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Influence of Surface Preparation on Morphology of Self-organized Nanotubular Oxide Layers Developed on Ti6Al4V Alloy

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Abstract

An ordered nanostructured surface of biomedical implants facilitates the enhancement of their osseointegration. It has been demonstrated that TiO_2 nanostructures (nanotubes/nanopores with 15-100 nm diameter) strongly promote bone cells adhesion, proliferation and differentiation. Present paper presents our results on development of ordered nanostructured TiO_2 layer on the surface of two phase (α+β) Ti6Al4V alloy by using electrochemical anodization in H_3PO_4/HF electrolytes. Our results show a successful deposition of oxide layers exhibiting requested morphology for a proper biological response, regardless of initial flat surfaces manufacturing process (polishing, conventional milling, sand blasting and acid etching,) and their initial roughness (R_a = 0.05-2.3 μm). On polished surfaces (R_a = 0.05 μm) and milled surfaces (R_a = 0.5 μm) we deposited well defined, self-ordered, nanotubular TiO_2 with internal diameter in the range of 50-100 nm. On sand blasted and acid etched surfaces (R_a = 2.3 μm) we developed nanoporous structures having pores diameter of 25-65 nm.

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1. Introduction

Metallic implants are used in hard tissues (teeth, bones) replacement and surgery. In this category, titanium and its alloys have been widely applied in dental and orthopedic implants manufacturing, as they present many advantages such as excellent biocompatibility, good mechanical strength, and high corrosion resistance. Titanium

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based implants have unique biocompatibility, due to the formation of a native TiO_2 compact layer, with a thickness of 2...10 nm, on their surface. The modification of the implant surface at the micro level has been shown to have a major effect on the rate and degree of osseointegration. Furthermore, recent studies show that the surface modification at nano scale level in order to produce an ordered nanostructured surface, promotes enhanced bone apposition demonstrated by the presence of active cells implicated in bone formation and regeneration (osteoblasts, osteoclasts, mesenchymal and haematopoietic stem cells, endothelial cells, etc.) surrounding the nanostructured implant surface [1-9]. Nanostructured oxide layers can be developed on titanium based surfaces by using sol–gel, template-assisted, hydro/solvo-thermal, and by electrochemical methods. Among these, electrochemical anodization can provide degree of control on the uniformity, self-arrangement and dimensions (nanopore/nanotube diameters, nanolayer thickness), structure and chemical composition of developed oxide layers and, by this, nanostructured surfaces with desired features can be developed by optimizing the process parameters of anodization. This control is very important in the context of recent studies showing the size-selective response of cells implicated in bone regeneration to the nanosurface: diameters of about 15 nm, strongly promote bone cells adhesion, proliferation and differentiation. This size-effect is likelihood to be the result of geometrical fitting between nanopore/nanotube opening of about 15 nm and surface proteins (about 10 nm diameter), who have the properties to be adsorbed onto surfaces (including implants surface) and which are sense by integrins (surface receptors of bone cells membrane) and to whom bone cells are attaching to. Also, recent literature arguments the favourable osseointegration around TiO_2 nanotubes of 15...100 nm diameters modified surfaces by over-expression of genes related to high activity of osteoblasts and mesenchymal stem cells, and by fast kinetics of hydroxyapatite (basic bone component) formation, surrounding titanium implant. In this context our project aims to develop TiO_2 nanostructures (nanotubes/nanopores) with 15...100 nm diameter.

As regards the technology used for surface modification, anodization leads to an oxidation of metal species that form a solid oxide on the metal surface. Depending on the anodization conditions, the solid oxide layer can be either compact, or nanotubular/nanoporous. Electrochemical anodization in aqueous fluoride solutions creates the conditions for ordered TiO_2 nanostructures development and offers control upon process parameters that can provide the requested specifications for nanostructures in order to be successfully used in biomedical applications [10-14].

The mechanism of nanostructures formation is a very complex one and occurs in interdependent conditions. The formation of nanostructures is governed by the competition between anodic oxide formation and chemical dissolution of the oxide as soluble fluoride complexes. The nanotubular layer develops in three stages: first is compact oxide formation, second is the initial porous structure formation, and third is self-organized nanotubes growth. A proper combination of electrolyte composition, anodization potential, anodization time, and a perfect balance between potentiodynamic stage and potentiostatic stage are required in order to develop uniform and highly-organized nanotubular oxide structures on titanium. Moreover, the formation of self-ordered nanostructures on two phase ($\alpha+\beta$) titanium alloys is a more demanding process, due to the selective dissolution of the less stable phase and/or different reactions rate of the different phases of the alloy [15].

In this context our major research direction is enhancement of surfaces of biomedical titanium based implants, both at micro and nano level, in order to improve their osseointegration. Our recently reported research led to successful development, using electrochemical anodization, of self-ordered nanostructured oxide layer on the surface of two phase Ti6Al4V alloy by using electrochemical anodization in H_3PO_4/HF electrolytes [16]. These results are fully comparable with the latest results reported by several research teams working in the field of nanostructured titanium based modified surfaces [3, 5, 6, 10, 13].

Based on these results, present paper aims to assess the influence of surface preparation, prior to anodization, on morphology of TiO_2 nanostructured layers. It is to be emphasized that the literature presents many results regarding TiO_2 nanostructured layers developed on flat, extra polished surfaces. However, these findings don't show the influence of surface preparation on nanostructures development. In this context our research presents a high degree of novelty, aiming to build premises for development of biomedical implants covered by TiO_2 nanostructures, where a cost effective solution for initial surface, prior to anodization, is of great importance.