# Is Barrier Layer Responsible for Cellular Structure Of Aluminum Oxide Film Anodized in Sulfuric Acid?

Dr. Moisey Lerner, Tomin Corporation, Wellesley, MA

Increasing AC voltage in DC+AC process can reduce DC voltage to ~7 VDC that creates a strong enough electric field, forming a barrier layer with three areas. The closest to aluminum area has composition  $A_{b+q}O_3$  with higher concentration of aluminum ions. Above it there is pure dielectric:  $A_bO_3$ -area. Area  $A_bO_{3+p}$  close to electrolyte has higher concentration of oxygen ions. A weak (for example, boric) acid does not dissolve barrier layer. A strong (for example, sulfuric) acid finds a spot and dissolves barrier layer until the lowest area  $A_{b+q}O_3$  surrounding the spot is reached and flooded with oxygen ions. These ions transform  $A_{b+q}O_3$  into  $A_bO_3$  that builds up wall around the spot, forming a pore. Each spot is complemented equidistantly with six spots, building hexagonal cells with a pore in the center of each cell.

For more information, contact: Dr. Moisey Lerner Tomin Corporation P.O. Box 812206, Wellesley, MA 02482-0015

*Phone:* 781-444-6529 *Fax:* 781-449-8923 E-mail: mltomin@gis.net

# Introduction

The main research effort dedicated during the last 50 years to understand the mechanism of oxide film formation targeted films formed by DC voltage only. Films formed by DC voltage with superimposed AC voltage were, as a rule, ignored. However, even in the early 1950's Campbell<sup>1</sup> invented and industrially implemented an aluminum hard-coating process that used a combination of high DC voltage with sinusoidal voltage of industrial frequency. This process forms the hardest coatings on aluminum ever anodized in sulfuric acid solutions. 25 years later, Fruzstajer and Lerner<sup>2</sup> invented a power source that combined low DC voltage with low sinusoidal voltage that was industrially applied for aluminum anodizing and hard-coating<sup>2</sup>. A combination of DC voltage with non-sinusoidal voltages also found industrial anodizing application since the beginning of 1980's. We offer here a humble attempt to explain formation of oxide film during anodizing with sinusoidal voltage added to DC voltage. This explanation shed additional light on the structure of oxide film formed with DC voltage only.

# Can we tin-plate a porous aluminum oxide with sinusoidal voltage?

An aluminum article, after it was covered with porous oxide film during the first step of architectural anodizing in a water solution sulfuric acid, becomes colored, for example, in tin-containing electrolyte during the second step of architectural anodizing. Tin (the coloring agent) is deposited into pores of the oxide film by electroplating. Most often, a source of sinusoidal voltage of industrial frequency is used to do tin plating. This is strange, because using AC source defies the Faraday Law that demands unidirectional transportation of Faraday electricity for depositing a proportional amount of tin.

On the other hand, Tareev, Lerner, Odine $z^3$  invented a process that used a three phase transformer for industrial anodizing of aluminum foil for electrolytic capacitors in the former Soviet Union. In this process, the rectifying properties of aluminum oxide film were employed. A DC voltage component was generated from the AC voltage applied to each tank of the three-tank system through which aluminum foil was pulled.

We will show below that the porous oxide film, when dipped into the tin-plating electrolyte, also has an ability to rectify the applied AC voltage. A DC voltage component is generated and is responsible for depositing tin into pores.

# The rectifying layer is 'barrier layer'

A porous oxide film is formed on aluminum in water solutions of either sulfuric acid or other strong acids (such as phosphoric, chromic, oxalic, etc.). Tareev<sup>4-5</sup> classified these films as the 'Second Class of oxide films'. On the other hand, weak acids, such as boric acid, can also be used to anodize oxide film. However, the formed oxide film is not porous – it is continuous. Tareev<sup>4-5</sup> classified these films as the 'First Class of oxide films'. They are very thin (not thicker than 1 micron) and

comparatively high density (of the order of  $3.2 \text{ g/cm}^3$ ). They have excellent insulating properties and are used as dielectric in electrolytic capacitors provided that aluminum is positive (anode) and electrolyte is negative (cathode). This First Class film is also called 'barrier layer' film. Should polarity be reversed, the barrier layer becomes conductive and the capacitor explodes. It is said that the barrier layer has 'unilateral conductivity' – it is conductive in one direction and non-conductive in the opposite direction<sup>5-6</sup>. A barrier layer functions as diode. This property of the barrier layer can be used to rectify AC voltage.

#### Basic unilateral conductivity data

The theory of unilateral conductivity of the oxide films has been elaborated by many investigators during the past 100 years, starting from the time of electrolytic rectifier invented by Mitkevich<sup>7</sup> in 1901. Tareev and Lerner<sup>8-9</sup> used new experimental facts together with the development of solid state physics to find an advanced explanation of unilateral conductivity of oxide films.

Let us take a pure aluminum without the oxide film on its surface (for example, after etching) and immerse it in a water solution of weak (such as boric) acid that does not-dissolve the film. Let us make aluminum the anode. Then, the oxygen will be generated on aluminum surface and a thin layer of aluminum oxide will be formed. Thickness d of the coating is proportional to the applied DC voltage where coefficient of proportionality is ~ 12.7 Å/ $V_{DC}^{10}$ . Due to thinness of this oxide layer, a very strong DC electric field acts in the film. The intensity of this electric field is of the order of  $10^{6}$ - $10^{7}$  V<sub>DC</sub> /cm even when very low voltage is applied across aluminum and electrolyte. Under the influence of electric field forces, negative oxygen ions will be moving through the oxide layer in the direction to aluminum and positive aluminum ions in the opposite direction, so that the thickness of the oxide film will increase. This process continues up to the moment when the growing thickness d of the oxide film (across which a constant film-forming voltage  $V_{DC}$  is applied) diminishes the electric field intensity. V<sub>DC</sub> /d drops so much that the force of this field becomes insufficient to move any longer the metal ions through the film. As a result, no ionic electric current flows through the oxide film and the film thickness d ceases to grow.

The non-uniformity in the concentration of ions in the oxide film is inevitable during the process of film formation<sup>8,9</sup>. The concentration of oxygen ions is maximal in the area of oxide film closest to the electrolyte (see Fig. 1 from<sup>9</sup>). The composition of the oxide film in this area (that we will identify as p-layer) may be written as  $Al_2O_{3+p}$ . As we move through the oxide film in the direction to aluminum substrate the oxygen ion concentration drops but the concentration of aluminum ions must grow and reach a maximum level at the metal surface. Hence, in the area of oxide film close to aluminum the deviation of composition of the oxide film from the stoichiometric composition may be written as  $Al_{2+q}O_3$ . Let us identify this area as n-layer. Between p-layer and n-layer of non-stoichiometric oxide compositions, there is an intermediate area (that we will identify as i-layer) with exact stoichiometric composition  $Al_2O_3$ . Aluminum ions, whose dimension is 2.6 times smaller then that of oxygen ions, diffuse more easily than oxygen ions. It is, therefore, obvious that the i-layer of stoichiometric

oxide is situated not in the middle of the oxide film but it is shifted in the direction of the electrolyte surface (see Fig. 1). If we define by a broken line the initial aluminum surface prior to anodizing, we may suggest that the "build-up" of oxide film in reference to this line is 50% and the "penetration" is also 50% (see stage 1 in Fig. 2).

It is known that aluminum oxide, containing surplus of oxygen, behaves like a semiconductor with 'hole' conductivity (p-type semiconductor). On the other hand, when it contains surplus of aluminum it behaves like a semiconductor with electronic conductivity (n-type semiconductor). Consequently, in the formed oxide film, p-n junction (with intermediate intrinsic layer of stoichiometric oxide, i.e. p-i-n junction) must be created. The p-i-n junction is one of the main reasons for unilateral conductivity of the first class oxide<sup>\*</sup>. When aluminum is made positive, the electric field shifts the excessive negative electrons of the solid-state n-semiconductor towards aluminum. This field also shifts positive holes of the p-semiconductor in the opposite direction. As a result, the thin intrinsic area  $AbO_3$  widens transforming the p-i-n junction into dielectric with high resistance to DC. The situation reverses when aluminum is negative: both - electrons and holes - run towards the intrinsic area making the p-n-junction conductive. That is how a diode functions in a first approximation.

## The process of forming a cell

If aluminum without the oxide film on its surface (after etching, for example) is immersed in a water solution of strong acid then a thin layer of aluminum oxide will be formed.

How thick is this layer? Let us consider conventional anodizing in a water solution of 170 g/l of sulfuric acid at room temperature. This process is ordinarily conducted at  $1.5 \text{ A/dm}^2$  that needs about 20 V of straight DC voltage across industrial anodizing tank.

If it were a weak (for example, boric) acid electrolyte, the oxide film would not dissolve. A barrier layer would be formed by 20  $V_{DC}$  with thickness equal to 12.7 Å/V  $\cdot$  20 V ~ 250 Å.

Sulfuric acid electrolyte is strong and will dissolve the film. Let us consider two scenarios: Scenario 1 – the process of dissolving is *uniform*, and Scenario 2 – the process of dissolving is *non-uniform*.

Fig. 2 illustrates behavior of oxide film in **Scenario 1**. We will show that the barrier layer formed on the aluminum surface will uniformly dissolve and gradually sink with time into aluminum substrate. This process may occur in the following order:

 If p-layer, that contacts electrolyte, begins dissolving, the thickness of the barrier layer is reduced and the electric field in the oxide increases. Therefore, resumes the flow of positive oxygen ions down to aluminum through the barrier layer. A portion of the intrinsic i-layer becomes enriched

<sup>&</sup>lt;sup>\*</sup> During preparation of article<sup>8</sup> for publishing (the article was submitted on August 29, 1959) Kabayashi<sup>11</sup> published a paper reflecting views close to those proposed by Tareev and Lerner<sup>7</sup>.

with oxygen and transforms into p-semiconductor restoring the initial thickness of p-layer.

- 2) Because of this conversion, the thickness of i-layer is reduced, the electric field in this layer increases and pushes oxygen ions deeper into n-layer to transform the electronic semiconductor  $Ab_{2+q}O_3$  into  $Ab_2O_3$  and restore the thickness of i-layer.
- 3) Since n-layer contributed a part of its thickness to restoration of i-layer, the electric field in n-layer increases and invites more aluminum ions into n-layer restoring its thickness.

Scenario 1 successfully describes *sinking the barrier layer* deeper and deeper into aluminum in reference to the broken line that indicates the initial aluminum surface prior to the process of anodizing (see Fig. 2 with three stages of dissolution where Stage 1 is initial barrier layer formed on bare aluminum). This *sinking* consumes an insignificant barrier-layer-restoring-current compared to Faraday current 1.5 A/dm<sup>2</sup> that forms the coating during sulfuric acid anodizing. Scenario 1 does not explain how this high Faraday current flows, and is therefore incomplete.

Fig. 3 illustrates behavior of oxide film in **Scenario 2** of non-uniform dissolution. Let us imagine a spot in which the rate of dissolution is higher than the rate of uniform dissolution considered in Scenario 1. During the accelerated dissolution of the spotbarrier-layer, this layer would sink creating a pore surrounded by the initial barrier layer that dissolves at a lower rate. The process of dissolution of the spot-barrier-layer will repeat steps described in Scenario 1 (see Fig. 2). Eventually, the top p-layer of the spot-barrier-layer, which contacts the electrolyte, will sink reaching the n-layer of the slowly dissolving barrier area surrounding the pore (see Stage 3 in Fig.3). Α conductive ring CR is created around the pore through which oxygen ions from the electrolyte tangentially enter conductive n-layer. Oxygen ions combine with aluminum ions (that are amply diffused in the n-layer) and create molecules of  $AbO_3$ underneath the intrinsic layer of AbO<sub>3</sub> surrounding the pore building up i-layer from underneath. How far can oxygen ions move tangentially feeding the growth of the ilayer of the slowly dissolving barrier layer? Apparently, the distance of tangential penetration of oxygen ions under the Al<sub>2</sub>O<sub>3</sub> area depends on the applied voltage drop (in our case 20  $V_{DC}$ ) across the n-layer. As a result, the i-layer within the 20  $V_{DC}$ -drop will grow up very fast at a ~70 Å/sec<sup>\*\*</sup> rate creating a cell (see Stage 4 in Fig.3). The spot-barrier layer sinking into aluminum shapes the area under the cell guided by the same 20V<sub>DC</sub>-drop rule (see Fig. 3). The process of non-uniform dissolution of the oxide film can better be described by term 'corrosion' (suggested by Runge<sup>13</sup>) meaning a gradual alteration by a chemical or electrochemical essentially oxidizing process.

We considered just a single spot through which the electrolyte succeeded to reach the n-layer and build up  $A_2O_3$  around the spot with the help of oxygen ions entering nlayer through the conductive ring CR. The fast growing cell protects the area under it

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<sup>&</sup>lt;sup>\*\*</sup> Because anodizing is conducted at 1.5 A/dm<sup>2</sup> at ~ 20 V of straight DC voltage across the tank and forms ~ 25 micron-thick coating in 60 minutes. Since 60 min = 3600 sec and 25  $\mu$  = 25x104 Å, then the rate of formation of the porous oxide film is about 70 Å/sec

from corrosion. The only vulnerable to corrosion area is limited to barrier layer at the bottom of the pore.

What about other cells, how are they created? Once the anodizing process in sulfuric acid electrolyte begins, corrosion will affect the whole area of bare aluminum. There will be an abundance of spots (which are centers of corrosion) on the aluminum surface with higher rate of oxide dissolution. Each cell will generate a pore, as described in Fig. 3. A structure of cells competing for the space will be created. There can be a square option of arrangement of cells, or hexagonal (Fig. 4) that looks thermodynamically more viable. As we know, Nature chose the hexagonal option.

#### Justification of barrier layer rectification in sulfuric acid electrolyte

Rectification of AC voltage by the barrier layer was observed during room temperature sulfuric acid anodizing using a power source that combined DC voltage with sinusoidal voltage of industrial frequency at different ratios between DC and AC voltage components<sup>12</sup>. It is shown in Fig. 5 (derived from<sup>12</sup>) that in Area 1 where AC voltage changes from 0 to 2 V<sub>ACrms</sub>, the DC voltage component increases up to 16 V<sub>DC</sub> from 14.5 V<sub>DC</sub> at V<sub>AC</sub> = 0. The additional 1.5 V<sub>DC</sub> was rectified by barrier layer at the bottom of pores (the power source was tuned to provide 14.5 V<sub>DC</sub> only).

Above we raised a question whether tin could be deposited in the pores of aluminum oxide by AC voltage. Since we proved that rectification in sulfuric acid electrolyte does occur, there is no doubt that a barrier layer would successfully rectify DC voltage in a less aggressive tin-plating electrolyte.

#### **Capacitance of the barrier layer**

As the AC voltage component of industrial frequency changes from 0 to 2  $V_{ACrms}$  in Area 1 in Fig. 5, the alternating current proportionally increases from 0 to 1.7  $A_{ACrms}/dm^2$  that exceeds the 1.5 A/dm<sup>2</sup> Faraday electricity level. A farther increase of AC voltage in Area 2 and Area 3 to levels twice or three times higher than 2  $V_{ACrms}$  does not cause proportional increase of AC. On the contrary, the AC demonstrated just insignificant increase. The explanation of this behavior needs farther investigation. A number of factors should be taken into consideration. And, first of all, a rather high capacitance of the barrier layer that functions as a dielectric in electrolytic capacitor in which aluminum is one electrode and electrolyte in pores is the other electrode. Capacitance can be calculated by formula (4-1) from<sup>6</sup>

$$C = 0.0884 \cdot \epsilon S / d$$

In this formula

- C capacitance in pF;
- S surface of the electrode in  $cm^2$ ;
- å dielectric constant;
- d thickness of the dielectric.

For a barrier layer 250 Å =  $250 \cdot 10^{-8}$  cm thick with  $\varepsilon = 10$  according to<sup>6</sup> and surface area S = 1 dm<sub>2</sub> = 100 cm<sub>2</sub>, capacitance is close to 0.5  $\mu$ F/dm<sub>2</sub>. If we suggest that the surface of the barrier layer dropped by half in the oxide film formed in sulfuric acid electrolyte (the other half of the surface is filled with cells) then capacitance will be about 2.5  $\mu$ F/dm<sup>2</sup>, which is still a rather high capacitance.

Besides capacitance, the increasing thickness of the barrier layer caused by superposition of the amplitude of AC voltage and DC voltage during a nonconductive portion of the period should also be taken into consideration to explain the unusual behavior of alternating current in Fig. 5. A contribution of the reverse current component during conductive portion of the period to total alternating current should also be considered.

# Conclusions

There are three relatively independent current processes that take place during anodizing second class oxide films (porous and at list 5-10 i thick) formed on aluminum in sulfuric acid electrolyte. The first process forms and maintains a barrier layer that has rather complicated p-i-n structure. Barrier layer thickness is proportional to the applied voltage but needs relatively insignificant Faraday electricity to be formed. This layer, being similar to the barrier layer formed in the boric acid electrolyte, is still different. The difference is that a strong sulfuric acid dissolves the barrier layer non-uniformly. This process can be called corrosion. In a spot with higher rate of dissolution, the spot-barrier-layer is restored simultaneously, and it gradually sinks dipper and deeper into aluminum substrate. Therefore, a pore is created in the initial barrier layer, and a conductive ring CR of n-semiconductor eventually appears just above the brim of the spot. This conductive area is responsible for initiating the **second process** of forming cells of the second class film, each cell surrounding a pore. Cells freely grow from underneath proportionally to the flow of Faraday electricity that amply supplies oxygen ions from electrolyte and aluminum ions from n-semiconductor-layer. Superimposing AC voltage over DC voltage initiates the **third process** - a rather high additional alternating current. If AC voltage of industrial frequency is sinusoidal then alternating current becomes close to and even higher than the Faraday current that forms cells.

#### Acknowledgement

I am thankful for the expressed by Dr. Jude M. Runge doubt in barrier layer being considered the only cause of creating cells in porous oxide films. This doubt haunted me and at last inspired to write this article. I was pleasantly impressed that the non-uniform dissolution that I employed was close to corrosion ideas of Dr. Runge.

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Thickness of the Film

Fig. 1 - Dependence of oxygen content of oxide film on the distance separating aluminum from the electrolyte (schematic)



Fig. 2 - Sinking of barrier layer according to Scenario 1 of uniform dissolution



Fig. 3 - Forming a cell according to Scenario 2 of non-uniform dissolution



Fig. 4 – Possible arrangement of cells caused by a non-uniform dissolution (corrosion) during sulfuric acid anodizing aluminum



Fig. 5 – Dependence of current and DC voltage from the sinusoidal voltage component during aluminum anodizing in 170 g/l water solution of sulfuric acid at room temperature (keeping direct current constant at  $1.5 \text{ A/dm}^2$ )