

# Cathodic deposition of silver particles on anodized titanium

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The paper presents the process of high voltage anodic oxidation of titanium in the electrolyte containing 2 M  $H_3PO_4$  + 1% HF. The anodization of titanium was performed at various potentials in the range of 30–210 V and the time of 30 minutes. As a result, a developed surface titanium oxide on titanium was obtained. Then, on the surfaces of the oxides, silver particles were deposited by cathodic method using the electrolyte containing 0.01 M  $HNO_3$  + 0.01 M  $AgNO_3$ . During the deposition of silver particles, a potential of –1 V was applied for 60 s with respect to the open circuit potential. In order to properly characterize the surface, research techniques were used such as XRD, EDS, SEM as well as corrosion testing. The XRD and EDS examinations have shown the presence of the silver particles on the surface of the titanium oxide. The SEM observations were used to assess the shape and surface morphology of the titanium oxide after anodizing and evaluate the amount of silver particles. The silver particles deposited on the anodized titanium surface exhibited a dendritic shape. On the basis of their arrangement and having monitored the deposition process, it can be assumed that they grow directly from the pores on the oxide surface. This is particularly evident in the most developed oxide surface obtained after oxidation of titanium at 210 V. This research allowed determining the suitability of combined anodic and cathodic treatment of titanium in various electrolytes for medical applications — implants. The resulting morphology of the titanium oxide was evaluated, taking into account the features necessary for the proper osseointegration process (structure, high corrosion resistance and surface morphology). Silver deposited on the anodic oxidized titanium surface causes the oxide layer to exhibit additional bactericidal properties, which is extremely advantageous in medical applications. Excess silver has a negative impact on the surrounding tissue in medical applications. For this reason, the dendritic shape of the obtained particles (high surface area) and their relatively small amount generates a potential in medicine applications.

**Key words:** titanium, anodic oxidation, silver, biomaterials.

## 1. INTRODUCTION

The present state of knowledge related to implantology, material engineering, biomechanics and physiology allows developing biomaterials meeting our basic expectations. Implants whose working time is expected in excess of 20 years must be continually adapted. The slow rate of degradation of the metal in the human body is unavoidable (infiltration of metal ions into the body) [1–3]. The implant is affected differently than the bone on the surrounding tissue. Troublesome is also the question of optimizing the osseointegration process. This phenomenon is still not fully understood. Therefore, it is difficult to predict the effect of modifications of the implant surface on the osseointegration process [4, 5].

The anodized layer exhibits the best properties of the modified surface layer on titanium [6]. Anodizing can change the surface properties, such as chemical composition, thickness, microstructure, and surface morphology. It is possible to produce oxides of approx. 1  $\mu m$  of thickness over the complex shape of the implant. Such possibilities place anodic oxidation before other methods of surface treatment of titanium.

In the field of surface treatment of titanium for biomedical purposes, we know what factors affect the effective process of osseointegration [7]. We can evaluate the impact of mechanical action of the implant on the surrounding tissue and then modify its shape in order to minimize the transmitted forces. The acquired clinical hands-on experience of osseointegration allows the use of better materials [8]. The present state of knowledge has contributed to a significant shortening of postoperative healing.

Anodic oxidation of titanium and its alloys in the electrolyte containing  $H_3PO_4$  is well known [9]. Currently no comprehensive research exists on the anodic oxidation of titanium in the electrolyte containing  $H_3PO_4$  with the addition of HF [10]. The obtained surface oxide didn't have a satisfactory morphology and biocompatibility [11]. Using appropriate process parameters, it is possible to obtain suitable properties for medical applications [12].

In order to improve the usability of implants, their surface is modified by the deposition of particles of other materials. The aim is to improve the process of osseointegration, bio-adhesion and to

minimize potential hazards that will result in rejection of the implant. An example of such research are issues related to the wettability of the surface and the possibilities of its modification [13], drugs modifying [14], bactericidal particles [15], and deposition of minerals apatite [16] on the surface of the implants.

During surgery, there is a high risk of infection and, for this reason, bactericidal implant surfaces are applied. Silver metallic state is neutral, but low corrosive in body fluids. For this reason, it is assuming a highly reactive ionized form, harmful to the bacteria. Excess silver prevents proper osseointegration. For this reason, silver used in the implants must have a large surface area (nanoparticle). Silver nanoparticles are cytotoxic to the cells of *E. coli* at a concentration of 8 g/cm<sup>2</sup> [17]. Attempts were made to deposit silver nanoparticles during the electrolytic oxidation of titanium plasma [18]. Application of solvothermal procedure caused the formation of dendrites of Ag on the surface of single crystal Si [19]. The type of substrate, the applied method and the conditions of deposition of Ag particles are decisive of the release of silver in different forms [20–22].

Currently, there are no publications about deposition of silver particles on the titanium surface after anodic oxidation process in different anodic potential. The bactericidal action of the applied process was confirmed by in-vitro studies [23].

## 2. EXPERIMENTAL PROCEDURE

The commercially pure titanium (99.6% Ti Goodfellow) was treated electrochemically. The samples were cut from a Ø10 mm titanium rod into a form of small tablets (10 mm in diameter and 5 mm in height). The surface was grinded up to a 1000 sand paper and then polished in  $Al_2O_3$  suspension to a mirror-like surface (without microcrack). The anodic oxidation process was carried out in the electrolyte containing 2 M  $H_3PO_4$  with an addition of 1 wt % HF for 30 min. The oxidation process took place in electric potential in the range 30–210 V at an interval of 60 V. Anodic oxidation uses high voltage Power Supply ATLAS SOLLICH (300 V/3 A) and a proprietary PTFE cell with a platinum counter electrode. After anodic oxidation the sample was rinsed and dried.

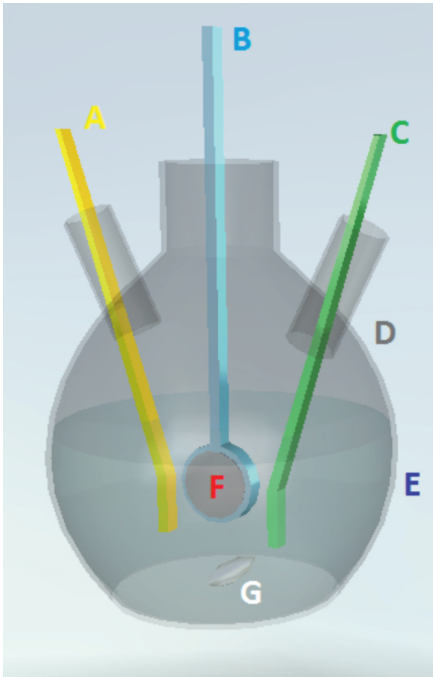
The silver deposition was performed in the electrolyte containing 0.01 M HNO<sub>3</sub> and 0.01 M AgNO<sub>3</sub> in water solution for 60 s. The deposition process was performed in electric potential -1 V vs open circuit potential. In the silver deposition, low voltage SOLA-TRON 1285 potentiostat and a glass chamber with silver counter electrode and platinum reference electrode were used (Fig. 1). After silver deposition the sample was rinsed and dried.

The structure was determined using Panalytical Empyrean XRD with CuKα<sub>1</sub> radiation, equipped with a crystallographic database. The XRD spectra were recorded in the range of 30÷120° 2θ angle. Using the Panalytical Highscore software, a crystal structure was determined on each sample. The surface topography was determined using VegaTescan SEM and Quesant Q-scope 250 AFM. The corrosion resistance was measured using the potentiodynamic method.

The corrosion cell was the same as in the anodic oxidation experiments. The potential was scanned at the rate of 0.5 mV/s from -1 to +3 V vs ocp. The Ringer electrolyte (Tab. 1) (bought in: Zakład Enzymow i Peptonow, Lodz, Poland) of the temperature of 37°C was applied as electrolyte. The corrosion current densities and corrosion potentials were estimated using the CorrView software.

### 3. RESULTS AND DISCUSSION

During anodizing the titanium in the 2 M H<sub>3</sub>PO<sub>4</sub> + 1% HF electrolyte, the oxidation of titanium surface occurs. At the moment when the power is turned on, a rapid oxidation of titanium takes place. Starting from the potential of 120 V, the oxidation process is



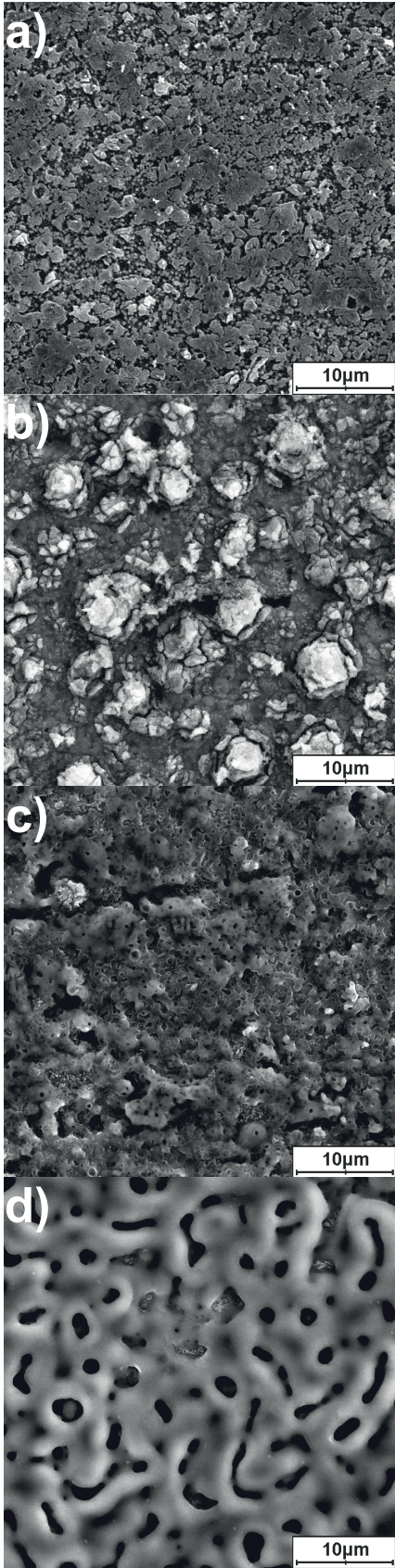
**Fig. 1.** Chamber for silver deposition: silver counter electrode A, sample holder B, platinum reference electrode C, glass chamber D, electrolyte E, sample F, magnetic stirrer G

*Rys. 1. Komora do osadzania srebra: przeciwelektroda srebrna A, uchwyt próbki B, elektroda referencyjna platynowa C, szklane naczynie D, elektrolit E, próbka F, mieszadło magnetyczne G*

**Table 1.** Chemical composition of the Ringer's solution  
*Tabela 1. Skład chemiczny roztworu Ringera*

Ion	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>
Concentration, mmol L <sup>-1</sup>	147.2	4.0	2.2	155.7

assisted by electrical sparks (PEO — *Plasma Electrolytic Oxidation*) [24]. The value of the anodizing potential significantly affects the resulting morphology of the surface layer (Fig. 2).



**Fig. 2.** SEM images of the Ti oxidized in the 2 M H<sub>3</sub>PO<sub>4</sub> + 1 wt % HF electrolyte at the potential of: a) 30 V, b) 90 V, c) 150 V, d) 210 V  
*Rys. 2. Zdjęcia SEM tytanu utlenionego anodowo w elektrolicie 2 M H<sub>3</sub>PO<sub>4</sub> + 1 wt % HF przy potencjale: a) 30 V, b) 90 V, c) 150 V, d) 210 V*



In low potential anodic oxidation of up to 60 V, a gray-blue oxide film is formed on the titanium surface. Such layers are characterized by underdeveloped oxide morphology. Anodization at low potentials has a low chance for application in long term implants. With the potential of 90 V, on the titanium surface form oxide features resembling products of corrosion. The samples are characterized by light gray color. That kind of surface, due to its more developed morphology can be used in medical applications. At higher voltages (starting at 150 V) oxidation assisted by electric spark discharges (PEO) was observed. During such oxidation an oxide layer forms with developed morphology, characterized by dark gray color. This surface has morphology suitable for good maintenance of the osteoblast cells during the process of osseointegration. The electrical sparks in the time of anodization break the forming oxide layer and remove it locally. The presence of hydrofluoric acid in the electrolyte favors the formation of the developed oxide layer. Hydrogen fluoride locally dissolves the oxide layer and reduces the thickness of all titanium oxides [9]. HF promotes the oxidation involving the presence of electric sparks inside the pores in the oxide layer, thus increasing the roughness of the surface [25].

Within 30 minutes of anodic oxidation, the process of forming of the titanium oxide occurs, especially in the Rutile form. It is a titanium oxide with a tetragonal crystallographic system. Titanium dioxide such as Rutile is necessary for proper osseointegration (Tab. 2).

Thick, compact, and developed oxide layer, obtained on the titanium surface, promotes the osseointegration processes [26]. During the oxidation with the assistance of electrical discharges at the potentials above 150 V, the components from the electrolyte are built in the top oxide layer [27]. The presence of such components as phosphorus and fluorine in the electrolyte can positively influence the process of osseointegration. These elements are naturally occurring in a bone tissue and assist the formation of bone around the implant after implantation.

The materials used for permanent implants are exposed to corrosive environment. For this reason, it is important to test their corrosion resistance in solutions chemically similar to the environment of the organism [28]. The produced oxide layers have a high corrosion resistance in the Ringer's solution, which is evaluated based on the polarization. All polarization curves show a shape suitable for the passivating materials (Fig. 3). Polarization curves after anodic oxidation of titanium are shifted to the right in comparison to the curves of the untreated titanium. Additional, current density values measured by means of Tafel tangential are lower than those measured for the untreated titanium (Tab. 3). The sample oxidized in high potential assisted with electrical discharges exhibits a different behaviour. The reason for this is the removal of a significant spot of the oxide layer during the spark discharge. Despite this, the samples still have a very good corrosion resistance in the Ringer's solution.

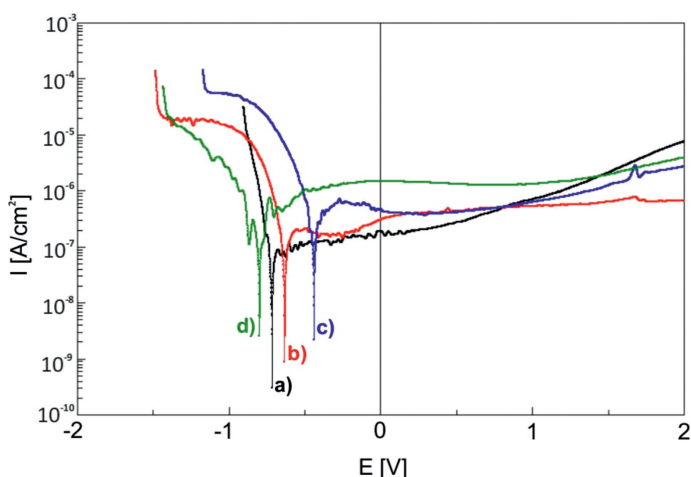
The deposition of silver on the surface of materials intended for medical devices is substantiated only when one achieves positive results. To do this, it is necessary to deposit the silver nanoparticles of high surface area to volume ratio. Upon the deposition of silver from the electrolyte in the cathodic process, the nanoparticles appear on the surface of the samples. On the surface anodized at the potential of 30 V, silver particles with a lot of dendritic branching were formed and their diameter did not exceed 0.8  $\mu\text{m}$  (Fig. 4a). On the surface oxidized at the potential of 90 V the deposition of silver failed (Fig. 4b). The reason for this phenomenon was the formation of passive and non-conducting oxide layer on this sample. The deposited silver particles on the anodized surfaces, starting from the 180 V potential, did not exceed a diameter of 0.7  $\mu\text{m}$ , and their branching often remains below 100 nm (Fig. 4c). This is related to the amount and size of the pores on the anodized surface. The process of growth of the silver dendrite begins inside the pores (Fig. 4d).

In the XRD spectral analysis, it was found that the deposited particles are silver (Fig. 5a). This analysis was done on the basis of deposits that fell from the sample surface after the process. The XRD spectrum of the anodized surface following the deposition of

**Table 2. Phases identified by XRD after anodic oxidation of titanium in different potential, Ti – Titanium, R –  $\text{TiO}_2$ , T –  $\text{Ti}_2\text{O}_3$**

*Tabela 2. Wyniki analizy XRD zidentyfikowanych faz po utlenianiu anodowym tytanu przy różnych potencjalach, Ti – Tytan, R –  $\text{TiO}_2$ , T –  $\text{Ti}_2\text{O}_3$*

Potential	30 V	90 V	150 V	210 V
Identified phase	Ti, R	Ti, R	Ti, R, T	Ti



**Fig. 3. Polarization curves recorded in the Ringer's solution for Ti surfaces: a) anodically unoxidized, and oxidized in 2 M  $\text{H}_3\text{PO}_4$  + 1 wt % HF at: b) 60 V, c) 150 V, d) 210 V**

*Rys. 3. Krzywe polaryzacji uzyskane w roztworze Ringera dla: a) czystego tytanu, oraz po utlenieniu anodowym w elektrolicie zawierającym 2 M  $\text{H}_3\text{PO}_4$  + 1% mas. HF przy: b) 60 V, c) 150 V, d) 210 V*

**Table 3. Corrosion current density  $I_{\text{corr}}$  and corrosion potential  $E_{\text{corr}}$  for the Ti after anodic oxidation in different potentials**

*Tabela 3. Gęstość prądu korozyjnego  $I_{\text{corr}}$  i potencjał korozyjny  $E_{\text{corr}}$  dla tytanu utlenianego anodowo w różnych potencjalach*

Potential, V	$I_{\text{corr}}$ , A/cm <sup>2</sup>	$E_{\text{corr}}$ , V
0	$1.23 \cdot 10^{-7}$	-0.760
30	$2.86 \cdot 10^{-8}$	-0.541
90	$6.65 \cdot 10^{-8}$	-0.500
150	$9.80 \cdot 10^{-8}$	-0.440
210	$5.68 \cdot 10^{-8}$	-0.799

silver reveals the presence of silver and titanium nitride on the surface (Fig. 5b).

The presence of the nitride phase in the surface layer of the titanium samples following the process of silver deposition is caused by the use of electrolyte based on the nitric acid and its reaction with titanium. The TiN phase is positive for medical application (the effect of nitrogen on the processes of osseointegration was found positive) [29].

An EDS point analysis carried out on the surface of the oxidized samples with a deposition of silver particles allowed determining their chemical composition. The EDS point analysis was performed in the areas of white dendrite deposits. Other measurements were performed in the areas without the said deposits (Fig. 6).

Based on the EDS analysis, it is not possible to do a quantitative assessment of the deposited silver. However, it was clear that on the sample after oxidation at 90 V the deposition of silver failed. On the sample oxidized with the assistance of electric sparks there is much more phosphorus and oxygen due to the high potential of the process and the absorption of the ions from the electrolyte.

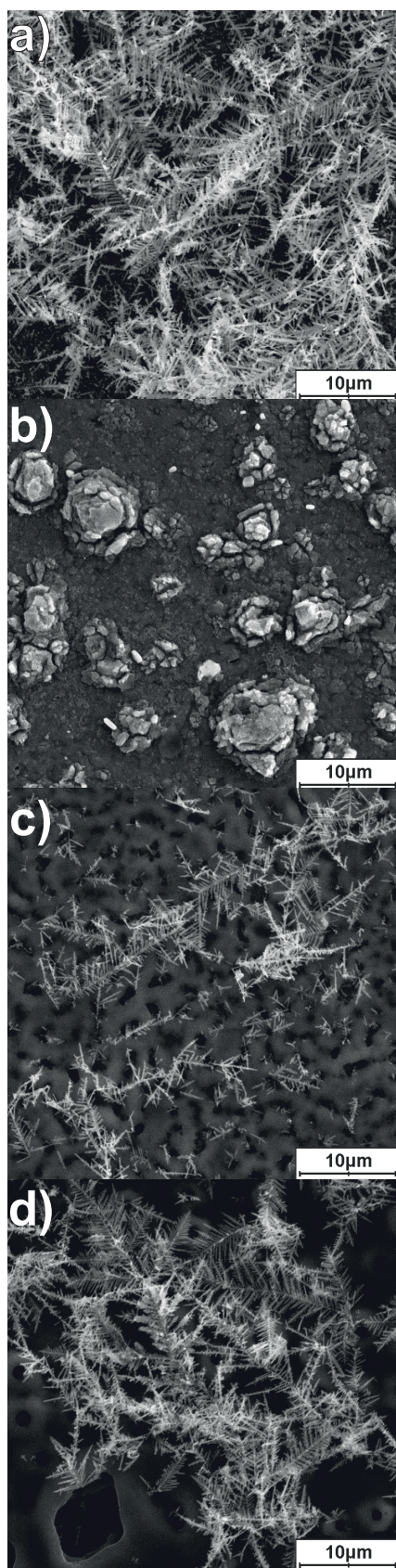


Fig. 4. SEM images of the Ti oxidized in the 2 M  $H_3PO_4$  + 1 wt % HF electrolyte at the potential of: a) 30 V, b) 90 V, c) 150 V, d) 210 V and after deposition of silver particles by the electrolytic method

Rys. 4. Zdjęcia SEM tytanu utlenionego anodowo w elektrolicie 2 M  $H_3PO_4$  + 1% mas. HF przy potencjale: a) 30 V, b) 90 V, c) 150 V, d) 210 V i po osadzeniu cząstek srebra metodą elektrolityczną

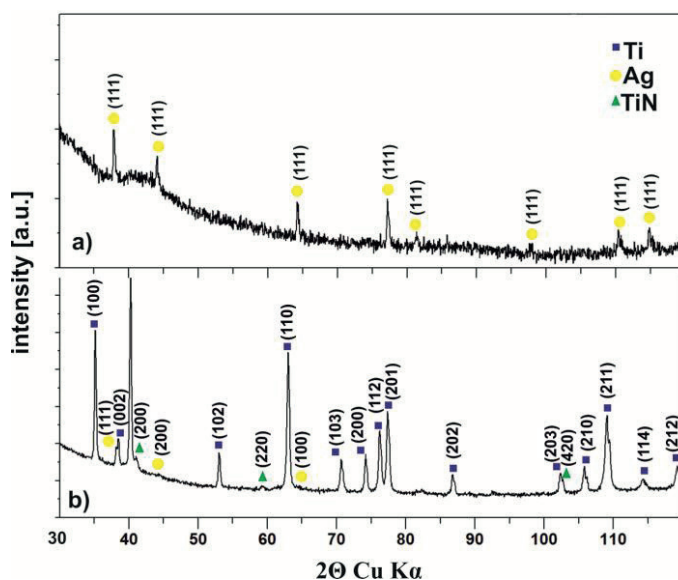


Fig. 5. XRD of silver deposits (a), and XRD from the titanium surface after anodic oxidation in the 2 M  $H_3PO_4$  + 1% HF electrolyte of the potential of 210 V and a deposition of silver particles (b)

Rys. 5. Widmo XRD osadu srebra (a) oraz widmo XRD powierzchni tytanu po utlenianiu anodowym w elektrolicie 2 M  $H_3PO_4$  + 1% HF i napięciu 210 V oraz osadzeniu cząstek srebra (b)

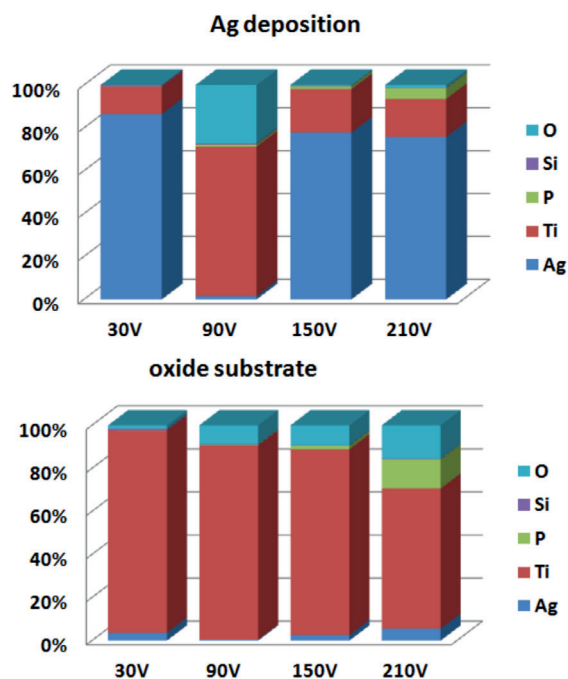


Fig. 6. Collected results of EDS analysis of the samples anodically oxidized in the 2 M  $H_3PO_4$  + 1% HF electrolyte and the deposited silver particles

Rys. 6. Zebrane wyniki z analizy EDS próbek utlenionych anodowo w elektrolicie 2 M  $H_3PO_4$  + 1% HF i z osadzonych cząstek srebra

The surface after anodic oxidation at the potential of 210 V has been tested *in vitro* with human fibroblast and osteoblast cells [24]. These studies have shown that the obtained surface after anodic oxidation has good biocompatibility. In addition, the silver particles deposited on the surface contribute to an increased cell survival and viability. This clearly confirms the possibility of application of the produced layers on titanium in medicine for permanent implants, provided the additional acceptance testing for medical application is carried out.



## 4. CONCLUSIONS

1. Anodic oxidation of titanium in the electrolyte containing 2 M  $\text{H}_3\text{PO}_4$  + 1% HF provides a developed surface of titanium oxide depending on the applied electric potential.
2. Titanium after anodic oxidation is characterized by good corrosion resistance on the same or better level than pure titanium. Such corrosion resistance allows this material to reside in the body for a long time like pure titanium.
3. During the process of anodic oxidation with electric sparks, the oxide surface on the samples was enriched with elements from the electrolyte. During the cathodic deposition of silver, the oxide surface was also enriched with elements from the electrolyte. In this way, it is possible to produce better materials for specific application (through electrolyte modification).
4. It is possible to deposit silver nanoparticles on anodized titanium by galvanic methods. Such deposited silver has the form of dendrites. For samples anodization at 150 and 210 V, the thickness will be less than 100 nm at the end of the dendrite arms.
5. The most promising surface for medical applications is titanium following oxidation at 210 V with deposited silver.

## ACKNOWLEDGEMENTS

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# Osadzanie katodowe cząstek srebra na tytanie utlenionym anodowo

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**Słowa kluczowe:** tytan, utlenianie anodowe, srebro, biomateriały.

## 1. CEL PRACY

W celu zapewnienia normalnego funkcjonowania organizmu pacjenta po urazie lub uszkodzeniu, wciąż poszukiwane są nowe materiały mogące zastąpić tkankę twardą. Jednym z materiałów dającym na to szansę jest tytan. Po wszczęciu implantu do organizmu dochodzi na jego powierzchni do osteointegracji. Od jej prawidłowego przebiegu zależy czas leczenia, skuteczność operacji oraz komfort pacjenta. Niniejsza praca wychodzi naprzeciw tym oczekiwaniom. Proces utleniania anodowego jest jedną z częściej stosowanych obróbek powierzchniowych implantów stałych, a utlenianie anodowe w elektrolicie kwasu fosforowego z dodatkiem kwasu fluorowodorowego wciąż nie jest dostatecznie poznane. W pracy dodatkowo przedstawiono możliwość wzbogacenia powstałej powierzchni tlenkowej w cząstki o właściwościach antybakteryjnych, niezbędnych w początkowych etapach osteointegracji. Przedstawione wyniki badań mogą się przyczynić do wytworzenia implantów o lepszych właściwościach powierzchniowych.

## 2. MATERIAŁ I METODYKA BADAŃ

Do badań użyto czystego tytanu (99,6% Ti Goodfellow) w postaci prętów o średnicy Ø10 mm. Wycięto z nich próbki w kształcie walców o wysokości 5 mm. Ich powierzchnię szlifowano papierem ściernym do gradacji 1000, następnie polerowano z zastosowaniem cząstek  $Al_2O_3$ , aż do uzyskania lustrzanego połysku (bez mikrorys).

Proces utleniania anodowego przeprowadzono w elektrolicie zawierającym 2 M  $H_3PO_4$  z dodatkiem 1% mas. HF przez 30 min. Podczas utleniania zastosowano potencjał od 30 do 210 V w odstępach co 60 V. Do procesu utleniania anodowego zastosowano zasilacz ATLAS SOL-LICH (300 V/3 A), elektrolizer wykonany z PTFE oraz katodę platynową. Po procesie utleniania anodowego próbki opłukano i suszono.

Osadzanie srebra przeprowadzono w elektrolicie wodnym zawierającym 0,01 M  $HNO_3$  i 0,01 M  $AgNO_3$  przez 60 s. Podczas osadzania zastosowano potencjał -1 V względem napięcia obwodu otwartego z wykorzystaniem potencjostatu SOLATRON 1285 i szklanego elektrolizera (rys. 1). Po procesie osadzania cząstek srebra próbki opłukano i suszono.

Strukturę próbek zbadano z użyciem dyfraktometru rentgenowskiego Panalytical Empyrean XRD z lampą miedzią  $CuK\alpha_1$  w zakresie kąta  $2\theta$ ,  $30 \div 120^\circ$ . Do analizy widm zastosowano dedykowane oprogramowanie Panalytical Highscore.

Topografię próbek zbadano z wykorzystaniem skaningowego mikroskopu elektronowego VegaTescan SEM i mikroskopu sił atomowych Quesant Q-scope 250 AFM. Badania korozyjne wykonano metodą potencjodynamiczną w roztworze Ringera (tab. 1) w temperaturze  $37^\circ C$  z wykorzystaniem elektrolizera stosowanego przy utlenianiu anodowym. Podczas badania mierzono natężenie prądu przy potencjałach od -1 do 3 V, stosując szybkość skanowania 0,5 mV/s. Uzyskane krzywe polaryzacji analizowano z wykorzystaniem oprogramowania CorrView.

## 3. WYNIKI I ICH DYSKUSJA

Uzyskane powierzchnie tlenkowe po utlenianiu anodowym w elektrolicie 2 M  $H_3PO_4$  + 1% HF charakteryzowały się rozwiniętą morfologią powierzchni (rys. 2). Na próbce utlenionej w 90 V zaobserwowano twory tlenkowe przypominające wykwyty korozyjne. Na próbkach utlenionych przy potencjale 150 i 210 V zaobserwowano powierzchnię charakterystyczną dla utleniania z udziałem wyładowań elektrycznych (PEO). Próbką utlenioną przy 210 V cechowała się obecnością porów najbardziej korzystnych dla zastosowań medycznych na implanty stałe. Badania XRD wykazały obecność tlenków tytanu w postaci krystalicznej (tab. 2). Badania korozyjne wykonane w roztworze Ringera wykazały dużą odporność korozyjną tytanu po utlenianiu anodowym. Analizowane krzywe polaryzacji charakteryzowały się kształtem odpowiednim dla materiałów pasywnujących się (rys. 3). Wyznaczona odporność korozyjna próbek po utlenianiu anodowym była większa niż dla nieobrobionego tytanu (tab. 3). Wyjątek stanowiła jedynie próbka utleniona w potencjale 210 V, jej minimalnie mniejsza odporność korozyjna wynikała z intensywnego iskrzenia (PEO) podczas utleniania anodowego i związanego z tym przebijania pasywnej warstwy tlenów. Podczas osadzania cząstek srebra metodą elektrolityczną na powierzchniach tytanu utlenionego anodowo powstały wydzielania w postaci dendrytów (rys. 4). Obecność srebra w postaci metalicznej potwierdzono badaniami XRD (rys. 5). Dyfraktogramy XRD wykazały również obecność TiN na powierzchni utlenionego tytanu. Analiza EDS potwierdziła obecność Ag na powierzchniach próbek po procesie osadzania srebra. Ponadto wykazała zwiększoną obecność P i O w próbkach utlenionych z udziałem wyładowań elektrycznych, co jest zgodne z literaturą.

## 4. PODSUMOWANIE

Utlenianie anodowe tytanu w elektrolicie zawierającym 2 M  $H_3PO_4$  + 1% HF prowadzi do utworzenia rozwiniętej warstwy wierzchniej tlenków tytanu, zależnej od przyłożonego potencjału.

Tytan po utlenianiu anodowym cechuje się dobrą odpornością korozyjną, na tym samym lub lepszym poziomie co nieobrobiony tytan. Podczas utleniania anodowego tytanu z udziałem wyładowań elektrycznych, powierzchnia próbek zostaje wzbogacona w pierwiastki pochodzące z elektrolitu. Podczas katodowego osadzania cząstek srebra również dochodzi do wzbogacenia warstwy tlenkowej w pierwiastki pochodzące z elektrolitu. Obydwa procesy cechują się odmiennymi mechanizmami, pozwalają jednak na wytworzenie lepszych materiałów dla wybranych zastosowań.

Możliwe jest osadzenie cząstek srebra na powierzchni tytanu utlenionego anodowo. Cząstki takie mają kształt dendrytów z ramionami o grubości poniżej 100 nm.

Najbardziej korzystną powierzchnią dla zastosowań medycznych na implanty stałe posiada tytan po utlenianiu anodowym przy potencjale 210 V z osadzonymi nanocząstkami srebra.