

Anodic Titanium Oxide and its Photoelectrochemical and Tribocorrosion Behavior

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Abstract — The obtained oxide films are continuous, amorphous, and the smoothest surface is obtained after Ti anodizing in 2 M H₃PO₄ + 0.05 M NH₄F solution. At concentration of NH₄F 0.2M, the nanotubes of TiO₂ are formed at the temperatures 10-20°C and voltage 20V. The length of nanotubes determined by FIB technique is in the range 650-730 nm, and the diameter of pores is 60-80 nm. The photocurrents and photopotentials correlate with fluorine incorporation into film, and the values of ones were obtained for films not included fluorine, i.e. for films obtained in pure 2M H₃PO₄. The anodic photovoltage up to 2 V (at constant current 1 mA/cm²) and photocurrent up to 5 mA/cm² (at constant anodic potential 1.8 V) have been detected in 0.05M NaOH solution. Tribocorrosion tests were performed in a neutral solution, and changes of open-circuit potential as well as electrochemical impedance spectra were recorded with/without 0.4 N load. The metallic Ti (“as is”) and anodized Ti covered by TiO₂ films immersed into 0.05 M H₂SO₄ + 0.2 M K₂SO₄ (pH 7) solution show passive behavior. TiO₂ films destroyed during sliding tend to restore within 300–400 s after unloading.

Index Terms — titanium anodization, titania film, photoelectrochemistry, tribocorrosion.

I. INTRODUCTION

Owing to the high mechanical strength, low specific weight, excellent thermal stability, and chemical inertness the titanium and titanium alloys are widely used in various recent technologies including used in medicine [1, 2]. The inertness of Ti surface is related to the spontaneous formation of Ti oxides on the titanium surface in the air and in aqueous solutions [3]. However, this TiO₂ film only several tenths of nanometers thick frequently exhibits a poor resistance against corrosion. It is common knowledge that additional chemical, or electrochemical oxidation of titanium allows increasing of the thickness of the natural titania (TiO₂) layer up to ~1 μm [4], or up to 12 μm by micro-arc oxidation of Ti [5], improving to some extent the chemical stability of this material.

The most commonly used electrolytes in titanium anodizing are phosphoric [6, 7] and sulphuric acids, at different degrees of dilution [8].

In the last years, a new class of anodization techniques has been developed, consisting of the anodic oxidation of titanium in electrolytes containing fluoride ions: particular surface structures can be achieved with this method, for example highly ordered arrays of TiO₂ nanotubes [9]. In fact, fluoride ions tend to perforate locally the TiO₂ barrier layer, which causes the oxide to thicken around the small holes while the ions consume the oxide forming on their bottom: the result is a nanotubular morphology, height and diameter of the

nanotubes depending on the fluoride ions concentration and solution pH [10-12].

Thus, it is developed relatively simple and effective methods to fabricate a slack and porous nanostructured TiO₂ with a large specific surface area and uniform nanopore distribution. The obtained oxide layers are subjected to medical technologies implementation, for ex.: TiO₂ is an attractive matrix to immobilize proteins and exhibits facile, direct electrochemistry without any electron mediator. The glucose sensor made by the material shows great sensitivity, good specificity, fast response time, and sound reliability. The new material could have great potential applications in biosensing and green energy systems [13]. TiO₂ photocatalysts have been found to kill cancer cells, bacteria and viruses under mild UV illumination, which offers numerous potential applications [14]. On the other hand, the unusual results have been obtained in which TiO₂ thin and composite films protect *E. coli*, *S. aureus* and *Bacillus* sp from UV light. The survival of *E. coli* with UV alone was 3.2 % while with UV and TiO₂ composite film was 91%. The UV absorbing coatings are transparent, colorless, and exhibit high optical quality. The UV-protective coatings offer an easy method to protect the living organisms against UV [15].

In addition, titania is of interest to use it for photovoltaic application, and to realize high energy conversion efficiency, mesoporous TiO₂ nanocrystalline electrodes of a large surface area have been investigated

extensively as a key material for dye-sensitized solar cells [16].

Rubbing or particle impacts may damage the oxide film and thus promote corrosion of substrate, as well as the functional properties of oxide film will be lost. The need to select or design new surfaces for future equipment as well as to minimize the operating costs, and extend the life of existing machinery has led to demands for a much better understanding of surface degradation processes. This has given rise to research area on tribocorrosion which seeks to address the concerns above and to understand the surface degradation mechanisms when mechanical wear and chemical/electrochemical processes interact with each other. S. Mischler et al [17] defined tribocorrosion as a material degradation process which results from simultaneous mechanical wear and chemical (or electrochemical) material removal mechanisms. It is important to point out that the two mechanisms of degradation do not proceed separately, but depend on each other in a complex way: corrosion is accelerated by wear and, similarly wear may be affected by corrosion phenomena. Additionally, according to [18], in practice the occurrence of tribocorrosion is not always recognized.

The aim of this study is photoelectrochemical and tribocorrosion behaviour of titanium oxide films electrodeposited by anodisation of titanium in solutions containing phosphoric acid and fluoride-ions.

II. EXPERIMENTAL PROCEDURE

Preparation of Ti substrate and its anodization. Prior to anodizing, Ti substrates with a size of 20×20×2 mm (99.2 % of purity, Alfa Aesar GmbH&CoKG, Germany) were mechanically polished using diamond paste followed by ultrasonic cleaning in acetone and then in distilled water. The anodization potentials (AP) between cathode (Cu) and anode (polished Ti) were varied 4 to 60 V. The anodization was carried at temperatures ranged from 0 to 20°C. As photocurrents depend on the surface morphology, in order to simplify the data interpretation, the thin TiO₂ films obtained at AP=4V and replicated mechanically polished surfaces of Ti substrate have been examined.

The surface of titanium was anodized in 2 M H₃PO₄ solution with different concentration of NH₄F, and exact formulations of electrolytes are presented in Table 1.

TABLE 1. Composition of solutions used for Ti anodization.

Lab code	Composition
Ti_1	2 M H ₃ PO ₄
Ti_2	2 M H ₃ PO ₄ + 0.05 M NH ₄ F
Ti_3	2 M H ₃ PO ₄ + 0.2 M NH ₄ F
Ti_4	2 M H ₃ PO ₄ + 0.5 M NH ₄ F

The morphology of the Ti substrate and the anodized Ti samples was investigated by scanning electron microscopy JEOL (JSM-T220A). The compositions of obtained passive films were studied by EDS analysis.

Photoelectrochemical study. A potentiostatic photocurrent and galvanostatic photopotential

examinations of obtained titania extremely thin films was carried out in the dark and under UV illumination with a potentiostat/monochromatic light source (Zahner Electric, 1M6ex and PP210 with $\lambda=365$ nm,) in a three-electrode cell equipped with a flat quartz window in front of the photoanode (working electrode). The electrolyte used for the illumination study was 0.05M NaOH at room temperature. The anodic reactant was the hydroxyl ion, and the photocatalytic reaction resulted in the generation of hydroxyl radical for the generation of O₂.

Protocol of tribocorrosion tests. Electrochemical measurements consisted of open-circuit potential (OCP), E_{oc} , measurements and recording of electrochemical impedance spectra, EIS in the corrosion media consisting on the mixture of 0.05 M H₂SO₄ and 0.2 M K₂SO₄ (pH 7) at the room temperature (22 ± 2 °C). These measurements were performed prior, during, and after sliding tests. A platinized titanium gauze was used as counter-electrode, and Ag/AgCl electrode in saturated KCl solution as reference electrode, and a working electrode was cleaned Ti substrate and anodized Ti test samples. All potential have been shown versus Ag/AgCl electrode. In course of tribocorrosion study the electrochemical measurements were done using a Solartron 1287 Electrochemical Interface and a Solartron 1255 Frequency Response Analyzer. EIS were recorded in frequency range 10^5 to 10^{-3} Hz.

The test set up consists of wear testing equipment allowing continuous circular ball-on-disk tests (Falex Tribology N.V., Belgium). Before the test, Ti substrate and the anodized Ti samples were cleaned in ultrasonic bath in acetone and then in ethanol for 5 min. each. Samples were kept for 24 h in the desiccator before the electrochemical and tribocorrosion tests. Test samples are used as plates and have to be fully immersed in the corrosion media. The tribocorrosion properties of exploratory Ti samples have been studied in a following sequence [19] as it is shown in Table 2.

TABLE 2. The sequence of measurements during tribocorrosion tests

Measured parameter	Time, min	Tribotester mode
OCP	60-240	Without sliding
EIS at OCP	136	Without sliding
OCP	2	Without sliding
OCP	18	Under sliding
EIS at OCP	16	Under sliding
OCP	45-60	Without sliding

Continuous unidirectional sliding tests have been started up immediately after the end of the EIS measurements at OCP. Record on-line the open-circuit potential under sliding, E_{oc}^s during 1,800 contact events under following conditions: counterbody- alumina ball (diameter 10 mm), the normal load applied - 0.4 N and 0.8 N which corresponds in these tests to a average Hertzian contact pressure P_{avg} of 240 and 258 MPa, in continuous circular sliding tests rotation speed - 100 rpm (1.67 Hz), radius of the wear track $R_{tr} = 4$ mm, the one mechanical contact event is counted per rotation cycle. After sliding tests, the area of the sliding track, A_{tr} , and

the wear track volume, V_{tr} were calculated based on the profilometric measurements (measuring station Micromesure STIL, France) at eight spots uniformly distributed along the sliding track. From these data, the corresponding mass loss was calculated as [20]:

$$A_{tr} = e \times L \quad (1)$$

$$V_{tr} = S \times L \quad (2)$$

$$V_{tr} = S \times L \times d \quad (3)$$

where L is the length of the sliding track ($L = 2\pi r$) (cm), e is an average width of track (cm), S is an average area of the cross-section of wear track (cm²), d is the material density (g/cm³).

III. RESULTS AND DISCUSSIONS

Anodic deposition of titania films. Titanium was anodized in the various solutions under anodization voltage (AV) 4-60 V. Dependently on the voltage used for anodization, it is possible to obtain either entire or ordered films. For photoelectrochemical and tribocorrosion study the samples containing entire titania films were selected. The typical elemental analysis data of obtained anodized compact films is presented in Table 3. However, inclusions of fluorine and phosphorous into oxide layer is observed in the presence of NH₄F, and that is caused probably by the formation of fluoride complexes with titanium and its migration via oxide films. The surface morphology of obtained films also slightly varies, and smoothest surface is obtained in the presence of 0.05M NH₄F (see Fig. 1).

TABLE 3. Elemental analysis data of anodized titanium samples after anodization in 2 M H₃PO₄ + 0 - 0.5 M NH₄F solutions. (%). Anodization voltage 12 V.

Lab code of solution	Content of elements, at. %			
	Ti	O	F	P
Metallic Ti	100	-	-	-
Ti_1	34.7	65.4	-	-
Ti_2	40.5	51.3	8.21	-
Ti_3	38.2	55.1	6.42	0.38
Ti_4	34.1	56.5	9.11	0.37

The passive state of surface after anodization also is confirmed by the shifts of OCP values towards positive values from -0.23÷ - 0.12 V to +0.4÷0.6 V. These films were used further for tribocorrosion study.

Photocurrents and photopotentials. As photocurrents depend on the surface morphology, in order to simplify the data interpretation, the extremely thin TiO₂ films obtained at AP=4V and replicated mechanically polished surfaces of Ti substrate have been examined. The photocurrent up to 5 μA/cm² (at constant anodic potential 1.8 V) and anodic photovoltage up to 2 V (at constant current 1 μA/cm²) and have been detected in 0.05 M NaOH solutions (see Fig. 2 and 3). The photocurrents and photopotentials correlate with fluorine incorporation into film, and the values of ones were obtained for films not included fluorine, i.e. for films obtained in pure 2M H₃PO₄.

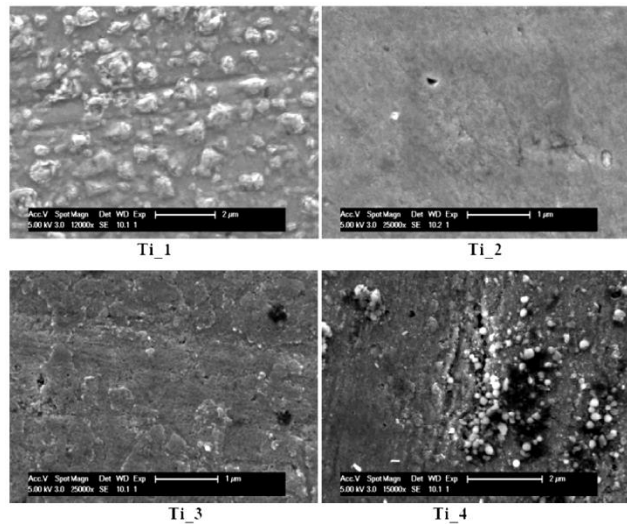


Figure 1. SEM photos of the surface of titania samples obtained in the various solutions at the AV= 12 V. Lab codes of solutions are indicated below photos.

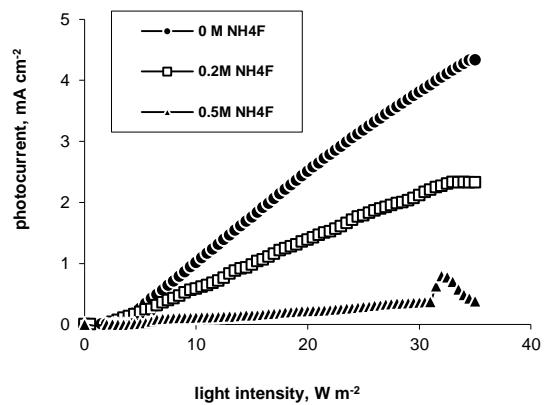


Figure 2. The effect of light intensity ($\lambda=369$ nm) on the photocurrent density in 0.05M NaOH generated byTiO₂ films obtained in 2M H₃PO₄ with various concentrations of NH₄F (indicated in the figure)

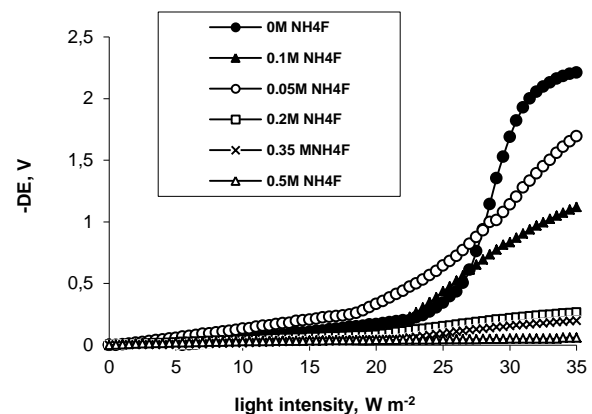


Figure 3. The effect of light intensity ($\lambda=369$ nm) on the decrease in anodic polarization in 0.05M NaOH of TiO₂ films obtained in 2M H₃PO₄ with various concentrations of NH₄F (indicated in the figure).

Electrodeposition of ordered porous films. The ordered porous films are formed under conditions facilitating the breakdown of passive film. In the case of Ti, the ordered nanoporosity is formed in the H₃PO₄ with NH₄F additive, where it plays a role of ligand for Ti⁺⁴. The anodization at 4-60 V in solutions containing NH₄F role of temperature was determined: the nanotubes of TiO₂ are formed at the temperatures 10-20°C and AV=20V (Fig. 4 a). The length of nanotubes determined by FIB technique is in the range 650-730 nm, and the diameter of pores is 60-90 nm (Fig. 4b).

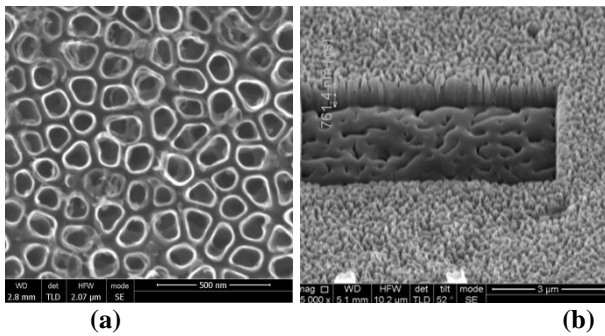


Figure 4. Nanotubes formed in the 2M H₃PO₄ + 0.2M NH₄F solution at 20°C (a); the FIB cross-section of obtained nanotubes (b).

Tribocorrosion of titania films. The formed TiO₂ films onto Ti at AV=12V exhibits relatively high corrosion resistance (up to 10⁶ ohm cm²) – see Nyquist plots in Fig. 5. The obtained electrochemical impedance spectra fit well with the equivalent circuit, containing the uncompensated solution resistance, the constant phase element representing the double layer capacitance, and the charge transfer resistance.

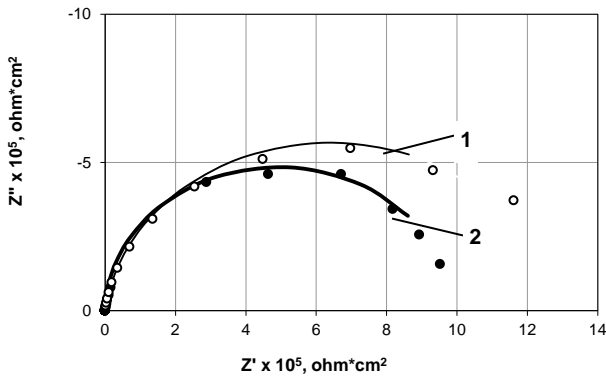


Figure 5. Nyquist plots for TiO₂ obtained in 2 M H₃PO₄ (1) and in 2 M H₃PO₄ + 0.5 M NH₄F (2). The corrosion media 0.05 M H₂SO₄ + 0.2 M K₂SO₄ (pH 7).

Unidirectional continuous sliding was proceeded at settled OCP values. Before sliding E_{oc} of non-processed Ti substrate reaches -0.04 V value, whereas E_{oc} of anodically obtained TiO₂ films are more positive, i.e. +0.150 ÷ +0.170 V. Under sliding, all values of OCP shift sufficiently towards negative potentials up to -0,480 ÷ -0,650 V. The rapid changes of OCP can be explained by the passive film abrasion, when oxide film becomes damaged and bare Ti surface is exposed. It was calculated that approximately 5 ÷ 10 % weight loss of top film from general area of exploratory samples. The E_{oc} value

recorded under sliding is a mixed potential resulting from the galvanic coupling of exploratory samples inside and outside the sliding track. During continuous unidirectional sliding, the values of OCP remain more or less constant at that lower value. During tribocorrosion tests under loading the E_{oc} of analyzed Ti samples dropped down sharply, it means that the passive film becomes fully destroyed at 0.4 N or 0.8 N normal loads.

The electrochemical impedance spectra were recorded during the second half of the sliding period. As follows from the obtained data, the EIS also fit well with the mentioned equivalent circuit, however, under sliding the values of corrosion resistance decreased at the least 5.1·10² times and mostly – 2.3·10⁴ times. It means, that the formed passive film on the anodized Ti samples can be mechanically destroyed during sliding at 0.4 N normal loads.

When sliding is finished, the values of OCP become more positive rapidly (see Fig. 6) that is caused by self-healing of passive film on the wear tracks. As it seen, the passive film re-growing on the wear track on the naked Ti surfaces takes ~400 s. Noticeably, the values of OCP reach similar range that was obtained for untreated metallic Ti before friction.

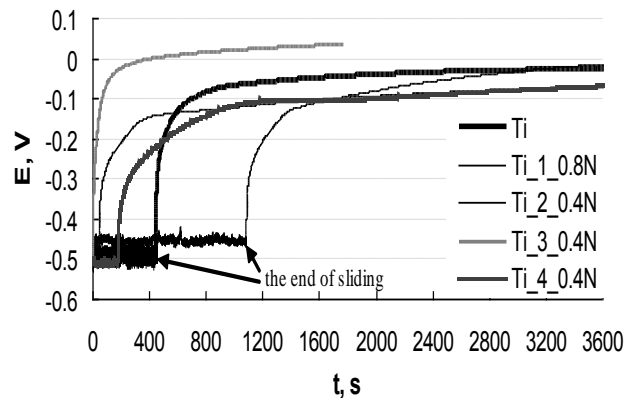


Figure 6. OCP evolution of Ti and TiO₂ films after sliding have been finished.

IV. CONCLUSIONS

The electrochemical behaviour of metallic Ti and TiO₂ films formed during anodization of Ti in 0.2M H₃PO₄ with addition of 0.0-0.5M NH₄F was investigated. Various oxide layers might be deposited (entire, ordered, extremely thin) dependently on the initial state of Ti substrate, composition of solution used for anodization and anodization potential.

The photocurrents and photopotentials correlate with fluorine incorporation into film, and the values of ones were obtained for films not included fluorine, i.e. for films obtained in pure 2M H₃PO₄. The anodic photovoltage up to 2 V (at constant current 1 μA/cm²) and photocurrent up to 5 μA/cm² (at constant anodic potential 1.8 V) have been detected in 0.05M NaOH solution.

The metallic Ti (“as is”) and anodized Ti covered by TiO₂ films immersed into 0.05 M H₂SO₄ + 0.2 M K₂SO₄ (pH 7) solution show passive behaviour. A significant degradation of oxide film in the sliding track on the anodized Ti samples was detected under sliding in 0.05 M

H₂SO₄ + 0.2 M K₂SO₄ (pH 7) at 0.4-0.8N loads. After sliding have been finished, the oxide film re-grow on the wear track of naked Ti surfaces within about 400 s. The values of open circuit potential for all samples reach the similar range that was obtained for the non-processed Ti sample.

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