The techniques of surface modification play a significant role in forming the physical and chemical properties of titanium and its alloys. Among many techniques for the layers’ application, chemical and electrochemical methods are particularly interesting, as they make it possible to control the process of depositing thin layers of the material and modifying their properties through a change of reagents and the parameters of the deposition process. A special advantage the methods bring is the possibility to obtain layers that offer a perfect coating for geometrically complex surfaces. Apart from improved haemocompatibility, a significant issue related to the creation of the layers is also a proper set of physicochemical properties. Therefore, the study comprised tests of the physicochemical properties of oxide layers deposited on the surface of samples taken from a Ti-6Al-7Nb alloy. The samples were subject to various surface modifications, i.e., grinding, electrolytic polishing, a SiO2 layer was applied using the sol-gel method and TiO2 by means of an anodic oxide and medical sterilisation methods (EO and steam). The corrosion-resistance tests were performed on the basis of registered anodic polarisation curves and the Stern method. Electrochemical Impedance Spectroscopy (EIS) was also used in order to evaluate the phenomena taking place on the surface of the tested alloys. As a part of the evaluation of the mechanical properties of surface layers created in such a way, hardness tests and tests of the adhesion of those layers to a metallic substrate were made. Measurements of the instrumental hardness were made with the Oliver & Pharr method, whereas the adhesion of the layers to the substrate was measured by means of a scratch test. The suggestion of proper surface treatment variants has perspective significance and will help to develop the technological conditions with specified parameters of the oxide coating’s creation on the surface of metallic implants.

Keywords: Ti-6Al-7Nb (Ti67) alloy, sol-gel, anodic oxide, scratch-test, nano-hardeness, EIS, potentiodynamic method

The haemocompatibility of titanium alloys, including the Ti-6Al-7Nb alloy, is increased by, e.g., modification of the surface layer of cardiovascular implants with surface-engineering methods. The methods used to modify the surface layers must ensure the repeatability and uniformity of their physical and chemical properties. The structure and chemical composition of the titanium and titanium-alloy implant layer may be modified with the use of various methods, among which the main ones are mechanical, chemical, electrochemical and thermal methods. Mechanical treatment techniques are used to modify the surface topography. The properties of the oxide layer after the application of these techniques are difficult to control. Chemical methods include primarily etching and passivation, which result in the formation of a thin (<10 nm) oxide layer composed mostly of TiO2 and oxides of the alloying elements, as well as impurities from chemical reagents. Repeatable layers with a fully controlled thickness, microstructure and chemical composition are obtained with high-temperature treatments, immersion in H2O2, alkaline etching, electropolishing, anodic oxidation and vacuum treatments. However, the

1 INTRODUCTION

The haemocompatibility of titanium alloys, including the Ti-6Al-7Nb alloy, is increased by, e.g., modification of the surface layer of cardiovascular implants with surface-engineering methods. The methods used to modify the surface layers must ensure the repeatability and uniformity of their physical and chemical properties. The structure and chemical composition of the titanium and titanium-alloy implant layer may be modified with the use of various methods, among which the main ones are mechanical, chemical, electrochemical and thermal methods. Mechanical treatment techniques are used to modify the surface topography. The properties of the oxide layer after the application of these techniques are difficult to control. Chemical methods include primarily etching and passivation, which result in the formation of a thin (<10 nm) oxide layer composed mostly of TiO2 and oxides of the alloying elements, as well as impurities from chemical reagents. Repeatable layers with a fully controlled thickness, microstructure and chemical composition are obtained with high-temperature treatments, immersion in H2O2, alkaline etching, electropolishing, anodic oxidation and vacuum treatments. However, the
method for increasing the haemocompatibility of titanium and titanium-alloy surfaces, which is increasingly often applied, involves using the sol-gel technique to produce thin oxide coatings based on Si. The advantage of this method is the low temperature at which the coating is produced, which guarantees unchanged mechanical properties of the metal base. Moreover, this method ensures the sol’s homogeneity, the possibility to register polycondensate molecules, a large number of metalorganic and inorganic metal salt compounds, used as precursors, as well as the possibility to obtain multi-ingredient coatings of high purity on different bases. Another important factor affecting the final quality of the products that come into contact with blood is the proper resistance of the modified surface to medical sterilisation. Presently, cardiovascular implants are usually sterilised with ethylene oxide (EO) and with pressurised-water steam in an autoclave. The positive results of already-published papers by the authors regarding the assessment of the usefulness of the surface-layer modification processes involving anodic oxidation, as well as the creation of a SiO₂ layer with the sol-gel method, enabled the selection of the most beneficial parameters for the process. An analysis of the literature data indicates that reducing the number of failed bloodstream disease treatments depends to a large extent on the electrochemical stability of the surface layer under the medical sterilisation conditions. Therefore, this article evaluates the effects of steam and ethylene oxide sterilisation processes on the physical and chemical properties of the surface layer of the Ti-6Al-7Nb (Ti67) alloy.

2 MATERIALS AND METHODS

The tested material was a titanium alloy Ti-6Al-7Nb (Ti67) in the form of discs of diameter \( d = 14 \) mm and thickness \( g = 2 \) mm. A number of surface-treatment methods were applied to the samples, including the following processes: grinding with the use of 1000- and 1200-grit sand paper, electrolytic polishing, the application of layers with the sol-gel technique, and anodic oxidation. The electrolytic polishing was conducted in a solution based on chromic acid \( z (E-395 \text{ by POLIGRAT Gmbh}) \), with a current density \( i = 10–30 \text{ A/cm}^2 \). The final stage of the surface treatment consisted of applying layers with two different techniques: sol-gel and anodic oxidation. In the case of the sol-gel method, a layer of SiO₂ was applied with the following process parameters: \( v = 2.5 \text{ cm/min, } T = 430^\circ \text{C, } t = 60 \text{ min.} \) The silica precursor used in the test was tetraethoxysilane \( \text{Si(OC}_2\text{H}_5)_4, \) TEOS, and tetramethoxysilane \( \text{Si(OCH}_3)_4, \) TMOS. The remaining starting ingredients contained ethyl alcohol (EtOH) and water. In the case of anodic oxidation a layer of TiO₂ was applied in an electrolyte based on phosphoric acid and sulphuric acid (TitanColor by POLIGRAT GmbH) at a potential of 90 V. Previous studies conducted by the authors made it possible to select the most favourable parameters, both for the sol-gel technique and for the anodic oxidation. Next, the prepared samples were sterilised with ethylene oxide and steam. The sterilisation with ethylene oxide was conducted in a 12-h cycle of exposure to ethylene oxide at 30 °C. After the process was completed, the samples were ventilated for 2 h with the use of an EOGas series steriliser from the Andersen Products company. The sterility assurance level (SAL) obtained during the cycle was \( 10^{-6} \). The process was controlled with a chemical and biological indicator, as well as an indicator of exposure to the ethylene oxide control. The steam sterilisation was conducted in a Basic Plus autoclave at \( T = 134 \text{ °C, under a pressure of } p = 2.1 \text{ bar for } t = 12 \text{ min.} \)

To evaluate the effect of ethylene oxide sterilisation and steam sterilisation on the mechanical and electrochemical properties of the proposed Ti67 surface modification, the authors suggested the following tests of the mechanical properties: measurements of the adhesion of the analysed layers to the base and their hardness. Electrochemical tests included potentiodynamic and impedance measurements.

First, as part of the mechanical properties’ tests, the measurement of a layer’s adhesion to the base was performed using the scratching method, with the use of an open platform equipped with a Micro-Combi-Tester from the CSM company, in accordance with the standard. The test consisted of making a scratch using a penetrator – a Rockwell diamond cone – with a gradually increasing normal force weighting the penetrator. To assess the value of the critical force \( L_c \), records of variations in the acoustic emission signals, the friction force and the friction coefficient were used, as well as a microscopic observation with the use of an optical microscope, and an integral component of the platform. The tests were performed with an increasing weighting force of 0.03–20 N, and with the following parameters: weighting speed 10N/min, table movement speed 1.5 mm/min, and length of the scratch ~3 mm.

Later, measurements of the nanohardness of the layers applied with the sol-gel method, and with the anodic oxidation method, were conducted. The instrumental hardness measurement was performed with the Oliver and Pharr method, using a Berkovich penetrator. The speed of the increasing weighting and relieving force was 0.40 mN/min. The measurement of the layer’s nanohardness was made with the Micro-Combi-Tester open platform from the CSM Instruments company, where the weighting force of the penetrator was 0.20 mN.

Subsequently, as part of the electrochemical properties testing, the resistance to pitting erosion was tested with the potentiodynamic method, recording the polarisation curves. They were used as a base to determine the values of specific parameters: the corrosion potential
The opening potential $E_{OCP}$ was determined without any electric current. Then, the anode polarisation curves were recorded. The measurements started for the potential of $E_{start} = E_{OCP} - 100$ mV, and the change of potential in the anodic direction was at a speed of $0.16$ mV/s, until the anodic current density reached a value of $i = 1$ mA/cm$^2$, or the measurement range of 4V was reached.\textsuperscript{14}

As part of the EIS testing, the impedance spectra of the analysed corrosive systems were determined, and then the obtained measurement data were adjusted to the corresponding substitute systems. The impedance spectra of the systems tested are presented on Nyquist diagrams for the different frequencies as well as on Bode diagrams. Also, the numerical values of the resistance $R$ were established, as well as the capacities $C$ of the analysed corrosive systems. The resulting spectra were interpreted after being adjusted with the least-squares method to the substitute electric systems. Based on the results obtained, it was possible to characterise the impedance of the phase boundaries, i.e., Ti-6Al-7Nb (Ti67) – surface layer – blood plasma, with an approximation of the impedance data using an electric model of a substitute circuit. The testing environment was an artificial blood-plasma solution of $T = 37\pm1 \, ^{{\circ}}\text{C}$. The measurements were performed using the AutoLab PGSTAT 302N measurement system, equipped with a FRA2 (Frequency Response Analyser) module. The reference electrode was a saturated calomel electrode SCE, type KP-113, whereas the supporting electrode was a platinum electrode type PtP-201. The system used made it possible to conduct tests within the frequency range $10^4$ to $10^{-3}$ Hz. The voltage amplitude of the sinusoid stimulating signal was $10$ mV.\textsuperscript{15, 16}

Table 1: The results of the adhesion of the layer on the Ti67 substrate

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Failure of the layer</th>
<th>Ti67+SiO$_2$</th>
<th>Ti67+TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>The value of registered indenter load $F_i$, N</td>
<td>initial state</td>
<td>steam</td>
</tr>
<tr>
<td>Measurement 1</td>
<td>Delamination $L_{c1}$</td>
<td>2.01</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>Complete break $L_{c2}$</td>
<td>3.57</td>
<td>2.24</td>
</tr>
<tr>
<td>Measurement 2</td>
<td>Delamination $L_{c1}$</td>
<td>2.48</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>Complete break $L_{c2}$</td>
<td>3.89</td>
<td>2.45</td>
</tr>
<tr>
<td>Measurement 3</td>
<td>Delamination $L_{c1}$</td>
<td>3.55</td>
<td>1.41</td>
</tr>
<tr>
<td></td>
<td>Complete break $L_{c2}$</td>
<td>5.02</td>
<td>2.12</td>
</tr>
<tr>
<td>Average</td>
<td>Delamination $L_{c1}$</td>
<td>2.68</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>Complete break $L_{c2}$</td>
<td>4.16</td>
<td>2.27</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>Delamination $L_{c1}$</td>
<td>±0.78</td>
<td>±0.12</td>
</tr>
<tr>
<td></td>
<td>Complete break $L_{c2}$</td>
<td>±0.76</td>
<td>±0.16</td>
</tr>
</tbody>
</table>

Figure 1: Results of the adhesion tests of the sample Ti67+TiO$_2$ (steam)

Slika 1: Rezultati preizkusov oprjemljivosti vzorca Ti67+TiO$_2$ (para)
3 RESULTS AND DISCUSSION

The test results for the adhesion of the analysed layers to the base made of Ti-6Al-7Nb (Ti67) alloy are presented in Table 1, Figures 1 and 2. It was found that in the case of samples in the initial state the critical value that caused the layer delamination, the external and the internal delamination, was \( L_{c2} = 4.16 \text{ N} \) – Ti67+SiO\(_2\) and \( L_{c2} = 7.42 \text{ N} \) – Ti67+TiO\(_2\). While using both steam and ethylene oxide sterilisation, the critical force value was reduced and for Ti67+SiO\(_2\) it was \( L_{c2} = 2.27 \text{ N} \) (steam), \( L_{c2} = 3.58 \text{ N} \) (EO), whereas for Ti67+TiO\(_2\) it was \( L_{c2} = 6.53 \text{ N} \) (steam), \( L_{c2} = 4.70 \text{ N} \) (EO). Regardless of the analysed sample type, an acoustic emission signal did not occur during the test, which indicates that the binding energy between the coating and the base was too low. Moreover, no significant differences between using steam sterilisation or ethylene oxide sterilisation were found.

Furthermore, the hardness of the analysed layers was tested. The test results are presented in Figures 3 and 4. On the basis of the results obtained, an increase in the hardness value following the steam sterilisation, as well as the ethylene oxide sterilisation, compared to the initial state was observed. The polarisation curves determined for the samples with a Ti67(TiO\(_2\)) layer are presented in Figure 5, and for the samples with a Ti67(SiO\(_2\)) layer in Figure 6.

Regardless of the surface-preparation method or the sterilisation technique, a hysteresis loop was not present in the anodic range up to 4 V, which is a positive phenomenon, indicating the absence of pitting erosion. The determined values of the corrosive potential \( E_{corr} \), and the polarisation resistance \( R_p \) for the individual variant of the samples tested were as follows: Ti67+TiO\(_2\) – \( E_{corr} = -112 \text{ mV} \), Ti67+SiO\(_2\) – \( E_{corr} = -123 \text{ mV} \).
The impedance spectra obtained for the Ti67+TiO2 and Ti67+TiO2 (steam) samples were interpreted by comparing them to the substitute electric system, which indicates the presence of an anodic layer composed of two sublayers:6–11 a compact internal layer and a porous external one, composed primarily of titanium oxide TiO2 (Figure 9b). It is indicated by the presence of the Warburg impedance, which in this case represents probable oxygen transport to the alloy surface. In addition, the CPEp element models the capacity of the surface material sphere with a significant surface extension, while Rp,

### Table 2: EIS analysis results

<table>
<thead>
<tr>
<th>Surface</th>
<th>$R_{se}$ Ω cm²</th>
<th>$R_{pore}$ Ω cm²</th>
<th>$CPE_{pore}$</th>
<th>$R_p$ kΩ cm²</th>
<th>$CPE_p$</th>
<th>$R_{ct}$ MΩ cm²</th>
<th>$CPE_{dl}$</th>
<th>$W$ μΩ cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti67(TiO2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>initial state</td>
<td>17</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>68</td>
<td>0,3580E-4</td>
<td>0,92</td>
<td>25,00</td>
</tr>
<tr>
<td>EO</td>
<td>18</td>
<td>54</td>
<td>0,5407E-6</td>
<td>0,93</td>
<td>1830</td>
<td>0,6381E-6</td>
<td>0,83</td>
<td>20,88</td>
</tr>
<tr>
<td>steam</td>
<td>17</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>42</td>
<td>0,2534E-6</td>
<td>0,96</td>
<td>0,96</td>
</tr>
<tr>
<td>Ti67(SiO2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>initial state</td>
<td>17</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>53</td>
<td>0,9823E-5</td>
<td>0,98</td>
<td>9,44</td>
</tr>
<tr>
<td>EO</td>
<td>18</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>52</td>
<td>0,7975E-5</td>
<td>0,92</td>
<td>11,87</td>
</tr>
<tr>
<td>steam</td>
<td>18</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>87</td>
<td>0,1213E-4</td>
<td>0,89</td>
<td>4,84</td>
</tr>
</tbody>
</table>
reflects the electrolyte resistance in this sphere of the material (Table 2).

The impedance spectra obtained for the Ti67+TiO2 (EO) sample were adjusted to the substitute system, which indicates the presence of three time invariables (Figure 9c). The symbols in Figure 9c signify the following: CPE_{pore} – capacity of the surface sphere of the material with a high level of surface extension (porous), R_{pore} – electrolyte resistance in pores, CPE_{double} – capacity of the double layer, R_{ct} – charge-transfer resistance at the phase boundary (it characterises the speed of the corrosive process), C_{dl} – capacity of the double layer, CPE_{P} – capacity of the passive layer (oxide), R_{P} – passive (oxide) layer resistance (Table 2).9–11

4 CONCLUSIONS

An important problem in the process of modelling the performance properties of the implants used in cardiology is the proper selection of the physical and chemical characteristics of their surface. The physico-chemical properties of the implant surface should be adjusted to the characteristics of the human tissue environment – in this case, to the blood environment. The safety of the device’s use is also associated with the need to follow the proper procedures preventing the transfer of pathogenic microorganisms into the human organism. The aim of these procedures is to remove and effectively destroy the microorganisms, i.e., to obtain sterile devices that meet the quality requirements defined in the standards. For medical devices that come into contact with blood, sterilisation with ethylene oxide or pressurised-water steam are the most frequently used. Therefore, accounting for the effect of these sterilisation processes on the properties of the analysed surface layer will enable their complete characterisation.17

The conducted impedance tests revealed that on the surface of the Ti-6Al-7Nb alloy, modified through anodic oxidation, a porous layer (TiO2) is found, in which parallel channels with an ionic conduction are formed. It is a layer that forms as a result of diffusion processes, which is indicated by the presence of the Warburg impedance. These processes intensify during the activity of pressurised-water steam in the sterilisation process. As a consequence, it leads to the partial dissolution of TiO2, as indicated by the lower value of the ionic transfer resistance R_{ct}. Sterilisation with ethylene oxide positively increases the R_{ct} value. This phenomenon may be caused by the increased oxygen concentration near the surface during the process, and the formation of an additional oxide layer. Diffusion processes associated with the partial dissolution of oxide in the solution were not observed in the samples with an applied SiO2 layer. This layer appears to be more compact than the TiO2. Regardless of the sterilisation method used, no changes in the properties of the layer were found. Only, as was the case with the samples undergoing anodic oxidation, a reduction in the ion-transfer resistance R_{ct} was observed. The conducted tests for layer adhesion to the base revealed a slight reduction in the adhesive force of the sterilised layers versus the samples in the initial state. The tests demonstrated the better adhesion of TiO2 than SiO2 to the Ti-6Al-7Nb alloy base. The hardness testing conducted in the study revealed that pressurised steam does not cause significant changes to the hardness of the TiO2 or SiO2, whereas sterilisation with ethylene oxide results in an increased hardness of the SiO2 and a significant reduction in the hardness of the TiO2. This phenomenon
may cause increased porosity of the TiO_2 layer, resulting from the effect of ethylene oxide, as demonstrated in the EIS tests. The SiO_2 layer also reacts when in contact with ethylene oxide. Its hardness significantly increases, which may be the cause of the formation on its surface of an additional oxide layer, based on Ti and Si, revealing better mechanical properties. To sum up, the conducted study of the modified surfaces of the Ti-6Al-7Nb alloy samples with the TiO_2 and SiO_2 layers demonstrated that the medical sterilisation process affects the physical and chemical properties of these layers. The selection of the proper surface layers should also depend on the manner and the method of sterilisation.

Acknowledgements

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