COMPARATIVE STUDY ON MECHANICAL AND BIOACTIVE PROPERTIES OF DIFFERENT NANOPATTERNED TiO_2 SUBSTRATES

Amanda Bartkowiak[1]*, Zarzycki Arkadiusz[1], Slawomir Kac[2], Marcin Perzanowski[1], Marta Marszałek[1]

[1] Institute of Nuclear Physics PAN, Poland
[2] AGH University of Science and Technology, Poland
*e-mail: amanda.bartkowiak@ifj.edu.pl

[Engineering of Biomaterials 158 (2020) 63]

Introduction

Nanostructured surfaces are considered as very attractive for orthopaedic applications. They are capable of combining different properties, such as high osseointegration with the ability to be used as drug delivery systems. Electrochemical anodization gives the opportunity to produce suitable nanotubular or nanoporous surface structure. Titanium oxide nanotubes (NT) have been extensively investigated for localized controlled release of therapeutics [1], however, their brittle nature could be significantly limiting factor for orthopaedic purpose. In this study, we have produced crystalline nanoporous u-shaped structure (US) of anodized TiO_2 with improved resistance to scratch compared to NT. Also, the US substrate was successfully modified with hydroxyapatite (HAp) coating and investigated for bioactivity.

Materials and Methods

Substrates were prepared on 14x14 mm^2 Ti plates by standard two electrode anodization at room temperature in potentiostatic mode. During the process voltage was kept constant at 50 V. Afterwards, NT and US were annealed in oxidizing atmosphere at 600ºC for 1 h. The US are formed when the NT are removed from the surface and thin layer of TiO_2 is covering patterned substrate. In order to produce HAp coatings, the hydrothermal process was carried out in an autoclave from solution containing: calcium salt hydrate, diammonium phosphate, calcium chelating agent. The morphology and structure of anodized and coated with HAp specimens were characterized using XRD, SEM-EDS and Raman spectroscopy. We evaluated adhesion strength of the nanopatterned samples using combination of SEM, EDS and Nano-Scratch Test System. Bioactivity was examined after 2 weeks of incubation in SBF.

Results and Discussion

SEM images presenting two nanopatterned structures of anodized titanium are shown in FIG. 1. The height of US (left image) is approximately ½ of their diameter, while NT exhibit micrometer-long tubular structures (right image).

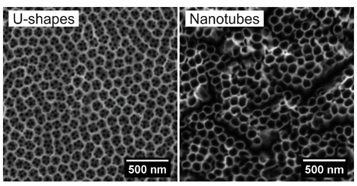

FIG. 1. SEM images of anodized and annealed at 600°C TiO_2 layer in the form of US and NT.

FIG. 2 presents SEM images of sample surfaces after the scratch test, where three main areas are identified: the beginning of scratch (left image); the intermediate area showing deformed but still continuous (according to EDS measurement) layer of the crystalline TiO_2 (middle image), and the area of layer delamination with substrate exposition (right image).

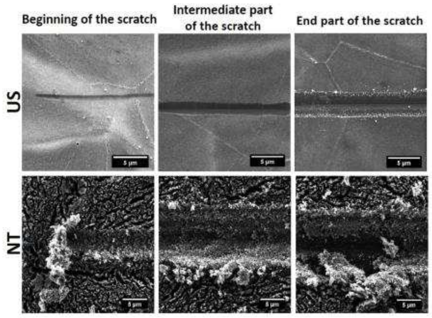

FIG. 2. SEM images showing sample surface of US and NT after the scratch test.

It is very important to consider, that at the time of implantation, orthopaedic implants are subjected to considerable mechanical stress. Most studies on implants with nanoscaled topography focus on their biological properties, however only few scientific reports consider investigating mechanical properties of TiO_2 nanotubes, especially regarding resistance to scratch [2]. In our opinion, nanoscaled topography requires more sophisticated approach than determining adhesion strength of nanopatterned layer only from acoustic emission examination, friction measurements or optical microscopy assessment. A deeper insight into evaluating the resistance against scratch of nanotextured surfaces can be achieved by combining the nano-scratch test with SEM imaging. During electrochemical growth of TiO_2 NT beneath the nanotubular layer a barrier layer of continuous oxide film is formed at the oxide/metal substrate interface [3]. Until now, none of the studies on adhesion considered the importance of this barrier layer, and thus determining the critical load at which delamination of the thorough oxide layer occurs (NT layer along with barrier layer). Using SEM imaging, it is possible to evaluate with good precision surface damage of the nanotubular structure from normal-load lateral scratches, however it is difficult to identify when the continuous oxide barrier layer starts to delaminate. For this purpose, we performed simultaneous SEM and EDS measurements after the scratch test, to investigate when TiO_2 layer experienced a complete delamination (i.e. NT/US layer along with barrier layer) with exposure of the metallic substrate. The determined critical normal with this method loads were of 22.0(3) mN for US and 11.0(3) mN for NT.
Functionalization of the US substrate with hydroxyapatite coating (HApUS) under hydrothermal conditions resulted in high bioactivity after 2 weeks of immersion in SBF.

Conclusions

In this study, we present crystalline nanoporous u-shaped structure of anodized titanium with twice higher resistance to scratch in comparison to brittle NT. We consider that this substrate could be an alternative material to nanotubes suitable as smart drug delivery platform. The HApUS coating may improve the currently used titanium based prosthesis.

Acknowledgments

This study was partially supported by NCN, grant UMO-2015/19/D/ST3/01843.

References

[1] W. F. Oliveira, I. R. S. Arruda, G. M. M. Silva, G. Machado, L. C. B. B. Coelho, and M. T. S. Correia, *Mater. Sci. Eng. C* 81 (2017) 597–606.
[2] M. Sarraf *et al.*, *Process. Appl. Ceram.*, 11 (2017) 311–321.
[3] P. Acevedo-Peña, L. Lartundo-Rojas, and I. González, *J. Solid State Electrochem.*, 17 (2013) 2939–2947.