Corrosion study of Ti6Al7Nb alloy after thermal, anodic and alkali surface treatments

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Materials

ABSTRACT

Purpose: The aim of the work was to work out methods to improve biocompatibility of the Ti6Al7Nb alloy by creating thick, porous layer which ensure corrosion resistance and which could be a base for biological reactions leading to improvements in the tissue bond with the implant.

Design/methodology/approach: Surface were prepared using electropolishing, thermal oxidation, thermal oxidation in TiO_2 powder, anodic oxidation in NaH_2PO_4, in NaOH and spark oxidation in $H_2SO_4+H_3PO_4$. The roughness was examined using MSP and LPM. Corrosion resistance tests were carried out in SBF with pH values characterized for neutral, inflammatory and stagnation state. Topographical features were determined using confocal microscope.

Findings: The surface treatments guarantee a smooth surface (low value of Ra and RZDIN) or porous surface structure and high corrosion resistance. Topographical parameters of the layer can be altered according to the duration of that process. The corrosion resistance of the specimens anodically oxidized in NaOH and spark oxidized possessed high corrosion resistance in SBF also in SBF with low and high pH value.

Research limitations/implications: For the layers, further mechanical, chemical, biological and composition examinations are planed.

Practical implications: The paper presents different surface treatments and their influence on corrosion and topographical properties and it could be useful for implant producers to take into consideration one of these methods. Anodic oxidation is a very simple method to ensure high corrosion resistance of implants.

Originality/value: The paper presented new approaches to the surface preparation by spark oxidation in the acids and anodic oxidation in NaH_2PO4 and NaOH at different parameters which haven't previously been used. There were proposed thermal oxidation in TiO_2 powder that was not presented before. The paper compares corrosion resistance and topographical features of the Ti6Al7Nb modified by the new proposed and commonly used techniques.

Keywords: Biomaterials; Thin and thick coatings; Surface treatment

1. Introduction

Nowadays polymers, ceramics and carbon materials dominate in the biomaterial engineering and they replace metallic materials.

However the metals are still in use in many medical procedures. Mechanical properties and relatively easy production process are the main reasons for using metals as implants. In general metallic implants are divided into three main groups: temporary, short and long term implants. The devices that stay in a body less than a

month are classified as short term implants, these which have to stay longer are classified as a long term implants. Nevertheless the month period is not a strict rule. The implants like bone pins, plates, nails and screws represent the first group and they could be made of stainless steel, titanium and its alloy and also cobalt alloy. The implants such as endoprosthesis, intramedullary nails, teeth implant, heart valves and pacemakers which remain slightly longer in the body are mainly produced of cobalt and titanium alloy and also other alloys of noble elements like gold, palladium, platinum, indium, and zirconium (eg. Ecogold, Eurogold). The surface plays the most important role of the implants from the biological point of view. The surface has direct contact with human tissue and is responsible for any adverse reaction of the tissues. Good biocompatibility or bioactivity of the surface guarantees positive biological tissues' response. Positive body response is followed by appearance of bonelike (tissue) artifacts on the surface and lack of infections. However, the implant may also cause severe adverse reactions. It could be a result of many factors such as allergy on some components of the implant, faults in clinical procedures, personal patients features connected with genes, age, gender, coexisting infections and immunological system. There is another possible reaction of the body on the insertion of the implant which is no response. It suggests that the implant is inert and completely inactive in the body. In general, implants surfaces may be prepared in many different ways accordingly to the implants function, time of implantation (remaining in the body) and their durability. Another classification could be also introduced. The classification would take into consideration surface reactions but also other previously mentioned properties. It distinguishes two main groups of implants: bioactive implants and inactive implants. The bioactivity or inactivity involves primarily surface properties of the implants which can be prepared by a large number of surface treatments. Actually, the most popular surface treatments used for implants are: polishing, electropolishing, chemical treatment, anodic oxidation, thermal oxidation, ion implantation (IBAD), PIII, PIII(D), PIRAC, CVD, PVD (also Rf enhanced) [1,8,13,14 16,17,22,25,26,27]. It should be said that surface layers or coatings have to ensure specific tissue responses, high corrosion resistance and also must be adjusted to the mechanical function of the implants. The coatings should be wear resistant and flexible enough too. They cannot be impaired by loads which they bear and during the clinical procedures (sterilization, prebending of implants). It indicates that wide interdisciplinary studies are required to launch new surface treatment.

Nowadays development of the metallic materials used for implants are associated with its increase in bioactivity. Bioactivity is understood as an ability of the surface to initiate chemical reactions that lead to tissue formation on the implant's surface. It causes the rise of implants acceptance in the body. At the same time it can accelerate the healing of hard tissue due to new tissue formation on the surfaces.

Currently research that is concentrated on an increase in bioactivity concern mainly titanium and its alloy and applied either chemical and mechanical methods. One of the simplest reported bioactive coatings on titanium is a titanium dioxide [1,8, 14]. Titanium dioxide occurs on the surface of titanium and its alloys in contact with air but this kind of layer is poorly defined and no more than 7 nm thick. However, much thicker and well defined layers can be produced by chemical and electrochemical methods like electropolishing, anodic oxidation or spark oxidation. These kinds of layers were widely described by Lausmaa [13] who conducted complex examinations of anodic oxide films formed on cp Ti and Ti6Al4V. The layers were prepared by anodic oxidation in H_2SO_4, H_3PO_4 or 1M acetic acid at potential 5-100V. Some of the specimens were sterilized by steam autoclaving or in the air by dry heat sterilization. The anodic layer was mainly composed of TiO_2 and small amount of anions SO_4^{2-} and PO_4^{3-}. The thickness of the layer was linearly dependent on the potential with rate $\alpha=2nm/V$. Sterilization caused small changes in the chemical composition, namely steam autoclaving resulted in the growth of Ca and H elements in the oxides. Further works of de Sena [8] and Liu [14] showed that cp Ti anodically oxidized in H_3PO_4 when soaked in SBF (simulated body fluid) for up to 35 days caused the precipitation of a layer containing calcium, phosphorus and other elements (magnesium and sodium). The layer was similar to a 'bone-like apatite'. On that basis it could be stated that a thin film of TiO_2 causes chemical reactions that result in apatite structures on the surface. It was also shown that thermally oxidized cpTi at 400°C and 500°C had an ability to form apatite in SBF [26]. However, the same author indicated that cpTi anodically oxidized in electrolytes of H_3PO_4, H_2SO_4 and acetic acid exhibited low capability of apatite deposition. These results are not in common with previously reported results.

There is numerous of works that showed that an increase in bioactivity is related to Ca, P and Na ions which are incorporated in the surface layer. Zhu [26] prepared cp Ti via anodizing and employing a constant current mode in the range of 30-100 A/m^2 in the electrolyte of Ca-GP (calcium glycerophosphate) and CA (calcium acetate). The layer was crystalline, porous and rich in Ca and P. Optimum conditions were obtained for the electrolyte containing 0.02M Ca-GP and 0.15M CA, and current density 70 A/m^2 and voltage 350 V. The layer was 5-7 μm thick and Ca/P ratio was 1.67. Micro arc oxidation (MAO) of cp Ti plates [22] using voltage 250-500 V in βGP (βglycerophosphate disodium salt pentahydrate) and CA resulted in formation of a layer containing TiO_2 and β-$Ca_2P_2O_7$, $CaTiO_3$, α-$Ca_3(PO_4)_2$,and $Ca_2Ti_5O_{12}$. Formation of tricalcium phosphate (TCP) is worthwhile due to its bioabsorbable properties. Carbonated HA (hydroxyapatite) was formed on the surface after immersion for 28 days in SBF. Differences in applied voltage affects the composition of the layer that caused different rate of apatite induction. It was demonstrated that oxide layers containing Ca an P (in the compound mentioned above) have an ability to induce apatite formation in the SBF.

The second group of methods that can be applied to produce bioactive coatings are physical ones. In this group plasma and ion implantation methods dominate. A method which is very promising but has very limited applications is IBAD (Ion Beam Double Assisted). The method enables the implantation of almost any element and compound onto the surface and it is possible to control the implanted dose of ions. Positive results of Ca, P, Na implantation were reported by Wierzchon [25]. It was shown that these elements increase corrosion resistance and bioactivity of the Ti6Al4V alloy. Application of this method to the production practice is almost impossible because it only allows (for now) the coating of flat and relatively small objects. It means that is useless

for implants complex geometry. Furthermore this technique is very expensive thus it would make with implants costly. Another method which is used to improve the bioactivity of titanium implants is PIII (Plasma Immersion Ion Implantation). The layers fabricated using PIII have a dense and open porous structure which characterize good adhesion [17]. Complex 3D objects (e.g. screws, plates, stems) can be coated using PIII. It is, similar to IBAD, a low temperature method that is favorable, but a vacuum is required. This method is not predisposed to modifying surfaces of biological materials but it is used to alter polymeric surface properties. There are some limitations, according to the polymers, which is a temperature and ion dose in the range of 10^{15}-10^{16} ion/cm^2. PIII is also applied to ceramics for surface hardening and modify hydrophobic properties. Also carbon substrate used to produce heart valves can be modified by PIII e.g. nitrogen PIII of carbon resulted in carbon nitride formation and increased the platelet adhesion and protein adsorption by a factor of 2-3. Titanium and its alloys are also coated using PIII e.g nitrogen PIII was used to modify the surface of Ti6Al4V. The TiN layer was up to 1μm thick and resulted in wear reduction. Oxygen PIII of titanium caused rutile formation on the surface. This titanium dioxide form shows better biocompatibility and ensures high corrosion resistance due to its closely packed structure. Mändl [17] affirmed that titanium alloys treated with PIII own better osseointegration properties than untreated alloys. But he indicated that bulk material is the most important to determine biocompatibility.

Liu [15] described the improvement in biocompatibility of titanium by plasma spraying. In spite of the poor adhesion and the presents of interface, titanium sprayed with hydroxyapatite, wollastonite and dicalcium silicate showed excellent bioactivity. But it is noticeable that the bonding strength of bioactive coatings by plasma spraying is weak and need to be improved.

A large amount of work concerns bioactive aspects in *in vitro* tests without the testing specific treatment influence on corrosion resistance. These aspects seems to be very important due to the possibilities of corrosion acceleration in body fluid, especially if the layers are not uniform and electrochemical properties of the coating are much different than the bulk material. From that point of view it also seems to be important to examine corrosion resistance after the deformation of the implant because if the coating is not flexible enough, deformation would cause some cracks, gaps etc, then it could decrease corrosion resistance (if the electrochemical properties of the coating and substrate are different). That kind of examination was done for Ti6Al4V ELI (TAV) anodically oxidized in CrO$_3$ solution and for stainless steel (SS) with carbon (DLC) coating [5,6,19,20,27]. It was shown that both coatings were not sensitive at a deformation angle of up to 90°. For oxidized TAV specimens deformed above 60° an insignificant rise of corrosion potential and anodic current density for potentials above 3 V was observed. It was stated that neither layer is flexible enough to be used for implants like intramedullary nails, deformed no more then 10° in physiological conditions [3] and maxillofacial miniplates deformed up to 90°.

Corrosion resistance for the modified surface was also investigated by Krasicka-Cydzik [10], Baszkiewicz [11] and Starosvetsky [23]. It was presented that anodicaly oxidated TAV in H$_3$PO$_4$ increase corrosion resistance and when soaked in Ringer's solution resulted in a deposition of the bioactive layer Ca-O-P [10]. Krupa and Baszkiewicz [11,25] reported that

implantation of Ca, P, Na and a combination of these elements on TAV had a positive influence on the corrosion resistance. Higher corrosion potential and polarization resistance were observed when compared with non treated specimens. Moreover a lower corrosion rate and current density was noted. Starosvetsky [23] investigated the corrosion resistance of TAV treated via PIRAC nitriding (powder immersion reaction assisted coating). The thin layer of TiN had excellent adhesion and high wear resistance. This method is useful for the complex geometry of some specimens so seems to be good for modifying implants. Corrosion tests revealed significantly lower anodic current density and a notable reduction in metal dissolution in Riger's solution.

This short revive of the latest development in titanium alloy surface preparation showed that currently bioactive coatings which guarantee high corrosion resistance are in demand. So the aim of the work was to examine corrosion resistance of Ti6Al7Nb alloy with surfaces prepared in variety of ways. Additionally in the work procedure of preparing porous coatings with pores of a diameter higher then 1 μm it was shown to enable the ingrowth of bone structures [8] that improve the implant bond with tissue.

The primary objective of the study was to work out methods to improve biocompatibility of Ti6Al7Nb alloy used for biomedical applications. It was done by producing porous oxide layers which guarantee high corrosion resistance and which could be a precursor of biological reactions that lead to improvement of tissue bond with the implant. Further chemical and biological studies are being carried out to prove usefulness of the proposed treatments.

2. Materials and methods

In the study titanium alloy Ti6Al7Nb (TAN) was used. The Samples surface (round bar φ7×20 mm) was prepared by grinding (600 SiC paper), electropolishing, thermal, anodic oxidation or alkali treatment.

The electropolishing was done in the bath that contained HF+H$_2$SO$_4$+ C$_2$H$_2$O$_5$ worked out by the author. The previous studies enabled to establish electrical and time duration parameters of the electropolishing [4,6,7,19].

After electropolsishing the surfaces were prepared using different treatments, which were divided into two following groups:

- heat treatment:
  - temp.500°C in the air, duration 15 min. and 60 min.,
  - temp 500°C samples placed in the container with TiO$_2$ powder, duration 60 min,
- electrochemical oxidation:
  - the anodic oxidation in NaH$_2$PO$_4$ water solution, at potential 30 V, duration 10 min.
  - the anodic oxidation in 1M NaOH, at potential 100 V for 10 min,
  - the spark oxidation in the bath composed of H$_3$PO$_4$ and H$_2$SO$_4$, potential 150 V, duration 1 and 3 min.

The samples were cleaned after each step of the preparation in the ultrasonic cleaner for 6 min. using ethyl alcohol. The thermal oxidation in TiO$_2$ powder was carried out in the ceramic dish which was filled up with the powder. The samples were placed inside the dish. Then the dish was placed in the furnace.

Each of the surface treatments was done on the samples that were initially electropolished.

Following examinations were carried out for every single sample:

- roughness measurements - R_a, R_{zDIN},
- potentiodynamic tests – corrosion study,
- topography observations.

To establish roughness of the sample parameters two measurements methods were used: MSP (mechanical stylus profilometry) using Surtronic R+ by Tylor-Hobson and LPM (non-contact laser profilometry) using confocal microscopy LEXT by Optimus. In these tests R_a and R_{zDIN} were determined.

The corrosion study was carried out in the SBF solution (Na^+ 142, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO_3^- 4.2, HPO_4^{2-} 1.0, SO_4^{2-} 0.5) [2]. The temperature of the solution was 36.6±1°C and pH∈(7.4-7.6). In the study electrochemical research set VoltaLab 21 was used. The anodic polarisation curves were recorded in the potential range (E_{cor}-100mV)-4000 mV. When current density reached 1mA/cm^2 direction of the polarization was reversed and the return curves were recorded. In the study corrosion parameter such as: corrosion potential – E_{cor}, corrosion current density – i_{cor}, polarization ressistance – R_p were evaluated. Supplementary, value of the current densities for 200 mV were determined – i_{200}. 200mV was reported as the highest potential observed in the body so it enabled to compare the specimens in the conditions which resembled body condition.

The samples surfaces topography was examined using the confocal microscope LEXT by Olympus. The diameter of the pores and their depth were measured during this study. The surface profile and 3D images of the surface were also recorded.

The analysis of the examination results enabled to chose two methods of surface preparation for further study. The chosen samples were then undertaken to the successive corrosion tests. The second round of the corrosion study was carried out in the same SBF solution but in two different pH values. The values represented inflammatory state – pH∈(9.7-9.9) and stagnation state – pH∈(5.0-5.2). This part of the study was performed to examine the surface corrosion properties in the harsh body conditions which can occur during healing process and to assess influence of pH value on corrosion resistance of TAN with modified surface.

3. Results

The roughness measurements revealed that results obtained for both methods MSP and LMP were alike. The electropolishing caused drop of the analyzed roughness parameters R_a and R_{zDIN} respectively to 0.12 and 0.5 µm. Following heat treatments and anodic oxidation with the exception of spark oxidation caused consecutive decrease of these parameters – Tab. 1. The results for the spark oxidized samples were significantly different, the rise of the roughness was observed. The R_a and R_{zDIN} parameters increased up to 0.404 and 2.513 µm for specimens oxidized at 150 V for 3 min. – Fig. 1. Shorter time of oxidation (1 min.) resulted in lowering of roughness parameters – R_a=0.35µm and R_{zDIN}=2.423µm – Fig. 2. Grater roughness of the spark oxidized samples was one of the primary aims of the study.
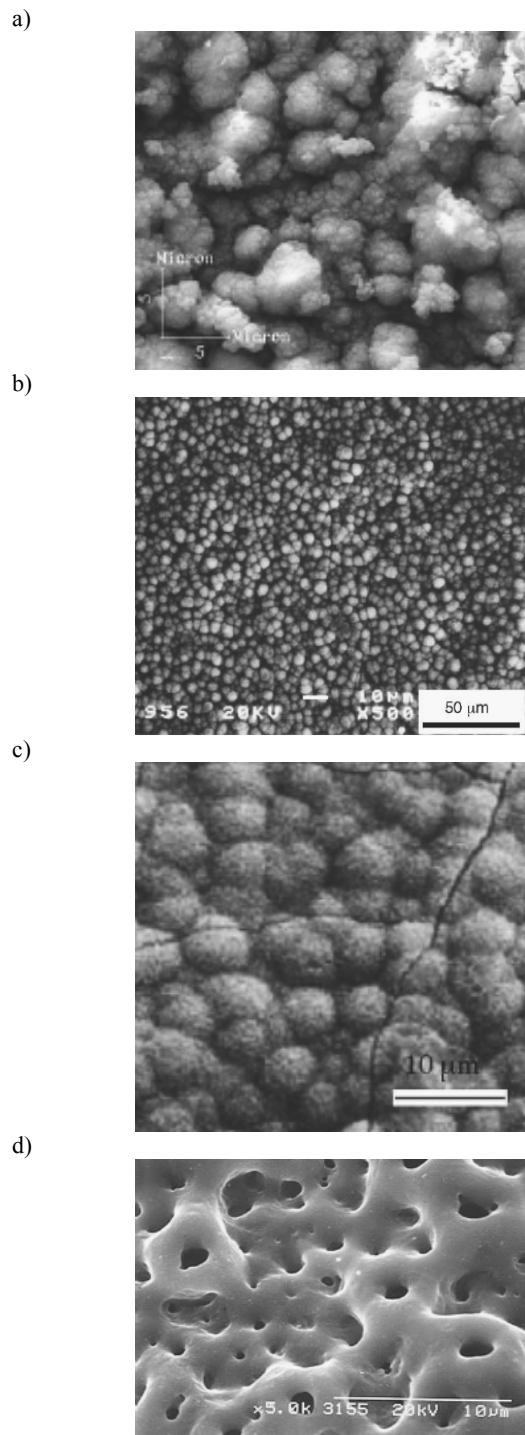
a)

b)

c)

d)

Fig. 1. Surface of the titanium and its alloys: a) Ti plate etched with H_3PO_4 and soaked for 21 days in SBF [8], b) SEM images of apatite particles deposited on the Ti surfaces after soaked in SBF for 5 days [14], c) cpTi oxidized in 1 MH2SO4 solution at 155 V and then soaked in SBF for 6 days [14], d) morphologies of anodic oxide films of titanium at 70 A/m^2, 348V (final voltage) [13]
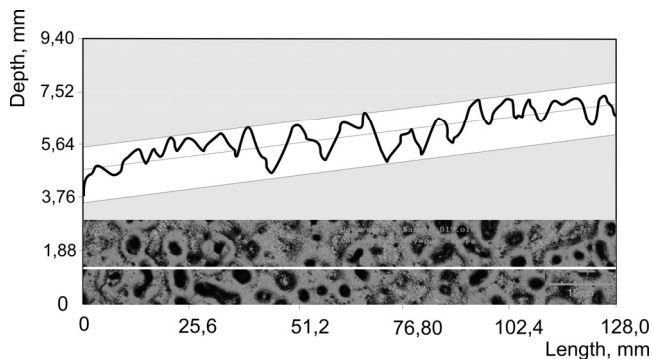
Fig. 2. Roughness profile for the spark oxidized specimen at 150 V for 3 min

The corrosion tests showed differences in the corrosion resistance of the specimens after different surface treatments. The electropolishing increased moderately determined corrosion parameters compared with the ground samples. The parameters for electropolished samples were: E_{cor}=-314 mV, i_{cor}=30.25 nA/cm^2 and R_p=523 kΩ·cm^2. The heat treatment at 500°C for 15 min. caused the additional improvement of the corrosion parameters which raised to: E_{cor}=-152 mV, i_{cor}=2.15 nA/cm^2 and R_p=3.16 MΩ·cm^2. The improvement of the corrosion parameters was less significant when the duration of the treatmnet was extended to 60 min and the parameters were then: E_{cor}=-210 mV, i_{cor}=25.4 nA/cm^2 and R_p=1.38 MΩ·cm^2 – Fig. 3. These results were highly unexpected and they are not consistence with previous research but done for different titanium alloys. The thermal oxidation in TiO$_2$ powder increased corrosion potential and corrosion current density (E_{cor}=-115 mV, i_{cor}=8.70 μA/cm^2) when compared with the ground and electropolished samples. However, a drop in the polarisation resistance for the thermally oxidised in TiO$_2$ samples was observed – R_p=446 kΩ·cm^2 – Fig. 3.

A notable increase of the parameters was noted for the specimens anodically oxidised in NaOH solution. The corrosion potential and polarisation resistance rose to +68mV and 4.12 MΩ·cm^2 and the corrosion currents were at the level of 4.9 nA/cm^2.

The corrosion parameters were significantly altered by the spark oxidation. After the 1 min. oxidation improvement of the parameters was observed: E_{cor}=+190 mV, i_{cor}=0.76 nA/cm^2 and R_p=13.5 MΩ·cm^2. The oxidation time extension to 3 minutes resulted in further improvement of the parameters: E_{cor}=+350 mV, i_{cor}=0.36 nA/cm^2 and R_p=27 MΩ·cm^2 – Fig. 5.

The current densities comparison recorded at the voltage of 200 mV for the samples showed analogical dependency. The electropolishing caused minor changes in the current density, a slight decline to 6.16 μA/cm^2 was observed. Surprisingly, a significant decrease of current density was observed after heat treatment for 15 min. (i_{00}=0.07 μA/cm^2), while 60 min. duration caused a less meaningful decrease (i_{200}=2.375 μA/cm^2). A drop of the current density at 200 mV was also observed for later treated samples. The current density was as follow: for anodically oxidized in NaH$_2$PO$_4$ – 1.89 μA/cm^2, for oxidized in NaOH – 50.8 nA/cm^2 and for spark oxidized for 1 min. – 1.1 nA/cm^2. It

was impossible to determine that value for spark oxidized for 3 min because the polarization curve was recorded from the potential 100 mV below corrosion potential. The start potential was grater than 200 mV – Table 1.
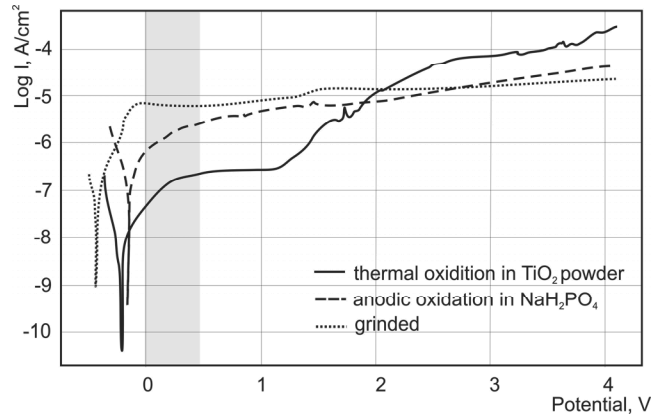

Fig. 3. Potentiodynamic curves recorded for grinded, thermally oxidised in TiO$_2$ powder (60 min.) and anodically oxidised in NaH$_2$PO$_4$ specimens

The confocal microscope observations revealed that the surface of the samples, except the ones obtained after spark oxidation, were smooth, mostly transparent, and didn't show crystalline features. Their thickness was below of the instrument resolution. The top layers reflected surface topography of the substrate. The spark oxidised samples had crystalline structure with numerous pinholes. The diameters and depths of the pinholes were 3.67 μm and 1.74 μm for specimens oxidised for 1 min. and for oxidised for 3 min. were 2.83 μm and 1.01 μm – Fig. 4. The longer oxidation process resulted in higher uniformity of the surface structure and grater numbers of holes which had slightly smaller diameters. The pinhole were also more regular – Fig. 5.
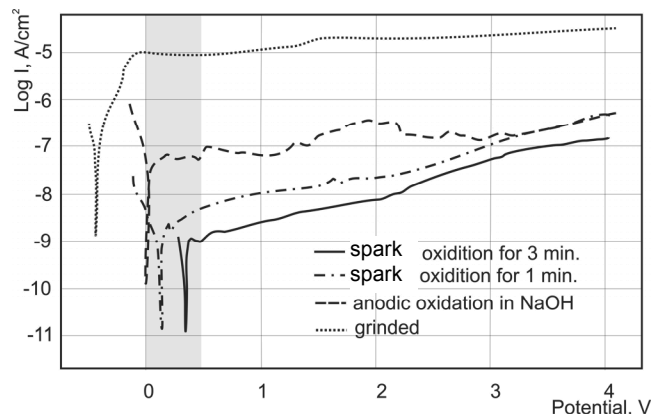

Fig. 4. Potentiodynamic curves recorded for grinded, anodically oxidised in NaOH and spark oxidized (1 and 3 min.) specimens

Table 1.
Results of the roughness and corrosion tests for TAN with surface modified in different ways

Determined parameter	Grinded	Electro-polished	Thermally oxidized, 500°C, 15 min.	Thermally oxidized, 500°C, 60 min.	Thermally oxidized, TiO$_2$ powder, 500°C, 60 min.	Anodic oxidation, NaH$_2$PO$_4$ water solution, 30 V, 10 min.	Anodic oxidation, 1M NaOH, 100 V, 10 min	Spark oxidation H$_3$PO$_4$ +H$_2$SO$_4$, 150 V, 1 min	Spark oxidation H$_3$PO$_4$ +H$_2$SO$_4$, 150 V, 3 min
Roughness tests									
R_a^{MSP}, μm	0.57	0.12	0.05	0.04	0.08	0.09	0.04	0.35	0.39
R_a^{LPM}, μm	0.55	0.09	0.04	0.03	0.07	0.07	0.04	0.35	0.404
R_{ZDIN}^{MSP}, μm	3.45	0.50	0.44	0.32	0.48	0.50	0.27	2.20	2.36
R_{ZDIN}^{LPM}, μm	3.41	0.51	0.38	0.29	0.49	0.51	0.26	2.42	2.51
Corrosion tests									
E_{cor}, mV (E[i=0], mV)	-357 (-347)	-314 (-315)	-152 (-190)	-210 (-212)	-115 (-162)	-131 (-152)	+68 (+30)	+190 (+168)	+350 (+361)
i_{cor}, nA/cm^2	70.9	30.25	2.15	25.4	8.4	186.7	4.9	0.76	0.36
R_p, MΩ·cm^2	0.217	0.523	3.16	1.38	0.446	0.165	4.12	13.5	27
i_{200}, μA/cm^2	6.93	6,15	0.07	2.375	0.35	1,89	50.8 nA/cm^2	1,1 nA/cm^2	In cathodic area

On the basis of the studies results two types of surface preparation were chosen for more complex corrosion study: the anodic oxidation in NaOH at 100V for 10 min., and the spark oxidation in the mixture of acids at 150V for 3 min. These two procedures ensured the high corrosion resistance. One of them treatments gave smooth surface (low R_a and R_{ZDIN} value) and the other porous surface structure. The porous surface structure seems to be very promising for biomedical applications, further modifications. This structure is supposed to have ability to initiate bone ingrown and form HAP on the surface.

The corrosion tests carried out in SBF which were buffered to pH 5 and 10 showed some differences in corrosion behavior for analyzed samples – table 2. The decrease in pH resulted in rise in the corrosion potential for the anodically oxidized samples to E_{cor}=+154 mV, additionally, the current density for 200 mV dropped to 18.5 nA/cm^2. Rest of the parameters remained close the values determined for neutral pH. The pH increase resulted in growth of the polarization resistance – R_p=27 MΩ·cm^2, and also in the corrosion current density and current density decrease for 200 mV – i_{cor}=0.32 nA/cm^2, i_{200}=1.8 nA/cm^2 – Fig. 6.

Analysis of the spark oxidized samples showed that either a growth or fall in the pH value resulted in the corrosion potential drop – Table 2. The lower pH value caused serious decrease of the polarization resistance which was then R_p=4.31 MΩ·cm^2, a rise of the current density to i_{cor}=4.43 nA/cm^2, i_{200}=18.7 nA/cm^2 was also observed. A higher pH value (9.7÷9.9) caused also the corrosion potential decrease and current parameters increase that were then: E_{cor}=+130 mV, i_{cor} =1.52 nA/cm^2, i_{200}=0.9 nA/cm^2. The polarization resistance remained at the similar level as recorded for the physiological pH – Fig. 7.
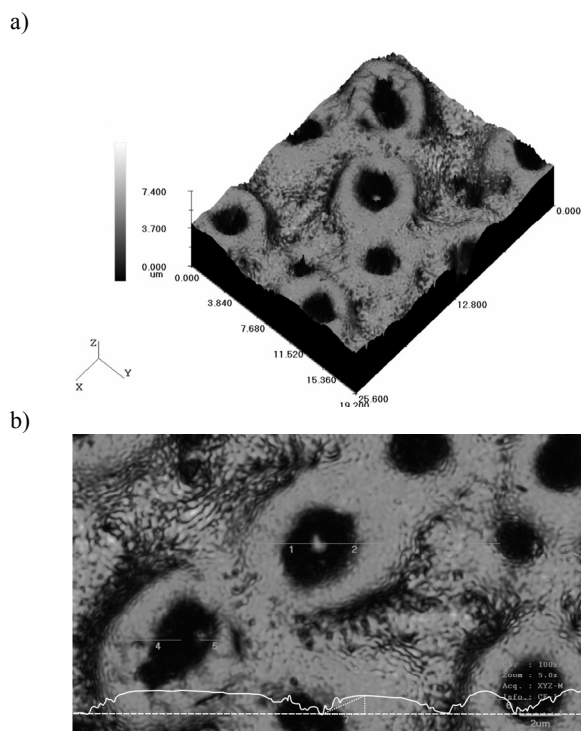
a)

b)

Fig. 5. The surface of the specimen after spark oxidation in potential 150V for 3min., a) 3D view of the structure, b) the measurement of the hole depth

Table 2.
Results of the corrosion tests carried out in SBF having pH 5 and 10

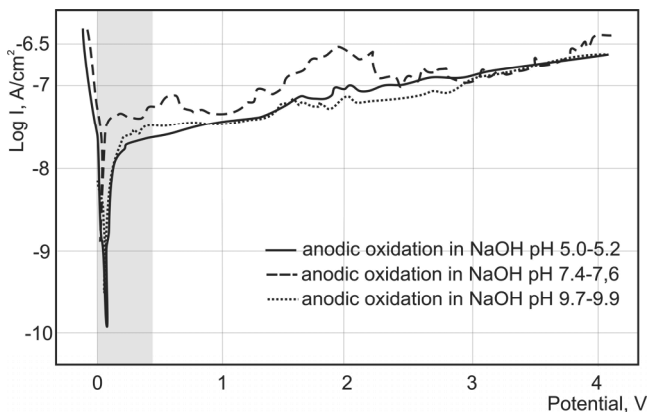| Determined parameter	anodic oxidation, 1M NaOH, 100 V, 10 min			spark oxidation H_3PO_4 +H_2SO_4, 150 V, 1 min		
	pH∈ (5.0-5.2)	pH∈ (7.4-7.6)	pH∈ (9.7-9.9)	pH∈ (5.0-5.2)	pH∈ (7.4-7.6)	pH∈ (9.7-9.9)
E_{cor}, mV (E=0, mV)	+154 (+102)	+68 (+30)	+63 (+75)	+125 (+80)	+350 (+361)	+130 (+139)
i_{cor}, nA/cm^2	4.99	4.9	0.32	4.43	0.36	1.52
R_p, MΩ·cm^2	3.86	4.12	27	4.31	27	28.5
i_{200}, nA/cm^2	18.5	50.8	1.8	18.7	In cathod. area	0.9

Fig. 6. Potentiodynamic curves recorded for anodically oxidised in NaOH specimens examined in SBF with different pH
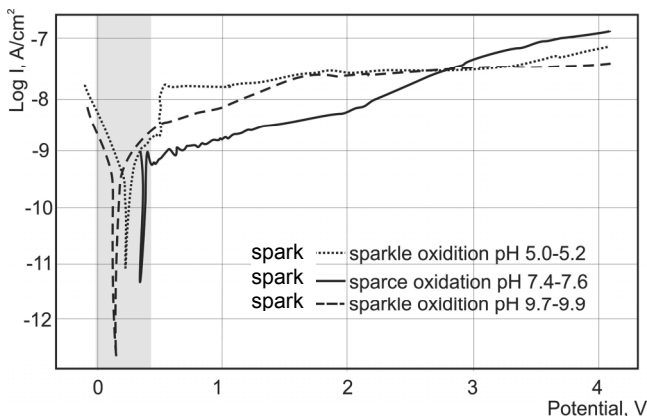

Fig. 7. Potentiodynamic curves recorded f spark oxidized specimens in SBF with different pH

4. Discussion

The results of the experiments and observations presented in this paper showed that the corrosion behavior, topography and surface layer structure of the Ti6Al7Nb alloy can be altered using different methods. In the work three groups of methods were taken into consideration: thermal, anodic and spark oxidation. They were carried out in variety of conditions. In general, roughness measurements showed that every single treatment made R_a and R_{ZDIN} parameters smaller compared with the electropolished specimens, with exception of spark oxidation. The last mentioned treatment caused an increase in this parameter due to its different structure which was crystalline and porous.

Corrosion tests showed that anodic oxidation in NaOH at potential 100V for 10 min., and spark oxidation (both described variants) had remarkable influence on the increase in corrosion resistance. A significant rise in the corrosion resistance and polarization resistance was observed after these modifications. The corrosion resistance grew about 650 mV after spark oxidation for 3 min. and about 390 mV after anodic oxidation in NaOH compared with the electropolished specimens. Polarization resistance rose up to 27 MΩ·cm^2 for spark oxidized specimens and to 4.9 MΩ·cm^2 for anodically oxidized in NaOH ones. Anodic current density was also very low for these specimens. The results showed that both treatments ensure very high corrosion resistance. Current density recorded for the specimens at the potential 200 mV showed very low value that indicated the low electrochemical activity of the surfaces. That kind of behavior is very positive because low current density in the body conditions means that corrosion shouldn't occur. The spark oxidized specimens presented better corrosion resistance compared with to the anodically oxidized in NaOH specimens. It could be the reason for the much thicker and crystalline layer on the spark oxidized specimens. The other treatments also had a positive influence on the corrosion behavior but it was not so outstanding.

Anodic oxidation carried out in NaH_2PO_4 caused a drop in the polarization resistance. Additionally, the analysis of the potentiodynamic curve showed that current density in the passive range was close to the current density observed for grinded specimens. These results showed that this treatment didn't ensure any significant growth in the corrosion resistance.

The topography assessment showed that thermal and anodic oxidation, presented in the paper, guarantees smooth, uniform, thin and transparent layer on the surface. Observation on the confocal microscope didn't reveal any crystalline features on the surface and their thickness was below the resolution of the microscope. Observation of the spark oxidized specimens showed that they were relatively thick and its structure was porous. Porosity was dependent on the duration of the oxidation. A longer

time ensured more regular structure with numerous pinholes. The depth and diameter of the pinholes was moderately smaller (about 0.7 µm in depth and about 1 µm in diameter) for 3 min. oxidation – Fig. 8. It showed that the longer oxidation duration gave a denser and better ordered layer that can be a base for further modification or can enable tissue to grow into the pores and improve its bond with the bone e.g. for bone screws [9,12,21,24,28].
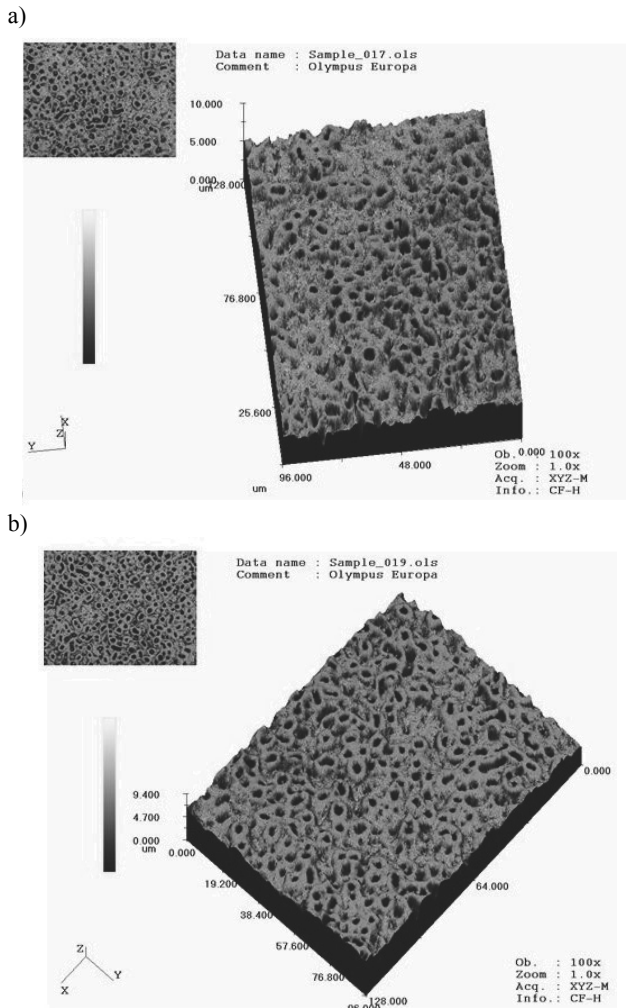
a)

b)

Fig. 8. Surface of the specimens surface after spark oxidation: a) 150V 1min., b) 150V 3 min

In the last part of the examinations corrosion tests in SBF at a pH 5.0-5.2 and 9.7-9.9 were carried out for anodically oxidized in NaOH and spark oxidized for 3 min. specimens. The tests showed that a higher amount of chloride anions Cl^- in the SBF decreased the corrosion potential and polarization resistance for both types of specimens. Also corrosion current density grew and showed that corrosion resistance dropped but it was still very high. That kind of behavior is caused by more aggressive corrosive environment of the SBF. It is notable that the lower value of pH

had less pernicious influence on anodically oxidized specimens. It is probably due to compounds incorporated into the surface during alkali treatment. It is highly possible that these compounds react with electrolyte and neutralize their activity.

The higher pH value didn't cause such a significant change. However, a drop in the corrosion potentials were observed for spark oxidized specimens. At the same time, polarization resistance remained at the same level while for specimens anodically oxidized in NaOH an increase of this parameter was observed. An insignificant rise in the current variables was observed for spark oxidized specimens. The opposite situation was observed for the other group.

The test showed that a drop in the pH value can slightly decrease the corrosion resistance, which seems to be important when we consider introducing the layer into the manufacture. But it must be said that the corrosion resistance after both treatments, was very high. The increase in the pH didn't cause any drastic changes in the corrosion resistance; it even improved some corrosion parameters for the anodically oxidized specimens. The analysis of the potentiodynamic curves showed that both changes didn't affect character of the curves. They possessed a wide passive range and very low current density value throughout the whole range of tests.

For these layers further mechanical, chemical, biological and composition examinations are planed. Further modifications of the porous layer are also planned.

5. Conclusions

On the basis of the studies results following statements were established:
1. It is possible to improve the samples roughness of the samples via electropolishing. Further improvement of the roughness parameters can be obtained through heat treatment (500°C, 15 and 60 min.), in TiO_2 powder (500°C, 60 min.), anodic oxidation in NaH_2PO_4 (30V, 10 min.) and in NaOH (100V, 10 min.).
2. The Spark oxidation (150V, 1 and 3 min.) resulted in increase of the R_a and R_{ZDIN} parameters compared with the electropolished samples.
3. Heat treatment, anodic and spark oxidation increased the corrosion resistance of the Ti6Al7Nb alloy. A significant rise in the corrosion resistance was observed after spark oxidation (150V 3 min.) and anodic oxidation in NaOH (100V, 10 min.). A drop of the polarization resistance was observed for the anodic oxidised in NaH_2PO_4 samples.
4. The thin films on the surface obtained via heat treatment and anodic oxidation were uniform and transparent. The spark oxidation resulted in porous top layer with relatively grater thickness. 3 minutes spark oxidation caused ensured regular porous structure of the top layer with numerous of pinholes (1.01 µm depth and 2.83 µm diameter). The depths and diameters of the holes were grater for 1 min. oxidation, respectively: 1.74 µm and 3.67 µm.
5. The corrosion study of the anodically oxidized in NaOH and spark oxidized for 3 min. in SBF solution with pH value (5.0-5.2) showed that the corrosion resistance for both types of the specimens decreased. It could be assumed that it is the

result of for higher concentration of Cl^- anions in the solution. The higher pH value (9.9-9.9) resulted in a drop of the corrosion potentials for the spark oxidized samples while the polarization resistance remained at the same level. For the samples anodically oxidized in NaOH a rise of polarization resistance was observed at a higher pH value.

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