

Characterization of Anodic Oxide Films on Titanium Formed by Transient Current/Voltage Application

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An electrolytic capacitor requires the anode to be covered by a film with high dielectric permittivity that does not pass anodic current and that can withstand a relatively high electric field. Commercial electrolytic capacitors are made of aluminum or tantalum (dielectric constants: 7.5 – 28)¹. Titanium offers potential advantages due to its much higher dielectric constant (up to 150),² lower cost and lower density. However, anodic films on titanium are known to incorporate defects that cause excessive leakage current and therefore have not been applied as capacitors.³ We characterize here titanium oxide films, formed through the application of various transients of current and voltage, focusing primarily on the leakage current and the oxide microscopic texture.

Anodic films were formed on high purity (99.999%) titanium foils using a high voltage bipolar power supply set to a current limit, typically corresponding to 10 mA/cm², and a voltage limit, typically 500 V. The anode substrate was electropolished prior to anodization.⁴ The cathode was a titanium foil. The electrolyte was 0.15 M phosphoric acid. Anodic leakage current and capacitance were measured.

A typical anodization cycle (Fig.1) was initially current limited until the pre-set maximal voltage was reached, whereupon the current would decrease to its near steady state leakage current. If the maximum voltage was set above 200V, then either silicone adhesive or a masking tape was applied at the air/electrolyte interface of the anode to prevent premature breakdown of the oxide. This also provided a consistent area of the electrode in the solution.

Scratching the titanium anode surface with various metals indicated the effect of impurities on the oxide: scratches of gold and copper increased the leakage current by a factor of about 30, while scratches of titanium and zinc had nearly no effect.

Tests involving the reapplication of voltage and current to previously anodized samples indicated that samples anodized above 15V required significant current to be reapplied before the previous anodization voltage was restored, while samples anodized below 15 volts did not require any additional anodizing current. The application of a higher current density during initial anodization led to a smaller current density that had to be reapplied upon re-anodization.

Anodization experiments involving pulsed current were carried out (Fig. 2). A typical pulse train involved square current pulses, with amplitude of 0 to 20 mA/cm² and a 20 sec period. Varying amplitudes and periodicity of pulses were explored, as well as pulses that involved a cathodic component. All experiments were run with the same total amount of charge. The pulsing did not reduce the leakage current, but showed that the oxide growth was not affected by the dynamics of the pulsing.

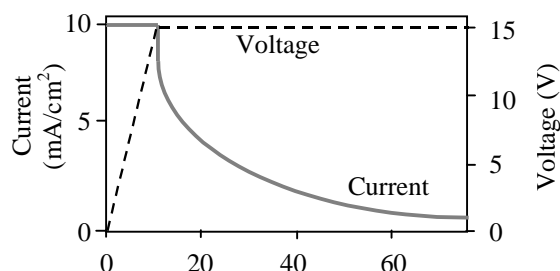


Fig. 1: Typical current (solid) and voltage (dashed) response to current and voltage limits (here, 10 mA/cm² and 15V) in anodization.

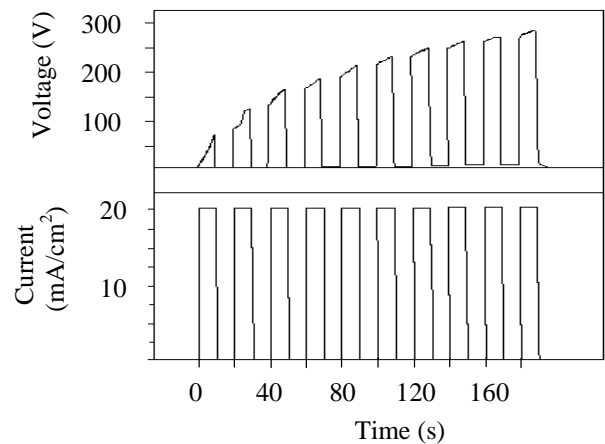


Fig. 2: Voltage (top) and current (bottom) pulse trains during titanium anodization

References:

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