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ELECTROCHEMICAL CHARACTERISTICS OF TITANIUM FOR DENTAL IMPLANTS IN CASE OF THE ELECTROLESS SURFACE MODIFICATION

In the paper the results of research under effect of electroless phosphate coating of titanium dental implants on potentiokinetic polarization characteristic obtained in artificial saliva were presented. On the basis of electrochemical studies it was concluded that the electroless process of phosphating beneficialy effect on corrosion characteristic of titanium determined in solution simulating the oral cavity. Furthermore, the proposed technique of chemical treatment of titanium surface is conducive to the homogeneous development of the surface, which is extremely important from the point of view of titanium implants biointegration. Phosphating treatment affect on the development of surface geometry, resulting in a slight increase in roughness parameters (*Ra*, *Rz* and *Rmax*). The temperature increase of electroless phosphating treatment promotes the rate of conversion layer formation, whereas the effect of temperature of the chemical treatment efficiency is secondary important at longer exposure times (e.g. 45 minutes).

Keywords: titanium implant, phosphating, conversion layer, artificial saliva, potentiokinetic curves

1. Introduction

Titanium and its alloys are among the most perspective group of metallic materials used in implantology. Comparing the properties of titanium with other biomedical material, titanium is characterized by: a small specific weight, preferred ratio of tensile strength to yield strength, a very high fatigue strength, among metallic biomaterials the lowest value of the Young's modulus, paramagnetic properties, very good biotolerance, tendency to spontaneous passivation, high local and general corrosion resistance [1-5]. All the discussed properties, with the low thermal expansion of titanium makes it the most widely used metallic material both in dental prosthetics and orthopedics. In practice, of titanium and its alloys are the most commonly performed joint prostheses and dental implants [3-6]. Due to fact that titanium easily passivate in the small amount of oxygen and easily covered with a permanent layer of oxide – mainly TiO_2 (rutile, anatase), is resistant to many corrosive media [7]. Classification of titanium as a biomaterial is caused by its surface passivation in body physiological fluids – protective properties of the passive oxide layer are significantly reduced until the pH (pH < 4). Whereas the local damages of the passive layer in the presence of oxygen rapidly repassivate [7,8].

The main limitation in the use of pure titanium is its poor resistance to abrasive wear. As a result of the friction forces the protective oxide layer can be easily damaged, and also malleable titanium can undergo deformation [8]. Issues increase the stability of the implant surface is a very important problem. Appropriate design in terms selection of biocompatible materials may announce the harmful effects of wear products (e.g. metallosis).

One of the methods to prevent damage to the titanium surface by abrasion is the use of appropriate technologies for surface engineering [9-12]. Preparation of the detail surface layer having improving resistance to abrasion and increases component lifetimes under operating conditions. The surface preparation of dental implants determines the formation of a permanent connection, and further reactions taking place on the border of the implant / biosystem.

The surface of titanium implants covering with oxide layers has beneficial effect on the osseointegration processes. In the area of the implant/bone tissue for oxidized titanium the increased amount of separated bone tissues have been observed (comparison to the polished titanium surfaces).

However, as can be seen from the literature, spontaneously formed oxide layers do not provide adequate adhesion, and in longer times of use can lead to resorption and demineralization of bone around the implant [12]. Against those negative effects, searching for other methods of implant's surface modification are reasonable. One of the technique is to apply the chemical conversion layer [10,11] Conversion deposition process, consists in producing tight layer on metal surface of sparingly soluble compounds formed from metal ions (from the substrate) and a solution of reactive environment (e.g., titanium phosphate) [10]. Phosphating process is commonly used to improve corrosion resistance, increase the adhesion of organic coatings to improve spreadability (to reduce friction and abrasive wear), or

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production of electrical insulation. Phosphating process is carried out in the presence of HPO_4^{2-} ions, usually in aqueous solutions of dihydrogen phosphates (e.g. NaH_2PO_4, sodium dihydrogen phosphate, zinc dihydrogen phosphate $Zn(H_2PO_4)_2$, magnesium dihydrogen phosphate $Mg(H_2PO_4)_2$) and/or in solutions of phosphoric acid H_3PO_4 [10]. In solution the metal-solution border phenomenon occurs transfer of the chemical equilibrium of dissolved salts, which allows to obtain on the metal surface the di- or trisubstituted salt of (insoluble in this environment).

$$Ti + HPO_4^{2-} \rightarrow Ti(HPO_4)_2 + 2e \quad (1)$$

The anodic applying of conversion layer in solutions H_3PO_4, on the titanium surface the layer of several components is formed, the layer includes TiO_2 and $Ti(HPO_4)_2 \cdot nH_2O$. The presence of a microporous structure of titanium oxide TiO_2 (rutile) and embedded in its titanium phosphate beneficialy effect on the processes of hydroxyapatite formation [10,11].

The aim of this study was to investigate the effect of electroless conversion layers application in aqueous solutions containing phosphate ions on the properties of pure titanium, which directly determines the quality of the surface of titanium for biomedical applications. The field of research has been targeted by the fact that even small change in the chemical composition of the alloy significantly effect on the corrosion behavior of metals in the environment of body fluids [13], as well as the fact that the surface treatment applied to metal alloys (biomaterials, as well as other alloys) strong impact on the potentiokinetic characteristics [14,15]. To determine changes in the surface layer during phosphating the potentiokinetic polarization test in medium simulating the environment of the oral cavity (artificial saliva), profilometry research and the Vickers hardness test were carried out.

2. Experimental procedure

The experimental material was commercial, technically pure titanium Grade 2 (*Bibus Metals*), one of the most commonly used variants of titanium in dental prosthetics. In order to determine the effect of the presence of a phosphate conversion layer on pure titanium, on the corrosion resistance, of the surface geometry and hardness, three variants of chemical treatment were used. The layers are applied using a phosphate aqueous solution containing phosphate ions:

- Variant 1 (V1) – 0,5M sodium dihydrogen phosphate (NaH_2PO_4) solution acidified to pH = 3, in temperature 20°C
- Variant 2 (V2) – 2M orthophosphoric acid solution (H_3PO_4) solution, in temperature 20°C
- Variant 3 (V3) – 2M orthophosphoric acid solution (H_3PO_4) solution, in temperature 50°C

The sample surface before exposure in phosphating bath carefully polished on water paper with gradation 800, then rinsed with distilled water, degreased with methyl alcohol. Each electroless phosphating process was carried out in fresh solution with a 50 cm^3 volume. To intensify the interaction of the aqueous medium to the metal surface treatment, the solution was stirred all the time. The sample was exposed by the above-mentioned variants (V1-3) using time 5, 15 and 45 minutes. In the next part of paper the marking for example were used as follows: e.g. W1-5, titanium treated by phosphating variant 1 for 5 minutes).

In the corrosion potentiokinetic studies the chloro-silver (reference electrode was used, $E^{eq}_{Agcl/Ag} = +0.22V$, The measurements were conducted in 25° ±0.1°C temperature, 10 mV/s potential scan rate from $E_{min} = -1.5V$, to $E_{max} = 2.5V$. Corrosion tests were performed in artificial saliva solution with the composition: 0.7 g/cm^3 NaCl, 1.2 g/cm^3 KCl, 0.28 g/cm^3 Na_2HPO_4, 1.5 g/cm^3 $NaHCO_3$, 0.33 g/cm^3 KSCN, 1.3 g/cm^3 urea.

The 2D roughness measurement was performed using a contact profilometer (Taylor Hobbson). Roughness measurement requires a research area of this size/segment on the surface of the material to be statistically representative and valuable area of research, i.e. an increase will not affect on the result. The section in this study has length about 250 µm. Linear measurements were made on three sections and each measurement was repeated 5 times, on the basis of these measurements average roughness and the standard deviation were determined.

3. Results and discussion

To determine the effect of the applied chemical treatment in aqueous solutions containing phosphate ions, the potentiokinetic polarization tests in medium simulating the of the oral cavity environment were carried out. In Figure 1 the corrosion characteristics of grade 2 titanium treated after phosphating with V1-3 are presented. All the obtained curves were compared to the curve obtained for titanium without treatment (surface polished and degreased).

Based on the characteristics shown in Fig. 1 can be unambiguously stated that the applied surface treatment in aqueous phosphate solutions has the beneficial effect on the behavior of titanium in an artificial saliva. With the extending exposure time (according to the proposed phosphating solutions), the corrosion potential shifts in more positive direction. Furthermore, the slope of the anodic curve in the active range shows that the material is more easily undergoes in passive state.

The biggest change in the potential was obtained after 45 minutes in 2M orthophosphoric acid solution, furthermore elevated temperature (50°C) also effect on the E_{corr} shift towards a more positive value. For example, 5-minutes exposure in a 2M orthophosphoric acid solution at room temperature caused a change in the potential about 50 mV, while applying the same solution and time but increasing the temperature to 50°C caused a change in the potential of nearly 100 mV. The effect of temperature is considerably less significant at longer times of phosphate layers application, and the change in the applied potential for the treatment variants V2-45 and V3-45 is approximately 200mV.

Based on roughness research with contact profilometer, the profiles for untreated titanium (after grinding), and two samples after phosphating (V2-45 i V3-45) were determined (Fig. 2) according to PN EN 10049:2014.

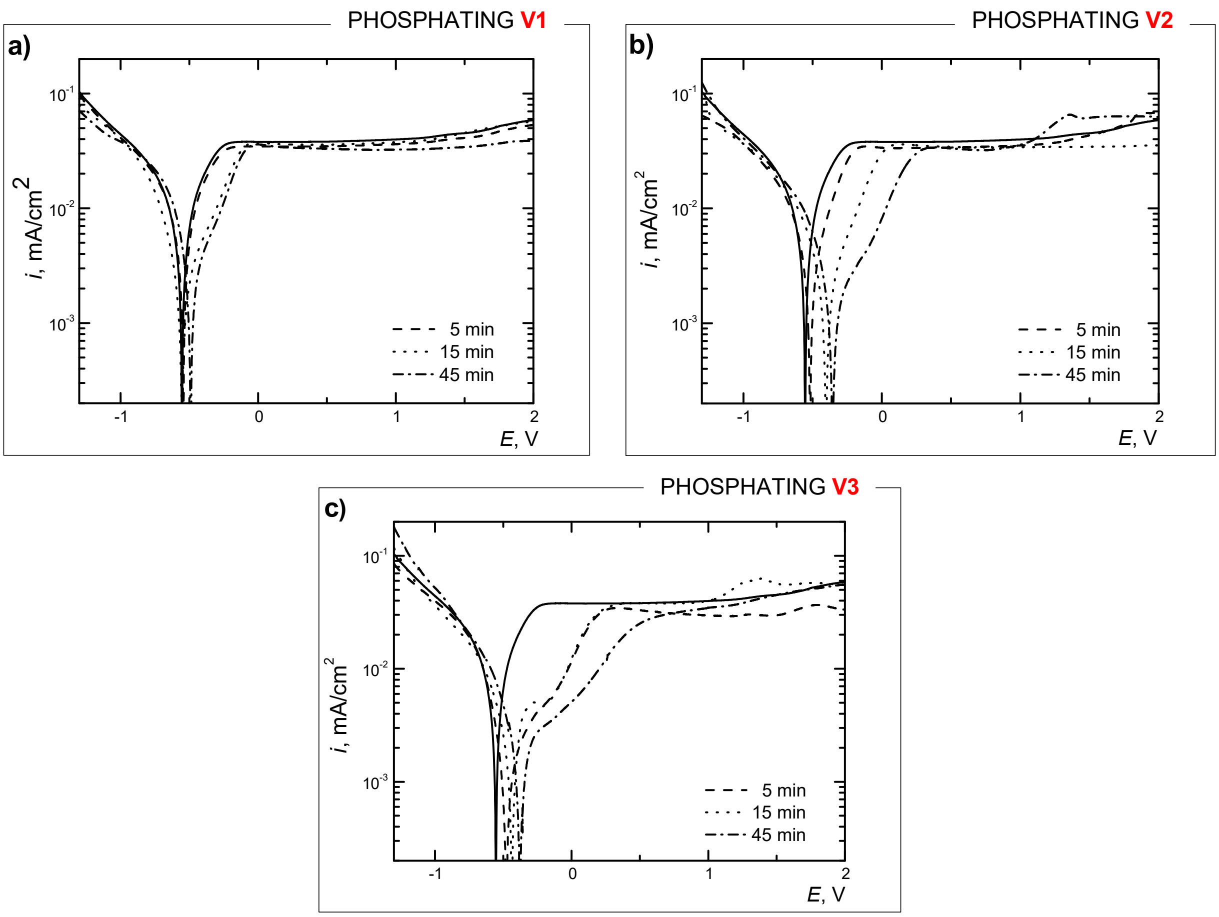
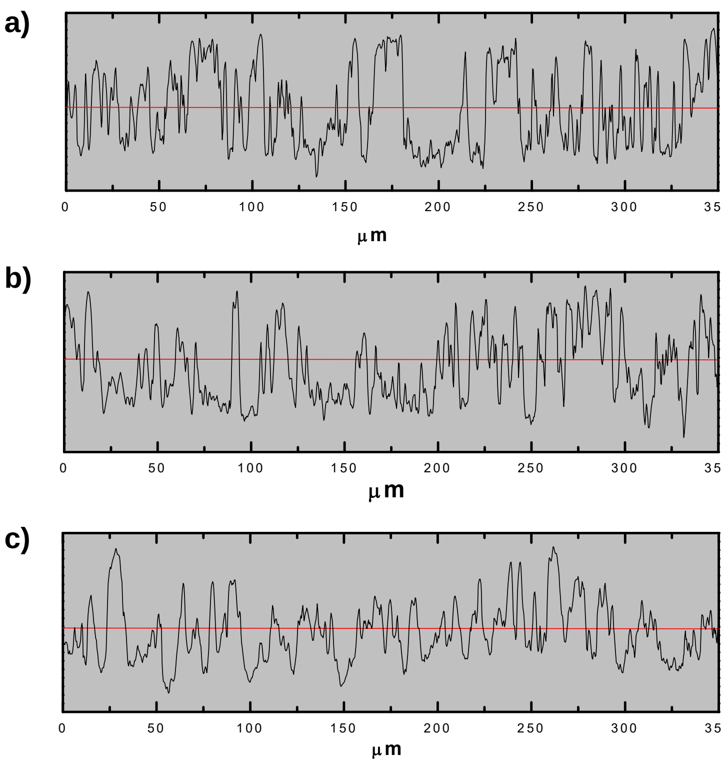


Fig. 1. Potentokinetic characteristics obtained in artificial saliva solution for titanium Grade 2 without surface treatment (— solid line) and after phosphating: a) V1 – 0.5M sodium dihydrogen phosphate (NaH_2PO_4) solution acidified to pH = 3, in temperature 20°C, b) V2 – 2M 2M orthophosphoric acid solution (H_3PO_4) solution, in temperature 20°C, c) V3 – 2M orthophosphoric acid solution (H_3PO_4) solution, in temperature 50°C



a)

Roughness parameters:
$R_a = 0.14 \pm 0.06$ μm
$R_z = 1.7 \pm 0.2$ μm
$R_{max} = 11.7 \pm 0.6$ μm

b)

Roughness parameters:
$R_a = 0.80 \pm 0.03$ μm
$R_z = 2.2 \pm 0.1$ μm
$R_{max} = 16.7 \pm 0.4$ μm

c)

Roughness parameters:
$R_a = 0.85 \pm 0.02$ μm
$R_z = 2.6 \pm 0.1$ μm
$R_{max} = 17.6 \pm 0.2$ μm

Fig. 2. Roughness profiles for titanium Grade 2 surface: a) without treatment, and after phosphating: b) V2-45 (2M orthophosphoric acid solution, in temperature 20°C, time 45 minutes), c) V3-45 (2M orthophosphoric acid solution, in temperature 50°C, time 45 minutes)

It has been reported that the phosphating treatment caused the development of surface roughness, however, the change between the tested surfaces is rather small. Other method to evaluate the beneficial influence of the titanium surface phosphating treatment of is the Vickers hardness test according to PN-EN ISO 6507-1:2007. The Vickers hardness of titanium samples: no chemicaly treatment, the phosphating solution in 2M phosphoric acid (temperature 20°C), the phosphating solution in 2M orthophosphoric acid (temperature 50°C) were respectively HV30 = 161 (reference), 222 (V2-45), 239 (V3-45). In line with expectations phosphating process caused an increase in hardness of the material. The increase in hardness is probably above all due to the changes that have occurred in the surface layer of titanium – saturation of the surface with oxygen and creating of $Ti(HPO_4)_2 \cdot nH_2O$.

4. Summary and conclusions

Based on electrochemical and material studies can be unambiguously stated that the process of electroless phosphating Has the beneficial effect on the corrosion behaviour and mechanical properties of titanium. Furthermore, the proposed chemical treatment technique of titanium surface is conducive to homogeneous development of the surface, which is extremely important from the point of view of biotolerance and biointegration of titanium implants.

- electroless plating process phosphating advantageously influences on the corrosion characteristics of titanium in an artificial saliva. Already five-minute treatment in solutions containing phosphate ions causes a corrosion potential (E_{corr}) shift towards more positive values,
- increase in temperature of electroless phosphating treatment promotes layer application rate, the effect of temperature on the chemical treatment efficiency is secondary important at longer exposure times (e.g. 45 minutes),
- electroless phosphating treatment supports the development of surface geometry, resulting in a slight increase in roughness parameters (*Ra*, *Rz* and *Rmax*),
- electroless phosphating process favors the growth of the mechanical properties of the titanium surface, causing an increase in hardness.

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