NANOSTRUCTURING OF TITANIUM FOR MEDICAL APPLICATIONS

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Abstract

There are several possible ways of fixation of titanium implants in human bone. One of them is direct contact of implant with bone i.e. theirs osseointegration. However, this process could be, depending on material’s surface properties, both long term and complicated. Research aimed at applications of metallic biomaterials is therefore focused on “bioactivation” of the implant surface. One of possible procedures is nanostructuring of the surface that means covering of the implant surface by a layer of nanotubes. Titanium dioxide can be prepared in the form of tubes with diameter in nanometres and lengths ranging from several nanometres to micrometers. Such nanostructure may be created on titanium by its electrochemical - anodic oxidation in fluoride containing electrolytes. Growth of nanotubes is in this case result of two simultaneous processes. First of them is anodic oxidation of the surface and the second one is a local dissolution of the growing titanium dioxide by fluoride ions.

First part of the presented work will be focused on theoretical background of titanium nanostructuring in fluoride-containing electrolytes. Influence of electrochemical parameters on nanotubes morphology will be discussed. Results of theoretical analysis will be subsequently compared with experimental data. Titanium grade 2 was used for experiments. Exposures were done in aqueous electrolytes containing fluoride ions. The influence of electrochemical parameters on the shape and degree of nanotubes organization will be presented.

Keywords: titanium dioxide, nanotube, self-organisation, anodization, medical applications

1. INTRODUCTION

1.1 General

Titanium and its alloys are commonly used in many medical applications. Reasons are especially mechanical properties and high corrosion resistance in human body environment. Surface of these materials is covered by thin passive layer (approximately $10^{-9}$ m) based on titanium dioxide and surfaces are bioinert. Implants aren’t usually rejected by the organism nevertheless they could be encapsulated by soft tissue. Direct connection with bone could be, because of this effect, long term and difficult process. Research in biomaterials field is therefore nowadays focused on improvement of surface properties. Many processes leading to increase of osseointegration were tested; inter alia modification of surface by DLC, ZrN and TiN layers [1-3]. The other way is formation of nanotubes on the surface. It is a layer of titanium dioxide (or other transient metal oxide) in the form of tubes with diameter in nanometres range and length from several nanometres to hundreds of micrometers. Structure of the tubes is amorphous and it is possible to modify it tune bioactivity (e.g. doping of the structure by phosphorous and calcium) [4-6]. Bioactive surface stimulate a deposition of the osteoblast cells which leads to easier interaction of the implant with a bone.
1.2 Nanotubes formation by anodization

The anodic growth of titanium oxide nanotubes is, in simplest approach, governed by a competition between two reactions. The first one is an anodic oxidation, which leads to formation of compact passive layer of TiO$_2$:

$$\text{Ti} + 2 \text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4 \text{H}^+ + 4 \text{e}^-$$  \hspace{1cm} (1)

The second one is a chemical dissolution of the oxide as soluble fluoride complexes, e.g.:

$$\text{TiO}_2 + 6 \text{F}^- \rightarrow [\text{TiF}_6]^{2-} + 2 \text{O}^{2-}$$  \hspace{1cm} (2)

The reaction (1) describes the oxide growth on an anodized metal surface, as schematically showed in Fig. 1 in a fluoride-free electrolyte (for example NH$_4$SO$_4$). Oxidized metal species react with O$_{2^-}$ ions (from H$_2$O) to form an oxide layer. The oxide growth is governed by ion transport through the growing TiO$_2$ lattice and thus competing with O$_{2^-}$ transport. The complex formation ability leads to a continuous chemical dissolution of formed TiO$_2$. The current response of system under applied potential is shown on Fig. 5. There are three stages of process: At the first stage, growth of compact titanium dioxide occurs (Fig. 1). The current response of the system is similar with that of the system without fluorides (Fig. 5-a). The second stage (Fig. 5-b) represents an initial stage of the nanotubes formation. The fluoride ions interact with titanium dioxide and selective dissolution on the high-energy places begins (Fig. 3). The increasing current is a consequence of competition between oxidation (electrochemical process) and chemical dissolution of the oxide layer. At the third stage, the equilibrium between oxidation and dissolution is reached. The current flow is constant (Fig. 5-c) and nanostuctured surface begins to form (Fig. 4) [7].

![Fig. 1. Growth of TiO$_2$ in fluoride-free electrolyte (based on [7]).](image1.png)

![Fig. 2. Current response of system under applied potential in fluoride-free electrolyte (based on [7]).](image2.png)
1.3 Influence of electrochemical parameters on surface geometry

The key factor controlling the tube diameter is the anodization potential. In the case of TiO$_2$ nanotubes layers, a wide variety of nanotube diameters can be achieved. For anodization experiments carried out in 1 M H$_3$PO$_4$ + 0.3 wt.% HF it has been shown that the tube diameter can be achieved in the range of 15–120 nm in the potential range between 1 and 25 V [8].

The nanotubes length is influenced by anodization time, however, only to the moment, when the equilibrium state is reached. Then the diffusion control of the process occurs (transport of fluoride ions and corrosion products) [9].

The nanotubes with length from 500 to 600 nm grow in the electrolytes containing fluoric acid (or acidic mixtures of fluorides). In buffered solutions, with respect to the pH gradient in tubes can be achieved length up to 2 µm. In viscous or water-free electrolytes 7 µm length tubes with smooth walls can be growth [7].

2. EXPERIMENTAL

Experiments were conducted with specimens of titanium grade 2 (0.23 wt.% O, 0.01 wt.% N, bal. Ti). Specimens were wet ground (up to FEPA P2500 paper) and polished by diamond paste with particles diameter 0.7 µm. The samples were sonicated in deionised water, isopropanole and acetone, and then dried in an air stream. Anodization was realised in electrolyte containing 0.2 mol/l (NH$_4$)$_2$SO$_4$ and 0.5 wt.% NH$_4$F. Experiments were carried out in standard three electrode setup with platinum gauze as a counter electrode, sample as a working electrode and silver/silver chloride (3 mol/l KCl) reference electrode. All potentials presented at this paper are related to this electrode. The electrochemical measurement consisted of a potential ramp from open circuit potential to the end potential 20 V with a chosen sweep rate and followed by holding the potential at the end potential for 1, 2 and 3 h. All anodization experiments were carried out at room temperature. After the electrochemical measurement, the samples were rinsed with deionised water and then dried in the air stream.

High voltage potentiostat Jaissle Potenciostat-Galvanostat IMP 88 PC-200V with controlling unit PGU-AUTO Extern was used at this work. For a morphological characterization of the samples, a scanning electron microscope (SEM) Hitachi S-4700 was used.
3. RESULTS AND DISCUSSION

In the first part of the study, the influence of the potential sweep ramp on the surface morphology was explored. Time dependencies of current densities are shown on Fig. 6. Growth of nanotubes wasn’t observed at the polarization rate 10mV/s. Titanium oxide layer wasn’t ordered and only nuclei of tubes were observed (Fig. 7). Different situation occurred with the polarization rate 100 mV/s. The nanotubes covered most of the surface, however degree of its organisation was low (Fig. 8). Highly ordered structure was observed after anodization with potential sweep ramp 1000 mV/s (Fig. 9). Nanotubes covered the whole surface and its diameter was approximately 100 nm.

![Fig. 6. Time dependencies of current density for different potential sweep ramps.](image_url)

![Fig. 7. SEM image of TiO$_2$ layer formed at 20 V in 0.2 mol/l (NH$_4$)$_2$SO$_4$ and 0.5 %wt. NH$_4$F electrolyte with potential sweep ramp 10 mV/s.](image_url)

![Fig. 8. SEM image of TiO$_2$ layer formed at 20 V in 0.2 mol/l (NH$_4$)$_2$SO$_4$ and 0.5 %wt. NH$_4$F electrolyte with potential sweep ramp 100 mV/s.](image_url)

![Fig. 9. SEM image of TiO$_2$ layer formed at 20 V in 0.2 mol/l (NH$_4$)$_2$SO$_4$ and 0.5 %wt. NH$_4$F electrolyte with potential sweep ramp 1000 mV/s.](image_url)

In the second part of the study, the influence of the total time on preselected potential was studied. After 1 hour of anodization at 20 V with the potential sweep ramp 1000 mV/s, the surface was covered by titanium
dioxide in an amorphous disorganized form. Nuclei for subsequent nanotubes growth weren’t observed (Fig. 10). Some nanotubes were detected after 2 hours of anodization. However, they were randomly distributed on surface. The major part of the surface was composed of the amorphous titanium dioxide (Fig. 11). Highly ordered structure was achieved after 3 hours polarization to 20 V (Fig. 9).

![Fig. 10. SEM image of TiO₂ layer formed at 20 V for 1 h with potential sweep ramp 1000 mV/s.](image1)

![Fig. 11. SEM image of TiO₂ layer formed at 20 V for 2 h with potential sweep ramp 1000 mV/s.](image2)

4. CONCLUSION

The major steps of the anodization process leading to the nanostructuring of the titanium surface were shown in this work. The influence of the electrochemical parameters on surface state was demonstrated. It was found, that the polarization rate 1000 mV/s, final potential 20 V and at least 3 hours delay are necessary to obtain ordered nanostructure on titanium in the sulphate based electrolyte.

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LITERATURE


