

## Corrosion behavior of Ti6Al7Nb alloy after different 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<sub>2</sub> powder, anodic oxidation in NaH<sub>2</sub>PO<sub>4</sub>, in NaOH and sparkle oxidation in H<sub>2</sub>SO<sub>4</sub>+H<sub>3</sub>PO<sub>4</sub>. 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 sparkle 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 sparkle oxidation in the acids and anodic oxidation in NaH<sub>2</sub>PO<sub>4</sub> and NaOH at different parameters which haven't previously been used. There were proposed thermal oxidation in TiO<sub>2</sub> 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 & thick coatings; Surface treatment

### 1. Introduction

Despite the fact that polymers, ceramics and carbon materials force out metallic materials in many medical procedures they are still in common use. The main reasons for using metallic implants are their mechanical properties and that they can be produced using conventional methods. In principle metallic implants are

divided into three main groups: temporary, short and long term implants. Implants which stay in a body less than 30 days are classified as an short term, these which have to stay longer are rather classified as a long term ones. But this 30 days period is not a strict rule. Implants like bone plates, pins, screws represent the first group and they can be made of stainless steel, titanium and its alloy and cobalt alloy. Endoprosthesis, intramedullary nails,

teeth implant, heart valves and pacemakers must remain in a body much longer and are mainly made of cobalt and titanium alloy and also other alloys of noble elements like gold, palladium, platinum, indium, zircon (eg. Ecogold, Eurogold). From the biological point of view the surface is the most important part of the implants. The surface has direct contact with human tissue and is responsible for acceptance of the implant. Surface reactions can lead to good acceptance and cooperation of the implant with the surrounding tissue. That situation is when on the surface a substance that resembles tissue appears. But the surface can also cause adverse reactions. This is mainly when a patient cannot accept some elements of the implant. There is one more possible reaction of the body after the insertion of an implant which is no response. It means that the implant is inert and completely inactive in the body. Broadly speaking, implants surfaces can be prepared in a different way accordingly to the implant's function, duration of stay in the body and durability. We could also introduce another classification that takes into consideration surface reactions but also other previously mentioned properties. This classification distinguishes two main groups: bioactive implants and inactive implants. Bioactivity or inactivity involves surface of the metallic implants which can be prepared by a variety of surface treatments. The most common surface treatment used for implants are: polishing, electropolishing, chemical treatment, anodic oxidation, thermal oxidation, IBAD, PIII, PIII(D), PIRAC, CVD, PVD (also Rf enhanced) [1-9,12]. It should be said that surface coatings have to ensure specific tissue responses, high corrosion resistance and also must be adjusted to the mechanical function of the implants. Coatings should be flexible enough and wear resistant too. They cannot be damaged while bearing load and during the operation (prebending of implants). It shows that interdisciplinary test are required to launch an implant or its coating technology.

The aim of this work was to work out methods to improve biocompatibility of Ti6Al7Nb alloy by creating thick, porous layer which ensure high corrosion resistance and which could be a precursor of biological reactions that lead to improvement of tissue bond with the implant. Biological experiments were not in the scope of the article.

## 2. Materials and methods

In the research Ti6Al7Nb (TAN) was used. The surface of the specimens (round bar  $\phi 7 \times 20$  mm) was prepared by grinding – SiC paper, electropolishing, coating creation. Electropolishing was carried out in the bath composed of  $\text{HF} + \text{H}_2\text{SO}_4 + \text{C}_2\text{H}_2\text{O}_5$  worked out by the author. On the basis of previous research electrical and time duration parameters were established [7,12]. In the next operation the surface was prepared in different ways. The treatments were divided into two groups as follows:

- thermal oxidation:
  - in the air, temp.  $500^\circ\text{C}$ , 15 min. and 60 min.,
  - in the  $\text{TiO}_2$  powder, temp  $500^\circ\text{C}$ , 60 min,
- electrochemical treatment:
  - anodic oxidation in  $\text{NaH}_2\text{PO}_4$  water solution, at potential 30 V for 10 min.
  - anodic oxidation in 1M NaOH, at potential 100 V for 10 min,

- sparkle oxidation in mixture of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$ , at potential 150 V, for 1 and 3 min.

After each step of preparation the specimens were cleaned in the ultrasonic cleaner for 6 min. using ethyl alcohol.

Thermal oxidation in  $\text{TiO}_2$  powder were carried out in the ceramic container which was filled with the powder and then the specimens were placed within it. The container were then located in the furnace. Each surface treatment was carried out on the electropolished specimens.

For the specimens the following examination were done: roughness tests, corrosion resistance tests, topography examination. MSP (mechanical stylus profilometry) using Surtronic R+ by Taylor-Hobson and LPM (non-contact laser profilometry) using confocal microscopy LEXT by Olympus were carried out to determine  $R_a$  and  $R_{ZDIN}$  parameters of the specimens.

The corrosion test were carried out in the SBF [10] solution at temp.  $36.6 \pm 1^\circ\text{C}$  and  $\text{pH} \in (7.4 \div 7.6)$  using the electrochemical research system VoltaLab 21. Potentiodynamic curves were recorded in the potential range  $E_{\text{cor}} - 100\text{mV} \div 4000\text{mV}$ , weather current density reached  $1\text{mA}/\text{cm}^2$  the polarization direction was reversed and return curve was recorded. Additionally, value of the current densities for 200 mV were determined –  $i_{200}$ . This potential represents the highest potential observed in the body so it enabled to compare the specimens in the condition found in the body.

The topography of the specimens surface was surveyed using the confocal microscope LEXT by Olympus. In the examinations the pores diameter and depth of the porous layers were measured. The profile of the surface and 3D images of the surface were recorded too.

On the basis of these results two methods of surface preparation were chosen to the further examination. Chosen options were then submitted to the successive corrosion tests. The tests were carried out in the SBF in two different pH values that represented inflammatory state –  $\text{pH} \in (9.7 \div 9.9)$  and stagnation state –  $\text{pH} \in (5.0 \div 5.2)$ . The latest tests were performed to examine the surface corrosion properties in the extreme body conditions.

## 3. Results

The roughness tests using MSP and LMP showed that both results were very similar. Both analyzed parameters  $R_a$  and  $R_{ZDIN}$  improved after electropolishing and they were respectively 0.12 and 0.5  $\mu\text{m}$ . Further thermal and anodic oxidation treatments with the exception of sparkle oxidation caused consecutive improvement of these parameters. The opposite results were observed for specimens which were treated via sparkle oxidation. Both parameters  $R_a$  and  $R_{ZDIN}$  increased up to 0.404 and 2.513  $\mu\text{m}$  for specimens oxidized at 150 V for 3 min. – fig. 1. These parameter were slightly lower for oxidation when the oxidation duration was 1 min. They were then  $R_a = 0.35\mu\text{m}$  and  $R_{ZDIN} = 2.423\mu\text{m}$ . The increase in roughness after sparkle oxidation was expected and purposeful.

Corrosion tests revealed differences in the corrosion resistance of the specimens after surface treatments. Electropolishing improved moderately determined corrosion parameters compared with the grinded specimens, and for electropolished specimens they were:  $E_{\text{cor}} = -314$  mV,  $i_{\text{cor}} = 30.25$  nA/cm<sup>2</sup> and  $R_p = 523$  k $\Omega$ ·cm<sup>2</sup>. Thermal oxidation at  $500^\circ\text{C}$  for

15 min. caused the further improvement of these parameters which raised to  $E_{\text{cor}}=-152$  mV,  $i_{\text{cor}}=2.15$  nA/cm<sup>2</sup> and  $R_p=3.16$  M $\Omega$ -cm<sup>2</sup>. The rise was less significant when the duration of the oxidation was extended to 60 min and these parameters were  $E_{\text{cor}}=-210$  mV,  $i_{\text{cor}}=25.4$  nA/cm<sup>2</sup> and  $R_p=1.38$  M $\Omega$ -cm<sup>2</sup>. Those results were rather unexpected and they are not in compliance with previous research but done for different titanium alloys. Compared with the grinded and electropolished specimens thermal oxidation in TiO<sub>2</sub> powder increased corrosion potential and corrosion current density ( $E_{\text{cor}}=-115$  mV,  $i_{\text{cor}}=8.70$   $\mu$ A/cm<sup>2</sup>) but a drop in the polarisation resistance was noted –  $R_p=446$  k $\Omega$ -cm<sup>2</sup> – fig 2.

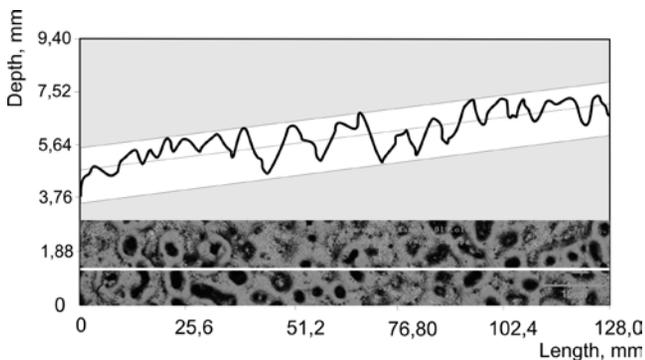


Fig. 1. Roughness profile for the specimen spark oxidized at 150 V and for 3 min.

A notable improvement of the parameters was noted for the specimens anodically oxidised in NaOH. The corrosion potential and polarisation resistance surged to +68mV and 4.12 M $\Omega$ -cm<sup>2</sup> and the corrosion current was equal to 4.9 nA/cm<sup>2</sup>. The sparkle oxidation altered these parameters and for 1 min. long oxidation they were  $E_{\text{cor}}=+190$  mV,  $i_{\text{cor}}=0.76$  nA/cm<sup>2</sup> and  $R_p=13.5$  M $\Omega$ -cm<sup>2</sup>. The extension of the oxidation time to 3 minutes improved the parameter. They were then  $E_{\text{cor}}=+350$  mV,  $i_{\text{cor}}=0.36$  nA/cm<sup>2</sup> and  $R_p=27$  M $\Omega$ -cm<sup>2</sup> – fig. 3.

The comparison of the current densities at 200 mV recorded for the specimens showed similar dependency. Electropolishing caused an insignificant decline in that value to 6.16  $\mu$ A/cm<sup>2</sup>. Remarkably decrease of current density was observed after thermal oxidation for 15 min. ( $i_{100}=0.07$   $\mu$ A/cm<sup>2</sup>), while 60 min. duration caused a less important decrease ( $i_{200}=2.375$   $\mu$ A/cm<sup>2</sup>). The decline of current density at 200 mV was observed for other treatments too and that parameter for anodically oxidized in NaH<sub>2</sub>PO<sub>4</sub> was 1.89  $\mu$ A/cm<sup>2</sup>, for oxidized in NaOH 50.8 nA/cm<sup>2</sup> and for sparkle oxidized for 1 min. was 1.1 nA/cm<sup>2</sup>. It was not possible to determine that value for sparkle oxidized for 3 min. because the polarization curve was recorded 100 mV below corrosion potential and was more than 200 mV. It can be said that this value is in the cathodic area of the curve.

Observation on the confocal microscope revealed that the surface layers, except the ones obtained after sparkle oxidation, were very smooth, transparent, didn't show crystalline features and were not thick enough to be measured using the microscope. The layers reflected the surface topography of the bulk material. The sparkle oxidised specimens possessed crystalline structure with numerous pinholes. The depths and diameters of the pinholes

were 1.74  $\mu$ m and 3.67  $\mu$ m for specimens oxidised for 1 min. while oxidised for 3 min. were 1.01  $\mu$ m and 2.83  $\mu$ m – fig. 4. The longer oxidation duration resulted in more uniform surface structure with larger numbers of holes which had slightly smaller diameter and were more regular.

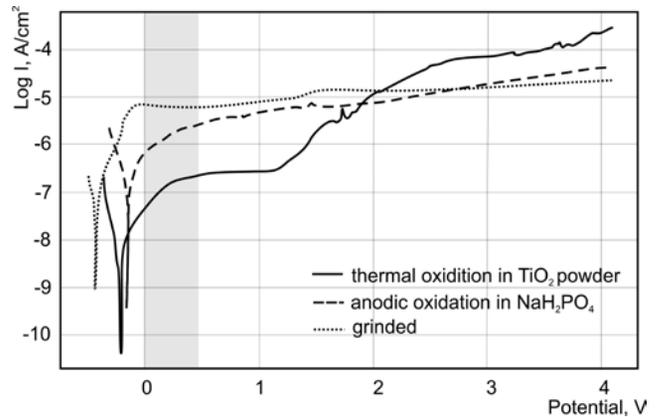


Fig. 2. Potentiodynamic curves recorded for grinded, thermally oxidised in TiO<sub>2</sub> powder (60 min.) and anodically oxidised in NaH<sub>2</sub>PO<sub>4</sub> specimens

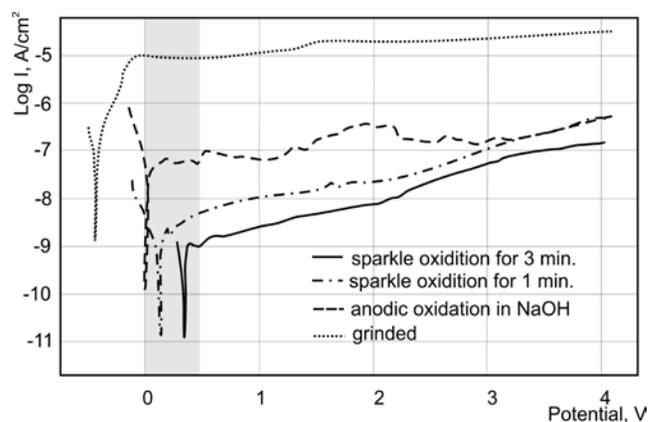


Fig. 3. Potentiodynamic curves recorded for grinded, anodically oxidised in NaOH and sparkle oxidized (1 and 3 min.) specimens

On the basis of the experiments' results two methods of surface preparation were chosen for further corrosion tests: anodic oxidation in NaOH at 100V for 10 min., and sparkle oxidation in mixture of acids at 150V for 3 min. These procedures ensure the highest corrosion resistance and had, one of them smooth surface (low  $R_a$  and  $R_{\text{ZDIN}}$  value) and the other a porous surface structure. The porous structure seems to be very promising for further modifications and assessment of their ability to initiate formation of HAP and bone ingrown.

The corrosion tests carried out in SBF with pH altered to 5 and 10 revealed some differences in corrosion behavior. The pH decrease caused a rise in corrosion potential for anodically oxidized specimens to  $E_{\text{cor}}=+154$  mV, at the same time the current density for 200 mV dropped to 18.5 nA/cm<sup>2</sup>. The other parameter stayed around the value determined for neutral pH. The increase

of the pH value resulted in the polarization resistance growth –  $R_p=27 \text{ M}\Omega\text{-cm}^2$ , decrease of the corrosion current density and current density for 200 mV –  $i_{\text{cor}}=0.32 \text{ nA/cm}^2$ ,  $i_{200}=1.8 \text{ nA/cm}^2$ .

For the sparkle oxidized specimens both a growth and fall in the pH value caused corrosion potential decrease. The lower pH value resulted in serious decline of the polarization resistance which was then  $R_p=4.31 \text{ M}\Omega\text{-cm}^2$ , it caused a growth of the current density to  $i_{\text{cor}}=4.43 \text{ nA/cm}^2$ ,  $i_{200}=18.7 \text{ nA/cm}^2$ . However, higher pH value (9.7÷9.9) led to corrosion potential decrease and current parameters increase that were then:  $E_{\text{cor}}=+130 \text{ mV}$ ,  $i_{\text{cor}}=1.52 \text{ nA/cm}^2$ ,  $i_{200}=0.9 \text{ nA/cm}^2$ . Polarization resistance remained at the same level.

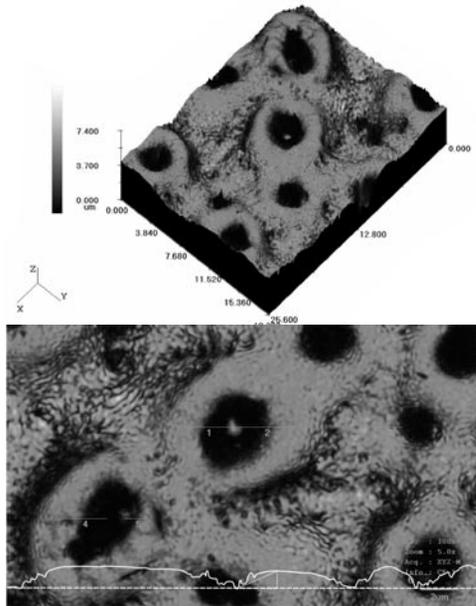


Fig. 4. The surface of the specimen after sparkle oxidation in potential 150V for 3min., a) 3D view of the structure, b) the measurement of the hole depth

## 4. Conclusions

In summarizing the experiments results we can state that:

1. The roughness of the specimens can be improved using electropolishing. Further improvement can be obtained through thermal oxidation (500°C, 15 and 60 min.), in  $\text{TiO}_2$  powder (500°C, 60 min.), anodic oxidation in  $\text{NaH}_2\text{PO}_4$  (30V, 10 min.) and in NaOH (100V, 10 min.). Sparkle oxidation (150V, 1 and 3 min.) increased the  $R_a$  and  $R_{ZDIN}$  parameters compared with the electropolished specimens.
2. The surface treatments: thermal, anodic and sparkle oxidation increase the corrosion resistance of the Ti6Al7Nb alloy. A remarkable rise in the corrosion resistance was noted after sparkle oxidation (150V 3 min.) and anodic oxidation in NaOH (100V, 10 min.). The anodic oxidation in  $\text{NaH}_2\text{PO}_4$  resulted in a drop in polarization resistance.
3. The thin films obtained via thermal and anodic oxidation were uniform and transparent. The sparkle oxidation resulted in a relatively thick, porous layer. Longer oxidation duration resulted in a more regular structure with numerous of pinholes

that had 1.01  $\mu\text{m}$  depth and 2.83  $\mu\text{m}$  diameter. Depths and diameters of the holes were bigger for 1 min. oxidation: 1.74  $\mu\text{m}$  depth and 3.67  $\mu\text{m}$  diameter.

4. The corrosion examination of the anodically oxidized in NaOH and sparkle oxidized for 3 min. in SBF with lowering pH value (5.0÷5.2) caused a decrease in the corrosion resistance for both types of the specimens. It could be the result of for higher concentration of  $\text{Cl}^-$  anions in the electrolyte. The higher pH value (9.9÷9.9) caused a drop in the corrosion potentials for sparkle oxidized specimens while polarization resistance remained at the same level. For specimens anodically oxidized in NaOH a growth in polarization resistance was observed at a higher pH value.

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