Effect of the voltage pulse frequency on the structure of TiO$_2$ coatings grown by plasma electrolytic oxidation

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Abstract. Plasma Electrolytic Oxidation (PEO) is used to synthesize titanium dioxide (TiO$_2$) ceramic coatings with the appropriate selection of an electrolyte. The dimension of the microcavities and the particle size at the surface can be controlled through the pulse frequency of the voltage that is applied between the electrodes. The change of surface morphology can increase the surface area-to-volume ratio. In this work, PEO of an ASME SB-265 titanium substrate (20×20×1mm) was made in a water solution containing 8g/L Na$_3$PO$_4$ and 0.4g/L NaOH. Hence, the coatings were fabricated using voltage pulses of 340V for 10 minutes with a 10% duty cycle and frequencies of 1000, 1500 and 2000Hz. According to the X-ray diffractograms of the obtained samples, the sintering process at 500°C during 1 hour generated Anatase titanium dioxide porous coatings. The grain size decreased approximately from 29nm for 1000 and 1500Hz pulse frequencies until 21nm for 2000Hz. On the other hand, from the micrographs of scanning electron microscopy was possible to see the uniform formation of the micro-cavities with the largest diameter, 900nm, for the lowest frequency value used in PEO.

1. Introduction
Plasma Electrolytic Oxidation (PEO) causes surface modifications of metal substrates and alloys, in order to produce ceramic coatings of high hardness, greater surface area and better tribological properties of the substrate [1]. This technique is environmentally friendly and widely used in the aerospace industry, biomedical implants and in wastewater treatment [2,3]. During the PEO process, the characteristics of the micro-discharges generated in the electrode surface change according to the voltage pulse frequency or the duty cycle; for this reason, these growth parameters are important in defining the structure and morphology of the oxide layer [4], specially the size and shape of the micro-cavities [5-6].

2. Materials and methods
2.1. Preparation of substrates and TiO$_2$ coatings growth
Titanium sheets, 99% purity grade 2 (ASME SB-265), with dimensions 20×20×1mm was used as electrode-substrate in this work. Before PEO, the plates were polished with 800 and 1000 grit SiC sandpapers successively and subsequently cleaned by ultrasonic bath (BRANSON 1510) in distilled water for 30 minutes [6]. A stainless steel chamber cooled with water was used for containing the electrolyte, an aqueous solution of 8g Na$_3$PO$_4$ with addition of 0.4g NaOH in 1L of distilled water. PEO process was carried out using a switching power source, output voltage of 340V. The coatings were made using three voltage pulse frequencies: 1000, 1500 and 2000Hz [6], with a 10% duty cycle for 10 minutes. The sintering treatment of the samples was performed at 500°C for one hour [7].

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2.2. Characterization of TiO$_2$ coatings

The composition of the coatings was studied using grazing-incidence X-ray diffraction in parallel beam geometry with an X-ray diffractometer (XBruker D8-Advance, Colombia), that was operated at 40kV and 40mA, with an X-ray source emitting Cu Kα radiation. The scans were acquired at 2θ range from 20° to 60° [8]. Pictures of the surface of the samples were taken using a Scanning Electron Microscopy (SEM, JEOL JSM-6390LV, México and ZEISS EVO MA 10 SEM, Colombia) and the roughness was measured with a contact-mode Atomic Force Microscope (AFM, CP Hitachi AFM5100N AFM-C).

3. Results and discussion

3.1. Characterization of TiO$_2$ coatings

A feature of PEO is the formation of specific surface structures as metastable phases under extreme conditions of pressure and temperature; the interaction phenomena that occur at a first stage of ionization in the discharge area, gives rise to the dissociation of compounds, generating discharges that occur in intervals of time less than 10$^{-6}$ s. At a second stage of condensation there is a temperature drop of about 10$^8$K/s and the plasma interaction between the electrode-substrate and the electrolyte components yield oxides and other compounds that are melt-quenched at high-temperature on the substrate [9].

The types of spark/arc micro-discharges are observed in the Figures 1 and 2; a vigorous gas evolution after the onset of the treatment system accompanies the whole process. Applying voltages pulses from the switching power supply between the electrodes, in the first moments a conventional anodizing appears [9] with a green-violet pattern on the substrate as shown in the Figure 1. When the voltage is increased until the rupture tension, white sparks/arc with high spatial density are produced as seen in the Figure 2 [8,10].

![Figure 1. Formation by PEO of green-violet area due to conventional anodizing.](image1)

![Figure 2. Formation by PEO of fine white sparks during TiO$_2$ superficial coating.](image2)

The X-ray diffraction patterns from the coatings are depicted in the Figures 3, 4 and 5; it can be seen that immediately after PEO all the coatings with the 10% duty cycle are amorphous phase material, possibly containing phosphorus. The peaks in diffractograms related to Anatase TiO$_2$ nanocrystals are visible for the coatings sintered at 500°C; the corresponding average particle sizes were determined by the Scherrer equation (1):

$$T = \frac{K \lambda}{d \cos(\theta)}$$  \hspace{1cm} (1)

Where $T$ is the crystallite mean size, $K$ the shape factor usually equal to 0.9, $\lambda$ the X-ray wavelength (0.154nm), $d$ is the full width at half maximum of the peak at 2θ≈25.4° and $\theta$ the relative Bragg angle. In Table 1, the average particle sizes corresponding to Anatase TiO$_2$ nanocrystals are reported for the
used voltage pulses frequencies; the minimum average crystal size, $20.71\pm 0.03\text{nm}$, was obtained with the highest frequency, while a size of $29\text{nm}$ approximately with the others frequencies.

| Frequency (Hz) | Duty cycle (%) | Average size (nm) |
|---------------|---------------|-------------------|
| 1000          |               | 29.30±0.01        |
| 1500          | 10           | 29.47±0.02        |
| 2000          |               | 20.71±0.03        |

**Table 1.** Particle size of nanocrystals in TiO$_2$ coatings grown by PEO on Ti substrates using voltage pulses frequencies of 1000, 1500, and 2000Hz at 10% duty cycle and sintering temperature of 500°C.

**Figure 3.** X-ray diffractograms of the TiO$_2$ coatings grown by PEO with 10% duty cycle, sintering process at 500°C and voltage pulse frequency of 1000Hz.

**Figure 4.** X-ray diffractograms of the TiO$_2$ coatings grown by PEO with 10% duty cycle, sintering process at 500°C and voltage pulse frequency of 1500Hz.

**Figure 5.** X-ray diffractograms of the TiO$_2$ coatings grown by PEO with 10% duty cycle, sintering process at 500°C and voltage pulse frequency of 2000Hz.

### 3.2. Surface morphology of the TiO$_2$ coatings

The elemental composition of the TiO$_2$ coatings samples was analyzed by Energy Dispersive Spectroscopy (EDS); Table 2 shows data related to the incorporation of phosphorous (P) and carbon (C) into the titanium oxide coatings, which can be centers of impurities. These species enter into the discharge channels from the electrolyte during PEO process [4]. The amount of P decreases with increasing voltage pulse frequency because the higher energy pulses put more elements of the electrolyte into the coating.

In the Figures 6, 7, and 8, from the SEM micrographs it can be observed that PEO generated micro-cavities on the Ti sheet surface. Uniform microcapsules with average pore diameter of $632\text{nm}$ for 1000Hz, $406\text{nm}$ for 1500Hz and $417\text{nm}$ for 2000Hz [10]; these sizes were estimated over an area of $10\times10\mu\text{m}^2$ approximately [10]. The pore surface density, number of micro-cavities per unit area, was $0.15\mu\text{m}^{-2}$ for 1000Hz, $0.27\mu\text{m}^{-2}$ for 1500Hz and $0.32\mu\text{m}^{-2}$ for 2000Hz. The size of the micro-pores varied between 295 and 1184nm with the voltage pulse frequency of 1000Hz in PEO, 60% of the micro-pores diameter between 295 and 500nm, 20% between 500 and 800nm and 20% between 800 and 1184nm; while for 1500Hz frequency this size varied between 202 and 983nm as follows: 85% between 202 and 500nm, 11% between 500 and 800nm and only 4% with a diameter greater than 800nm; Finally, for 2000Hz the size varied between 215 and 681nm as follows: 72% between 202 and 500nm and 28% between 500 and 800nm [11]. In this way, it is possible to deduce that the size of the micro-pores become
smaller with increasing voltage pulse frequency in the PEO, thus the frequency controls the micro-discharges power through pulse activation time [6,12].

Table 2. Surface composition by EDS and average micro-cavity diameter of samples grown by PEO (voltage pulse frequency with 10% duty cycle and 500°C sintering temperature).

| Voltage pulse frequency (Hz) | Atoms (%) | Minimum diameter (nm) | Maximal diameter (nm) |
|-----------------------------|-----------|-----------------------|-----------------------|
|                             | Ti        | O                     | P                     | C         |                               |                               |
| 1000                        | 21.36     | 72.29                 | 6.35                  | --       | 295                             | 1184                           |
| 1500                        | 22.82     | 70.22                 | 4.44                  | 2.51     | 202                             | 983                            |
| 2000                        | 16.69     | 67.95                 | 4.41                  | 7.31     | 215                             | 743                            |

Figure 6. SEM micrographs of TiO₂ coatings grown by PEO with voltage pulse frequency of 1000Hz, 10% duty cycle and 500°C sintering temperature.

Figure 7. SEM micrographs of TiO₂ coatings grown by PEO with voltage pulse frequency of 1500Hz, 10% duty cycle and 500°C sintering temperature.

Figure 8. SEM micrographs of TiO₂ coatings grown by PEO with voltage pulse frequency of 2000Hz, 10% duty cycle and 500°C sintering temperature.

The topographic roughness images of 10×10μm² of the surface of the coatings are illustrated in the Figures 9, 10 and 11. From the analysis of these micrographs the roughness parameters were registered in the Table 3; where Ra is the arithmetic average of the peak heights and valleys from the mean line, Rms the root mean squared value of these profile height deviations and Rz is the average of the distance from the five highest peaks to the five lowest valleys. It can be seen that the increase of the frequency generated a rise in the micro-cavities depth. In addition, the formation of the oxide layer is observed with perpendicularly oriented pores to the metal surface.

Table 3. Roughness of the TiO₂ coatings from AFM micrographs. Growths by PEO at 10% duty cycle and 500°C sintering temperature.

| Voltage pulse frequency in the PEO (Hz) | Ra (nm) | Rz (nm) | Rms (nm) |
|----------------------------------------|---------|---------|----------|
| 1000                                   | 73      | 393     | 89       |
| 1500                                   | 95      | 494     | 235      |
| 2000                                   | 116     | 620     | 144      |
4. Conclusion

TiO$_2$ coatings were achieved by the PEO technique using a switching power supply with pulses of 340V, with frequencies of 1000, 1500 and 2000Hz and 10% duty cycle, on ASME SB-265 titanium sheets using an aqueous solution of Na$_3$PO$_4$ and NaOH as electrolyte. The X-ray diffractograms showed the formation of Anatase TiO$_2$ nanocrystals after sintering process at 500°C for 1h. In the oxide layer, the grain size of these nanocrystals decreased approximately from 29nm for 1000 and 1500Hz voltage pulse frequencies in the PEO to 21nm for 2000Hz.

From SEM micrographs, the micro-cavities size diminished when the voltage pulse frequency was increased. The elemental map showed a uniform distribution of the phosphorus and oxygen on the substrate. From AFM micrographs, the roughness of the TiO$_2$ coatings increased in function of the voltage pulse frequency.

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