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Corrosion Stability of the Anodized Ultrafine-Grained Titanium in the Human Body Solution

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ABSTRACT

Nanostructured surface modification was performed on the ultrafine-grained commercially pure titanium (UFG cpTi) using electrochemical anodization. The characterization of the morphology of the nanostructured surface obtained during different times of electrochemical anodization was done using scanning electron microscopy (SEM). The corrosion resistance of the materials was examined using the potentiodynamic method and electrochemical impedance spectroscopy (EIS), during which the electrochemical characteristics of oxide layers and the evaluation of the corrosion resistance of the mentioned materials were determined. These materials were exposed to a solution simulating conditions in the human body (artificial saliva solution) with a pH of 5.5 at a temperature of 37 °C. The obtained results indicate the extensive influence of time, as a parameter of electrochemical anodization on the surface morphology. The electrochemical anodization of 60 minutes can lead to the creation of the nanotubular oxide layer on the UFG cpTi surface, while the electrochemical anodization of 30 and 90 minutes did not lead to the creation of the nanotubular oxide layer, but it is up to the surface modification of UFG cpTi. Electrochemical tests showed a slight increase in the corrosion resistance in a solution of artificial saliva after electrochemical anodization. Also, the electrochemical impedance spectra for anodized and non-anodized UFG cpTi show the characteristics of corrosion resistance, but the anodized UFG cpTi has better resistance to the oxide layer. It can be concluded that anodized UFG cpTi has better corrosion stability, but both non-anodized and anodized UFG cpTi show exceptional corrosion stability in simulated conditions of the human body, which makes them equally suitable for use in medicine.

Keywords: High-Pressure Torsion, Electrochemical Anodization, Commercially Pure Titanium, Corrosion Resistance, Human Body Solution.

1. Introduction

The surface oxide layer, formed on metal materials, has a significant role as an inhibitor of the release of free metal ions, but after that, its behavior changes due to the reaction of the metal with the surrounding living tissue. Even a low concentration of dissolved oxygen, inorganic ions, proteins, as well as the influence of the cell itself, can accelerate the metal ions release [Kasemo et al. 1986]. Also, the amount of released ions depends on how much time it takes to restore the surface oxide layer after the damage. The surface layer, created on metal materials, plays a big role not only because of its resistance to corrosion but also because of its biocompatibility with the surrounding tissue. Biomedical implants should be tested using both in vivo and in vitro methods. In vitro experiments simulate the conditions in the body and indicate the behavior of the material that can be expected during its application, but the result of this type of test cannot be fully authoritative and recommended for the application of the material in the human body. The thin surface layer of oxide is not always stable in the human body; therefore, it is also necessary to understand the behavior in vivo to understand the phenomenon of corrosion in this way. Animal models are used in in vivo tests, in which a sample is taken after implantation and the corrosion resistance of the material is measured. Conditions in the body are simulated when it comes to in vitro testing using Hank's [Bundy et al. 1994], Ringer's [Gonzalez et al. 1999] solution, or artificial saliva [Preetha et al. 2005]. It is known that the pH value of the solution affects the corrosion resistance of the material, so it has been shown that commercially pure titanium has higher corrosion stability in the solution of artificial saliva with a higher pH value [Barjaktarević et al. 2017].

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Metal ions, released from the implant surface during corrosion, affect several biological parameters in the human body. As the material begins to corrode, the dissolution of metal ions can lead to erosion, which causes the implant to fracture. When the material is damaged due to the loss of the protective oxide layer and due to the increased exposure of the surface to the surrounding environment, the corrosion process accelerates. If the damaged metal parts are not surgically removed, further fragmentation and dissolution of metal ions can occur, which can further cause inflammation of the surrounding tissue. Bearing in mind all of the above, as a solution to prevent corrosion damage to implants, the choice of a better and better quality implant material, on which a suitable coating has been applied or its surface has been modified, is imposed. Chemical methods for surface modification of materials are used to improve biocompatibility, corrosion resistance, wear resistance, and contamination removal [Barjaktarević et al. 2021]. Some of the most commonly used chemical methods are chemical treatment, and electrochemical treatment, i.e., electrochemical anodization (anodic oxidation), the sol-gel process, and chemical vapor deposition. As a result of electrochemical anodization, a nanostructured oxide layer composed of nanotubes is obtained. The morphology and structure of the obtained nanostructured oxide layer depend on the characteristics of the substrate, the composition of the electrolyte, and the parameters of the electrochemical anodization procedure [Kulkarni et al. 2014, Hu et al. 2009]. Electrochemical anodization usually results in a nanostructured oxide layer composed of TiO_2-based nanotubes with a thickness of 10 nm to 40 μm. The specific topography of the surface formed in this way improves corrosion resistance, biocompatibility, and bioactivity, and reduces the value of the surface modulus. The diameter and length of the nanotubes can strongly change the corrosion stability of anodized commercially pure titanium [Park et al. 2010, Al-Swayih 2014, Liu et al. 2011]. Many authors have shown the influence of electrochemical anodization on the corrosion stability of commercially pure titanium. A. Al-Swayih et al. [Al-Swayih et al. 2014] showed that electrochemical anodization led to improved corrosion stability of commercially pure titanium, while nanotubes formed at 20 V have the best corrosion stability. Also, anodizing time can change the corrosion stability of cpTi. B Munirathinam et al. [Munirathinam et al. 2015] showed that the annealed nanotubes showed higher impedance and lower passive current density than the formed nanotubes on the commercially pure titanium. W. Yue et al. [Yu et al. 2009] showed that titanium with TiO_2 nanotube layers showed better corrosion resistance than that of non-anodized titanium. Our previous papers also show that the application of electrochemical anodization and nanostructured morphology formed on titanium-based materials has an effect on the corrosion stability as well as on the surface modulus of elasticity and the topography of the surface, which directly affect the biocompatibility of the materials [Barjaktarević et al. 2018, Barjaktarević et al. 2021].

In this paper, we measured the corrosion of commercially pure titanium with an ultrafine-grained structure before and after electrochemical anodization, all to examine the effect of the formation of a nanostructured oxide layer on the surface of the material on the corrosion resistance in the conditions of the human body.

2. Materials and Methods

Materials: Commercially pure titanium grade 2 (coarse-grained cpTi, CG cpTi) was selected for testing purposes. The material was made by conventional methods and obtained in a cast state in the form of a rod of 28 mm in diameter. The chemical composition of CG cpTi is in accordance with the ASTM F67-89 standard [ASTM F67-89, 2013]. To obtain an ultrafine-grained structure, CG cpTi was subjected to severe plastic deformation using the high-pressure torsion procedure (HPT). The HPT procedure was performed at a temperature of 24 ± 1 °C under a pressure of 4.1 GPa and a speed of 0.2 rpm with 5 rotations, at the Erich Schmid Institute of Materials Science, Austria. The HPT process is carried out by pressing a thin disk between two pistons, under high-pressure, and the rotation of the two pistons in opposite directions causes large shear deformations of the material. The applied HPT procedure caused a change in the dimensions of the disk, in such a way that the thickness of the disk decreased while the diameter of the disk increased.

Electrochemical anodization: Electrochemical anodization was performed using a system of two electrodes: platinum, as the cathode, and a sample of UFG cpTi as the working electrode, or anode. The samples were square-shaped, with dimensions of 10cm x 10cm x 1mm. Electrochemical anodization was performed at room temperature, at a voltage of 25 V. 1M H3PO4+0.5 wt. % NaF was chosen as the electrolyte, while the duration of electrochemical anodization was 30, 60, and 90 minutes. After the electrochemical anodization procedure, the samples were washed with distilled water and left to air dry for 24 hours. To analyze the modified surface, scanning electron microscopy (SEM) was used. SEM was performed using a TESCAN MIRA 3 XMU microscope at an operating voltage of 20 keV.

Corrosion measurement: The corrosion stability of the UFG cpTi before and after electrochemical anodization was tested employing two methods: the potentiodynamic method and electrochemical impedance spectroscopy (EIS) using the Gamry Reference 600 potentiostat/galvanostat/ZRA device. Tests were performed in an artificial saliva solution (Apoteka Belgrade, Serbia), with a pH value of 5.5 and at a temperature of 37 °C to simulate conditions in the human body. The apparatus for electrochemical tests consisted of a system of three electrodes. The working electrode consisted of a tested material sample in the form of a square with a 1 cm2 area. The auxiliary (counter) electrode was a platinum wire, while the reference electrode was a saturated calomel electrode (SCE) in the form of a probe.

Potentiodynamic method: With the Gamry Instruments Framework software package, the potential change in the open circuit (Eoc) was monitored for 30 minutes, and after establishing a stationary state, measurements were made using the potentiodynamic method in the potential range from -1.0 V to 4.0 V. Anode and cathode polarization curves were recorded at a potential change rate of 1.0 mVs-1.

Electrochemical impedance spectroscopy (EIS): Impedance measurements were performed at open circuit potential in the frequency range from 100 kHz to 10 MHz with an alternating voltage amplitude of 10 mV. The analysis of impedance values is presented in complex Nyquist and Bode planes. A model of a two-layer oxide film, consisting of an internal compact barrier layer and an external porous layer, and a model of a homogeneous nanotubular oxide layer formed by electrochemical anodization were used. The corresponding equivalent circuit (EC) was used to fit the results.

3. Results and Discussion

3.1. Surface morphology of the anodized UFG cpTi

Figure 1 presents the morphology of the nanostructured modified UFG cpTi surface after electrochemical anodization for 30, 60, and 90 minutes. Table 1 shows the mean values of the dimensions of the formed nanotubes, i.e. their diameters and wall thicknesses.

As can be seen in the SEM micrographs, the electrochemical anodization after 60 minutes led to the formation of a nanotubular oxide layer, Figure 1 (b). Nanotubes obtained during this surface modification are open at the top, and they have a diameter of 100 nm, while the wall thickness is 30 nm. The values of SD for both dimensions are small, Table 1, which shows a homogeneously formed nanotubular oxide layer on the surface of UFG cpTi. It has been demonstrated that the electrochemical anodization of UFG cpTi in an electrolyte with fluoride ions can lead to the creation of the nanotubular oxide layer. On the other hand, electrochemical anodization of 30 and 90 minutes did not lead to the creation of the nanotubular oxide layer, but it was sufficient for surface modification of UFG cpTi.

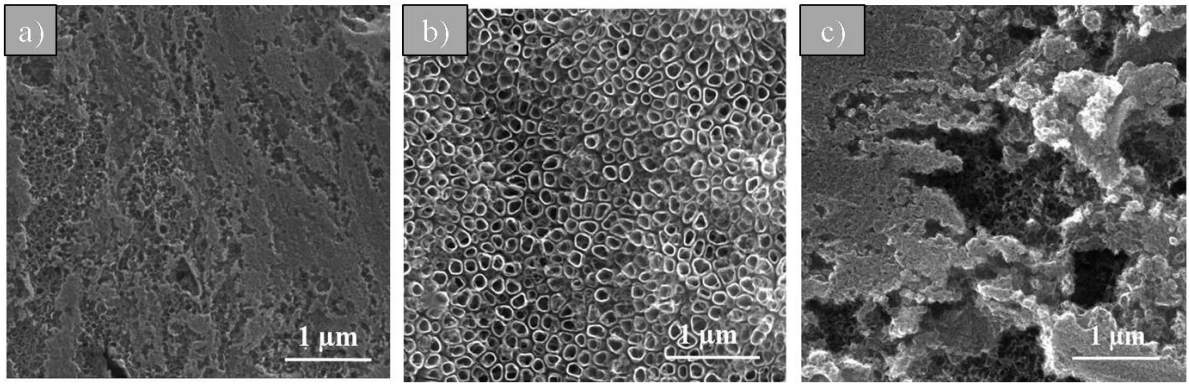

Fig. 1. Morphology of the nanostructured surface of UFG cpTi after electrochemical anodization of (a) 30, (b) 60, and (c) 90 minutes

Table 1. Average values of the dimensions of nanotubes formed after electrochemical anodization of 60 minutes

Material	Anodizing time (min)	Dimension of nanotubes (nm)			
		Wall thickness	Standard deviation, SD	Diameter	Standard deviation, SD
UFG cpTi	60	30	0.69	100	8.60

3.2. Corrosion stability of non-anodized and anodized UFG cpTi

Figure 2 presents polarization curves for non-anodized UFG cpTi and anodized UFG cpTi after 60 minutes in the artificial saliva pH 5.5 solution, while estimates of corrosion potential, E_{corr}, and corrosion current density, j_{corr}, are shown in Table 2.

The corrosion properties of the material can be evaluated by the value of the corrosion current density, j_{corr}, where a lower value of j_{corr} indicates better corrosion behavior of the material. Low corrosion current density values of the order of magnitude greater than 10^{-7}Acm^{-2} for non-anodized and anodized UFG cpTi, indicate exceptional corrosion stability in simulated oral cavity conditions. From the curves shown in Figure 2 and the results in Table 2, it can be seen that the corrosion current density values are slightly lower for the anodized UFG cpTi compared to the non-anodized UFG cpTi. Commercially pure titanium (purity grade 2) after 60 minutes of electrochemical anodization, showed j_{corr} value ($31.6 \cdot 10^{-9}$Acm^{-2}), which is slightly lower than the corrosion current density value for non-anodized UFG cpTi, ($40.0 \cdot 10^{-9}$Acm^{-2}).

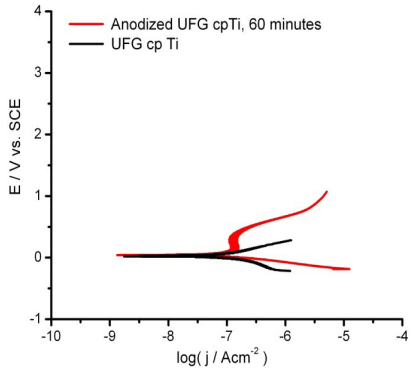

Fig. 2. Potentiodynamic polarization curves of non-anodized and anodized UFG cpTi

By comparing the results obtained during the characterization of the corrosion resistance of anodized ultrafine-grained and coarse-grained Ti-13Nb-13Zr alloy, presented in the previous paper [Barjaktarević et al. 2019], it can be concluded that the corrosion resistance of UFG cpTi anodized after 60 minutes ($31.6 \cdot 10^{-9}$Acm^{-2}) is slightly better than the corrosion resistance of CG TNZ and UFG TNZ alloys anodized after 60 minutes ($47.9 \cdot 10^{-9}$ Acm^{-2} and $41.6 \cdot 10^{-9}$ Acm^{-2}, respectively). This corrosion behavior was influenced by the formation of a homogeneous nanotubular oxide layer on the surface of UFG cpTi with nanotubes whose diameter is larger than the diameter of the nanotube obtained on the surface of TNZ alloy after electrochemical anodization for 60 minutes.

Table 2. Electrochemical parameters of non-anodized and anodized UFG cpTi

Material	UFG Ti	Anodized UFG TI, 60 min
Ecorr (V)	0.021	0.044
jcorr (nA/cm2)	40	31.6

The electrochemical impedance spectra for anodized and non-anodized UFG cpTi are presented through Nyquist (Figure 3) and Bode (Figure 4) diagrams. Both examined samples show the characteristics of corrosion resistance; it can be seen from the size of the semicircle diameter that the anodized UFG cpTi has a better resistance to the oxide layer.

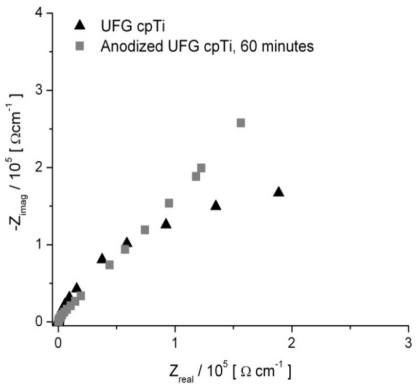

Fig. 3. Nyquist plot of non-anodized and anodized UFG cpTi

Bode plots have two-time constants that describe the two oxide layers. SEI data were successfully calculated using equivalent circuits (EC). For non-anodized UFG cpTi, the time constant at high frequencies

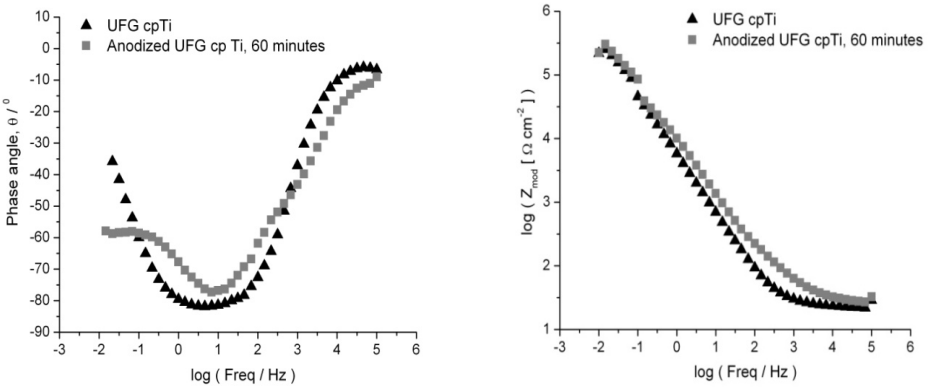

Fig. 4. Graphical representation of Bode plots of (a) phase angles and (b) modulus for non-anodized and anodized UFG cpTi

Table 3. Electrochemical impedance spectroscopy results of non-anodized and anodized UFG cp Ti

Material	Anodizing time (min)	R_o (Ω)	R_1 (Ω cm²)	*CPE1*		*R2* (Ω cm2)	*CPE2*		*„Goodness of Fit"*
				$Y_o \cdot 10^7$ (snΩ^{-1} cm^{-2})	*n*		$Y_o \cdot 10^7$ (snΩ^{-1} cm^{-2})	*n*	
UFG cpTi	/	24.81	130.40	8.66 ·10^{-6}	0.85	2.77·10^5	2.08·10^{-6}	0.93	5.66 ·10^{-3}
	60	26.68	5.07·10^4	2.47·10^{-7}	0.92	4.36·10^5	2.75·10^{-7}	0.92	7.23 ·10^{-3}

(R_1CPE_1) corresponds to the outer porous layer, while the time constant at low frequencies (R_2CPE_2) corresponds to the barrier inner layer [Dimić et al 2017]. Anodized UFG cpTi has two layers: the nanotubes walls (R_1CPE_1) and the bottom of the nanotubes, which is the same as the inner barrier layer (R_2CPE_2) [Saji et al. 2009, Wu et al. 2012]. R_o represents the resistance to the electrolyte. The "Goodness of Fit" parameter is used to evaluate the similarity between experimental and simulated results, and its values are of the order of 10^{-3}, indicating good agreement.

The obtained results for the tested materials are shown in Table 3. It can be noted that the corrosion resistance of the outer porous layer R_1 (*Rp*) is up to three orders of magnitude lower than the resistance of the inner barrier layer, R_2 (*Rb*). In this way, it was shown that the protection of the surface provided by the outer porous layer is worse than the protection provided by the compact barrier layer. The improvement in corrosion stability of UFG cpTi after electrochemical anodization is visible based on the results shown in Table 3.

The resistance of the nanotube bottom, R_2 (*Rnb*), is greater than the resistance of the nanotube walls, R_1 (*Rnv*). These results confirm the better stability of the barrier layer compared to the porous layer. The oxide layer thickness on the surface of the anodized UFG cpTi is greater than that of the non-anodized UFG cpTi.

As can be seen from the results shown in Table 3, the constant phase angle element is well defined by the *n* coefficient, which has values ranging from 0 to 1. When *n* has a value of 0, the system is an ideal resistor, and when n has a value of 1, the system is a capacitor. The coefficient *n* has values ranging from 0.85 to 0.93. The results show that the formation of a nanotubular oxide layer on the surface of UFG cpTi significantly increases the corrosion resistance compared to the non-anodized UFG cpTi.

Increasing the corrosion resistance of commercially pure titanium is primarily achieved by changing the microstructure of the material, i.e. by reducing the grain size. In a previous work [Barjaktarević et al. 2017], it was shown that the corrosion resistance of UFG cpTi, in artificial saliva solution, is higher than that of CG cpTi. The grain size shows a significant influence on the corrosion resistance of titanium-based materials, while the method of processing the material, surface modification, and the electrolyte all play an important role in corrosion stability. Also, parameters of electrochemical anodization have a significant influence on the corrosion stability of titanium-based materials. Many papers show that increasing the anodizing time influences the corrosion resistance, but indirectly through the obtained morphology of the modified surface for a defined anodizing time [Barjaktarević et al. 2019, Al-Mobarak et al. 2014, Al-Swayih et al. 2016]. In a previous paper [Barjaktarević, et al. 2019], it was shown that increasing the anodizing time leads to an increase in the corrosion resistance of the Ti-13Nb-13Zr alloy. Also, increasing anodizing time should lead to an increase in surface roughness and, therefore, increased cell adhesion in the human body.

4. Conclusions

The electrochemical anodization procedure successfully led to the formation of a nanostructured oxide layer on the surface of UFG cpTi in the electrolyte of orthophosphoric acid with the presence of F-ions at different times. SEM microphotographs of UFG cpTi after surface nanostructural modification showed that only the electrochemical anodization procedure lasting 60 minutes led to the formation of a nanotubular oxide layer, with nanotubes having an average diameter of 100 nm, while the average wall thickness of the nanotubes was 30 nm. Electrochemical tests have shown that after the surface nanostructural modification, there was an increase in the corrosion resistance in the artificial saliva solution with a pH value of 5.5. Commercially pure ultrafine-grained titanium showed similar corrosion resistance in an acidic artificial saliva solution before and after electrochemical anodization. The results should allow a better understanding of the behavior of implant metal materials based on titanium with an ultrafine-grained microstructure after surface nanostructural modification in the conditions of the human body.

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