The porous layers for medical application made by a process of high-voltage anodic oxidation of titanium

Abstract

Purpose: Examination the process of high voltage anodic oxidation of titanium in electrolyte containing 2M orthophosphoric acid with addition of hydrofluoric acid for biomedical applications (implants).

Materials and Methods: On the study used titanium samples (99.6%) having a diameter of 10mm and a height of 5mm. Samples were anodized in an electrolyte 2M H_3PO_4 + 0÷2% HF at a voltage of 30÷240V during 30min. Obtained oxide surface was examined by scanning electron microscope (SEM), Atomic Force Microscope (AFM), X-ray diffractometer (XRD) and corrosion resistance in Ringer solution. The obtained results allow identified a series of samples for further testing. On the selected series was executed deposition process of silver particles carried out by the electrolytic method. In time the deposition of silver used electrolyte containing 0.01M HNO_3 + 0.01M $AgNO_3$ at a voltage of -1V (vs. OCP) during 60s. Some specimens were wettability tested (dynamic and static) with additional annealing at a temperature of 120^0C. Investigations of photoelectron spectroscopy (XPS) and biocompatibility *in vitro* on human cells fibroblasts and osteoblasts was done. Anodic oxidation process was carried out on commercially implant.

Results: Samples of titanium after anodization have morphology that is strongly dependent on the specific electrolyte and anodic voltage. Low concentration of HF in the electrolyte promoted the formation of flat layers and the presence of corrosive efflorescence. The content of 2% HF in the electrolyte conducive to strong etching of oxide surface. The electrolyte containing 1% HF give the balance between the rate of oxide formation and the etching. For all samples starting from the voltage 180V oxidation process was assisted with the foci of plasma. All the samples have good corrosion resistance and the crystalline structure suitable for medical application. On the selected series of samples, oxidized in an electrolyte 2M H_3PO_4 + 1% HF was carried out the deposition process of the silver particles. Deposited particles took the form of dendritic and grow directly from the pores in the oxide layer. Static wettability test classify the majority of samples in the field of strong bioadhesion ($<55^0$). The study of dynamic wettability test for selected samples have shown their superhydrophilicity. Annealing the samples resulted in their further oxidation and crystallization of the oxide TiO_2 from amorphous phase and the deterioration of wettability. XPS analysis showed the presence of Ti^{+3} in the surface layer corresponding to the oxides Ti_2O_3. Biocompatibility studies *in vitro* on a sample oxidized in the electrolyte 2M H_3PO_4 + 1% HF at a voltage of 210V indicate its usefulness for medical purposes. The deposited silver particles allowed for increased viability and survival rate of human cells in studies of biocompatibility. Anodizing process of commercial implant indicates the possibility of transferring the developed technology for different materials and substrate without losing the quality of results.

Summary: It is possible to produce the anodic oxide layer on titanium with properties suitable for medical applications. The best oxide layer was obtained during the anodizing the titanium in the electrolyte 2M H_3PO_4 + 1% HF at a voltage of 210V with additional deposition of the silver particles. The resulting oxide film was characterized by a high roughness, good wettability, high corrosion resistance and appropriate biocompatibility.

Keywords: titanium, anodic oxidation, electrochemistry, silver, wettability, *in vitro* biocompatibility