Proceedings of TEAM 2015

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of the International TEAM Society

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CONTENT

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7th International Scientific and Expert Conference TEAM 2015
Technique, Education, Agriculture & Management
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THE ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY STUDY OF ULTRAFINE-GRAINED TITANIUM IN ARTIFICIAL SALIVA

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Abstract

The enhancement of mechanical properties of commercially pure titanium (cpTi) can be achieved by grain refinement obtained by severe plastic deformation, but corrosion resistance of ultrafine-grained (UFG) cpTi is still under discussion. Therefore, the aim of this study was to estimate electrochemical behavior of UFG cpTi obtained by high pressure torsion under a pressure of 7.8GPa with a rotational speed of 0.2 rpm up to 5 rotations at room temperature. Electrochemical measurements were performed in artificial saliva with pH value of 4.0 at 37°C in order to simulate oral environment, because UFG cpTi is primarily developing for dental implant applications. UFG cpTi was investigated by electrochemical impedance spectroscopy (EIS). The obtained results indicate that HPT process significantly reduces the grain size and UFG cpTi shows better corrosion resistance compared to its coarse-grained (CG) counterpart.

Keywords: titanium, corrosion resistance, electro–chemical behavior, artificial saliva

1. Introduction

Commercially pure titanium (cpTi) is the most commonly used metallic biomaterial. Several applications of titanium can be found in biomedicine, for instance, in devices for artificial hearts, structural applications such as screws and dental implant pins, and prostheses [1]. CpTi and Ti-alloys have demonstrated high mechanical strength, low elastic modulus, excellent biocompatibility and corrosion resistance [1]. To determine the suitability of a material for body implant applications, several properties must be evaluated. Among these properties, the corrosion behavior is of crucial interest, because the metallic ion release from the implant to the surrounding tissues may give rise to biocompatibility problems. The corrosion resistance is of great importance, not only because it determines the device's useful life, but also due to the harmfulness of corrosion processes taking place in the living organism. It has been established that the corrosion products may affect cell metabolism [2]. CpTi shows very good corrosion resistance in many media due to the formation of passive TiO_2 thin film on its surface upon exposure to air. It should be noted that corrosion rate of cpTi is significant in concentrated acid solutions at room temperature because the protective oxide film tends to dissolve in aggressive media [3].

Therefore, it can be concluded that formation and protective rate of the passive film layer is dependent on the environment conditions.

Although cpTi is considered to be the best biocompatible metallic material for dental application because its surface properties result in the spontaneous formation of a stable passive oxide layer, it does not have high enough strenght for more applications. Therefore, in order to improve mechanical properties of cpTi, different thermomechanical treatments had been examined. Further enhancement of mechanical properties of metallic materials may be achieved by severe plastic deformation (SPD) procedures, leading to the formation of finer microstructures. Large number of different SPD methods, such as equal channel angular pressing (ECAP), high pressure torsion (HPT) and others similar processes, have been extensively studied in recent years [4]. High pressure torsion (HPT) is SPD method where deformation is obtained mainly by simple shear. This method applies very large strains in a material due to the applied hydrostatic pressure during deformation. An equivalent strain (ε) imposed on the sample can be estimated using the formula [4]:

$$\varepsilon = \frac{2\pi N r}{\sqrt{3}t} \quad (1)$$

As can be seen, the equivalent strain depends on the number of rotations (N), the radius (r) and the thickness (t) of the sample obtained by HPT process. Ultrafine-grained (UFG) metals and alloys produced by severe plastic deformation (SPD) techniques have better mechanical and physical properties compared to their coarse-grained (CG) counterparts. There are numerous studies about mechanical and physical properties of UFG cpTi produced by severe plastic deformation (SPD) techniques [5,6], but only a few about corrosion resistance of this material [7-14]. Furthermore, most of papers investigated ultrafine-grained cpTi produced by equal-channel angular pressing (ECAP) [15]. Therefore, the purpose of this study was to evaluate corrosion resistance of UFG cpTi obtained by high pressure torsion. Schematic overview of performed experiments is presented in Fig. 1.

2. Method

The cpTi grade 2 (Goodfellow, Germany) in the shape of a rod with 16 mm in diameter was used in

this study. The cpTi samples were cut into disc-shaped samples with 8.0 mm in diameter and 1.0 mm in thickness.

The one group of cpTi samples was subjected to HPT process under a pressure of 7.8 GPa with a rotational speed of 0.2 rpm up to 5 rotations at room temperature. The obtained samples of UFG cpTi was disc-shaped with 8.0 mm in diameter and 0.7 mm in thickness. In order to analyse micro–structure of cpTi before and after HPT process, scanning electron microscope (SEM) MIRA3 TESCAN was used. The SEM operated at an accelerating voltage of 20 keV.

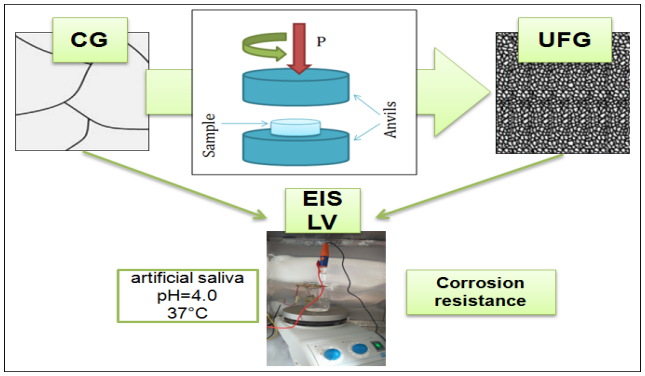

Figure 1. Schematic overview of performed experiments

Electrochemical measurements were performed in a artificial saliva solution (Pharmacy Belgrade, Serbia) with pH value of 4.0, using a Gamry Reference 600 potentiostat with in a Faraday cage, at 37°C ± 1°C. The composition of artificial saliva solution is shown in Table 1. The apparatus used in this study is shown in Figure 2.

Table 1. Chemical composition of artificial saliva

Component	Contetnt, %
NaCl	0.0844
KCl	0.1200
$MgCl_2$ x $6H_2O$	0.0052
$CaCl_2$ x $2H_2O$	0.0146
Sorbitol	0.3000
KH_2PO_4	0.0342
Carboxymethylcellulose sodium	0.1000
Water	99.3416

Figure 2. Faraday cage with system of electrodes

Fresh solution was used for each experiment. The assembly was embedded into an epoxy resin in order to form working electrode.

After that, the samples were ground with SiC abrasive paper (up to 2000 grit). Ultimately, the samples were cleaned in methanol in ultrasonic bath followed by rinsing with deionized water. After immersion into artificial saliva solution, the cpTi and UFG cpTi disc specimens were held for 30 min to achieve a steady open-circuit potential (OCP). Electrochemical impedance spectroscopy (EIS) was performed at OCP over a frequency range from 100 kHz to 0.01 Hz using a sinusoidal AC voltage amplitude of ±10 mV. Subsequently, potentiodynamic polarization was carried out in the range of -0.25 to 0.25 V with respect to the OCP at a scan rate of 0.15 mV s^{-1}. In order to maintain a high statistical accuracy, all electrochemical measurements were repeated at least three times.

3. Results

Ti has two allotropic forms: *α* - the atoms are arranged in a hexagonal close-packed (hcp) array (up to 882.5 °C) and *β* - the atoms are arranged in a body-centered cubic (bcc) array (above 882.5 °C) [16]. Thus, the *β*-to-*α* transformation temperature of pure Ti either increases or decreases based on the nature of the alloying elements [16]. Accordingly, the *β* phase is found only at high temperatures unless Ti is alloyed with other elements which maintain the *β* phase at lower temperatures. The characteristic microstructures of the examined materials are shown in Figure 3. Figure 3a shows equiaxed *α* grains in the cpTi microstructure. As can be seen from the SEM micrographs, HPT progressively leads to the transformation of the initial structure into a new ultrafine structure upon continued straining.

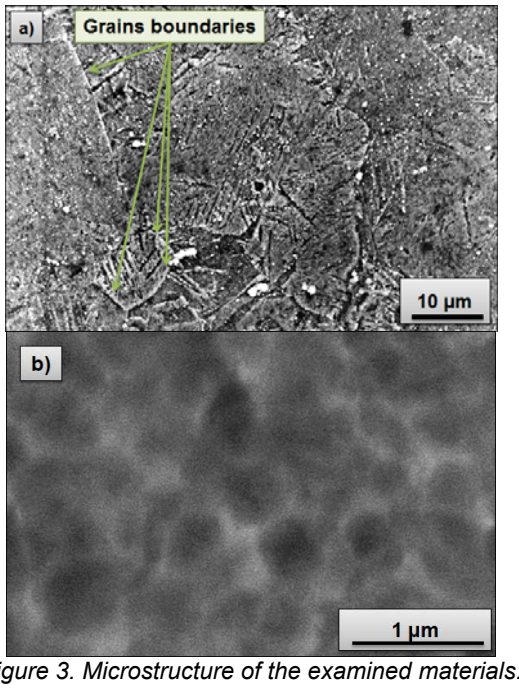

Figure 3. Microstructure of the examined materials: a) cpTi, b) UFG cpTi

Sergueeva et al. [17] revealed that the microstructure of UFG cpTi is sufficiently homogeneous after HPT deformation under 5 GPa pressure up to 5 rotations at room temperature, but there is evidence of significant lattice distortions associated with large internal stresses.The presence of large internal stresses in UFG structure of cpTi was also confirmed by in [18]. They showed that a large fraction of the grain boundaries have high angles of misorientation, but they are ill-defined and lack the banded contrast that is a characteristic feature of the well-formed grain boundaries observed in annealed metals. Additionally, the grain boundaries in HPT-processed materials are typically wavy, curved or corrugated, indicating their non-equilibrium character [18].

The Bode plots for the examined materials in artificial saliva with pH value of 4.0 were shown in Fig. 4, while the Nyquist plot was shown in Fig. 5.

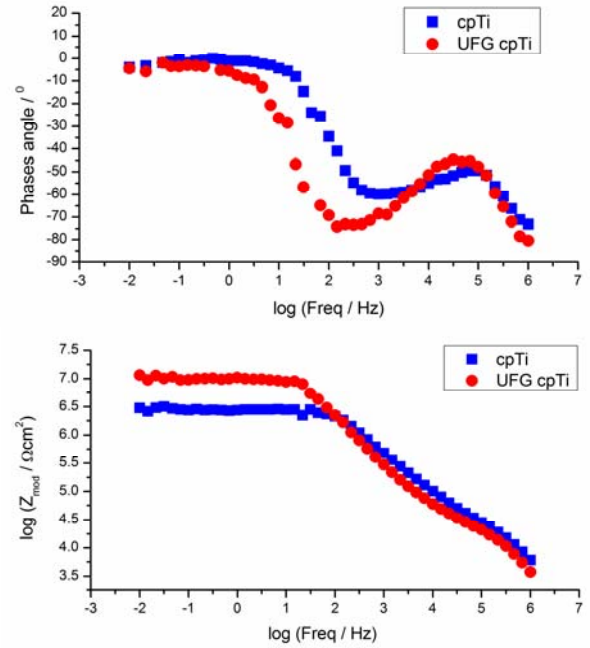

Figure 4. The Bode plots of cpTi and UFG cpTi

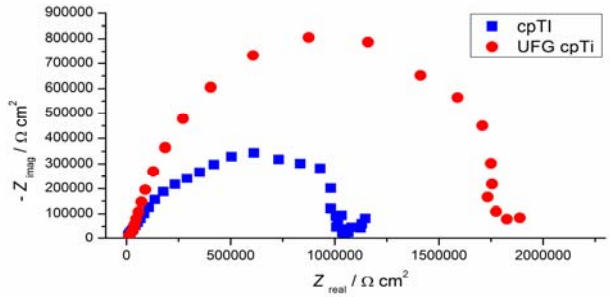

Figure 5. The Nyquist plot of cpTi and UFG cpTi

As can be seen in Figure 5, Z_{imag} and Z_{real} values for UFG curves are higher than that of CG sample. Therefore, it can be concluded that cpTi had less corrosion resistance than UFG cpTi. Furthermore, the total impedance value for the UFG sample is higher than that of the CG sample according to Bode plots, Figure 4.

The equivalent circuit related to the data extracted from EIS test is presented in Figure 6 [19]. R_Ω, R_b and R_p represent the resistance of the electrolyte, inner barrier layer and porous outer layer, respectively. On the other hand, C_b and C_p represent the capacitance of the inner barrier layer and porous outer layer, respectively. A good agreement between the measured and simulated data was achieved when a constant phase element (CPE) with the exponent *n* was utilized for data fitting instead of an ideal capacitor. The value of mentioned parameters for both CG and UFG cpTi is presented in Table 2.

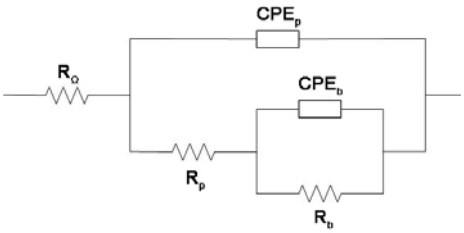

Figure 6. The equivalent circuit of the examined materials in electrochemical tests

Table 2. The electrochemical parameters - EIS data

Material		cp Ti	UFG cpTi
R_b [Ωcm^2]		2.89 x10^4	3.89x10^2
CPE_b	Y_o [S^{n}Ω^{1}cm^2]	2.49x10^{-9}	1.28x10^{-5}
	n	0.803	0.877
R_p [Ωcm2]		1.47x10^6	1.05x10^5
CPE_p	Y_o [S^{n}Ω^{1}cm^2]	7.96x10^{-10}	1.72x10^{-10}
	n	0.822	0.907

The values of the 'Goodness of Fit' were 2.64x10^{-3} for cpTi and 3.19x10^{-3} for UFG cpTi.

4. Discussion

Corrosion resistance of the implant material depends on the material composition and sample dimensions, as well as on the type, composition, temperature, pH value and volume of testing solution. For instance, Qu et al. [20] analyzed the corrosion behavior of cpTi in artificial saliva with and without lactic acid by OCP, polarization curves and EIS. The corrosion of cpTi in artificial saliva was resulted in a slight decrease in the pH value of the solution. The corrosion of cpTi was distinctly affected by lactic acid and the corrosion rate increased with increasing the amount of lactic acid. Lactic acid is suitable to form a chelate compound ($[Ti(OH)_3]\cdot L$), which dissolves in water. The formation of $[Ti(OH)_3]\cdot L$ accelerates the dissolution of passivation film (TiO_2) on cpTi, and this causes the deficiency of the protective film, leading to a tendency of pitting corrosion. Similarly, Balyanov at al. [21] also investigated the corrosion behavior of cpTi with both UFG and CG microstructures. In that study, they found that UFG cpTi produced by ECAP had better corrosion resistance than CG cpTi in both HCl and H_2SO_4 solutions.

In addition, compared with CG cpTi, UFG cpTi has lower corrosion current densities, more positive corrosion potential, lower critical currents, i_c, at the passive potential, and more positive passive potential, E_p. Higher concentration of HCl or H_2SO_4 led to higher corrosion rates for both UFG and CG cpTi. The corrosion resistance of UFG cpTi is believed improved by rapid formation of passive films at surface crystalline defects including grain boundaries and dislocations. Likewise, Balakrishnan at al. [22] analyzed the corrosion behaviour UFG cpTi produced by equal channel angular process (ECAP) in simulated body fluid (SBF). Tafel extrapolation studies showed the corrosion resistance of the UFG cpTi to be 10 times higher compared to coarse-grained (CG) cpTi. On the similar way, Kim et al. [1] showed that UFG cpTi obtained by (HRDSR) high-ratio differential speed rolling had better corrosion properties than CG counterpart in H_2SO_4 solution.

In all those papers, as in our work, the obtained results indicate that UFG cpTi shows better corrosion resistance compared to its coarse-grained (CG) counterpart. The difference between corrosion behavior of CG and UFG cpTi may be related to the volume fraction of grain boundaries [13].

5. Conclusion

The obtained results indicate that HPT process significantly reduced the grain size. Furthermore, UFG cpTi produced by HPT has better corrosion resistance compared to CG cpTi. The difference between corrosion behavior of CG and UFG cpTi may be related to the volume fraction of grain boundaries. Further examinations will include electrochemical testing of CG and UFG cpTi in different testing conditions (different pH values of artificial saliva, presence of lactic acid and fluoride, etc.) in order to prediction of behavior of these materials in oral environment.

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