Modification of titanium and its alloys implants by low temperature surface plasma treatments for cardiovascular applications

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Impairment of the cardiovascular system is a major cause of mortality in humans. Cardiac implants are made mostly of titanium and its alloys and various methods have been used to improve their surface properties. Titanium nitride — TiN and titanium oxide — TiO₂ surface layers are promising materials to improve biocompatibility in this respect. Modifying their surface properties in the nanoscale may impact their protein adsorption and cellular response to the implant. Nitriding and oxynitriding processes in low-temperature plasma, also involving the use of an active screen, seem to be prospective methods in the production of titanium nitride and oxide forming a diffusive outer zone of titanium nitride TiN (nanocrystalline) + TiN + α-Ti(N) or oxynitried TiO₂ (nanocrystalline) + TiN + Ti₂N + α-Ti(N) surface layers on titanium alloy. Also a hybrid method that combines oxidizing and the RF CVD process for producing a-C:N.H (amorphous carbon modified with nitrogen and hydrogen) + TiO₂ (nanocrystalline titanium oxide-rutile)-type composite surface layers on NiTi shape memory alloys is noteworthy in the context of medical applications. The paper presents the characteristics of these diffusion multi-phase layers in terms of their microstructure, topography, hardness, residual stress, corrosion and wear resistance, wettability as well as biological properties such as: adsorption of proteins — fibrinogen and albumin, and platelet adhesion during interaction with blood components (human plasma and platelet-rich plasma).

The results suggest that these layers, produced using the new hybrid processes, exhibit a high potential for improving cardiac implant properties. The article is based on research carried out by the authors and the interpretation of the obtained results is made on the basis of literature data regarding the surface layers of titanium oxides and titanium nitride produced by various methods. 

Key words: titanium and its alloys, NiTi shape memory alloy, surface treatments under glow discharge conditions, hybrid processes, biocompatibility, cardiovascular implants.

1. INTRODUCTION

Titanium and its alloys have been increasingly used in medicine as cardiological implants such as artificial heart valves, elements of heart assist devices, e.g. centrifugal pumps [1, 2]. This is so because of the advantageous properties of these materials, among which the high corrosion resistance, good mechanical properties accompanied by twice lower density compared to steel and CoCrMo alloys commonly used in medicine. However, the results of the investigations performed thus far show that the possibility of optimization of the mechanical and biological properties of titanium and its alloys by modifying their chemical and phase compositions or by subjecting them to various thermal or thermoplastic treatments have reached their upper limit. Meanwhile the request for implants increases and the requirements are directed towards the production of biomaterials that are safe in long-term use [3, 4]. Although currently or modified titanium alloys are used for the manufacture of cardiological implants, a risk of complications still persists, chiefly due to the coagulation of blood in contact with the implant surface [5, 6]. In seeking the solution to this problem, the prospective methods seem to be surface engineering techniques which permit producing surface layers and coatings with precisely specified structure, chemical and phase compositions, porosity, surface topography, good adhesion to the substrate, and also high resistance to biological corrosion and friction properties which guarantee good biocompatibility. Surface engineering processes can also produce coatings that transfer anticoagulants. However, even in these techniques, some new problems arise. For example, clinical observations of titanium stents covered with a resorbable polymer coatings containing anti-thrombogenic drugs indicate that the migration and proliferation of smooth muscle cells of the blood vessel walls are enhanced and the regeneration and functions of the endothelium are hampered, which is followed by inflammatory reactions [7, 8].

The anti-thrombogenic properties of cardiac titanium implants can be improved by subjecting the implants to surface treatments such as anodic oxidation, radio frequency chemical vapour deposition (RF CVD), microwave CVD (MWCVD), glow discharge-assisted nitriding, ion implantation, and hybrid technologies such as, e.g. those combining nitriding processes with glow discharge oxidation, glow discharge processes with CVD processes or PLD processes which permit producing multi-layer coatings [9–13]. The layers produced on cardiological implants include amorphous hydrogenated silicon carbide (α-SiC:H), nanocrystalline diamond (NCD), diamond-like coatings (DLC), titanium oxide (TiO₂), or amorphous nitrogen-modified hydrogenated carbon (α-C:N:H) [11–18]. Moreover, by modifying the microstructure, chemical composition and phase composition of the surface layers as well as their surface topography and thickness it is possible to produce layers with low residual stress state and low surface energy, and also to control the performance properties of the cardiological implant, such as corrosion resistance, wear resistance, hardness, fatigue strength, and hemocompatibility. Simultaneously, the layers eliminate the migration of titanium and the components of its alloy into the surrounding biological environment, which is known as the metallosis effect. Biological investigations show that the nanostructured layers not only inhibit the blood coagulation, but also improve the adhesion and proliferation of endothelial cells [7, 19, 20]. A prospective hemocompatible materials seem to be titanium nitride (TiN) and titanium oxide (TiO₂) [6, 11]. The properties of the biomaterials can be changed by subjecting them to low-temperature
plasma treatments conducted under glow discharge conditions, i.e. nitriding processes and their modifications (e.g. oxynitriding, carbonitriding, oxycarbonitriding). These processes permit modifying the chemical composition of the outer zone of the nitried diffusive layer (TiN + Ti2N + Ti(N)) by, for example, producing an outer surface zone composed of titanium oxide (TiO2), titanium oxynitride (Ti(ON)), titanium oxycarbonitride (Ti(OCN)), or titanium carbonitride (Ti(CN)) with various chemical compositions, surface topography, morphology, microstructure (or nanostructure), so that the biological properties of the surface of the biomaterial can be tailored to the requirements of its application. In the case of TiO2, it is possible to produce rutile, anatase, brukite which exhibit different biological properties [6].

Also, hybrid processes combining two surface treatments are an effective way to modify the surface of biomaterials. In this way, it can give results that can not be achieved by using only one method. An example of this can be the modification of the NiTi shape memory alloy’s surface in a hybrid process combining glow discharge oxidizing or oxynitriding with the production of a-C:N:H amorphous carbon coating via RF-CVD process [21, 22]. The TiO2 or TiO2 + TiN layers formed in the glow discharge process increases the corrosion resistance and protects against the phenomenon of metallosis (migration of alloy components into the biological environment which is disadvantageous especially in the case of NiTi alloy containing above 50% nickel). On the other hand, the amorphous carbon coating ensures limiting platelet clotting and adequate endothelialisation of the surface, which is a key aspect in long-term cardiac implants [21].

These properties influence on the adsorption of blood proteins and thereby they can additionally restrict thrombogenicity and improve the hemocompatibility of titanium and its alloys [12, 16, 23, 24]. The modification of the surface of titanium and its alloys by surface engineering methods improve the interactions between the implant, the blood vessel walls, and blood cells. With the proper selection of the surface treatment, the implant can properly function for a long time, and its long-term durability is one of the basic goals to be achieved by the new generation of implants (including titanium implants).

2. GLOW DISCHARGE-ASSISTED TREATMENTS OF TITANIUM AND ITS ALLOYS

Titanium exhibits the chemical affinity to oxygen, nitrogen, and carbon (Fig. 1). Hence, in an air atmosphere, the surface of titanium (or its alloy) is covered with a titanium oxides film, about 4÷6 nm thick, which ensure their high corrosion resistance [1]. Titanium oxides formed under glow discharge conditions can be different thicknesses, microstructures, and phase compositions [26]. The active nitrogen, oxygen and carbon particles, as well as the in-status-nascendi atoms of these elements which appear under glow discharge conditions, and also their ions and radicals which are very active chemically, together with defects of the crystalline structure of the surface external zone (generated during the glow discharge treatment at the cathode potential [27, 28]) enable lowering the process temperature. Thus, glow discharge treatment accelerates the formation of the diffusion layer on the parts with complicated shapes. This enables low temperature processes (in the case of a NiTi shape memory alloy even at temperature up to 300°C) (Fig. 2), for example in glow discharge oxynitriding process [18, 21, 25, 29], what permits preserving the advantageous mechanical properties of the implants made of titanium, and, in the case of alloys with shape memory (NiTi), preserving their specific property together with the super-elasticity characteristic [30]. This process allows also producing the homogeneous surface layer on the implants with complicated shape [31, 33].

It should also be noted that titanium nitride, carbide, and oxide (TiO2) exhibit the same crystallographic structure and mutual solubility, which enable producing layers of the Ti(O, C, N) type with various contents of oxygen, carbon, and nitrogen and, thus, with various properties such as e.g. resistance to corrosion (Fig. 3). The chemical composition of these layers can be modified by choosing adequately the process parameters, i.e. the temperature, reactive atmosphere, and glow discharge process duration.
By controlling the technological parameters of the glow discharge-assisted nitriding and oxycarbonitriding, it is also possible to modify the microstructure, topography and surface morphology of the surface layers, and, hence, their surface energy, wettability, and their residual stress state that determine the performance properties of the implants (including their biological properties).

The glow discharge-assisted nitriding processes can be conducted at the cathode potential (a classical glow discharge treatment) or with the active screen (glow discharge surface treatment at the plasma potential) (Fig. 4) which leads to additional advantage from the point of view of biological properties of the layer permitting to produce additionally an outer nanocrystalline titanium nitride (TiN) zone with a 30÷50 at. % nitrogen content [32].

This is so since during nitriding at the plasma potential the effect of cathode sputtering on the formation of the diffusive surface layer is limited, therefore the TiN + Ti2N + α-Ti(N) type surface layer is smoother and thinner compared to layers produced at the cathode potential and has homogenous thickness on parts with complicated shapes (Fig. 5).

The thickness of the diffusive nitried layers increases also with increasing process temperature which is accompanied by an increase of its surface roughness [27].

As shown by the analysis of the phase composition of the TiN + Ti2N + α-Ti(N) nitried layers produced on Ti6Al4V titanium alloy at the cathode potential as well as at the plasma potential at a temperature between 600÷700°C, the layer produced at the cathode potential contains more the Ti2N phase. This, in turn, entails a change of the residual stress state present in the layers and a change in the wettability angle of the titanium nitride (TiN) surface (Tab. 1).

Table 1. Roughness parameters (AFM) of the nitried layers produced on the Ti6Al4V titanium alloy by glow discharge nitriding at the plasma potential (PP) and the cathode potential (PK), residual stress state measured by the sin^2ψ method and wettability

<table>
<thead>
<tr>
<th>Material</th>
<th>TiN layer thickness μm</th>
<th>Surface roughness</th>
<th>Residual stress MPa</th>
<th>Wettability °</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ra μm</td>
<td>Rq μm</td>
<td>Rt μm</td>
<td></td>
</tr>
<tr>
<td>Ti6Al4V – I</td>
<td>—</td>
<td>0.020</td>
<td>0.026</td>
<td>0.514</td>
</tr>
<tr>
<td>Ti6Al4V – II</td>
<td>—</td>
<td>0.600</td>
<td>0.748</td>
<td>6.172</td>
</tr>
<tr>
<td>TiN – I</td>
<td>1.1</td>
<td>0.177</td>
<td>0.229</td>
<td>3.244</td>
</tr>
<tr>
<td>TiN – II</td>
<td>0.6</td>
<td>0.019</td>
<td>0.025</td>
<td>0.913</td>
</tr>
<tr>
<td>TiN – III</td>
<td>1.8</td>
<td>0.597</td>
<td>0.757</td>
<td>6.472</td>
</tr>
</tbody>
</table>

1 – distilled water; 2 – diiodomethane; 3 – ethylene glycol; Ti6Al4V – I – polished Ti6Al4V titanium alloy; Ti6Al4V – II – grinded Ti6Al4V titanium alloy; TiN – I – nitried (TiN + Ti2N + α-Ti(N)) surface layer on polished Ti6Al4V produced at the cathode potential; TiN – II – nitried surface layer on polished Ti6Al4V produced at the plasma potential; TiN – III – nitried surface layer on grinded Ti6Al4V produced at the cathode potential.
While in the oxy-nitriding process (Fig. 6) under glow discharge conditions a thin TiO₂ titanium oxide layer (rutile with a nanocrystalline structure) is produced by glow discharge-assisted oxidizing of titanium nitride TiN (the outer zone of the TiN + Ti₂N + α-Ti(N) layer). This layer changes the wettability, residual stress state, and hardness of the titanium surface (Tab. 2) which significantly influence on the biological behaviour of the titanium biomaterial [24, 26, 32, 34, 40]. Furthermore, the diffusive oxy-nitrided layers exhibit good resistance to frictional wear and corrosion.

The thickness, chemical composition, and surface topography of the layer are controlled by the technological parameters of the glow discharge process [16, 26]. This oxide improves the hemocompatibility of titanium (or its alloys), including its anti-thrombogenicity [16, 24].

After low temperature plasma nitriding conducted at the cathode potential, the outer TiN zone of the nitrided layer is not stoichiometric and, depending on the process parameters, contains from 32% to 38% of nitrogen. Moreover, the layer has a nanocrystalline structure and a strongly developed (rough) surface in both macro and micro-scales [39, 41, 42] which can be additionally modified by various surface preparation techniques such as e.g. grinding or mechanical or electrochemical polishing.

These properties of the non-stoichiometric titanium nitride (TiN) permit the formation of an outer titanium carbonitride (Ti(CN)) zone as a result of the final annealing of the nitrided layer under glow discharge conditions in the atmosphere that contains active carbon particles (carbonitrizing process) [43]. It should be noted that during the plasma sterilization (in hydrogen peroxide – H₂O₂) of nitride surface layer TiN + Ti₂N + α-Ti(N) type the nanometric thickness titanium oxide is also formed [42]. This process offers an additional possibility of improving the performance properties of the titanium alloy according to its application, also when it is intended for use in medicine.

![Fig. 6. Microstructure (TEM) of the diffusion TiO₂ + TiN + Ti₂N + α-Ti(N) layer produced on the Ti6Al4V titanium alloy (a) and the content profiles of nitrogen, titanium, and oxygen in the layer (b).](image)

**Table 2. Some properties of the TiO₂ + TiN + Ti₂N + α-Ti(N) layer formed on the Ti6Al4V titanium alloy by glow discharge oxidizing of the TiN + Ti₂N + α-Ti(N) nitride layer.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Microhardness HV0.05</th>
<th>Surface Roughness</th>
<th>Residual stress δx MPa</th>
<th>Wettability μ ± 90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>1420</td>
<td>0.369</td>
<td>0.479</td>
<td>4.94</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1020</td>
<td>0.673</td>
<td>0.886</td>
<td>8.19</td>
</tr>
</tbody>
</table>

1 – distilled water; 2 – ethylene glycol

3. MODIFYING THE HEMOCOMPATIBILITY OF CARDIOLOGIC TITANIUM IMPLANTS

The hemocompatibility of titanium implants depends on their surface physicochemical and topography properties which are further of fundamental significance for surface wettability and formation of a protein biofilm participating in the interaction between the implant surface and the blood cells such as the blood platelets or endothelium. Moreover, the processes of adhesion and activation of the blood platelets can be inhibited by modifying chemically outer functional groups of the material [44] or by covering the implant surface with resorbable anti-coagulants carriers, e.g. heparin, blood platelet aggregation inhibitors, or plasmogen activators [45, 46], or else by depositing an albumin biofilm [47] or substances that imitate the components of the biological membranes such as e.g. phosphorylcholine [48].

One of the principal properties that affect the biocompatibility of the material is the topography of its surface. It has been shown that when the surface is strongly developed in the nanoscale, the adhesion and activation of the blood platelets may be inhibited while endothelial cells growth and differentiation may be promoted [49]. It is known that the nanoparticles of titanium improve the adhesion of the endothelial and smooth muscles cells of blood vessels [50, 51]. This is why efforts have been made to achieve an appropriate surface roughness, in both macro- and micro-scales. Investigations of the response of the cells to the nanostructure of the surface indicate that human cells, such as leucocytes, and endothelial cells, are sensitive to changes of the surface topography in the nano-scale [52, 53]. This was also confirmed by our studies on glow discharge nitrided layers with the topography varied in the nano-scale [53], which have shown that the adhesion of blood cells is decreased and on the TiN + Ti₂N + α-Ti(N) layer produced at the cathode potential, the layer with higher nanoroughness compared to the layer produced at the plasma potential (Tab. 1, Fig. 7a). In the same study the adhesion of HUVECs was increased by both types of nitrided layers in comparison to the Ti6Al4V alloy in initial state (Fig. 7b). It is however worth noting that, according to many literature reports, the biomaterials with a nano-rough surface inhibit the adhesion and blood platelets aggregation and intensify the adhesion and proliferation of the endothelial cells [54]. At the same time, the authors of ref. [52] however state that the dimensions of the topographical features with a nano-scale of 13 nm are critical to human microvascular endothelial cell lines and HUVECs surface reactions. It is therefore not surprising that the authors [54] observed different proliferation of endothelial cells on titanium oxide (TiO₂) with various surface roughness and hydrophilic properties. Additionally, it has been found that endothelial cells incubated on nanostructured surfaces produce and release more nitrogen oxide (NO) and prostaglandine I₃ (PGI₃) which inhibit the proliferation of the blood vessel smooth muscle cells.
The differences between the reactions of the blood cells to the surface nano-topography result from the changes of the activation of the membrane receptors and molecules bound with the actin filament, such as G-proteins, and also proteins of the ionic channels and calcium pathways, or their response to the biofilm proteins absorbed on the surface [55]. As result the surface topography affects the organization of the actin filament and the focal adhesions whose organization leads to changes in cell morphology, adhesion and proliferation, and decides about the preservation of cells biological functions [56]. This is the reason why the cells incubated on a titanium nitrided layer with a higher surface roughness ($Ra = 0.177 \mu m$), produced on cathode potential – PK, compared to these in contact with a lower surface roughness ($Ra = 0.019 \mu m$), produced on plasma potential – PP, exhibited different morphology (Fig. 8). Thus, platelets on smooth surfaces were spread compared to dendritic-like on the surface with higher roughness, while endothelial cells respectively elongated multiformed. Simultaneously changes in the number and size of focal adhesions were observed. It has been found that the focal adhesion at the cells growing on surfaces of the higher roughness, formed dots distributed over the entire contact surface with the material, whereas on smoother surfaces it has the form of dashes located at the cell edges (Fig. 9).

Other important factor affecting the hemocompatibility of biomaterials is presence of oxides on the surface of titanium and its alloys. It has been demonstrated that the biocompatibility of the titanium oxide layer chiefly depends on its thickness, phase composition and microstructure [23, 24].

M. C. Sunny and C. D. Sharma [57] observed that if the layer was thicker, albumins were deposited in greater amounts than fibrinogen and, in consequence, the adhesions of the blood cells and their activation are lower. It is known that among the titanium oxides (TiO, TiO$_2$, Ti$_2$O$_3$, Ti$_3$O$_5$), the best hemocompatibility is exhibited by rutile with a tetragonal structure [34, 58]. It is also possible to improve the antithrombogenicity properties by modifying the phase composition of TiO$_2$ by, e.g., doping with lanthanum oxide (La$_2$O$_3$), or by producing...
a layer composed of a titanium nitride and titanium oxide (TiN/TiO₂) mixture [36] or TiO₂-doped nitrogen – TiO₂(N)-type [59].

The mechanism of the influence of the thickness, microstructure, and surface topography of the oxides on the hemocompatibility of titanium and its alloys is not entirely understood. It is suggested that titanium oxide in contact with water forms hydroxide groups on the surface, which, depending on the pH of the environment, become positively or negatively charged and thereby determine the kind of the deposited proteins i.e. whether negatively charged albumins or positively charged fibrinogen [6].

On the other hand, the surface energy of titanium oxides is low, and can be additionally reduced by increasing the density of atoms in the crystalline lattice of rutile. Therefore on surfaces characterized by lower surface energy, the amounts of attached fibrinogen, which is responsible for the adhesion and activation of blood platelets, are smaller [59]. This was confirmed by our investigations of the platelets aggregation and activation in the context of surface energy of titanium and the Ti6Al4V alloy untreated and with the layers produced under glow discharge conditions (Fig. 10, Tab. 3).

In general opinion, the materials with low surface energy are characterized by high wettability contact angle which is correlated with less abundant adhesion of fibrinogen and weaker interactions between the material surface and proteins, which, in turn, means that these materials show less conformational changes responsible for thrombogenicity. However, the authors of ref. [53] have demonstrated that in materials with highly hydrophilic surface the blood platelet adhesion is higher than in less hydrophilic materials, but it does not occur when endothelial cells are present.

It is suggested that the materials which promote the settlement of endothelial cells are titanium oxides, with a thickness below 10 nm, with a nanostructured surface [61] which imitates the natural nanostructure of the blood vessel walls. It is reported in ref. [62] that on the oxide layer produced on commercially pure titanium and the Ti6Al4V titanium alloy by ionic plasma deposition, the adhesion of endothelial cells increased with increasing surface nano-roughness. The final success in intensifying the settlements of endothelial cells on the biomaterial surface would be achieved when we will manage to produce a cell monolayer with the proper biological functions. As shown in ref. [54], the endothelial cells settled on a nano-structured titanium surface released 1.5 times greater amounts of NO than those adhered on a polished control surface. These cells also exhibited the amplification of gene for the nitric oxide synthase. Similar results were obtained by the authors of ref. [63]. Our investigations (unpublished) also confirm these observations. This effect is attributed to the presence of appropriate proteins in the extra-cellular matrix which forming a biofilm on the material surface [64]. It is known that the adhesion of endothelial cells on the biomaterial surface is initiated by the presence of fibronectin. Then they adhere on collagen I, III, and IV [65]. However the growing cells form tight junctions only on collagen IV, but proliferate most actively on collagen III and laminine [66].

According to ref. [66], titanium oxides with an appropriate surface roughness can enhance the proliferation of endothelial cells. In our experiments we observed that most of the cells present on the surface of nanocrystalline titanium nitride (the outer zone of the TiN + Ti₂N + α-Ti(N) nitrided layer produced on the Ti6Al4V titanium alloy) had a spindle-like shape, whereas some of those observed on nanocrystalline rutile (TiO₂) (the outer zone of the oxynitrided layer) were flattened or multiform (Fig. 11). The spindle-like shape of the cells on nanocrystalline TiN was correlated with their enhanced proliferation activity (Fig. 12), which permit us to suppose that the surfaces of the nanocrystalline titanium nitride produced by nitriding in low-temperature plasma favor the settlement of the vascular endothelial cells.

Another way to improve the antithrombogenic properties of the surface is to apply an additional coating, e.g. various types of carbon coatings, which are known to be of antithrombogenic nature. The modification of the NiTi shape memory alloy’s surface in the aspect of applications for cardiac implant, can be applied by hybrid process combining glow discharge oxidizing with the RFCVD process [21]. The microstructure of the produced a-C:N:H + TiO₂-type composite layer and the distribution of the elements on its cross-section is shown in Figure 13 [21, 29].

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### Table 3. Surface energy of titanium and Ti6Al4V alloy in initial state and with a layer with the outer zone containing TiN and TiO₂ produced under glow discharge conditions

<table>
<thead>
<tr>
<th>Material surface energy</th>
<th>Ti6Al4V polished</th>
<th>TiN on polished Ti6Al4V</th>
<th>Ti6Al4V ground</th>
<th>TiN on ground Ti6Al4V</th>
<th>TiO₂ on polished Ti6Al4V</th>
<th>Ti Grade2 polished</th>
<th>TiN on polished Ti Grade2</th>
<th>TiO₂ on polished Ti Grade2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEP, mJ/m²</td>
<td>25.20</td>
<td>24.34</td>
<td>26.31</td>
<td>24.70</td>
<td>25.21</td>
<td>31.47</td>
<td>35.74</td>
<td>30.44</td>
</tr>
</tbody>
</table>

1– TiN – nitrided surface layer TiN+Ti₂N+α-Ti(N); 2 – TiO₂ – oxynitrided surface layer TiO₂ + TiN + Ti₂N + α-Ti(N)° SEP was calculated using Owens-Wendt method [60]
During our study we have showed that the a-C:N:H amorphous carbon coating modified with nitrogen and hydrogen reduced platelet adhesion and aggregation to a much greater extent than using only a titanium oxide layer (Fig. 14). What’s more, the carbon coating also ensures proper proliferation of endothelial cells, which is a key aspect in the context of cardiac application of the material (Fig. 15) [21].
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REFERENCES

Modyfikacja powierzchni implantów z tytanu i jego stopów w niskotemperaturowej plazmie w aspekcie zastosowań kardiologicznych

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Słowa kluczowe: tytan i jego stopy, stop NiTi, obróbki jarzeniowe, procesy hybrydowe, biozgodność, implanty kardiologiczne.

1. CEL I ZAKRES PRACY

Choroby układu krążenia są jedną z głównych przyczyn śmiertelności u ludzi. Biozgodność i inne właściwości implantów kardiologicznych, wytwarzanych z tytanu i jego stopów, można kształtować, stosując różne metody inżynierii powierzchni. W pracy przedstawiono charakterystykę wielofazowych, dyfuzyjnych warstw powierzchniowych typu TiN + Ti2N + α-Ti(N) oraz TiO2 + TiN + Ti2N + α-Ti(N) wytwarzanych w niskotemperaturowej plazmie na stopie tytanu Ti6Al4V, także z wykorzystaniem aktywnego ekranu, pod kątem ich mikrostruktury, topografii powierzchni, twardości, stanu naprężeń własnych, odporności na korozję i zużycie, zwilżalności oraz właściwości biologicznych, takich jak: adsorpcja białek — fibrynogenu i albuminy oraz adhezja płytek krwi podczas inkubacji z ludzkim osoczem i osoczem bogatym w platelety. Przedstawiono także wyniki badań warstw typu TiO2 oraz a-C:NH + TiO2 wytwarzanych na stopie z pamięcią kształtu NiTi. Artykuł prezentuje wyniki badań przeprowadzonych przez autorów, a interpretacji uzyskanych wyników dokonano w porównaniu z danymi literaturowymi dotyczącymi powierzchniowych warstw złożonych z tlenku tytanu i azotku tytanu wytwarzanych różnymi metodami.

2. WSTĘP

W rozdziale przedstawiono zalety tytanu i jego stopów jako biomateriałów do zastosowań medycznych w kontekście danych literackich. Omówiono też możliwości obróbek powierzchniowych z użyciem niskotemperaturowej plazmy wyładowania jarzeniowego, a także istotę procesów hybrydowych.

3. OBRÓBKI JARZENIOWE TYTANU I JEGO STOPÓW

W tym rozdziale przedstawiono charakterystykę obróbek tytanu i jego stopów — w tym stopu Ti6Al4V oraz stopu z pamięcią kształtu NiTi — w niskotemperaturowej plazmie. Na rysunku 2 pokazano przykładową mikrostrukturę warstwy TiO2 wytworzonej na stopie NiTi. Opisano procesy obróbek jarzeniowych na tzw. potencjałe katody (klasyczny proces) i z użyciem tzw. aktywnego ekranu, tj. określonego jako obróbka jarzeniowa na potencjałe plazmy w przedstawieniu schematu urządzenia do realizacji tych procesów (rys. 4). Opisano mikrostrukturę i właściwości wytwarzanych warstw typu TiN (nanokrystaliczny) + Ti2N + α-Ti(N), TiO2 (nanokrystaliczny-rutyl) + TiN (nanokrystaliczny) + Ti2N + α-Ti(N) takie jak: odporność korozyjna, twardość, stan naprężeń własnych, chropowatość i zwilżalność powierzchni.

4. KSZTAŁTOWANIE HEMOZGODNOŚCI IMPLANTÓW KARDIOLOGICZNYCH

W rozdziale przedstawiono porównanie homokompatybilności tytanu i jego stopów bez i z wytworzonymi warstwami powierzchniowymi. Omówiono czynniki wpływające na homogzoidność powierzchni, m.in. wpływ topografii na adhezję i agregację płytek krwi oraz adhezję śródbłonków naczyniowych. Na zdjęciach z mikroskopów elektronowego i konfokalnego przedstawiono zmiany w morfologii płytek krwi inkubowanych na warstwach azotku tytanu TiN o różnej topografii, kształtowanej sposobem jej wytwarzania, tj. azotowaniem na potencjałe plazmy lub na potencjałe katody.

5. PODSUMOWANIE

Dyfuzyjne warstwy azotowane TiN + Ti2N + α-Ti(N) oraz tlenoazotowane TiO2 + TiN + Ti2N + α-Ti(N) wytwarzane na stopach tytanu mogą być stosowane w kształtowaniu właściwości implantów kardiologicznych z tytanu i stopów tytanu, podobnie jak warstwy TiO2 oraz a-C:N:H + TiO2, na stopie z pamięcią kształtu NiTi. Stępując parametrami technologicznymi procesów obróbek jarzeniowych, można kształtować ich topografię powierzchni, zwilżalność, zwiększając odporność korozyjną i biozgodność stopów tytanu. Są to warstwy dyfuzyjne, które można wytwarzać na detalach o złożonym kształcie, co jest istotne w przypadku implantów kardiologicznych. Warstwy te ograniczają adhezję i agregację płytek krwi, a jednocześnie umożliwiają adhezję śródbłonków naczyniowych.