Formation of TiO₂ nanostructure by plasma electrolytic oxidation for Cr(VI) reduction

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Abstract. Plasma electrolytic oxidation (PEO) is an environmentally friendly technique that allows the growth of ceramic coatings without organic solvents and non-toxic residues. This method was applied to ASME SB-265 titanium (Ti) plates (2×2×0.1cm) using voltage pulses from a switching power supply (340 V) for 10 minutes at frequency of 1000Hz changing duty cycle at 10, 60 and 90% and the electrolytes were Na₃PO₄ and NaOH. The treated sheets surfaces were analysed by X-ray diffraction and scanning electron microscopy. According to the diffractograms, the duty cycle increase produces amorphous TiO₂ coating on Ti sheets and the thickness increases. After sintering at 900°C during 1 hour, the 10% duty cycle generated a combination of anatase and rutile phases at the sample surface with weight percentages of 13.3 and 86.6% and particle sizes of 32.461±0.009nm and 141.14±0.03 nm, respectively. With this sample, the total reduction of hexavalent chromium was reached at 50 minutes for 1 ppm solution. This photocatalytic activity was measured following the colorimetric method ASTM-3500-Cr B.

1. Introduction
The surface modification of metal substrates and alloys using plasma electrolytic oxidation (PEO) for the formation of ceramic coatings with high hardness and large surface area is an environmentally friendly technique, simple for the porous material production and low-cost. In PEO, microdischarges are produced by high potential difference between the metal sheet and another electrode and modifying the frequency or duty cycle of the voltage pulses, which are important parameters for determining the growth characteristics and morphology of the oxide layer [1]. Titanium dioxide (TiO₂) is a semiconductor widely studied due to its large variety of applications such as environmental purification, sewage treatment, metal reduction, biomedical implants and others. TiO₂ has three crystallographic phases: rutile, anatase and brookite, which play an important role according to applications [2,3]. The TiO₂ photocatalytic activity is a solution to attack environmental problems related to contamination by high metals as hexavalent chromium (Cr(VI)); especially, it is one of the most notorious in tanning industry, mining activity and pigment manufacture causing health problems by ingestion, inhalation or absorption through the skin [4,5].

2. Materials and methods
2.1. Preparation of samples and TiO₂ coatings growth
Titanium sheets, 99% purity grade (ASME SB-265), with dimensions 20×20×0.1mm were used in this work. Before to PEO, the plates were polished with 1000 and 1200 grit SiC sandpapers successively and subsequently cleaned by ultrasonic bath (BRANSON 1510, Colombia) in distilled water for 30
minutes. A DC pulse power supply designed to deliver a maximum peak voltage of 340V between the electrodes, with variable frequency of 1000Hz and duty cycle of 10, 60 or 90%, was employed in the PEO system. A water cooled stainless steel chamber, containing an aqueous electrolyte 8 g/L Na3PO4 and 0.4g/L NaOH, was used as electrode and the Ti sheet was the other electrode. Subsequently, the sintering of the samples was performed at 500, 700 and 900°C for one hour [1].

2.2. Characterization of TiO2
The coatings’ thickness was measured using a micrometer (Mitutoyo 543-460B Digital, Colombia) with an accuracy of ±0.1μm. The thickness was measured at 20 different locations on the sample surface. The phase composition of the coatings was studied by glancing angle XRD measurements in parallel beam geometry using X-ray diffractometer (XBruker D8- Advance, Colombia). The Pictures of the samples’ surface were taken using a scanning electron microscopy (SEM, JEOL JSM-6390LV, CICATA, México) [6].

2.3. Photocatalytic activity
The analysis of the photocatalytic activity reduction of Cr(VI) to Cr(III) was done following the colorimetric method (ASTM-3500 B-Cr) with 20 mL aqueous Cr(VI) solution with a concentration of 1ppm. The light from 125W UV-lamp, which has main emission at 253.7nm, was used to radiate the sample in contact with the solution into a beaker; TiO2/Ti catalyst was placed in the middle of this beaker and the process was completed at two hours.

The TiO2 coating absorbs UV light so the electrons are excited from valence band to conduction band; this electron-hole pair generates oxidization and radicals OH- [7,8] as seen in the Equations (1) and (2):

\[
\begin{align*}
O_2 + 4H_2O + 4e^- & \xrightarrow{TiO_2/hv} 4OH^- \\
CrO_4^{2-} + 4H_2O + 3e^- & \rightarrow Cr(OH)_3 + 5OH^- 
\end{align*}
\]

A UV–Vis spectrophotometer (Thermo Scientific Evolution 201/220 UV-Vis system, Colombia) was used to measure the absorbance of the treated solutions under the maximum absorbance wavelength (540nm). In the range of low concentration, the reduction rate in the solution of Cr (VI) to Cr (III) was calculated through the Equation (3):

\[
\text{Removal rate (\%) } = \frac{C_0 - C}{C_0} \times 100\% 
\]

Where C is the concentration of Cr(VI) at a certain interval of time (mg/L) and C0 is the initial concentration of Cr(VI) [5].

3. Results and discussion

3.1. Characterization of TiO2 coatings
During PEO, white sparks appear when critical voltage is achieved; later the tension stabilizes and orange sparks appear as in Figure 1 [9]. The coating thickness presents a progressive increase with the duty cycle 10, 60 and 90% of 0.32%, 5.4% and 9.49%, respectively at 1000Hz [10]. We assumed that this thickness increase occurs on ton and solidifies during toff; this suggests that the heat is absorbed by the coating and the micro-discharge colour changes. The coatings by PEO were examined using SEM, revealing uniform microstructures by voltage pulse frequency 1000Hz and duty cycle of 10%, as shown in Figure 2. When this frequency is applied the pores density is large enough; because of the high density of the sparks [11]. The pores diameter was approximately between 356 and 1200nm. The
weight and atomic chemical composition were determined by EDS [12] giving 48.66% of oxygen, 43.06% of titanium and 8.28% of phosphorus. The phosphorus presence in the films shows that electrolyte enters in discharge channels during the growth process; although SEM analysis shows a significant amount of phosphorus, it was not found by XRD, because it is in amorphous shape or the crystalline component may be below diffractometer detection limit [11].

![Formation of orange sparks during the TiO\textsubscript{2} superficial coating by PEO on the Ti plate.](image1)

**Figure 1.** Formation of orange sparks during the TiO\textsubscript{2} superficial coating by PEO on the Ti plate.

![Surface morphology by SEM of TiO\textsubscript{2} on Ti sheet at 1000Hz, duty cycle of 10% and 500°C: (a) low magnification x500 and (b) high magnification x10000.](image2)

**Figure 2.** Surface morphology by SEM of TiO\textsubscript{2} on Ti sheet at 1000Hz, duty cycle of 10% and 500°C: (a) low magnification x500 and (b) high magnification x10000.

The XRD patterns of titanium substrate and coatings (10, 60 and 90% duty cycles) are shown in Figure 3, where peaks of titanium and amorphous TiO\textsubscript{2} can be seen (2\(\theta\) between 20° and 30°).

Sample diffractograms after thermal treatment at 500, 700 and 900°C can be seen in Figure 4. The average particle size was determined by the Scherrer Equation (4), involving the Bragg angle (2\(\theta\)) and the Full Width at Half Maximum (FWHM); the values were listed in Table 1 [13].

\[
T = \frac{0.9\lambda}{\text{FWHM} \cos \theta} \tag{4}
\]
From Figure 5, anatase and rutile weight fractions during sintering of TiO$_2$ coatings were calculated using the Spurr and Myers’s Equations, (5) and (6) [14]:

$$X_R = \frac{1}{1 + 1.26 \frac{I_A}{I_R}}$$

$$X_A = 1 - X_R$$

Where $X_A$ and $X_R$ are the phase’s percentages and $I_A$ and $I_R$ are the maximum-intensity of the XRD peaks of anatase (101) and rutile (110) phases. The results are shown in Table 1.

![Figure 3](image1.png)
**Figure 3.** Diffractograms of TiO$_2$ coatings; PEO with duty cycle: 10, 60 and 90%.

![Figure 4](image2.png)
**Figure 4.** Diffractograms of TiO$_2$ coatings; PEO with 1000 Hz and 10% duty cycle and different sintering temperature.

**Table 1.** Particle size; phase percentage and reduction of Cr (VI) using Ti sheets modified by PEO with 1000 Hz and 10 % of duty cycle.

| Sintering Temperature (ºC) | Anatase average size (nm) | Rutile average size (nm) | Anatase (%) | Rutile (%) | Percentage reduction of Cr (%) |
|---------------------------|---------------------------|--------------------------|--------------|------------|--------------------------------|
| 500                       | 16.567±0.004              | ---                      | 100          | ---        | 99.488±0.004                   |
| 700                       | 24.40±0.01                | 73.819±0.069             | 75.2         | 24.6       | 98.848±0.004                   |
| 900                       | 32.46±0.009               | 141.143±0.029            | 13.3         | 86.6       | 26.442±0.004                   |
3.2. Photocatalytic activity

For the evaluation of the photocatalytic activity of TiO$_2$ coatings, a 1ppm Cr(VI) calibration curve was done as shown in Figure 6, using Standard Methods 3500-Cr. Absorption capacity of coated plates was analysed locating it into the same solution in darkness. The Cr(VI) reduction performance with UV irradiation at 2 hours is reported in Table 1; for 900°C sintering, a deterioration of the coating was found and this sample had the lowest performance (approximately 26%); while at 500°C sintering, the sample had the highest performance (approximately 99%). However, this value was achieved after 50 and 90 minutes for 1ppm and 10ppm Cr(VI) respectively, according to Figure 7 that shows reduction percentage in function of time.

![Figure 5](image1.png)  
**Figure 5.** Diffractogram of TiO$_2$ films sintered at 900 °C and formation of crystalline anatase and rutile phase.

![Figure 6](image2.png)  
**Figure 6.** Calibration curve for quantification of Cr (VI) reduction.

![Figure 7](image3.png)  
**Figure 7.** Percent reduction of 1 ppm (squared dots) and 10 ppm (circle dots) Cr(VI) and the effect by solution adsorption in the darkness (triangle dots).
4. Conclusion
TiO$_2$ ceramic coatings on titanium sheets were accomplished by PEO technique using voltage pulses frequency 1000Hz and changing the duty cycle. These porous films were sintering for growing TiO$_2$ nanostructures of a mixed phase with particle sizes between 16 and 32nm for anatase and between 74 and 141nm for rutile phase; the SEM pictures showed a topography of microcavities; the EDS analysis shows small phosphorus amounts, which were not detected by XRD, but it could be present in the sample as an impurity.

The equilibrium time of maximum adsorption (7%) was 30 minutes and a reduction almost complete was achieved after 50 minutes of radiation with the TiO$_2$ coating made with 10% of duty cycle.

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