TITANIA COATINGS PRODUCED BY ELECTROCHEMICAL AND CHEMICAL OXIDATION OF TITANIUM ALLOYS SURFACE AND THEIR APPLICATION IN CONSTRUCTION OF IMPLANTS

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Introduction

The titanium alloys are widely used in the construction of implants, which complement the bone defects in patients e.g. after complicated spine surgery or bone fractures. Although titanium based implants are typically expected to be longlasting, the lack of the integration with the bone often leads to implant failure and to the need to replace it. Therefore, one of the key challenges in bone healing and regeneration is the engineering of an implant, which provides osteointegration with enhanced bioactivity and improves implant-host interactions. One of the surface modification directions aiming at enhancement of bioactivity and osteointegration, is the formation of TiO_2 based coatings of defined structure, architecture, physicochemical, and mechanical properties, on the surface of titanium based implants. The low cost of electrochemical and chemical oxidation methods, and easy production of titanium dioxide nanotubular coatings, possessing the high surface-area-to-volume ratio, the strong oxidizing properties, the chemical stability, non-toxicity, the good mechanical properties, the excellent corrosion resistance and the high biointegration activity, caused a wide interest of these implants surface modification methods. The evaluation of relationship between structure, morphology and biological activity of titania nanotube coatings (TNT), produced by electrochemical oxidation of the implant surface, and titania fibrous layers (TNF), produced by titanium alloy surface chemical oxidation, were the aim of our investigations.

Materials and Methods

The amorphous TNT coatings were produced based on previously optimized anodic oxidation procedure [1-3], using Ti6Al4V alloy substrates and potentials U = 5-40 V. The samples of TNF coatings on the surface of Ti6Al4V substrates were produced using chemical oxidation method [2]. The surfaces of the substrates were chemically etched in a ca. 5.8 M HCl or 2M HF, then samples were heated in 30% H_2O_2 solution at 358 K, for different oxidation times. Samples surface morphologies were studied using the scanning electron microscope with field emission. Analysis of Raman spectra and XRD patterns of produced titania coatings allowed their structure determination. The photobleaching properties of TNT and TNF coatings were studied in accordance to ISO 10678; 2010 by the degradation of methylene blue [2]. The nanoindentation and nanoscratch-test analysis were performed to nanomechanical properties determination of studied TNT and TNF samples. The MTT assay was used to test specimen's influence on cells proliferation (measured after 24 and 72 h) [1,3,4]. We have studied the proliferation level of three cell lines growing on the surface of tested nanocoatings, i.e. adipose-derived human mesenchymal stem cells (ADSC), MG-63 osteoblasts and L929 fibroblasts were seeded onto the autoclaved TNT and TNF nanocoatings. Analysis of SEM allows observing the morphology changes of ADSCs co-cultured with MG-63 osteoblasts or L929 fibroblasts on the surface of tested nanolayers.

Results and Discussion

Among the applied oxidation methods, the direct chemical oxidation of Ti6Al4V substrates surface led to the produce of hydrophobic fibrous TiO_2 coatings (TNF), which mechanical properties and the biointegration activity was better in comparison to titania nanotube layers (TNT) produced by surface anodization (FIG. 1).

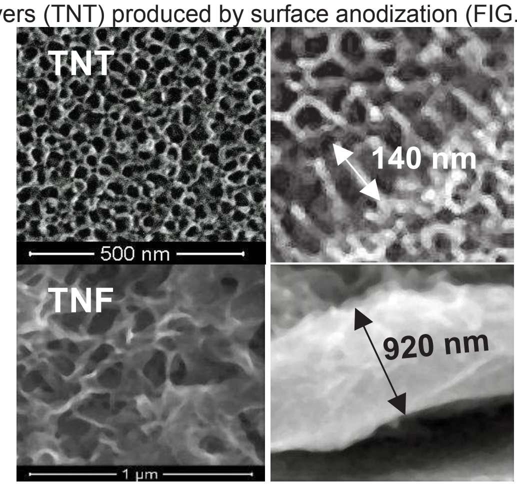

FIG. 1. SEM images of the surface morphology and cross-section of TNT and TNF coatings.

The results of nanoindentation studies proved that TNF coatings characterized good adhesion to the substrate surfaces, higher values of the Young's Modulus, and lower roughness. The viability level of all cell lines (mouse L929 fibroblasts, human osteoblasts-like MG-63 cells, and adipose-derived human mesenchymal stem cells (ADSCs)) increased after 72 h of culture on completely amorphous TiO_2 nanofibers surfaces versus TNT layers and the control sample (Ti6Al4V alloy). Simultaneously, it should be noted that also the photocatalytic activity of TNF coatings was higher in comparison to TNT ones. This would suggest that TNF coatings are also able to actively support the sterilization process of medical devices carried out in the presence of UVA radiation, increasing the speed and efficiency of the process of degradation of organic pollutants.

Conclusions

The research exhibited more favourable bioactivity and photocatalytic properties of titania nanofibrous coatings in comparison to titania nanotube ones. This suggest that the use of TNF layers obtained by chemical oxidation of the implant surface is more prove to be beneficial and can be applied as a novel alternative for bone tissue regeneration.

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