The Future of Aluminum Anodizing in Sulfuric Acid Electrolytes

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If a linearly increasing AC power were added to the anodizing tank then the consumed DC power would linearly drop to a half of its initial value in room-temperature-anodizing with unchanged DC. The increasing AC voltage is a carrier of AC power because AC practically does not grow once it exceeded DC. The carrier of AC power should have a sinusoidal waveform. Otherwise, pollution of the industrial power net and of the environment becomes prohibitively high. Adding high AC power with the sinusoidal carrier to DC power is the future of anodizing.

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Phone: 781-444-6529 Fax: 781-449-8923 E-mail: mltomin@gis.net The year 2000 was a turning point in the 80-year-long history of 'conventional^{*} anodizing of aluminum'. It was discovered in the summer of 2000^{1, 2} that only a half of DC power sent to a tank is spent on formation of aluminum oxide. The other half generates heat in the film adversely affecting its quality.

The practical significance of this 'heat-in-film' discovery can be illustrated with the example of a 10,000A straight DC tank used for the first step of architectural anodizing. A full load of this tank consumes over 200 kW of DC electricity. The discovery revealed that only 100 kW was spent on formation of the oxide film. The other 100 kW was wasted on a) generating heat in the film, b) deteriorating film's quality and c) demanding a matching chilling capacity to throw this heat out of the tank and using close to 50 kW of additional power.

The 'heat-in-film' discovery was stumbled upon in the Tomin Corporation while measuring active power sent directly to the tank. Dr. C. Colombini³ urged to conduct this experiment using electrodynamic wattmeter for measuring the active power. The power to the tank was sent from a Continuous Mixer of DC voltage sinusoidal AC voltage⁴ (called "Cont-Mix" and marked '1' in Fig. 1).

The experiment demonstrated that the heat-generating-DC-power gradually disappears as the added AC power increases. Therefore, the DC power consumed by the tank drops by half.

Elimination of heat in the film allows the anodizer to safely increase the level of Faraday electricity forming the film. Instead of so far safe 1.5 A/dm² in straight DC conventional anodizing (that forms a 25-micron-film in 60 min) the current density can be two-three times higher at room temperature of the electrolyte in the unified anodizing process with superposition of AC voltage over DC voltage.

On the contrary, forming thick coatings with straight DC can be done only in 0°Celectrolyte (so called 'hard-coating process') with obscenely high voltages up to 100V and obscenely high heat generation in the oxide film.

The discovery of a huge excessive DC power that heats and harms coating during straight DC anodizing leaves no future for this process.

Instead, a new source should be used to power the anodizing tank. This source should send two powers: a) DC power to form the coating and b) high AC power to prevent high levels of heat to generate in the film. So, the source is a pulse-generator using AC voltage carrier of AC power with close to sinusoidal waveform.

Experimental Procedure

A simple schematic was used (see Fig. 1) for measuring active power consumption in the aluminum anodizing tank. The Cont-Mix power supply '1' has two knobs: a DC knob that controls V_{DC} (this voltage is plotted on the DC voltage vertical axes in Fig.

^c Conventional anodizing is usually conducted in water solutions of 170-g/l sulfuric acid at room temperature and can produce a 25 micron-(1 mil)-coating in one hour using up to $20 V_{DC}$.

2a). An AC knob controls the added sinusoidal V_{AC} of industrial frequency (this voltage is plotted on the AC voltage horizontal axes in Fig. 2a).

DC-meter '2' measured V_{DC} (in milliVolt) across a shunt. AC-meter '3' measured V_{AC} across the same shunt. Electromagnetic DC-voltmeter '4' measured V_{DC} across the tank. The true-root-mean-square-value (rms) tester '5' measured V_{AC} across the tank. Electrodynamic wattmeter '6' measured the total active power spent in the tank.

A standard 170-g/l sulfuric acid electrolyte at room temperature with no agitation was used for anodizing samples of aluminum alloy 6061-T6.

The experiment evolved through two stages. In Stage 1, the sent to the tank straight DC power was increased by turning DC knob of Cont-Mix '1' clock-wise until direct current reached the 1.5 A_{DC}/dm^2 level. This level of current density is habitually used in industrial straight DC anodizing. In Stage 2, the AC sinusoidal power of industrial frequency was added to the tank by turning AC knob clock-wise.

The following provision was observed during Stage 2: the direct current density through the tank (1.5 A_{DC} /dm²) was kept unchanged. If DC increased by the raised V_{AC} then DC knob would be turned counter-clock-wise to restore the 1.5 A_{DC} /dm² level.

Results

Fig. 2a and Fig. 2b demonstrate measurement results. Curve (1) of Fig. 2a shows total active power W(active) in W/dm² measured by the electrodynamic wattmeter '6' and sent to the tank. Curve (2) reflects the behavior of V_{DC} while V_{AC} increased. Curve (2) also reflects DC power in W/dm² sent to the tank. This power was calculated by the formula $W_{DC} = V_{DC} \times b_C$. Since the direct current b_C remained unchanged, Curve (2) describes both - DC power and V_{DC} with different scales. Curve (3) reflects the active AC power $W_{AC}(active)$ in W/dm² calculated by subtracting DC power from the total active power of Curve (1) ($W_{AC}(active) = W(active) - W_{DC}$).

The constant Line (4) reflects the unchanged DC (1.5 A/dm²), while Curve (5) depicts the rms value of the alternating current component.

The constant Line (6) reflects the Faraday Power needed to form oxide film and do nothing else^{1, 2}. The Faraday Power is calculated from the minimum level of DC power reached as the added sinusoidal AC power increased.

Discussion

Fig. 2a shows that AC power added to the tank would dramatically reduce the consumed DC power while direct current was kept unchanged at a level of 1.5 A_{DC}/dm^2 .

How large is this "dramatic" reduction? Let us call by "initial DC power" and "initial DC voltage" values of W_{DC} and V_{DC} that produce 1.5 A_{DC} /dm² without adding

AC power. We can discover from Fig. 2a that these initial values are 22 W_{DC}/dm^2 and 15 V correspondingly. The same figure demonstrates that the added to the tank AC power would cause DC power (and V_{DC}) drop to about a half of their initial value (11 W_{DC}/dm^2 and 7.5 V_{DC} correspondingly).

- Let us consider the following questions about the 'heat-in-film' discovery:
- 1. Which roles do both halves (the remaining and the removed one) play in straight DC anodizing?
- 2. Which half of DC power is a Joule power that heats the electrolyte?
- 3. Can the added active AC power be considered a Joule power too?
- 4. How beneficial was the removal of a half of DC power to aluminum anodizing?
- 5. Which kind of voltage should carry AC power to the anodizing tank? Sinusoidal? Non-sinusoidal? Which frequency should be chosen?

Question 1: Which roles do both halves (the remaining and the removed one) play in straight DC anodizing?

The **remaining** DC power was about 11 W/dm² at high levels of AC power. This minimum of DC power is close to the Faraday Power defined in references^{1, 2} that produces $1.5 A_{DC}/dm^2$ of flow of Faraday electricity forming about .5 micron of oxide film per minute. The Faraday Power, apparently, does not depend on the level of AC voltage and AC current. The Faraday Power is proportional to direct current. For a given level of DC (say, $1.5 A_{DC}/dm^2$) the area of Faraday Power is indicated in Fig. 2b derived from Fig. 2a. The Faraday Power area demonstrates what the remaining half of DC power does during anodizing – it forms the oxide film.

The potentially **removed** DC power is demonstrated in Fig. 2b if we turn the AC knob counter-clock-wise making AC voltage drop. We can observe how DC power gradually exceeds the level of Faraday Power. When V_{AC} and AC power dropped to zero (i.e. we returned to straight DC anodizing) the excessive DC power became as large as the Faraday Power. We arrive at a conclusion that the excessive power is that half of DC power that is removed if high AC power is added to the tank.

What does this excessive half of DC power do in straight DC anodizing? To answer this question we will use hypothesis of arcs ignited in free oxygen collected in the pores⁵⁻⁷. Pores of the oxide film are filled with molecules of free oxygen that create an impediment to the flow of Faraday electricity in straight DC anodizing. The presence of oxygen in the pores is proved, in particular, by explosions of the oxygen and hydrogen mixture in industrial anodizing tanks covered with a blanket of foam⁸. As 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 A_{DC}/dm^2 the voltage across the tank remains practically steady and the current remains steady regardless of the coating thickness. In 15 minutes, a 6-micron coating will be produced; in 30 minutes, a 12-

micron coating and so on with the voltage remaining unchanged at a level below 20 V_{DC} . The apparent contradiction between the logical deduction that "DC voltage should grow" versus a practical observation "DC voltage does not grow" was resolved if we admit⁵⁻⁷ that an arc was created in the pillar of oxygen. 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.

Therefore the excessive DC voltage and excessive DC power (that can be removed by AC power) are spent on maintaining the oxygen plasma and increasing resistance to the flow of Faraday electricity that forms the coating.

Question 2: Which half of DC power is a Joule power that heats the electrolyte?

In fact, this question deals with heat dissipation in the tank that eventually warms the electrolyte.

A half (11 W/dm²) of DC power that **remained** after high AC power was added to the tank, was spent predominantly on oxide film creation. This half is close to the Faraday Power that does not produce heat (the power is used only to form the coating). Only a small portion of the remaining half of DC power transforms into heat by direct and alternating currents flowing through the electrolyte. We can assume that the heat released in the electrolyte is about 1 W/dm² leaving 10 W/dm² for the Faraday Power^{1, 2}. Apparently, only this 1 W/dm² heat should be thrown out of the tank with the help of a chiller to keep the electrolyte temperature unchanged.

The other half (11 W/dm²) of DC power that was **removed** by the high enough AC power is spent on creating and maintaining the oxygen plasma and increasing resistance to the flow of Faraday electricity that forms the coating. Does this half generate heat? Yes, it does as measurements of heat dissipation in the electrolyte indicated. The 20-year experience of using close to forty DC power plus AC power sources for hard-coating demonstrated that we need, on average, a three times more powerful chiller for straight DC system than for the DC+AC system with the same current delivering ability. This means that the removable half of DC power is predominantly responsible for generating heat in the electrolyte during straight DC anodizing. We can conclude that the potentially removable half of the DC power is a Joule power. This power is 11 times higher than heat generated by the remaining half of DC power.

Question 3: Can the added active AC power be considered a Joule power too?

In other words, does the active AC power, that is added to the tank to reduce DC power, produce heat? As it follows from Fig. 2 and Fig. 3 the AC power increases proportionally to AC voltage reaching a rather high level equal to a half of the initial DC power. As we discovered, the AC power does the work of unclogging pores from the oxygen plasma pushing it out. Does this power also produce heat? Yes, it does but very insignificantly. The heat is generated only by alternating current flowing through the electrolyte. This means that the active AC power, predominantly, is a non-Joule power.

Question 4: How beneficial was the removal of a half of DC power to aluminum anodizing?

The removal of a half of DC power in the DC power + AC power process provides a long list of advantages. We will mention here just 5 of them:

- a) preventing coatings from "burning" and making it possible to increase current density in the tank more than 10 times,
- b) allowing the anodizer to use the same tank with the same electrolyte and with the same power supply to produce safely both thin and thick coatings,
- c) preventing the anodized articles from edge defects,
- d) allowing the coloring agents to fill more space in the pores and make the colored coatings brighter^{1, 2},
- e) bringing big savings of electrical energy, especially during anodizing thick coatings.

We will concentrate here just on **a**) and **b**) **advantages** of anodizing with DC power + DC power source.

Advantage a) preventing coatings from "burning" and making it possible to increase current density in the tank more than 10 times.

The eighty years of industrial experience proved that 1.5 A/dm² is a safe level of current density in room temperature straight DC anodizing. At the same time it was recognized that increasing current density above this safe level should be carefully avoided to escape catastrophic dissolving or as it is called "burning" the aluminum article.

On the other hand, if a half of DC power is removed by a high AC power, no plasma is left in the pores. The heat released in the tank electrolyte would drop from 11 W/dm² to the level of 1 W/dm² at 1.5 A_{DC}/dm^2 . In these conditions the current density can safely be doubled or tripled in the room-temperature electrolyte without the fear of 'burning'. The DC voltage component across the tank would increase insignificantly just to overcome the resistance of the electrolyte. It was also proved that the DC-power + AC-power process can form an oxide film close to 60 microns in 10 minutes at V_{DC} close to 20 V providing current density 12 times higher than1.5 A_{DC}/dm^2 .

Advantage b) allowing the anodizer using the same tank with the same electrolyte and with the same power supply to produce safely both - thin and thick coatings. Traditionally, in straight DC anodizing, different tanks have been used to form thin coatings and thick coatings. Thin coatings were formed in room-temperature electrolyte at voltages up to 20 V_{DC}. Thick coatings were formed at lower electrolyte temperatures using different concentration of sulfuric acid and a power supply with a much higher voltage.

The DC-power + AC-power process needs only one low-voltage power supply and have a single tank to produce thin and thick coatings. The concentration of sulfuric acid in electrolyte can be the same. Only temperature can be changed to achieve different integral colors of the coating.

Question 5: Which kind of voltage should carry AC power to the anodizing tank? Sinusoidal? Non-sinusoidal? Which frequency should be chosen?

This question appears to be nonsensical. Who cares which kind of voltage is used to carry AC power provided that it removes a half of DC power in anodizing?

It is the plant that cares about which waveform of voltage is used to carry AC power. Imagine a 10,000A-source that supplies power to the-first-step-architectural -anodizing tank. The power supply consumes over 200 kW of DC electricity at a full load of the tank. In order to remove a half of this DC power we need 100 kW of active AC power to send additionally to the tank (see Fig. 2a that demonstrates removal of a half of DC power by the increased AC power).

If the sinusoidal voltage carried this large AC power then the process of removing DC power would be harmless.

On the other hand, if 100 kW of rectangular pulses were sent into the tank, the whole electric power network of the plant would start pulsating – blinking. It can cause disaster if the anodizing system (or systems) consumes the major portion of energy that enters the plant.

Power blinking can be escaped if a much smaller level of pulsating AC power (say 10 kW instead of 100 kW) were sent to the tank. However, 10 kW of AC power may be too little to remove any DC power. The level of removed DC power in this situation would be as insignificant as it were with straight DC power supplies with a ripple.

Using AC voltage with close to sinusoid waveform as a carrier of AC power is the only practical way to drop DC power consumption in the tank to a half of its value in straight DC anodizing. As to the frequency, apparently, the best is industrial frequency of 50 - 60 Hz. Then, no additional transformation of frequency taken from the net is needed.

Conclusions

A high AC power should be sent to aluminum anodizing tank to push the oxygen plasma out of the pores and dramatically drop the consumed DC power that generates heat in the film and deteriorates its quality.

If the carrier of high AC power were non-sinusoidal voltage it would cause prohibitively high levels of pollution of the plant power net and of the environment. Pulse anodizing sources sending small levels of AC power to the tank with nonsinusoidal voltage do not cause considerable pollution. However, they do not cause any drop of DC power either and are, therefore, as ineffective as straight DC power supplies.

To escape pollution of the net and environment, the waveform of the AC voltage that carries high AC power should be close to sinusoidal.

Instead of two straight DC traditional processes ('conventional anodizing' to form thin coatings and 'hard coating' to form thick coatings) we can use a single unified anodizing process that forms both – thin and thick coatings. This 'unified anodizing process' demands a single anodizing tank having a fixed composition of electrolyte and powered from a single DC plus AC power supply. In this unified DC+AC process there is no excessive heat generation that harms the coating.

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Figure 1 - Schematic of active power measurements.



Figure 2 - Test results



Time

Figure 3 - Steady-voltage-Steady-current Process.