Abstract: Present paper deals with the investigation of the surface morphology of pure titanium after anodization. Round samples of CP Ti were anodized at different voltages (16V, 20V, 25V, 30V and 40V) in an electrolyte containing 0.5 wt.% HF. The process duration varied from 30min to 7 hours. The samples’ surface was observed and EDX analysis was made by SEM. Surface morphology of CP Ti after anodization is defined by the surface roughness before anodization, electrolyte type and process parameters – voltage and duration. It was established that the surface of pure titanium after 3h-7h anodization at all voltages characterizes with large number of craters increasing the surface micro-roughness. At short-term processes only pores with about 2µm diameter were observed. Depending on the regimes used different oxide nanostructures were observed. After short-term anodization in lower voltages the titanium surface was covered with nanodots, nanorods and nanoflakes. Increasing the voltage up to 25V led to originating of nano-tubular structure in some areas and sponge-like nano-structure at 30V and 40V. Increasing the process duration caused increase of the proportion of nanotubes and sponge-like structure to that of nanorods.

Keywords: PURE TITANIUM, ANODIZATION, SURFACE MORPHOLOGY, TITANIUM OXIDE NANOTUBES AND NANOSTRUCTURES

1. Introduction

An implant is an artificial structure whose purpose is to replace or stabilize damaged body functions and include many different types such as hip and knee joints, spinal implants, dental implants etc. [1]. The principal requirements of all medical implants are corrosion resistance, bio-compatibility, bio-adhesion, bio-functionalities, processability and availability. The design of implants could be divided into four levels: macro-design, mini-design, micro-design and nano-design. The last two aspects refer to the surface roughness at micro-level and to the molecular organization of the implant surface at nano-level. From that point of view, the surface topography of the implant should consist of hierarchical structure, composed of micro- and nano-components, which mimic the structure of the natural bone [2,3].

Pure titanium is preferable material for production of implants because its mechanical properties and elastic modulus are close to that of the bone tissues. Its good corrosion resistance and biocompatibility depends upon the formation of a solid oxide layer. As the geometry, roughness and other surface characteristics importantly influence the surface–tissue interaction, the biocompatibility of the implant can be enhanced by surface modification. Transformation of the solid oxide layer into porous or tubular structure can give such a decision, because TiO2 NanoTubes (NT) can mimic the dimensions of the components of natural bone [4,5].

The simplest, rapid and inexpensive method for preparation of strongly adherent layer of TiO2 NT is anodization [4,5]. The nano-tubular structures are obtained during anodization in fluorine electrolyte solutions with applied voltage lower than the dielectric breakdown. In the most electrolytes containing fluorides, nanotubes can be grown with diameter of 40-150nm at anodic voltages in the range of 5-30V [3-5]. It was found that the diameters of the nanotubes were determined by applied voltage while the final length of the tubes was independent of the anodization time. The thickness of the formed tubular-structure oxide layer can be from a few hundred nanometers up to a few microns by controlling pH and electrolytes.

As the geometry and roughness of the surface strongly influences on the implant’s biocompatibility, the aim of the present paper is to investigate the surface morphology of pure titanium after anodization in water solution of HF at different regimes.

2. Experimental methods

Round samples with dimensions 24mm x 3mm (diameter x thickness) were made of commercially pure (CP) Ti Grade-2 (99.5%). The samples’ surface was ground with sandpaper 300, 600 and 800. After grinding they were ultrasonically cleaned consecutively in acetone, ethanol and deionized water for 15 min in each media and dried with compressed air. On the next stage the samples were etched for 30 min in 0.5 wt.% HF acid, immediately rinsed with deionized water and dried. They were anodized at different voltages (16V, 20V, 25V, 30V and 40V) in an electrolyte containing 0.5 wt.% HF acid using a DC power supply with a graphite electrode as cathode. The process duration varied from 30min to 7 hours. Immediately after anodization the samples were rinsed several times with deionized water and dried with compressed air. The surface morphology was observed and EDX analysis was made on high resolution field emission scanning electron microscope FEI Quanta 400 ESEM FEG (ESEM2). The phase composition was investigated by XRD analyzer Rigaku D/Max in Cu Kα irradiation.

Fig. 1 Surface morphology of pure Ti-Gr2, after 30 min anodization at different voltages: 20V - a); 30V - b); and 40V – c).
3. Results and analysis

Results obtained

The surface of CP Ti after anodization characterizes with large number of craters increasing the surface micro-roughness. The first single pores with diameter of about 2 µm are observed in 1 h anodization even in lower voltages – 16 V. Their quantity slowly increases with increasing of the voltage up to 40 V (Fig. 1), while their sizes remain unchanged. The process duration influences stronger. With increase the time from 30 min up to 6h (Fig. 2) the number of pores and their diameter increase while their shape changes to crater-like. Fig. 2c-1 and Fig. 2d-1 show large number of well-shaped craters with different sizes on the sample’s surface after 3h and 6h anodization. The new formed pores of about 2 µm can be seen both inside the craters with larger sizes and outside them. The craters’ diameter after 1h anodization varies between 5-7 µm; it is up to 15 µm after 3h and up to 25 µm after 6h processes.

The grain boundaries can be clearly seen on the samples surface after anodization in all regimes, whether increasing the voltage (Fig. 3) or the process duration (Fig. 2d-2). White formations with irregular shape and dimensions of about 1-2 µm are observed on the joints of three grains and mainly along the grain boundaries (Fig. 3).

![Fig. 2 Surface morphology of pure Ti-Gr2, after anodization at 30V in different duration: 30min - a); 1h - b); 3h - c); and 6h - d).](image-url)
They originate at the all anodization voltages after 1h and can be even seen after 6h process (Fig. 4). They are composed of titanium oxide (Fig. 3f and Fig. 4).

The surface morphology after short term (30 min) anodization in low voltages (20 V) is very similar to that of the etched sample (Fig. 5). Only porous sponge-like nanostructure (Fig. 2a-3) originates in several spots on the surface after anodization at 30 V and 40 V, while the rest part is covered by nanorods. Increasing the process duration leads to formation of different type of titanium oxide nanostructures. After 1h anodization in lower voltages (16 V and 20 V) the samples surface is covered with nanodots, nanorods and nanoflakes (Fig.3a-d). The first nano-tubular structure originated in small spots scattered over the entire sample’s surface after 1h anodization in 25V. The structure is rather sponge-like consisting of pores with irregular shape and sizes [6]. Well-shaped NTs with average internal diameter 82 nm could also be observed in some zones. The rest surface is covered with nanorods. The sample surface after 1h anodization in 30 V is covered with porous sponge-like nanostructure (Fig.2a-3) and nanorods in ratio 30%/70%. Increasing of the process duration leads to increase the portion of nanotubes and sponge-like structure to that of nanorods and increasing the NTs diameter as well. After 6h anodization at 25 V the average NTs diameter is 109 nm and the NTs/nanorods ratio is 60-70%/40-30% (Fig. 4). While after 30 V process with the same duration the sponge-like/nanorods ratio is 60%/40% (Fig. 2d-2). EDX analysis on Fig. 4 shows that all types of nanostructures consist of titanium oxide with amorphous structure [6].

**Discussion**

Surface morphology of pure titanium after anodization is defined by the surface roughness before anodization, electrolyte type and process parameters – voltage and duration. During anodization field-enhanced oxidation and field-enhanced dissolution run simultaneously with the chemical dissolution of the titanium and titanium oxide in HF acid. But the field-enhanced processes run with different rate at the particular micro-regions because of the micro/nano-roughness of the surface, obtained after etching [6]. As a result the formation of thin oxide layer on the sample’s surface is embarrassed and the first TiO2 nanostructures originate in small spots. The fluorine electrolyte solutions determine the nano-porous or nano-tubular structure of the oxide layer during anodization which is obtained in voltages much lower than the dielectric breakdown – 93 V [5, 7, 8]. Our results show TiO2 nano-tubular structure at 25 V and nano-porous sponge-like structure at higher voltages - 30 V and 40 V. The formation of nano-porous sponge-like structure at higher voltages is probably due to the intensive release of oxygen on the anode (1) which occurs during anodization in water solutions [7] and may cause inhomogeneity of the ordered structure.

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\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \\
\]

\[\text{(1)}\]

The titanium oxide is a dielectric and has higher resistivity than the electrolyte and the metallic substrate. Therefore the applied voltage will mainly drop over the oxide film on the anode. High O₂ at the anode means that there are high electric currents through the oxide films, which may lead to dielectric breakdown of the film [7]. Moreover in our experiments the thickness of the anodized layer is not uniform, so there are conditions in some weak points the potential drop to exceed the dielectric limit causing sparking [5]. The sparking causes micro-pits and spots along the grain boundaries [8]. As a result we observed micro-pits with about 2µm diameter in 30 min process at all voltages (Fig. 1 and Fig. 2a-2). This process is accompanied with increasing the local temperature up to several thousand degrees causing local melting [5], thus transforming pores into craters. Thermal stress of the anodized layer leads to cascading process of multiplication of weak points and consequently breakdown of the dielectric. As a result large number of craters is formed on the surface of pure titanium after anodization in 3h and 6h (Fig. 2).

As the grain boundaries characterizes with high degree of lattice disorder of the neighboring grains and condensation of vacancies [9], the diffusion of metal cation in these regions during anodization is higher. As a result oxide formations with different shape can be seen along the grain boundaries and in joints of three grains after short term anodization at all of the voltages (Fig. 3) which keep in
time increase up to 7h. But, because of the high vacancies’ accumulation, local decohesion of the oxide layer from the metal could occur thus weakening the anodized layer and creating conditions for dielectric breakdown. That is why the pores, growing further into craters, are mainly along the grain boundaries.

4. Conclusions

Samples’ surface of pure titanium after anodization in water solution of HF acid at different regimes was investigated. Surface morphology is defined by the surface roughness before anodization, electrolyte type and process parameters – voltage and duration.

It was established that the surface of pure titanium after 3h-7h anodization at all voltages characterizes with large number of craters increasing the surface micro-roughness. At short-term processes only pores with diameter of about 2µm are observed. Increasing of time leads to increase of the number of pores and their diameter while their shape changes to crater-like with dimensions up to 25 µm (6h, 30 V).

Different oxide nanostructures are observed depending on the regimes used. After short-term anodization in lower voltages (16 V and 20 V) titanium surface is covered with nanodots, nanorods and nanoflakes. Increasing the voltage up to 25 V leads to originating of nano-tubular structure in some areas and sponge-like nano-structure at 30 V and 40 V. Increasing of the process duration leads to increase the proportion of nanotubes and sponge-like structure to that of nanorods up to 60%-70%/40-30% (6h, 25V) and 60%/40% (6h, 25V) accordingly.

Surface morphology of pure titanium after anodization characterizes with higher micro-roughness and different morphology of the oxide layer which varies from nanodots,

![Fig. 5 Surface of pure Ti-Gr2 after etching – a) and after subsequent 30 min anodization at 20V - b).](image-url)
nanorods and nanoflakes in lower voltages and short-term processes to nanotubes/nanorods and sponge-like/nanorods with different ratio in higher voltages and long-term anodization.

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6. References