### **Technical Article**

# Practical Effects of Unclogging Pores With AC Power During Aluminum Anodizing in Sulfuric Acid Electrolytes

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Faraday power is the DC power needed only for the formation of aluminum oxide in anodizing. The total DC power used in DC anodizing at  $20^{\circ}$ C ( $68^{\circ}$ F) exceeds the Faraday power by more than twice, and in hard coating at  $0^{\circ}$ C ( $32^{\circ}$ F), it is about three times higher. The total DC power is reduced if AC power of industrial frequency is sent to the process tank along with DC power. The AC power unclogs the pores of the oxide film from accumulated free oxygen. This reduces opposition to DC flow, reducing the DC voltage needed to maintain the required level of DC. The lower DC voltage proportionally reduces DC power, until it drops to nearly Faraday power. The negative effects of excessive DC power on the quality of coatings are demonstrated.

Aluminum anodizing in water solutions of sulfuric acid found industrial application in the early 1920s. Since then, it was believed that the power supplied by a direct current (DC) source was spent on formation of the porous oxide film and on heating the electrolyte. It can be shown <sup>a</sup> that



heating the electrolyte with Joule power generated by DC consumes about 5 percent of the total DC power sent to a tank.

A newly developed power source that supplies DC and AC voltages at continuously changing proportions<sup>1</sup> helped refute the traditional perception that the bulk (95%) of the total DC power is spent on formation of the oxide film. To arrive at the correct perception, the notion of "Faraday power" should be introduced. Let us define the Faraday power to be the minimum DC power required for forming only the oxide film and doing nothing else. The tests described below prove that Faraday power is much lower than the total power spent in room temperature anodizing with straight DC. In fact, the Faraday power equals about half the total DC power.

### Experimental

We anodized samples of aluminum alloy 6061-T6 in room temperature (20°C; 68°F) electrolyte with 1.5  $A_{DC}/dm^2$ direct current. The electrolyte was traditional for this type of anodizing; an aqueous solution of 170 g/L of sulfuric acid. The level of aluminum concentration in this electrolyte was 4 percent. We used lead for a cathode and titanium for racks. There was no air agitation in this process. Aluminum samples were pretreated in a soap solution, rinsed and then deoxidized for 30 sec instead of etching.

### Results

Figure 1 shows the dependence of different anodizing process parameters on the sinusoidal AC voltage component  $(V_{AC})$  of industrial frequency (50 or 60 Hz) supplied to the anodizing tank along with the DC voltage.  $V_{AC}$  was plotted on the horizontal axis and was measured as a root mean square value (rms).<sup>b</sup> In Figure 1(a), the DC voltage across

<sup>a</sup> Power spent on heating can be calculated once we know the voltage drop across the electrolyte. It can be measured with a probe immersed in the electrolyte and located as close as possible to the anodized workpiece. A DC voltmeter should be connected between the probe and the tank cathode. Tank measurements conducted under shop conditions demonstrated that the voltage drop across the electrolyte (such as a 170 g/L water solution of sulfuric acid) would be ~1.0 V<sub>DC</sub> at 1.5 A<sub>DC</sub>/dm<sup>2</sup>, which is a common level of current density in room temperature anodizing. Multiplying voltage by current density, we arrive at ~1.5 W/dm<sup>2</sup>, which is the Joule power spent on heating the electrolyte. The total DC voltage drop between anode and cathode under these conditions is about 15 V<sub>DC</sub>. Subtracting the voltage drop across the electrolyte from the total tank voltage, we arrive at ~14 V<sub>DC</sub> that can be said to form the oxide film. The power spent on oxide formation equals ~14 V<sub>DC</sub> x 1.5 A<sub>DC</sub>/dm<sup>2</sup> = ~21 W/dm<sup>2</sup> or 95% of the total power.

<sup>b</sup> The amplitude (maximum) value of the sinusoidal voltage can be calculated by multiplying the rms value by 1.41:  $V_{AC}(max) = 1.41 V_{AC}(ms)$ 



the tank and currents (DC and AC) through the tank are plotted on the vertical axis. This figure demonstrates that there are four distinct areas of  $V_{\rm DC}$  change, as  $V_{\rm AC}$  grows with the direct current held constant at 1.5 A/dm<sup>2</sup>:

 $\begin{array}{l} \mbox{Area 1: } V_{AC} \mbox{ from 0 to } {\sim} 2.0 \ V_{rms} \\ \mbox{Area 2: } V_{AC} \mbox{ from 2.0 to } {\sim} 3.5 \ V_{rms} \\ \mbox{Area 3: } V_{AC} \mbox{ from 3.5 to } {\sim} 7.8 \ V_{rms} \\ \mbox{Area 4: } V_{AC} \mbox{ above 7.8 } V_{rms} \\ \end{array}$ 

In Area 1, the DC voltage increases to its maximum value, exceeding the initial level of 14.5  $V_{DC}$  at  $V_{AC} = 0$  by ~1.5 V. In Area 2,  $V_{DC}$ gradually returns back to the initial level. In Area 3, we observe a more rapid linear reduction of the DC voltage until  $V_{DC}$  reaches 9.5 V. In Area 4, the DC voltage drops abruptly to the ~8 V level.

Figure 1(a) also contains a time graphic shown over the  $V_{\mbox{\tiny DC}}$ curve. This graphic can be observed on the oscilloscope. The graphic illustrates the dependence of the  $V_{AC} + V_{DC}$  waveform on time at a particular location on the  $V_{DC}$  curve. At the point refer-enced,  $V_{DC} = 10.4$  V, reached at  $V_{AC} = 7.4$  V<sub>ms</sub> (or  $V_{AC}(max) = \sim 10.4$ V). This location, therefore, has a ratio  $V_{AC}(max)/V_{DC} = 10.4$  V/10.4 V = 100 %. For values of V = higher than 10.4 V, the ratio becomes V = 100 %. For values of  $V_{DC}$  higher than 10.4 V, the ratio becomes lower than 100 percent, because the corresponding values of  $V_{AC}$ are lower. Conversely, as  $V_{\rm DC}$  drops further along the curve, the ratio becomes more than 100 percent.

The level  $V_{DC} = -8$  V reached in Area 4 can be used to calculate Faraday power. c Calculations demonstrate that the Faraday power spent with a current density of 1.5  $A_{pc}/dm^2$  was about 10 W/dm<sup>2</sup>. Apparently, the Faraday power, being an active power, is also a non-Joule power because it does not create heat. It creates the oxide film. The total power spent in straight DC anodizing was equal to approximately 21 W/dm<sup>2</sup>, or roughly twice the Faraday power.

Figure 1(a) also illustrates the dependence of the alternating current (as the rms value) on  $V_{AC}$  while the direct current density remains constant at 1.5 A/dm<sup>2</sup>. The alternating current curve begins at zero and reaches a near-plateau at the end of Area 1. The alternating current component changes insignificantly within this plateau through Areas 2 and 3, while the DC voltage undergoes a significant reduction in Area 3. Only in Area 4 is a sharp increase in alternating current observed.

In Fig. 1(b), three other parameters of the anodizing process are

considered: (1) the DC power calculated by the formula  $W_{DC} = V_{DC} \times I_{DC}$ ; (2) total W(active) power measured directly in the tank with an electrodynamic wattmeter; and (3) the active AC power calculated by the formula  $W_{AC}(active) = W(active) - W_{DC}$ . In consultation with Dr. C. Colombini,<sup>2</sup> I was urged to directly measure the active power spent in a tank. He argued that direct measurements might add information to the strong industrial evidence in hand about the smaller power required for chilling electrolyte in the DC+AC process compared to a straight DC process. Less chilling power indicated that less Joule power was released in the tank. The direct power measurements described here proved that the active AC power spent in the tank was much higher than anticipated. Surprisingly, this extra active power did not cause heat generation. It was a non-Joule power spent on unclogging pores.

### Discussion

According to Fig. 1, extra DC voltage and extra DC power are spent in straight DC anodizing, over and above the DC voltage and Faraday power required for creating the oxide film. In room temperature anodizing, the extra DC power is high enough; it is close to the power spent on oxide film creation. Figure 1 also shows that the extra DC power can be partially reduced or completely eliminated, depending on the level of sinusoidal AC voltage (of standard industrial frequency) applied across the tank in addition to the DC voltage.

The above discussion gives rise to two questions: (1) "What is the function of the extra DC voltage and power we discovered here?" and (2) "What drives free oxygen out of the pores of oxide films?"

#### Question 1: What is the function of the extra DC voltage and power?

These two "extras" are responsible for the following three (at least) phenomena:

- Ensuring the steady-voltage-steady-current process in straight DC room temperature anodizing,
- Making the quality of colored coatings vulnerable in two-step straight DC architectural anodizing,
- Preventing thick coatings from having colors as bright as those of coatings that are half as thick.

For an explanation of the first phenomenon, *i.e.*, steady-voltagesteady-current process in straight DC room temperature anodizing, we will use the Keller-Hunter-Robinson3 model of porous oxide films (see Fig. 2). The porous films grow from the aluminum sur-



Fig. 3-Steady-voltage steady-current process.

<sup>&</sup>lt;sup>c</sup> It was mentioned above that at 1.5  $A_{pc}/dm^2$  the voltage drop across the electrolyte was ~1  $V_{pc}$ . Subtracting this voltage from the minimum level of ~8  $V_{pc}$ we arrive at ~7  $\tilde{V}_{DC}$  across the anodized article. Multiplying this voltage by the current (1.5 /dm<sup>2</sup>), we find that the Faraday power spent under the current test conditions on formation of the oxide film is equal to ~10 W/dm<sup>2</sup>. At  $V_{AC} = 0$ , the DC power spent in the tank to create the same mass of oxide is equal to  $(15 V_{DC})$  $-1.0 V_{DC}$ ) x 1.5  $A_{DC}/dm^2 = \sim 21 W/dm^2$ .



(c) 12µm (d) 12µm Fig. 4—Chromatographic test of oxide film structure.

face during anodizing in water solutions of strong acids, such as phosphoric or sulfuric. In strong acids, two processes that create the pores occur simultaneously: (1) oxide film creation, and (2) oxide film dissolution. According to the model,<sup>3</sup> the pores have a small diameter of ~150 Å. The distance between pores increases proportionally to the DC voltage applied across the process tank. A thin non-porous layer of oxide film located between the pores and the aluminum is called the "barrier layer" with unilateral conductivity.<sup>4</sup>

In our explanation, we will also employ the hypothesis that arcing takes place in the free oxygen collected in the pores of the oxide film.<sup>5-7</sup> According to this "arc-hypothesis," the pores of the oxide film are filled with molecules of free oxygen that create additional resistance to current flow in straight DC anodizing. The presence of oxygen in the pores is proved, in particular, by explosions of a mixture of oxygen and hydrogen in industrial anodizing tanks covered with a blanket of foam.<sup>8</sup> As the film thickness grows during the process, the height of the pillars of free oxygen in the pores increases, as seen over the direct current line in Fig. 3. Apparently, higher pillars of oxygen in a thicker coating would create more resistance to the flow of direct current, and would demand a higher DC voltage during a run to keep the same level of current.

This logic does not conform to practical observations in straight DC room temperature anodizing. At 1.5 App/dm<sup>2</sup>, the voltage remains practically steady and the current remains steady regardless of the coating thickness. In 15 min, a 6-micron coating will be produced; in 30 min, a 12-micron coating, and so on, with the voltage remaining unchanged at a level below 20  $V_{_{\rm DC}}$ . The apparent contradiction between the logical deduction that "DC voltage should grow," versus a practical observation "DC voltage does not grow" was resolved by the "arc-hypothesis."5 According to this hypothesis, the extra DC voltage in straight DC anodizing initializes an electrical breakdown (an arc) in the oxygen pillars in the pores, as in the diagram below the current line of Fig. 3. The arcs generate oxygen plasma that drops the resistance of the pillars to a much lower level. It is significant that this level of resistance remains constant, even as the height of the pillars increases with the thickness of the oxide. The extra DC voltage and extra DC power are spent on maintaining this plasma. As  $V_{_{AC}}$  grows, the plasma in the pores gradually vanishes, as was demonstrated in Fig. 1(a), showing the drop of  $V_{\text{DC}}$  in Area 3. Opposition to DC

flow becomes minimal when DC voltage drops to a minimum.

The second phenomenon-making the quality of colored coatings vulnerable in two-step straight DC architectural anodizing-is supported by the well-known fact9 that, when producing colored coatings, any significant delay between the first step (anodizing) and the second step (tin coloring) should be avoided in industrial production that uses a straight DC power supply. Otherwise, the quality of the final product can be seriously compromised. Moreover, if a coating dries completely after the first step, there is little chance that a nicely colored product will be made with a straight DC process. The reason for this phenomenon is simple. Plasma created in the pores is a very aggressive media. The aggressiveness of the plasma is added to the aggressiveness of the strong acid itself. Plasma catalyzes chemical reactions occurring in the pores. As a result, the pores become filled with debris made of aluminum sulfates and aluminum hydroxides-products of these reactions. Any delay between the two production steps facilitates the solidification of this debris, and reduces space in the pores otherwise available for coloring agents.

On the other hand, in the DC+AC process with a 100 percent ratio between  $V_{AC}$  (amplitude) and  $V_{DC}$ , very little plasma is left at the top of each pore. Practice shows that whether the items are allowed to dry or not, there is no difference between the quality of the coloring of DC+AC coatings.

The third phenomenon—preventing thick coatings from having colors as bright as those of coatings that are half as thick-is a 6 to 8-micron thickness limitation in large-volume, two-step architectural anodizing with straight DC. In Fig. 4, we have a chromatographic comparison of the oxide films with the same thickness produced by different processes in the same electrolyte. The chromatographic test is based on plating tin into the pores under the same conditions, changing only the duration of the process. In comparing Fig. 4(b) for 6-micron coating with Fig. 4(d) for a 12-micron coating, each picture shows a sample with four layers: (1) no coloring, (2) tin-colored for 15 sec with 12  $V_{AC}$ , (3) colored for 30 sec, (4) colored for 75 sec. The comparison shows that, contrary to common sense, in straight DC anodizing, a thicker coating that allegedly should have more free space in the pores to take a coloring agent is not as bright in color as the half-thickness coating. On the other hand, the coatings in Figs. 4(a) and (c) are about equally bright, though the coating in Fig. 4(c) is twice as thick. These two coatings were anodized with DC+AC when the presence of free oxygen in the pores in the plasma state was dramatically smaller. The volume of debris in the pores was lower as well.

## Question 2: What drives free oxygen out of the pores of oxide films?

This is a very important question that deals with the mechanism of reducing the extra DC voltage and DC power. Tests demonstrated that the additional AC voltage superimposed on DC voltage drives the plasma of free oxygen out of the pores. The question is, "How?"

Is the alternating current a factor here? For a long time we were under the impression that AC played a major role in eliminating oxygen in the pores of the oxide film. Being encouraged by the experience in electroplating, we believed that with a higher AC, the reverse current also became higher. The higher reverse current released more hydrogen in the pores. This hydrogen would neutralize the oxygen, thereby wiping away the substance that created the plasma.

Figure 1(a) refutes this hypothesis. As  $V_{AC}$  increases, the alternating current also increases. However, the AC reaches a plateau at the end of Area 1. The level of AC remains about the same within Area 2 and especially within Area 3, where the DC voltage drops considerably. Moreover, the rms value of AC in this plateau

exceeds the direct current flowing through the tank. This means that the reverse current in the beginning of the plateau was high enough to generate enough hydrogen to completely eliminate oxygen in the pores. The test did not support such a suggestion. The drop in DC voltage was negligible at the beginning of the plateau in Area 2. This indicates that it is not the growth of AC that brings about the gradual reduction of the DC voltage and DC power. All these parameters drop, but the AC remains approximately the same.

Figure 1(b) demonstrates that it is the active AC power that is responsible for the reduction of the DC voltage and for driving the oxygen out of the pores. The higher the active AC power, the lower the excessive DC power becomes. This suggests that active AC power pushes the plasma out of the pores. The plasma collapses in the electrolyte once it is pushed out of the pores. The oxygen, from which the plasma was created, returns to the atomic or molecular state. No more free oxygen remains in the pores. The presence of sufficient AC power prevents oxygen from collecting and once more creating plasma in the pores.

Figure 1 unfolds the drama of the fight between the AC and DC powers. The fight begins at a very low level of  $V_{AC}$ . In Area 1, the DC voltage across the tank does not drop at all. On the contrary,  $V_{pc}$  even increases by ~1.5 V. The barrier layer in the bottom of each pore has unilateral conductivity<sup>4</sup> that provides the barrier layer with the ability to rectify AC voltage.<sup>d</sup> We could not detect a tangible increase of the direct current caused by the additional  $V_{DC}$ that was rectified by the barrier layer. Once the alternating current reached the plateau at the end of Area 1, a slow reduction of  $V_{DC}$ began as the AC power was increasing in Area 2. It was only in Area 3, where the active AC power became high enough to begin forcefully pushing the plasma out of the pores to cause a more rapid linear drop of  $V_{_{DC}}$  versus that of Area 2. The AC plateau does not extend into Area 4, and the alternating current increases dramatically here, indicating that the anodizing process suffers a major transformation in this area.

If the process of increasing the AC power sent to the tank were reversed, the sequence of events would also reverse. The lower AC power would permit free oxygen to enter the pore and create plasma, requiring the additional DC power to maintain it. If  $V_{AC}$  reverses and is gradually reduced to zero,  $V_{DC}$  would increase by closely following the curves of Fig. 1 in the opposite direction.

### Conclusions

A power source supplying sinusoidal AC voltage of industrial frequency and DC voltage in different proportions appeared to be very helpful for discovering previously unknown facts about aluminum anodizing.

The Faraday power required to form a porous oxide film on aluminum is close to a half the total power spent in straight DC room temperature anodizing.

The other half is spent mostly in forming and maintaining oxygen plasma in the pores, making straight DC room temperature anodizing a steady-voltage-steady-current process. The plasma formed by the extra DC power fills the pores with additional debris that prevents more coloring agents from entering the pores. The brightness of the colored oxides becomes adversely affected. The same occurs if debris solidifies (*i.e.*, the oxide is partially or completely dried before coloring). This means that the quality of the final product can be harmed by the extra DC power. The extra DC power is reduced in room temperature anodizing as the AC power of industrial frequency is added to the tank. The active AC power component unclogs the pores, pushing the oxygen plasma out of the pores.

Coatings can safely be dried after the first step of architectural anodizing if they are unexposed to plasma effects. The color of the coating is of the same quality, whether it has been dried or not. Also, thicker coatings (nearly double) can be produced with the same high quality of color that could only be obtained with thinner coatings in straight DC anodizing.

In hard anodizing, even more stunning observations were made when the AC power of industrial frequency was added to the DC power. In particular, the harmful DC power sent to the tank exceeded the Faraday power by nearly threefold. Effects of AC power on hard anodizing will be described in a separate paper.

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sulfuric acid hard coating of aluminum. Since 1992, Dr. Lerner has broadened his research in hard coating to include application of the DC+AC technology to room temperature (conventional) anodizing. He has written close to 200 publications, including five books, and holds more than 20 patents.

<sup>&</sup>lt;sup>d</sup> It was mentioned above that at  $1.5A_{pc}/dm^2$ , the voltage drop across the electrolyte was ~1  $V_{pc}$ . Subtracting this voltage from the minimum level of ~8  $V_{pc}$ , we arrive at ~7  $V_{pc}$  across the anodized article. Multiplying this voltage by the current (1.5/dm<sup>2</sup>), we find that the Faraday power spent under the present test conditions on formation of the oxide film is equal to ~10 W/dm<sup>2</sup>. At  $V_{ac} = 0$ , the DC power spent in the tank to create the same mass of oxide is equal to 15  $V_{pc}$  - 1.0  $V_{pc}x 1.5 A_{pc}/dm^2 = ~21$  W/dm<sup>2</sup>.