

**Recent advances on the influence of microstructural characteristics
on corrosion resistance in H₂SO₄ of anodized titanium**

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ABSTRACT

Commercially pure titanium has been anodized with the use of a pulsed signal in unipolar regime, with 25 % of anodic contribution at low frequency (20 Hz). This anodizing regime can effectively enhance thickness and crystallinity of the barrier region directly in contact with the metallic substrate. The latter condition will be particularly advantageous for corrosion resistance enhancement in strong reducing acidic environment, as concentrated hot sulfuric acid (10 %v/v at 60 °C). Corrosion response has been investigated through the use of Electrochemical Impedance Spectroscopy (EIS) and results compared with weight-loss tests and Linear Polarization Resistance (LPR). The higher degree of crystallinity of the coating, in the interfacial region, will be found to provide an effective barrier against proton diffusion thus retarding debonding of the oxide promoted by hydrogen evolution reaction (HER).

Keywords: PEO, EELS, acid corrosion, EIS, titanium, anodize.

INTRODUCTION

Industrial usage of Plasma Electrolytic Oxidation (PEO) has grown consistently in recent years, thanks to the improved characteristics imparted to the oxide film in terms of surface adhesion, hardness, crystallinity, uniformity, and corrosion resistance. The metallic substrate is not subjected to elevated temperature and the overall equipment complexity is relatively simple, making the technique a good candidate for surface functionalization. In PEO treatments, high voltages are employed ($\sim 150\text{-}750\text{ V}^{\dagger}$) allowing for the formation of an insulating, or at least semiconductive, oxide layer that's limits ion transport responsible for the initial coating growth. Beyond the spark voltage (prerequisite to enter the PEO regime) oxidation does not occur only as the result of a continuous flow of ions but rather it takes place after the cooling of a plasma discharge. This makes a PEO coating particularly affected by the heat developed during the plasma emission, allowing to obtain high hardness according to the abundant amount of crystalline phase developed. It is possible to estimate PEO on Ti as a process with a technology readiness level (TRL) $\sim 4\text{-}6$, indicating the need of several effort to consolidate its industrial application. Ti is abundantly used in many fields like aerospace where the metal is mainly employed in turbine components. A PEO coating may be strategic for this application as the high thickness combined with the relatively high porosity results in enhanced thermal barrier properties. Titanium is also used in many car components: valves, rods and turbocharge rotor are an example of possible applications. Here PEO can be beneficial to enhance overall surface properties like corrosion resistance and anti-galling. From a morphological point of view PEO coatings can be described according to a double layer structure, i.e., a porous outer layer mainly imparting thickness, wear and abrasion properties and a barrier layer responsible for the corrosion resistance and substrate isolation. Recently a detailed stoichiometric investigation² of PEO barrier layers on Ti was proposed for both PEO in direct current and pulsed regime. It was shown how the application of a DC field allows to retain the peculiar structure assumed by the natural oxide layer, i.e.: a first layer in contact with the metal composed of TiO (Ti^{2+}) followed by Ti_2O_3 separating the former by a well developed TiO_2 (Ti^{4+}) component.

The use of a pulsed signal instead was found to favor oxidative conditions almost eliminating the TiO component (responsible for metallic conductivity) enhancing the formation of $\text{Ti}^{3+}/\text{Ti}^{4+}$ bearing oxide phases. Keeping this in mind the present research wants to correlate the barrier layer stoichiometry and microstructure, investigated through electron energy loss spectroscopy (EELS), to the response of Ti oxide towards a harsh environment commonly encountered during metal pickling operations: 10 %v/v sulfuric acid at 60 °C.

EXPERIMENTAL PROCEDURE

Metal coupons with size $10 \times 10 \times 1.6\text{ mm}^3$ were sheared from a Ti grade 2 plate. PEO treatment was performed in a 1 L vessel containing a solution of 0.5 M sulfuric acid. A cylindrical activated Ti net was used as counter electrode considering a radius of 50 mm. Conversion treatment was performed in potential-control until a final voltage of 160 V was reached through a ramp with constant slope of 0.5 V/s (total treatment time of 320 s) considering a duty cycle (unipolar) composed by 25 % of anodic polarization and 75 % of rest (no polarization applied at all) repeated at 20 Hz.

After the anodization of the samples, a Focused Ion Beam (FIB) Zeiss NVision 40[†] was used to mill and extract an electron transparent sample ($\sim 100\text{ nm}$ thickness) for TEM analysis. Then, the phase distribution was investigated with EELS using a FEI Titan[‡] 80-300 microscope, operated at 300 keV with a field emission electron gun equipped with an electron monochromator, providing an overall energy resolution down to 0.11 eV. EELS spectra were extracted according to a in house program developed in Python environment with the help of Hyperspy³, details regarding the program can be found elsewhere ².

[†] Trade Name

[‡] Trade Name

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All the electrochemical tests were performed using a Metrohm Autolab PGSTAT[§] equipped with a FRA32M module for Electrochemical Impedance Spectroscopy (EIS) using a standard three-electrode cell with a KCl saturated silver/silver chloride (SSC) reference electrode and an AMEL^{**} Pt counter electrode in a solution of 10 %v/v sulfuric acid kept at 60 °C. All tests were repeated three times to confirm the quality of the results. EIS analysis were performed at the corrosion potential (E_{corr}) considering a sinusoidal input voltage with amplitude of 10 mV_{rms} applied in a frequency window between 10⁻²-10⁵ Hz and collecting 10 points per decade of frequency.

Linear Polarization Resistance (LPR) was performed after each impedance test polarizing the electrode ± 20 mV from E_{corr} according to a scan rate of 10 mV/min. Weight-loss was evaluated according to immersion for 24 h in a solution of 10 %v/v H₂SO₄ at 60 °C using a Mettler-Toledo MS105^{††} balance with a resolution of 10⁻⁵ g.

RESULTS

Figure 1 shows the bright-field overview of the TEM lamella after FIB preparation. The overall oxide thickness can be estimated to be around 3.2 μm , in line with common thickness values obtained on Ti oxide coatings synthesized in sulfuric acid. In fact, it is accepted that the PEO process is less effective on Ti with respect to other valve-like metals like Al or Mg. The reason derives from the semiconductive nature of TiO₂ (and relative sub-oxide) not allowing the formation of intense internal electric field as the ones established in Al₂O₃ or MgO, which are both important insulators. As a consequence, lower thicknesses are generally achieved on Ti, however with the possibility of exploiting its outstanding stability towards several harsh environments.

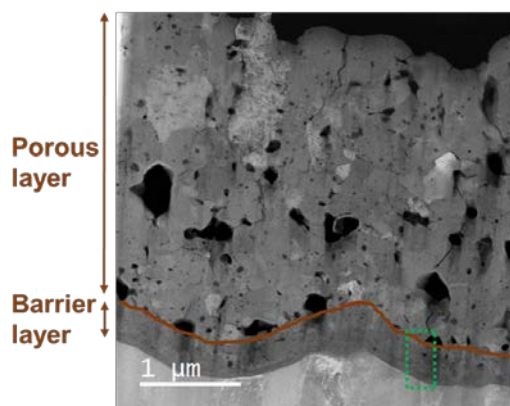


Figure 1: bright-field oxide overview with barrier and porous layer distinction. The green box outlines the region of interest (ROI) barrier layer portion analyzed by EELS

EELS analyses were performed on the barrier layer region and displayed in the form of component map where each component was identified with a color assigned to a particular oxide structure as highlighted in Table 1.

Table 1: color code assigned to structures present in the barrier layer region

Color	Green	Yellow	Purple	Gray	Black	Light blue
Structure	Ti ₂ O ₃	Anatase	Rutile	titanium	Hole	Mix Ti ³⁺ /Ti ⁴⁺

[§] Trade Name

^{**} Trade Name

^{††} Trade Name

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