Effect of Additives on Faraday Power Reduction In Sulfuric Acid Anodizing of Aluminum

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DC voltage (V_{DC}) linearly drops during anodizing with the constant flow of Faraday electricity while a linearly increasing AC voltage (V_{AC}) is applied across the tank. The reached minimum of V_{DC} was used to calculate the Faraday Power that formed the oxide film and did nothing else. Farther increasing of V_{AC} would cause a non-linear drop of V_{DC} and a non-linear increase of AC power. A mysterious additive to the electrolyte used to prevent catastrophic dissolution ("burning") of the oxide film in straight DC anodizing would also mysteriously prevent the non-linear behavior of V_{DC} and AC power. This phenomenon can be used as a test and a measure of "anti-burning" efficiency of the chemical additive and also to calculate the Faraday Power more precisely.

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Phone: 781-444-6529 Fax: 781-449-8923 E-mail: mltomin@gis.net A catastrophic dissolution (so called 'burning') of aluminum article anodized in a water solution of sulfuric acid at current densities exceeding 1.5 A_{DC}/dm^{2*} twice, three times or more was a concern since the first hard anodizing process was introduced in the USA in the 1950s (so called "Martin-process"). Cooper-containing aluminum alloys belonging to 2000 series have been especially vulnerable. Soon, a chemical additive to the electrolyte was offered¹⁻⁴ with the purpose of protecting aluminum parts from 'burning'. Since then, different additives became abundant in the market leaving a potential customer puzzled which additive to choose. The best choice could be identified after years of accumulating statistical data. It would be beneficial to have an objective method of a prompt laboratory evaluation of the additive efficiency.

The 'heat-in-film' discovery of 2000^{5, 6} provides a basis for developing this method. In the described below experiment the AC voltage component was applied across the anodizing tank in addition to the DC voltage component that caused the Faraday electricity to flow and form the coating.

It was discovered that DC voltage (V_{DC}) would linearly drop during anodizing with the constant flow of Faraday electricity while a linearly increasing AC voltage (V_{AC}) is applied across the tank. The reached minimum V_{DCmin1} of linearly dropping V_{DC} can be used to identify the Faraday Power that forms the oxide film^{5, 6} and does nothing else. A higher AC voltage than V_{AC} that corresponds to V_{DCmin1} may cause a non-linear increase of AC power and farther non-linear drop of V_{DC} to another minimum level V_{Dcmin2}. The traditional anti-'burning' chemical additive to the electrolyte such as¹⁻⁴ prevented this non-linear drop to the V_{Dcmin2} level and ensured the strictly linear drop of V_{DC} and DC power as V_{AC} increased. The degree of the additional linear drop can be used as a measure of the "antiburning" efficiency of the additive and be employed both a) for a quality test of the delivered additive and b) for a periodic test of the tank electrolyte.

Experimental Procedure

A simple schematic was used (see Fig.1) for applying V_{AC} across the anodizing tank besides V_{DC} . A Continuous Mixer of DC power and sinusoidal AC power⁷ fed the tank. The mixer was called 'Cont-Mix" and marked by '1' in Fig.1. Two knobs control the mixer: a DC knob controls V_{DC} (this voltage is plotted on the DC voltage vertical axes in Fig. 2). An AC knob controls the added sinusoidal V_{AC} of industrial frequency (this voltage is plotted on the AC voltage horizontal axes in Fig. 2).

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

Aluminum samples of 6061-T6 alloy were used in this experiment. A 300 g/l water solution of sulfuric acid electrolyte (with and without the anti-'burning'-

^{*} A habitual current density used in conventional anodizing in water solution of sulfuric acid at room temperature.

additive prepared according to^{1 - 4}) was used for anodizing in room temperature electrolyte. The 300-g/l electrolyte is very aggressive and it has never been used in industrial room temperature conventional anodizing with straight DC. 170-g/l was a safe concentration used in conventional anodizing to produce oxide films up to 25-micron-thickness with 1.5 A/dm².

However, once the DC power was reduced to a half of its initial value by sending high enough AC power to the tank then twice or three times increase of current density in room-temperature anodizing can be coupled with the increase of sulfuric acid concentration to 300-g/l level.

The experiment evolved through two stages. In Stage 1, the straight DC power sent to the tank was increased by turning the DC knob clock-wise until direct current reached 3 A_{DC}/dm^2 . In Stage 2, the AC power of industrial frequency was added to the tank by turning the AC knob clock-wise.

The following provision was observed during Stage 2: the direct current density through the tank (3 A_{DC}/dm^2) was kept unchanged. If the raised AC voltage increased DC, then the DC knob would be turned counter-clock-wise to restore the 3 A_{DC}/dm^2 level.

Results

Measurement results are demonstrated for the electrolyte without the additive in Fig. 2a and with the additive - in Fig 2b. The additive was prepared according to¹⁻⁴. In both cases the initial V_{DC} level is marked directly on the V_{DC} axis where V_{AC}(rms) is zero. The next level of V_{DC} is shown beginning with V_{AC}(rms) > 3 V when V_{DC} starts linearly declining.

Fig. 2a shows that as the AC voltage component increases causing the active AC power $W_{AC}(active)$ to linearly increase (see curve (2)) then V_{DC} would drop to the V_{DCmin1} level (see curve (1)) if DC were kept unchanged at the 3 A_{DC}/dm^2 level. Besides V_{DC} , curve (1) also describes the drop of DC power calculated by multiplying V_{DC} by the constant current: $W_{DC} = V_{DC} \times 3 A_{DC}/dm^2$. On the other hand, $W_{AC}(active)$ was calculated by subtracting W_{DC} from the total active power W(active) sent to the tank and measured by wattmeter '6'. Curve of the active power W(active) is not shown in Fig. 2a, however the curve data can be calculated by summing up W_{DC} and $W_{AC}(active)$ curves. We can see that the linear increase of $W_{AC}(active)$ and the linear drop of W_{DC} ends at about 7.5 V_{AC} . Both curves behave non-linearly at V_{AC} beyond this threshold. V_{DC} non-linearly drops to V_{DCmin2} that remains constant in spite of the sharp increase of $W_{AC}(active)$.

On the contrary, we do not observe any non-linear increase of active AC power in Fig. 2b for the electrolyte with the additive. Apparently, the additive succeeded to prevent the non-linear drop of V_{DC} and non-linear increase of active AC power.

In Fig. 2b we find an additional information about the DC+AC process compared to Fig. 2a. In Fig. 2b we can see time graphics illustrating sinusoidal pulses at different ratios between the amplitude of the sinusoid and the level of V_{DC} (the amplitude was calculated by formula $V_{AC}(max) = V_{AC}(rms) \times 1.41$). Three

ratios are illustrated in Fig. 2b: ratio 0.5 : 1 for $V_{AC}(max) = 0.5 V_{DC}$ at the top of curve (1), then ratio 1 : 1 for $V_{AC}(max) = V_{DC}$ at the middle of curve (1), and at last ratio 1.5 : 1 for $V_{AC}(max) = 1.5 V_{DC}$ at the bottom of curve (1). These time graphics illustrate more vividly the dynamics of changing the waveform of sinusoidal pulses as the AC voltage component across the tank increases.

Discussion

Using DC+AC Mixer as additive tester

The experiment in the 300 g/l electrolyte without the additive in Fig. 2a demonstrated that the drop of V_{DC} occurred strictly linearly when V_{AC} (rms) increased up to 7.5 V that corresponds to about 1 : 1 ratio of the amplitude of V_{AC} to V_{DC} (compare with the location of this ratio in Fig. 2b). Consumption of the active AC power increases nonlinearly beyond 7.5 V_{AC} (rms) until this increase becomes very high at V_{AC} over 9 V_{AC} (rms).

On the other hand, anodizing in same conditions but with the additive¹⁻⁴ (see Fig. 2b) demonstrated that the strictly linear drop of V_{DC} and the linear increase of active AC power continued until 10.5 V_{AC} (rms) that corresponds to 1.5 : 1 ratio of the amplitude of V_{AC} to V_{DC} . Limitations of the Continuous DC+AC Mixer used in this experiment did not allow us to reach higher ratios of V_{AC} (max) to V_{DC} . However, if we prolong with broken lines linear dependencies of W_{DC} and W_{AC} (active) we can reach the point where these lines cross (at about 12.5 V_{AC} (rms) and 7.5 V_{DC}). The ratio between the amplitude of V_{AC} and V_{DC} at the point of crossing is close to 2.5 : 1. In other words, when the amplitude of the sinusoidal voltage component 2.5 times exceeds V_{DC} then the active AC power and the DC power in the tank become equal (at least in theory). It would be interesting to experimentally verify with a specially designed DC+AC Mixer whether the additive that we used in this experiment (or any other available additive) would still prevent non-linear events during anodizing at ratios close to 2.5 : 1.

Why does the additive behave as described?

The additive^{1 - 4} that we used in our experiment contains weak organic acids. It has always been a mystery why these weak acids when added to the water solution of strong sulfuric acid tame the catastrophic dissolution ("burning") of the anodic film in straight DC anodizing.

Now we discovered a new property of this additive – taming the non-linear behavior of V_{DC} and AC power added to the tank. This new behavior of the additive differs from the traditional preventing the "burning" of the oxide film with DC power in straight DC anodizing. What unites these two cases – they both are mysterious.

May be the weak-acid-AC-power-taming-phenomenon is another reminder that regardless of our progress in understanding the nature of anodizing we should remain humble – aluminum anodizing was and will be a constant challenge.

Calculating the Faraday Power

The notion of the Faraday Power was introduced in^{5, 6} as the minimum DC power spent just on formation of the aluminum oxide. For calculating the Faraday Power it was suggested to use the linear drop of V_{DC} while the level of sinusoidal V_{AC} applied across the tank increased provided that the level of direct current was kept the same. The reached minimum of V_{DC} (close to 10 V - see Fig. 2a) multiplied by $3 A_{DC}/dm^2$ would yield the minimum DC power 30 W/dm² that was considered to be close to the Faraday Power. We would arrive at the Faraday Power if we deducted from this minimum the power spent on heating the electrolyte by flowing direct current. If we assume that the V_{DC} drop across the electrolyte at $3 A_{DC}/dm^2$ were close to 1 V (say, 0.75 V) then the Faraday Power would be close to 30 W/dm² - 0.75 V_{DC} x $3 A_{DC}/dm^2 = ~28 W_{DC}/dm^2$.

On the other hand, we can continue the linear drop of V_{DC} with a broken line to meet with the broken line continuation of the increasing active AC power in Fig. 2a and Fig. 2b. The point of crossing corresponds to approximately 7.5 V_{DC} in both cases - with and without the additive. This information allows us to more precisely calculate the Faraday Power needed to form the coating at 3 A_{DC}/dm² in 300-g/l electrolyte. We assumed that the V_{DC} drop across the electrolyte at this level of current density equals 0.75 V that reduces the 7.5 V_{DC} minimum to the level of 6.75 V_{DC}. Then, the Faraday Power will be close to 6.75 V_{DC} x 3 A_{DC}/dm² = ~ 20 W_{DC}/dm² or about 30% lower than the level 28 W_{DC}/dm² that we defined using the minimum V_{DC} in Fig. 2a with no additive. This 20 W_{DC}/dm² Faraday Power will form about 1 micron of oxide film per minute (or 50 microns per hour) in the described above conditions.

Straight DC anodizing can not be safely conducted at room temperature with $3 A_{DC}/dm^2$ in 300 g/l electrolyte. Industrial practice accepted 1.5 A_{DC}/dm^2 and the 170-g/l electrolyte at room temperature as a safe straight DC process.

Anodizing thick coatings

To reach 3 A_{DC}/dm^2 in the 300-g/l electrolyte in straight DC process the electrolyte temperature should be dropped to 0°C (this process was called 'hard coating'). Hard coating demands 40 V_{DC}. The total DC power spent in the tank equals 40 V_{DC} x 3 A_{DC}/dm^2 = 120 W_{DC}/dm² or 6 times higher than the Faraday Power. We will address reasons why DC power skyrocketed in straight DC hard coating in a separate publication.

Ultra-low-voltage unified anodizing process

Test results of Fig. 2a and Fig. 2b discussed above, in fact, demonstrate a new ultra-low-voltage unified anodizing process that can be conducted at below 10 V_{DC} in a single tank. The composition of the electrolyte is kept the same regardless of its temperature. Lower temperatures are used to get different shades of integral color of the coating. This process uses a generator of sinusoidal pulses that differs from the prior art by the option of using much higher ratios of the amplitude of AC voltage to DC voltage than the 1:1 ratio introduced in the late $1970s^{6-10}$ and perfected in the $1990s^{11}$. The unified process anodizes

all aluminum alloys in the wide range of thickness and uses DC power close to the Faraday Power spent on oxide film formation if the electrolyte contains an additive such as^{1 - 4}. Without the additive, the 1:1 ration secures safe anodizing that was proved by a decade of industrial experience.

Conclusions

A device for testing the efficiency of anti-'burning' additives to the electrolyte is offered. The device is based on the ability of properly manufactured additives to guarantee linear reduction of the DC voltage component across the tank while the sinusoidal AC voltage component is increased.

A more precise methodology of calculating the Faraday Power that forms the oxide film is based on extrapolating the linear reduction of V_{DC} .

A unified anodizing process for any aluminum alloy and for wide range of thickness is feasible. This process uses generators of sinusoidal voltage pulses with the DC voltage component below 10V for 1.5 A/dm². The ten times higher current densities (and more) can be achieved with DC voltage component not exceeding 20 V.

No additive is needed in this process if the ratio between the amplitude of V_{AC} and V_{DC} is close to 1 :1.

An additive is needed if the ratio exceeds 1:1 providing the opportunity to reach lower levels of DC power consumption that are closer to the Faraday Power.

References

- 1. P. Sanford, U.S. Patent 2,743,221, (1956).
- 2. J. Franklin, et al., U.S. Patent 2,897,125, (1959).
- 3. J. Franklin, et al., U.S. Patent 2,905,600, (1959).
- 4. J. Franklin, et al., U.S. Patent 2,977,294, (1961).
- 5. M. Lerner, Proceedings of AESF SUR/FIN 2001 Conference, Light Metals Section, June 25-28, Nashville, Tennessee (2001)
- 6. M. Lerner, *Plating and Surface Finishing*, February (2002).
- 7. M. Lerner, B. Fruzstajer, U.S. Patent 4,170,739 (1979).
- 8. M. Lerner, J. Morse, U.S. Patent 4,089,756, (1978).
- 9. M. Lerner, J. Morse, U.S. Patent 4,133,725, (1979).
- 10. M. Lerner, J. Morse, *Proceedings of 67th AESF Annual Technical Conference, Milwaukee ,WI*, June, (1980) (SUR/FIN[®] '80, Section E).
- 11.M. Lerner, U.S. Patent 5,620,582 (1997).



Figure 1 - Schematic of active power measurements.



