Light Metals Finishing

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Pulse Anodizing of Aluminum: The Recovery Effect

Control of heat produced and efficient dispersion during anodizing are very important process aspects that define the technical properties of an oxide coating.

If the time between pulse conditions is sufficiently long, pulse anodizing allows utilization of the "recovery effect." When a voltage is abruptly reduced, current will fall to low values, and after a time readjust to the new conditions.[1] During this "recovery," heat is given time to escape the oxide film.[2]

Before going into pulse anodizing details, let's look at the options for designing pulse conditions. Just like metal plating, the current/voltage design can be unipolar or bipolar.

Options for Conditions

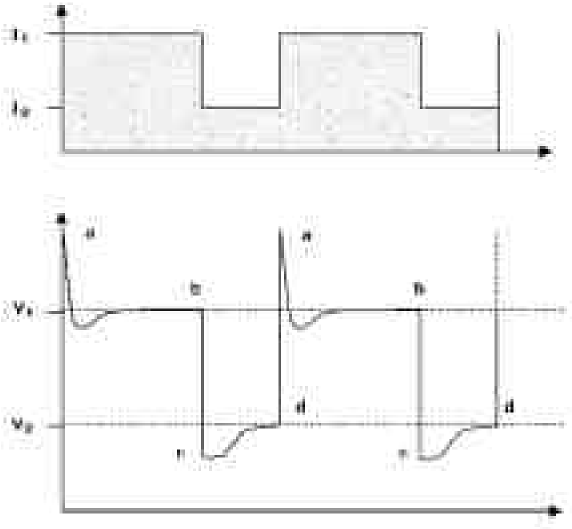
During unipolar conditions (anodic), the time between the pulses must be long enough to ensure that the capacitive effects of the barrier layer are not distorting the pulse design applied by the rectifier.

It is important to differentiate between the pulse design delivered by the rectification unit and the design that is experienced by the electrochemical processes. This is not necessarily a 1:1 transition.[3] Charging and discharging of an electrochemical process is different from conditions related to charging and discharging within an electronic component rectifier.

Because aluminum oxide is an efficient capacitor, pulse periods less than one sec must be used with caution, and if applied, the electrochemical system must be adjusted accordingly.

In the anodic period, the goal is to produce aluminum oxide. If we reverse the polarity of the current or voltage to cathodic conditions, hydrogen is produced. Naturally, the gas that is produced at the bottom of the pores must escape, thereby, providing an additional mechanism of dispersing heat generated during the previous anodic period.

The oxide structure, which is the dimension of each hexagonal unit cell, depends on the processing conditions. Cell diameter, the size of a pore, and thickness of the "barrier layer" change with the formation voltage, which is a value that must be reached before oxide formation will occur.



Voltage/current relation during anodizing.

During low-temperature, low-acid concentration, or high current density, the result is formation of large, hexagonal unit cells, resulting in a more compact oxide structure.[1]

For now, let's focus on the current density and the oxide structure (see table). The thickness of the barrier layer is calculated by assuming an increase corresponding to 1.15 nm/V. The value is typically between 1.0 nm/V and the theoretical maximum of 1.45 nm/V.[1] As current density increases, the diameter of each hexagonal unit cell, the pore diameter, and the thickness also increase.

DC Anodizing in 15% w/w Sulfuric Acit at 20°C[1]

Current	*Forming*		*Diameter*	
Density, A/dm²	*Voltage, V*	*Pore, nm*	*Cell, nm*	*Barrier, nm*
1	14.5	14.5	40	16.7
2.5	17.8	16	46	20.5
5	19.6	18	53.5	22.5
8	23.5	21.5	58.5	27.0

When the anodizing condition suddenly changes from 1 A/dm² to 5 A/dm², the production of Joule's energy increases almost seven times, from 14.5 J/dm²/sec to 98 J/dm²/sec.

In addition, the thickness of the barrier layer increases approximately 33 percent, from 16.7 nm to 22.5 nm. The cell diameter and the pore diameter also become larger.

The degree of utilizing the recovery effect is closely related to the time during a transition from high current to lower current (see figure). The measured response during such a change in anodizing conditions must be explained within our basic understanding of aluminum oxide formation. It is a balance between electrolytic formation of oxide and chemical dissolution of formed oxide, the latter being assisted by the applied electrical field. Recalling Le Châtelier's principle, this balance can be shifted: *When a stress is applied to a system at equilibrium, the position of the equilibrium tends to shift in such a direction as to diminish or relieve that stress.*

Assuming anodizing at 5 A/dm² under steady-state conditions, the oxide structure is as shown in the table. At some point, the applied current is changed to 1 A/dm² (b in figure), and by doing so a voltage drop will appear.

The thickness of the barrier layer is much too thick for steady-state anodizing at this lower current density, however. By reducing the current, the balance in favor of oxide formation is shifted toward oxide dissolution.

Gradually, the thickness of the barrier layer is reduced by field-assisted dissolution and reaches a minimum value (c in figure), after which the conditions at the bottom of the pore are slowly shifted back toward a balance in favor of oxide formation. Gradually, the voltage stabilizes at a level corresponding to the applied current (d in figure). The dimensional structure of each hexagonal cell produced is shown in the table.

During the transition from b to d, no heat (or only very small amounts) is produced, therefore, the energy produced during the previous pulse period has time to escape the porous oxide structure.

After conditions are stabilized to a constant voltage at an applied 1 A/dm^2, the current is increased to 5 A/dm^2. Naturally, the voltage will increase until it reaches a maximum (a in figure). After maximum, it gradually decreases and oscillates toward a stabilized level corresponding to the applied current density, just like the movement of a metal spring after being stretched and freely attaining relaxation equilibrium.

When the current is increased to 5 A/dm^2, the electrochemical conditions are similar to the first 10–20 sec of anodizing under conventional DC conditions. First, a barrier layer is formed, and as it gradually increases in thickness, so does the voltage. After reaching a critical thickness, a porous structure is formed, and gradually, the balance between formation and dissolution is established. The transition from barrier layer formation toward porous formation results in a voltage decrease, which gradually reaches steady-state conditions, and the voltage becomes stable.

The transition from b to d in the figure takes time. Depending on the alloy anodized, electrolyte chemistry, and pulse design, it can vary from a few sec to more than 30 sec. Typically, the transition time is from 15–25 sec when anodizing in sulfuric acid.

During a period with low current density, the growth of the oxide film is small. It is during the pulse conditions that compact oxide is formed at a high rate. When the duty cycle (γ in Eq.1) is 75 percent or higher, thickness growth is “ON” during most of the total processing time.

If the overall formation must be high, and the recovery effect utilized, the base pulse design should be 50–70 sec with high current, followed by 15–25 sec at low current.

Compared to pulse plating, where the durations of current are in the millisecond range, pulse anodizing is a completely different ball game. From an equipment point of view, this is an important advantage. Not the only one, but important, none the less.

The requirements and investment in a pulse rectification unit cannot be compared to pulse plating rectifiers. Actually, at low costs, many DC anodizing rectifiers can be modified and turned into pulse units, and by adding an appropriate programming unit, equipment should no longer be a barrier. ***P&SF***

References

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3. J.C. Puippe and F. Leaman, *Theory and Practice of Pulse Plating*, AESF, 1986.