The effects of a SiO₂ coating on the corrosion parameters cpTi and Ti-6Al-7Nb alloy

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The aim of this paper was to evaluate the usefulness of the sol-gel method application, to modify the surface of the Ti6Al7Nb alloy and the cpTi titanium (Grade 4) with SiO₂ oxide, applied on the vascular implants to improve their hemocompatibility. Mechanical treatment was followed by film deposition on surface of the titanium samples. An appropriate selection of the process parameters was verified in the studies of corrosion, using potentiodynamic and impedance method. A test was conducted in the solution simulating blood vessels environment, in simulated body fluid at \( t = 37.0 \pm 1 \) °C and \( \mathrm{pH} = 7.0 \pm 0.2 \). Results showed varied electrochemical properties of the SiO₂ film, depending on its deposition parameters. Correlations between corrosion resistance and layer adhesion to the substrate were observed, depending on annealing temperature.

Introduction

Titanium and titanium alloys have been used as an implant material for blood contact. This type of biomaterials is used to produce mainly rings of prosthetic heart valves. Implants used in blood system should not undergo degradation or adsorb any blood components and should minimize the occurrence of blood clot formation. Proper bond between an implant and a tissue environment is guaranteed by appropriately prepared surface of medical product. Combination of the advantages of implant metal constructions and biotolerance required for medical use is achieved by various methods of the implant surface treatment, i.e. electropolishing, chemical passivation, oxide films fabrication using sol-gel method. Modification based on the sol-gel technology is one of the most progressive methods of coating surface of different morphology and geometry with thin films, which gives surface desirable roughness and appropriate combination of mechanical properties. Siliceous films, depending on chemical composition of sols as well as parameters of the surface coating process, are characterized by i.e., good adhesion to the metal substrate, controlled macroscopic structure of gels, very high biotolerance and improved corrosion resistance comparing to non-coated material. Literature data indicate many undefined phenomenon accompanying oxide films fabrication involving silicon on surface of metal biomaterials. Selection of proper coatings production parameters, as well as complex studies presenting their behavior in conditions of implantation and long-lasting contact with tissue environment during use of an implant, are still an unsolved problem. Currently there are no reports on use of silicon-based coatings on metal implants used in blood vessels surgery. Few studies conducted in this field mostly do not comprise analysis of deformations that occur during implantation or use of this kind of implants. Authors of papers equally often omit issues connected to the influence of technological parameters of the sol-gel method on physicochemical and mechanical properties of siliceous coatings.¹¹ Therefore, in this paper authors attempted to analyze physicochemical and mechanical properties of the SiO₂ films deposited in defined technological conditions on titanium Grade 4 and Ti-6Al-7Nb alloy surface using sol-gel method.

Results

Results of the pitting corrosion resistance tests of the Ti6Al7Nb alloy and titanium Grade 4 samples with differentiated surface preparation method, performed with potentiodynamic method, are presented in (Table 1; Figs. 1 and 2).

The obtained results showed that the average corrosion potential of the titanium Grade 4 samples in their initial state (grinding and mechanical polishing) was \( E_{\text{corr}} = -130 \) mV. Thereby determined anodic polarization curves indicated existence of the passive range to the potential value \( E = +4000 \) mV. In this case, no rapid increase in the anode current density in the analyzed measurement range, which would prove pitting corrosion initiation was observed. In addition, polarization resistance amounting \( R_p = 530 \) kΩcm² and corrosion current density amounting \( i_{\text{corr}} = 0.049 \) µA/cm² were determined using Stern method. Next,
samples coated with SiO2 layer using sol-gel method, at different annealing temperatures were tested. The results showed that this process caused advantageous increase of polarization resistance $R_p$, compared with the initial state samples, regardless of applied variant. Passive range also occurred in all anodic range. Corrosion potential $E_{corr}$ value in turn, slightly increased (Table 1; Fig. 1).

Next, Ti6Al7Nb alloy samples shaped by different surface modifications were analyzed. At the initial stage (grinding and mechanical polishing) corrosion potential amounted $E_{corr} = -275$ mV. As in case of titanium, analyzed alloy indicated existence of the passive range to the potential value $E = +4000$ mV. Also in this case no rapid increase in anode current was observed. Determined polarization resistance and corrosion current density amounted respectively $R_p = 237 \, k\Omega \, cm^2$, $i_{kor} = 0.10 \, \mu A/cm^2$. Subsequently, samples coated with SiO2 using sol-gel method at different heating temperatures were tested. Based on the results it was ascertained that this process caused advantageous increase of corrosion potential value and polarization resistance compared with the initial state samples, regardless of applied variant. It is showed by the values of parameters characterizing their corrosion resistance (Table 1; Fig. 2).

Results of the films adhesion tests show diverse adherence of the SiO2 layer to the Titanium Grade 4 and Ti-6Al-7Nb alloy substrates. It is showed by differentiated values of particular parameters determined on the basis of performed measurements (Table 2). On the basis of the results it was ascertained that samples coated with SiO2 layer annealed at the temperature $t = 430$ °C (2) were characterized with the best adhesion. Critical load value, which caused inside and outside layer delamination for this type of layer amounted $L_c = 6.5$ N for Ti6Al7Nb alloy substrate and $L_c = 9.6$ N for titanium Grade 4 substrate (Figs. 3 and 4).

At the next stage of tests, electrochemical impedance spectroscopic measurements were conducted. Impedance spectrums recorded for titanium 4 and Ti-6Al-7Nb alloy samples with mechanically polished surface and coated with SiO2 film. Nyquist diagrams determined for such prepared samples present fragments of large incomplete semi-circles, which are a typical impedance response of thin oxide films. Presented on the Bode diagrams, maximum values of the phase shift angles in the wide range of frequencies amount $\theta \approx 85^\circ$. Slopes of $\log |Z|$ in the all range of frequencies are close to -1, which demonstrates the capacitive character of passive film (Table 3). High impedance values $|Z| > 10^6 \, \Omega \, cm^2$ in turn, in the range of the lowest frequencies, indicate good dielectric and protective properties of the oxide film fabricated on the commercially pure titanium and Ti-6Al-7Nb alloy samples.

Electrode-oxide layer-solution phase boundaries impedance was characterized by approximation of the experimental data using equivalent electrical circuit model (Fig. 5). In the equivalent electrical circuit (Table 3) Resistor $R_c$, and constant phase element (CPE) represent respectively the ions transition resistance and the capacity of the passive oxide film fabricated on the biomaterial surface. In turn, $R_s$ resistor represents the resistance of the simulated body fluid, in which the tests were performed.

### Discussion

Processes of blood coagulation and restenosis are classified as factors limiting efficacy of using medical products in the cardiovascular diseases treatment. They are a result of not completely adjusted electrochemical properties of their surfaces

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**Table 1. Results of the potentiodynamic tests**

| The method of surface preparation of samples | $E_{corr}$ [mV] | $I_{corr}$ [µA/cm²] | $R_p$ [kΩ/cm²] |
|--------------------------------------------|----------------|-----------------|----------------|
| **cpTi Grade 4**                           |                |                 |                |
| Initial state                              | -130           | 0.049           | 530            |
| 1                                          | -185           | 0.014           | 1790           |
| 2                                          | -205           | 0.007           | 3370           |
| 3                                          | -187           | 0.011           | 2210           |
| 4                                          | -139           | 0.010           | 2590           |
| **Ti6Al7Nb alloy**                         |                |                 |                |
| Initial state                              | -275           | 0.10            | 237            |
| 1                                          | -108           | 0.010           | 2390           |
| 2                                          | -90            | 0.006           | 3970           |
| 3                                          | -136           | 0.022           | 1181           |
| 4                                          | -93            | 0.012           | 2030           |

**Figure 1.** Polarization curves of the titanium Grade 4 samples after different stages of surface modification

**Figure 2.** Polarization curves of the Ti6Al7Nb alloy samples after different stages of surface modification
Table 2. Results of the SiO₂ films adhesion

| Surface modification | Ti-6Al-7Nb alloy | cpTi (Grade4) |
|----------------------|------------------|---------------|
|                      | Measurement 1    | Measurement 2 | Measurement 3 | Average | Measurement 1 | Measurement 2 | Measurement 3 | Average |
| 1                    | 2.7              | 3.2           | 1.2           | 2.3     | 8.63          | 6.6           | 3.3           | 6.1     |
| 2                    | 6.7              | 5.53          | 7.5           | 6.5     | 10.54         | 11.65         | 6.79          | 9.6     |
| 3                    | 11.38            | 3.94          | 4.03          | 6.4     | 5.43          | 5.36          | 6.72          | 5.8     |
| 4                    | 7.04             | 6.54          | 4.04          | 5.8     | 4.02          | 2.23          | 14.6          | 6.9     |

Figure 3. Exemplary test results of the SiO₂ film adhesion (variant 2) to the Ti6Al7Nb alloy substrate

Figure 4. Exemplary test results of the SiO₂ film adhesion (variant 2) to the titanium Grade 4 substrate
to the specificity of the vascular system. So far, mechanisms of generation and development of these adverse processes have not been discovered. An important issue, in view of the processes of generating and propagating action potentials of cardiac muscle cells, are the electrical and magnetic properties of the used metal biomaterials. Metal implant insertion in the blood vessels must not disturb these processes. Physical properties of the biomaterials have a special meaning due to the possibility of hemostasis process initiation as a result of implant insertion in the vascular system. Literature data indicate that the process of interaction between blood and implant materials has not been fully learned. Currently, different types of surface modifications, in order to improve hemocompatibility of the blood contact implants, become more common. Fundamental criterion of usefulness of a particular surface modification method, is obtaining a product with appropriate functional properties. These properties largely depend on the corrosion resistance in the environment of human blood. Hence, in the paper there was proposed a method of surface modification of the pure titanium Grade 4 and Ti-6Al-7Nb alloy with SiO2 oxide in the controlled conditions, differentiating the annealing temperature in the range of 400 °C to 500 °C. Efficacy of the proposed technology of SiO2 layer deposition was evaluated basing on voltammetric and impedance measurements. Supplementarily, in order to determine film adhesion the scratch-test was performed. Regardless of the type of metal substrate, beneficial influence of the surface modification with SiO2 oxide was observed. Potentiodynamic and impedance tests showed differences in the electrochemical properties of the layers annealed in different temperatures. The most beneficial combination of electrochemical properties had SiO2 film, annealed in the temperature of t = 430 °C (2). For this variant, the force causing layer delamination was the highest and amounted f = 6.5 N for Ti-6Al-7Nb and for the cpTi (Grade 4) it amounted f = 9.6 N.

Suggesting appropriate variants of the surface treatment using sol-gel method is perspectively significant, and will contribute to the development of technological conditions with precise parameters of oxide coatings fabrication on the metal implants designed for blood contact, made of titanium alloys.

**Materials and Methods**

Material for the tests were Ti6Al7Nb alloy and titanium (Grade 4) discs, with diameter d = 14 mm and thickness g = 3 mm and chemical composition presented in Table 4.12,13

Samples were subjected to surface treatment including: grinding (Ra = 0.40 µm), mechanical polishing (Ra = 0.12 µm) prior to SiO2 film deposition with sol-gel method (1 - v = 2.5 cm/min, t = 400 °C, t = 60 min, 2 - v = 2.5 cm/min, t = 430 °C, t = 60 min, 3 - v = 2.5 cm/min, t = 460 °C, t = 60 min, 4 - v = 2.5 cm/min, t = 490 °C, t = 60 min). Silicon precursors used in the tests was tetraethyl orthosilicate Si(OCH3)4 (TEOS), and tetramethoxysilane Si(OCH3)4 (TMOS). The rest of initial components included ethyl alcohol (EtOH) and water. Hydrochloric acid (HCl) was used as a catalyst. In the sol-gel method of film fabrication the following stages are distinguished:9,11,14-16

### Table 3. Results of the EIS test

| Surface modification | R, Ω·cm² | R, kΩ·cm² | CPE | Y, Ω⁻¹·cm⁻²·s⁻¹ | n, cm⁻¹ |
|----------------------|---------|-----------|-----|----------------|---------|
| cpTi | 1 (E = -142 mV) | 72 | 6940 | 0.4979E-5 | 0.92 |
| | 2 (E = -157 mV) | 2 | 71 | 18790 | 0.6280E-5 | 0.92 |
| | 3 (E = -158 mV) | 70 | 8570 | 0.6205E-5 | 0.91 |
| | 4 (E = -185 mV) | 68 | 11980 | 0.5866E-5 | 0.93 |
| Ti-6Al-7Nb | 1 (E = -114 mV) | 69 | 1920 | 0.5160E-5 | 0.91 |
| | 2 (E = -21 mV) | 72 | 11840 | 0.4323E-5 | 0.92 |
| | 3 (E = -129 mV) | 70 | 6470 | 0.4415E-5 | 0.93 |
| | 4 (E = -98 mV) | 71 | 8830 | 0.4447E-5 | 0.93 |
1) Production of colloidal suspension (sol), in which used precursor is a dispersed phase and proper alcohol and water are a dispersing phase
2) Complete or partial hydrolysis, which depends on the amount of solvent and presence of catalyst:
   \[ M(OR)_4 + H_2O \rightarrow HO - M(OR)_3 + ROH \] (1)
   or
   \[ M(OR)_4 + 4H_2O \rightarrow M(OR)_3 + 4ROH \] (2)
   where \( M \), metal atom; \( R \), alkyl group; \( ROH \), alcohol
3) Generation of manomer. Particles that were hydrolyzed earlier may now join together and form a manomer:
   \[ (OR)_4M + OH + OH - M(OR)_2 \rightarrow (OR)_2M - O -M(OR)_2 + H_2O \] (3)
   or
   \[ (OR)_2M + OH + OH - M(OR)_2 \rightarrow (OH)_2M - O -M(OR)_2 + ROH \] (4)
4) Gel is formed as a result of manomer polymerization and growth of particles, which join together forming chains and then networks
5) Deposition of sol layer on a substrate
6) Drying and annealing of deposited layers

A condensation reaction begins before the end of hydrolysis. Proportions of initial elements used, type and amount of catalyst used as well as parameters characterizing particular stages of the process influence the properties of obtained films.\(^{16}\)

One of the methods of verifying usefulness of this kind of surface modification are electrochemical tests. For this purpose, potentiodynamic and impedance test were performed to determine corrosion resistance (Fig. 6).\(^{17–20}\)

Potentiodynamic tests were performed in accordance with PN-ISO 17475 recommendations. Polarization curves were recorded using Radiometer PGP-201 potentiostat. Saturated calomel electrode (SCE) type KP-113 was used as a reference electrode. Platinum electrode Pt-P-201 was an auxiliary electrode. At the beginning of the study, open-circuit voltage \( E_{OCP} \) under zero current conditions was measured. Then, anodic polarization curves were recorded. Measurements began when voltage came to \( E_{OCP} + 100 \) mV, with voltage change in anode direction at a rate of 3 mV/s. When the anode current density reached \( i = 1 \) mA/cm\(^2\), polarization direction was changed and return curve was recorded. To designate parameters characterizing corrosion resistance of tested materials, Stern method was also used.

In order to obtain additional information about physicochemical properties of analyzed samples’ surfaces, tests using electrochemical impedance spectroscopy were conducted. Measurements were performed using Auto Lab PGSTAT 302N measurement system, equipped with FRA2 module (Frequency Response Analyzer). Used measurement system enabled to conduct studies in the frequency range \( 10^4 \div 10^3 \) Hz. In the studies, impedance spectrums of the circuit were determined and obtained measurement data was matched to the equivalent circuit. On this basis, numerical values of resistance \( R \) and capacity \( C \) of analyzed circuits were determined. Impedance spectrums of the studied circuit were presented in a form of Nyquista diagrams for different frequency values, and in a form of Bode diagrams. Obtained EIS spectrums were interpreted after matching, using least squares method, to the equivalent electrical circuit.

All electrochemical tests were performed in simulated body fluid at the temperature of \( t = 37 \pm 1 \) °C and \( pH = 7.0 \pm 0.2 \) (Table 5).

Additionally, authors of the paper attempted to evaluate mechanical properties of films deposited with this method by testing adhesion to the titanium Grade 4 and Ti6Al7Nb alloy substrate. Adhesion tests of the deposited films were performed with a scratch test, using open platform equipped in CMS Micro-Combi-Tester in accordance with standard.\(^{21}\) The test was based on generating a scratch using a penetrator—Rockwell diamond cone—with a gradual increase in the normal force loading the penetrator. Critical load, which is a measure of adhesion, is the lowest normal force which leads to the loss of the layer adhesion to the substrate. To evaluate a critical load \( L_c \), record of acoustic emission signals changes were used, as well as friction force and friction factor and microscopic observations under an optical microscope, which is an integral part of the platform. Acoustic emission AE, also called stress-wave emission is defined as an elastic wave generated by release of an internally stored energy from the structure of material. AE detection can be recorded during scratch-test, only if the energy of the bond between layer and the substrate is high enough. As a result of damage generation and propagation during scratch-test, stress wave impact occurs, which leads to the spectrum signal emission, which amplitude corresponds to the damage generated in the interfacial layer-substrate area. Thus, the acoustic signal includes information about sizes and amount of damages. Tests were performed using increasing loading force at the range of \( 0.03 \div 30 \) N and following operation parameters—loading speed 100 N/min, speed of the table displacement 10 mm/min, length of the scratch ~3 mm.

### Table 4. Chemical composition of titanium Grade 4 and Ti-6Al-7Nb alloy

| Type of material         | C    | N    | O    | Fe   | H    | Al   | Nb   | Ta   | Ti   |
|--------------------------|------|------|------|------|------|------|------|------|------|
| cpTi (Grade 4)           | 0.05 | 0.03 | 0.4  | 0.4  | 0.005| -    | -    | -    | rest |
| Ti-6Al-7Nb alloy         | 0.008| 0.03 | 0.08 | 0.22 | 0.003| 6.24 | 6.84 | 0.37 | rest |

### Table 5. Chemical composition of artificial plasma

| Ingredients | Ingredients concentration, g/dm\(^3\) distilled water |
|-------------|------------------------------------------------------|
| NaCl        | 6.800                                                |
| CaCl\(_2\)  | 0.200                                                |
| KCl         | 0.400                                                |
| MgSO\(_4\)  | 0.100                                                |
| NaHCO\(_3\)| 2.200                                                |
| Na\(_2\)HPO\(_4\)| 0.126                                             |
| Na\(_2\)PO\(_4\)| 0.026                                              |
Disclosure of Potential Conflicts of Interest

No potential conflicts of interest were disclosed.

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References

1. Shibli SM, Mathai S. Development and bio-electrochemical characterization of a novel TiO_2-SiO_2 mixed oxide coating for titanium implants. J Mater Sci Mater Med 2008; 19:2971-81; PMID:18360799; http://dx.doi.org/10.1007/s10856-008-3409-2
2. Karasinski P, Jaglarz J, Reben M, Skoczek E, Mazur J. Porous silica xerogel films as antireflective coatings – Fabrication and characterization. Opt Mater 2011; 33:1989-94; http://dx.doi.org/10.1016/j.optmat.2011.03.003
3. Huan Z, Chang J. Study on physicochemical properties and in vitro bioactivity of tricalcium silicate-calcium carbonate composite bone cement. J Mater Sci Mater Med 2008; 19:2913-8; PMID:18357870; http://dx.doi.org/10.1007/s10856-008-3423-4
4. Ni S, Chang J, Chou L. In vitro studies of novel CaO-SiO_2-MgO system composite bioceramics. J Mater Sci Mater Med 2008; 19:359-67; PMID:17607509; http://dx.doi.org/10.1007/s10856-008-3423-4
5. Patel A, Knowles JC. Investigation of silica-iron-phosphate glasses for tissue engineering. J Mater Sci Mater Med 2006; 17:937-44; PMID:16977391; http://dx.doi.org/10.1007/s10856-008-3186-3
6. Areva S, Arazito V, Tiusa S, Jokinen M, Lindén M, Peltona T. Sol-Gel-derived TiO_2-SiO_2 implant coatings for direct tissue attachment. Part II: Evaluation of cell response. J Mater Sci Mater Med 2007; 18:1653-42; PMID:17483880; http://dx.doi.org/10.1007/s10856-007-3064-x
7. Grivishi R. Fast sol–gel technology: from fabrication to applications. J Sol-Gel Sci Technol 2009; 50:241-53; http://dx.doi.org/10.1007/s10971-008-1885-y
8. Belori MM, Rollo JM, Irman Filho A, Rosa AL. In vitro biocompatibility of duplex stainless steel with and without 0.2% niobium. J Appl Biomater Biomech 2004; 2:162-8; PMID:20803434
9. Karasinski P. Influence of technological parameters on the properties of sol-gel silica films. Optica Applicata 2005; 1:253-63
10. Walko W, Paszenda Z, Karasinski P, Basiga M. The silica-titania layer deposited by sol-gel method on the AISI 316L for contact with blood. Journal of Achievements in Materials and Manufacturing Engineering 2013; 15:75-82
11. Brinker CJ, Scherer GW. Sol-gel science. Academic Press, Inc. San Diego 1990.
12. ISO 5832-2:1999 Implants for surgery - Metallic materials - Part 2: Unalloyed titanium.
13. ISO 5832-11:2007 Implants for surgery - Metallic materials - Part 11: Wrought titanium 6-aluminium 7-niobium alloy.
14. Klein LC. Sol-gel optics, processing and application. Kluwer Academic Publishers 1994.
15. Karasinski P. Sol-gel derived optical waveguide films for planar sensors with phase modulation. Optica Applicata 2004; 34:467-75
16. Karasinski P, Gondek E, Drewniak S, Kityk IV. Nanosized blue spectra shift in sol-gel derived mesoporous titania films. J Sol-Gel Sci Technol 2012; 61:195-61; http://dx.doi.org/10.1007/s10971-011-2634-1
17. Basiga M, Walko W, Paszenda Z, Karasinski P. Research on electrochemical properties SiO_2 layer, intended for contact with blood, deposited by sol-gel method. Eur Cell Mater 2013; 26:157
18. Zheludkevich ML, Serra R, Montemorbe MF, Yaukau KA, Salvado JM, Ferreira MGS. Nanostechnology sol-gel coatings doped with cerium nitrate as pretreatments for AA2024-T3, Corrosion protection performance. Electrochim Acta 2005; 51:208-17; http://dx.doi.org/10.1016/j.electacta.2005.04.021
19. Basiga M, Popik P, Paszenda Z, Pochrzast M. The research of electrochemical properties of silica layers used in medical devices intended for contact with blood. Electrical Review 2013; 89:374-8
20. Szewczenko J, Jaglarz J, Basiga M, Kurzyk J, Paszenda Z. Optical methods applied in thickness and topography testing of passive layers on implantable titanium alloys. Optica Applicata 2013; 43:173-80
21. PN-EN 1071-3:2007 Advanced technical ceramics - Methods of test for ceramic coatings Part 3: Determination of adhesion and other mechanical failure modes in an attempt to scratch.