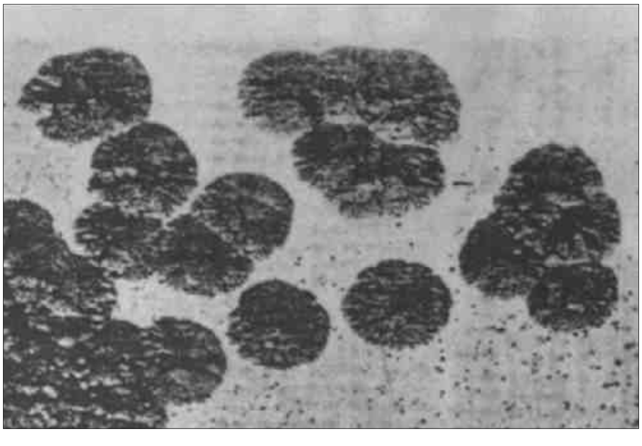

Figure 7—*Example of primary oxidation sites as observed by Csokan.*[37]

What has been largely ignored in the past is the effect of lattice defect structures on film formation and growth. They include the following:

- The presence of foreign atoms (alloying or impurity) in the lattice.
- Lattice distortion arising from hot and cold working operations.
- Localized concentration of vacancies, which may arise from manufacturing.
- Individual vacancies in the lattice.

It has to be remembered that many of these defects are below 100 nm in size. It seems a reasonable assumption that the various lattice defects can be expected to affect the formation and structure of individual anodic cells, which are mainly of several hundreds of nanometers in size.

The foregoing also raises the question of the origins of the pores which develop as anodic coating formation commences. The author finds it difficult to accept the KH&R theory that they originated from oxide dissolution. As has already been pointed out with one out of three aluminum atoms not converted to oxide there is a huge surplus of aluminum ions on the surface of the transition zone which will prevent oxide dissolution. This effect will be enhanced as pores develop. In addition, there is the work of Franklin who has established the presence of pores in barrier coatings and is firmly of the opinion that all anodic coatings have a similar formation mechanism.

Macdonald has examined anodic film formation and breakdown in a number of metals,[43] including aluminum, for which he has developed a point defect model. In a further contribution, he considers its application to anodizing aluminum in more detail.[44] He considers that, under the influence of a potential, vacancies coalesce to form "voids." He has also observed that the voids increased in size with increasing voltage. His analysis accepts the "barrier layer" theory and ignores Sato and Kaminga, as well as Csokan's contributions. The other problem is that investigators have so universally based their work on existing theory, which ignores the effect of the material, particularly its nanostructure, so that one is left with dependence on logical inferences from the data available.

The role of the electrolyte

The addition of an acid to water results in its dissociation into its constituent ions and the water into hydrogen and oxygen ions so that the formation of anodic oxide can readily take place. In the case of weakly dissociated boric acid, the lack of oxide solvency when the pH is around 5.5 means that electrolyte above the coalesced vacancies has no significant effect on the oxide formed as the coating grows. Although there is a "shadow" pore base, as the oxide thickens, there is no attack on the oxide growing around the pore shadow, as shown by Franklin. These incipient ("shadow") pores become smaller and almost disappear as the coating grows because of the volume increase as the coating grows. On the other hand, if the pH is steadily increased, a porous structure is obtained. However, there appears to be virtually no BO_4 built into the film, mainly because boric is a weak acid.

The electrolytes used industrially are highly dissociated acids having varying degrees of oxide solvency. As the oxide surrounding the shadow pore thickens, the electrolyte has a limited attack on the pore walls. The increase in pore diameter $H_2SO_4 \rightarrow (COOH)_2 \rightarrow H_3PO_4 \rightarrow H_2CrO_4$ reflects the increase in oxide solvency. The factor probably only comes into play for the short period when the first 20 to 50 Å are formed, because from this point onwards it is the mass action effect of the egress of aluminum ions neutralizing the electrolyte attack that prevents any further widening. The above order is also that of the amount of electrolyte anion incorporated, which has a significant effect on the potential required to maintain a useful current density.

Academic attention seems to have focused on electrolyte attack at the hypothetical "barrier layer." This seems to be rather misdirected because, in the author's experience, there has never been reported an incident of breakdown of the "barrier layer" leading to film attack on the underlying metal. What appears to have been inadequately recognized is the serious problem of electrolyte attack producing degradation of film quality on the outer layers of the coating, especially when producing films over 15 μm in thickness.

Most architectural work is anodized to a minimum thickness of 20 μm. This usually results in film thicknesses on the range of 20 to 26 μm. The problem has been that, although passing the usual quality tests, on exposure for six to 18 months, "chalking" has taken place. This is due to degradation from electrolyte attack. The problem has been that this seems to occur despite anodizing conditions remaining unchanged, but the occurrence is of a random nature. It is the effect of prolonged contact of the electrolyte with the outer layers of the coating that is of great industrial importance, not the "barrier layer."

Hypotheses for a new model of anodic coating formation

It should be appreciated that the following hypotheses are ones that are considered to follow logically from the data and analysis presented in the foregoing. Even so, it is recognized that they involve some inferences which lack the support of experimental data. The concepts offered involve a new view of the structure of anodic coatings, which has a particular importance at a time when the potential of nanotechnology is attracting much attention. It is based on a view of how the arrangement of atoms, vacancies and other lattice defects appear likely to affect the initial formation of the individual cell and subsequent film growth and structure.

Factors affecting the morphology of the individual cell

As shown above, the distance between the pore centers will affect cell morphology:

- The morphology of each cell will show a variation from that of its neighbor.
- These variations are due to variability in the field around each pore because of variations in the lattice defect structure.
- The presence of foreign atoms at the metal surface and in the oxide film, *i.e.*, alloying metals and impurities, can also reduce conductivity at the nano-level and thereby result in an irregular cell shape.
- Differences in packing density of atoms on different planes will affect conductivity and therefore the rate of cell growth - initially laterally, then vertically once the film covers the surface.
- Mobile atoms, such as magnesium and zinc, produce increased cation vacancies in the metal substrate and in the anodic oxide. This results in a higher current density as compared the pure metal.
- Some metals at quite low levels can significantly reduce conductivity, which can be significant at the nano level.

All the above factors will produce a non-uniform cell around each pore.

Factors affecting nucleation and initial growth

The hypotheses developed here are based on the Franck-Csokan model with modifications:

N1. When current is applied, a coalescence of vacancies occurs, as has been referred to in the previous text.

N2. There is a time interval to this process which seems to be mainly around 5 to 10 seconds (based on Csokan's work).

N3. Cells will start to grow within the primary nuclei which contain clusters of "voids."

N4. Where there are a number of adjacent cells, as in the primary nuclei, the KH&R model would apply if the underlying metal were perfectly uniform. However, the foregoing analysis shows there are lattice defects which would be expected to produce a non-uniform polygonal cell structure as a consequence of the non-uniform field produced.

N5. Those cells forming at the edges of growth nuclei will continue to grow until restricted by expansion of the adjacent nuclei.

N6. As the coating grows, it produces resistance and formation of the primary nuclei slows. Meanwhile the coalescence process will have produced new nucleation centers and the process will be repeated until the whole surface is covered and an overall film is produced.

Pore formation and characteristics

The foregoing text suggests the following hypotheses may be valid:

P1. When an appropriate potential is applied to aluminum in an electrolyte, cation vacancies will be produced. There will also be lattice vacancies present in the metal structure.

P2. As the anodic film begins to grow cation vacancies are produced in the first 20 to 50 nm of the inner transition layer. Correspondingly, there will be anion vacancies in the outer 20 to 50 nm of the layer.

P3. The application of a suitable potential results in a coalescence of these vacancies into "voids."

P4. These voids remain in place as anodizing proceeds.

P5. The spacing between the centers of these voids is voltage dependent.

P6. The voids are incipient pores, which are preserved as the anodic coating grows. All anodic coatings have an incipient pore structure due to the presence of these voids.

P7. The size and spacing of the pores will be affected by the electrolyte and anodizing conditions.

P8. Evidence of pore size variability suggests that it will also be influenced by the lattice defect structure and material composition.

P9. These pores provide a ready path for the movement of cations from the metal into the electrolyte. They have an imperfect aluminum skeleton which will form anodic oxide, but it will be variable and imperfect depending on the underlying structure.

P10. Since one out of three of the aluminum atoms is dissolved in the electrolyte, the mass action effect of this large supply of aluminum ions prevents dissolution of the film once the initial oxide layer is formed.

Factors affecting coating thickness

The following factors will affect film thickness:

T1. Differences in packing density of atoms on different planes will affect conductivity and therefore rate of growth and amount of oxide formed.

T2. This will also produce film thickness variations - usually below ±1 μm except on thick films, but this effect increases with current density.

T3. These factors will also affect surface smoothness and appearance.

T4. Compositional variations due to segregation of alloying elements will also produce thickness variations.

T5. The film is not uniform, due to the variable nanostructure, although the variations are less than ±1 μm. These variations affect the appearance and surface finish of the work.

T6. The effects of added elements at a fixed potential on the current density, and therefore the film thickness formed per unit of time, will vary. This is well documented in the literature.

The new model in perspective

Inasmuch as the work of Keller, Hunter and Robinson was made possible by the improvements in electron microscopy, it should now be practicable to look at anodic coatings in a new way using the improved tools available as a result of advances in the means available to determine the structure of materials at the nano level.

The above text is an attempt to focus attention on areas critical to understanding anodic coating formation, especially the metal nanostructure. It has to be remembered that anodic cell dimensions are on the order of a few hundred nanometers. Since the lattice structures involved are less than 100 nm, it seems reasonable to conclude that lattice defect structures will affect the formation and characteristics of anodic coatings. There are now techniques available which can help to confirm or modify the outline of the model presented here.

Summary

After a survey of the development of industrial anodizing and the theory of the formation of the anodic coating on aluminum, the present "barrier layer" theory has been subjected to a detailed critical analysis. This has shown it to be misleading and inaccurate. It is demonstrated that there is adequate evidence that it is not a layer, but a transition zone between the metal and the anodic oxide film. Additionally, the theory fails to account for the effect of material composition and structure on the formation, structure and growth processes. It is concluded that the theory is no longer valid.

Literature on coating morphology is examined critically to provide a better understanding of what is actually produced at the level of the individual cells. Statistical analysis of data on cell sizes of an oxalic acid coating and of the pore sizes of a 7-μm sulfuric acid coating showed that published values are simply mean values, with variances of ±21 and ±27% respectively, which is not consistent with the original theory.

This has led to consideration of published literature that contained results that were not expected by the "barrier layer" theory. The most interesting studies were those of Franck, which were further developed by Csokan. They viewed growth as taking place from random oxide nuclei initiated from high energy centers associated with structural defects.

Examples of the surface chemistry of aluminum are given which support the observations of Franck and Csokan that growth of surface films originates from nucleation centers, as opposed to currently accepted film formation theory. Franklin has shown that there is a pore structure in barrier coatings and concluded that there is a common formation mechanism for all anodic coatings. More recently, MacDonald has developed a model of anodic coating breakdown based on evidence that suggests vacancies agglomerate under the influence of an electric field. Their spacing is voltage dependent. The present author has integrated, modified and extended the above concepts into a series of hypotheses which relates the above findings to features of the nanostructure of the metal.

It is suggested that with the initial application of current, there is an agglomeration of vacancies whose spacing is voltage dependent. This agglomeration forms the basis of the pore structure. Because there is a significant variability in the material lattice structure at the nano level, the distance between the pore centers is variable. This variability in turn affects the size and morphology of the individual cells and results in the polygonal cell structure seen in photomicrographs. A series of hypotheses are developed which provide a new model of anodic formation.

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About the author

Dr. Arthur Brace, CPE, AESF Fellow, FIMF, FIMMM, was born in Bristol, England and attended a local grammar school, leaving at 16 to become a laboratory assistant in a plant producing aluminum and magnesium castings. He remained associated with aluminum for most of his subsequent career. In the late 1940s, he joined the Aluminum Development Association, being involved is several projects promoting the use of aluminum. In this period he first became involved in anodizing and a few years later joined Alcan's Laboratories at Banbury, where he built up an anodizing R & D team which subsequently established itself as one of the leading centers for anodizing. This led to his promotion as Head of the Chemistry Division, Several years later he left Alcan and became a plant manager, gaining experience in architectural and hard anodizing. He went on to establish himself as a professional consulting engineer. He assisted a number of companies in setting up anodizing plants. Over the years he also established a reputation for problem solving in anodizing.

Noting the large increase in the use of hard anodizing and the growth of offshore contracts, he played a leading role in setting up the International Hard Anodizing Association to provide a forum for its members to discuss issues of mutual interest. He was one of a small committee that formed the Aluminum Anodizers Association. He also served as President of the International Branch of the American Electroplaters and Surface Finishers Society and was a member of its Light Metals Committee. He also served on the Council of the Institute of Metal Finishing and as Chairman of its Aluminum Finishing Committee. He was author of two books, and numerous papers relating to aluminum and anodizing.

He holds a B.Sc. (Economics) from the London School of Economics and a Ph.D. from the University of Aston in Birmingham. He has also received the following awards:

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