

**M. Supernak-Marczewska<sup>1\*</sup>, A. Ossowska<sup>2</sup>, P. Strąkowska<sup>2</sup>, A. Zieliński<sup>2</sup>**

*Gdańsk University of Technology, Faculty of Ocean Engineering and Ship Technology, Department of Ship Manufacturing Technology, Quality Systems and Materials, Narutowicza 11/12, 80-233 Gdańsk, Poland*

*Gdańsk University of Technology, Faculty of Mechanical Engineering, Department of Materials Science and Welding Engineering, 11/12 Narutowicza, 80-233 Gdańsk, Poland*  
*\*milsuper@pg.edu.pl*

## **NANOTUBULAR OXIDE LAYERS AND HYDROXYAPATITE COATINGS ON POROUS TITANIUM ALLOY Ti13Nb13Zr**

### **ABSTRACT**

The surface condition of an implant has a significant impact on response occurring at the implant-biosystem border. The knowledge of physical-chemical and biological processes allows for targeted modification of biomaterials to induce a specified response of a tissue. The present research was aimed at development of technology composing of obtaining the nanotube oxide layers on a porous titanium alloy Ti13Nb13Zr, followed by the deposition of phosphate coating. The porous substrate (porosity about 50%) was prepared by a selective laser melting of the Ti13Nb13Zr powder with the SLM Realizer 100 equipment. The nanotubular oxide layers were fabricated by electrochemical oxidation in H<sub>3</sub>PO<sub>4</sub> + 0.3% HF mixture for 30 min. at a constant voltage of 20V. The calcium phosphate coatings were formed by the electrochemically assisted deposition (ECAD). The presence of nanotubular oxide layers with their internal diameters ranging from 30 to 100 nm was observed by SEM (JEOL JSM-7600F). The nanotubes have dimensions that facilitated the deposition of hydroxyapatite.

**Keywords:** *titanium alloy Ti13Nb13Zr, electrochemical oxidation, nanotubular titanium oxides, hydroxyapatite coatings, SEM*

### **INTRODUCTION**

Titanium and its alloys are materials the mostly used for load-bearing implants, like endoprostheses of the hip joint. They possess a very good strength, high corrosion resistance, relatively low Young's modulus and above all they are highly biocompatible [1-8]. Among many titanium alloys used for implants, the most common is the Ti6Al4V alloy. However, aluminum present in its composition may result in bone softening [2,6]. As the next candidate, the Ti13Nb13Zr alloy can be considered, which is completely biocompatible and has lower Young's modulus (70 GPa) as that of the Ti6Al4V alloy (80 GPa) [6,15]. High Young's modulus is disadvantageous when designing the endoprosthesis; the significant difference in elasticity modulus between metal and a bone may result in a change of stress distribution inside a bone, resulting in undesirable bone resorption and a lack of strong and

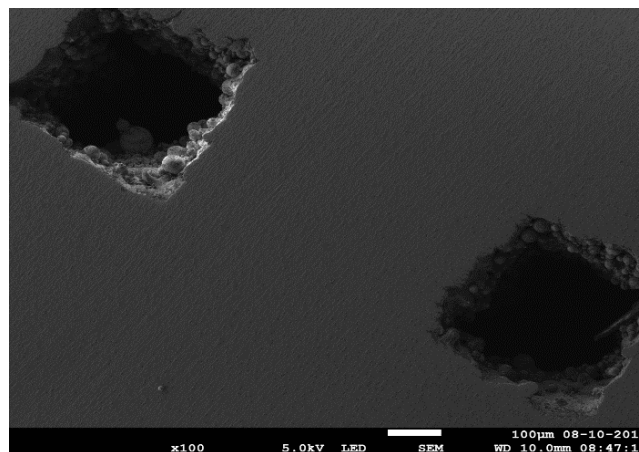
stable implant-tissue connection [11-12]. Despite the improvement of biomaterials and technologies for their production, about 15-25% of metallic implants is destroyed after some fifteen years of use. Such negative behavior may be associated with a loosening of the implant caused by insufficient joining between a body and the bone implant. There is then a need for such metal modification, which would increase the biological activity on the interface between the implant and an environment of tissues and body fluids. The receipt of bioactive surfaces is possible by performing their oxidation resulting in titanium nanooxide layer, followed by deposition of hydroxyapatite coating binding the implant and the body [5, 9, 11]. The anodic oxidation parameters such as time, voltage and electrolyte allow to control the effect the morphology of the resultant layer. The nanocrystalline structure of titanium oxide is composed of crystals of anatase possessing the same crystallographic structure as hydroxyapatite [1, 10]. The bioactivation of the surface of titanium implants increases the potential biomechanical contact at the border implant-bone and affect the rate of adsorption of proteins [14]. In vitro, the surface roughness effects on osteoblasts, shaping their proliferation and differentiation [13-15].

Even if these phenomena were very extensively studied for titanium alloys, there was no such research on the porous Ti13Zr13Nb alloy. The application of porous substrate with a pore diameter of 200  $\mu\text{m}$  allows for better adherence of the metal to the bone tissue [2,10]. However, the porous/scaffold structure may or may not make the oxidation and phosphate deposition processes more difficult or even impossible. Therefore this research was aimed development of technology composing of obtaining the nanotube oxide layers on a porous titanium alloy Ti13Nb13Zr, followed by the deposition of phosphate coating.

## MATERIALS AND METHODS

### *Substrate preparation*

Tests were carried on porous specimens (Fig. 1) made of the Ti-13Nb-13Zr alloy by the selective laser melting of powders using the SLM Realizer 100 equipment. The mean porosity, examined with the SEM, was about 50%. The specimens were polished with a waterproof paper with a final grit 2500. Then the samples were cleaned in an ultrasonic cleaner in three different reagents - acetone, 2-propanol, and distilled water. The morphology of surfaces after polishing process were made with the JEOL JSM-7600F scanning electron microscopy (SEM).



**Fig. 1.** Surface top view (SEM) of porous sample made of titanium alloy Ti13Nb13Zr

### *Electrochemical oxidation*

The electrochemical oxidation was performed in the 1M H<sub>3</sub>PO<sub>4</sub> + 0,3%wt. HF environment, during 30 min. at a voltage of 20 V. The Pt cathode of dimensions 20x20x0.5 mm was used. The distance between the cathode and anode was 20 mm. The surface morphology was examined with the JEOL JSM-7600F SEM.

### *Deposition of hydroxyapatite coating*

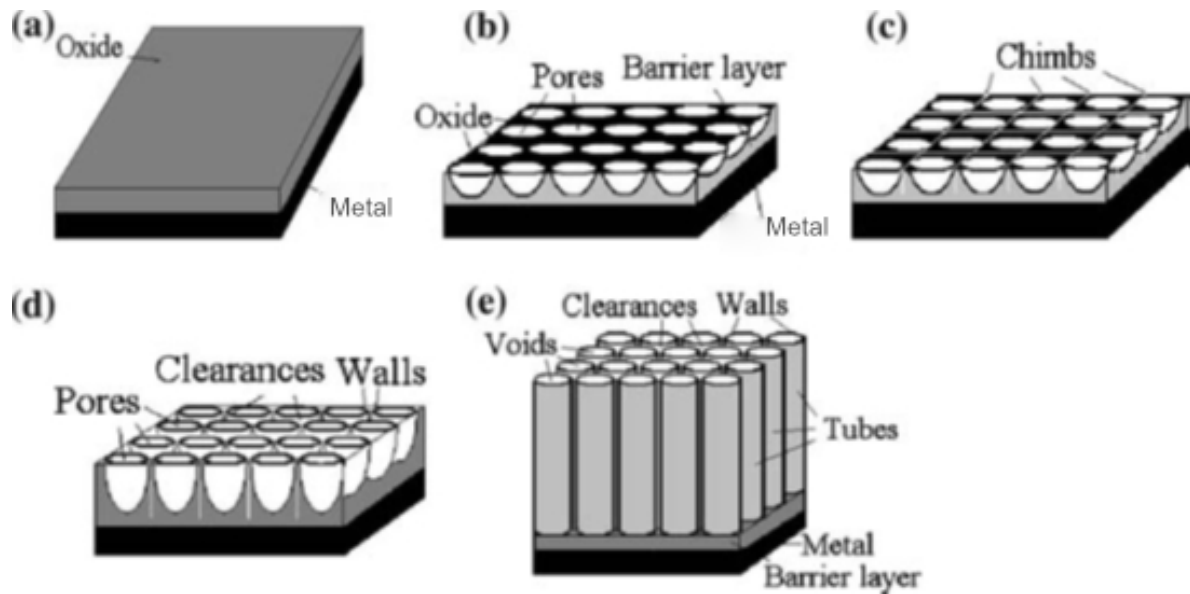
Calcium phosphate coatings were formed by the ECAD (Electrochemical Assisted Deposition method). The electrolyte used for deposition was prepared from solutions of 0.033 M CaCl<sub>2</sub> and 0.02 M NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. The final pH of the electrolyte was adjusted to 6.4 with 0.5% ammonium hydroxide solution. The ECAD was performed in a galvanostatic mode using a combined potentiostat/galvanostat (Jaisle IMP 88-100) in a two-electrode assembly at temperature 36±1°C. The potentials were measured as cell potentials via the platinum net counter electrode. The surface morphology was observed with the JEOL JSM-7600F SEM. The chemical composition of obtained coating was found in another research as close to that of hydroxyapatite.

## RESULTS AND DISCUSSION

Formation of nanotubes on the surface of the two-phase alloy is a complex process, determined by the crystallization of the acid solution in the presence of fluoride. The process of TiO<sub>2</sub> tube growth can be divided into three stages, as explained in detail by Crawford *et al.* [16]:

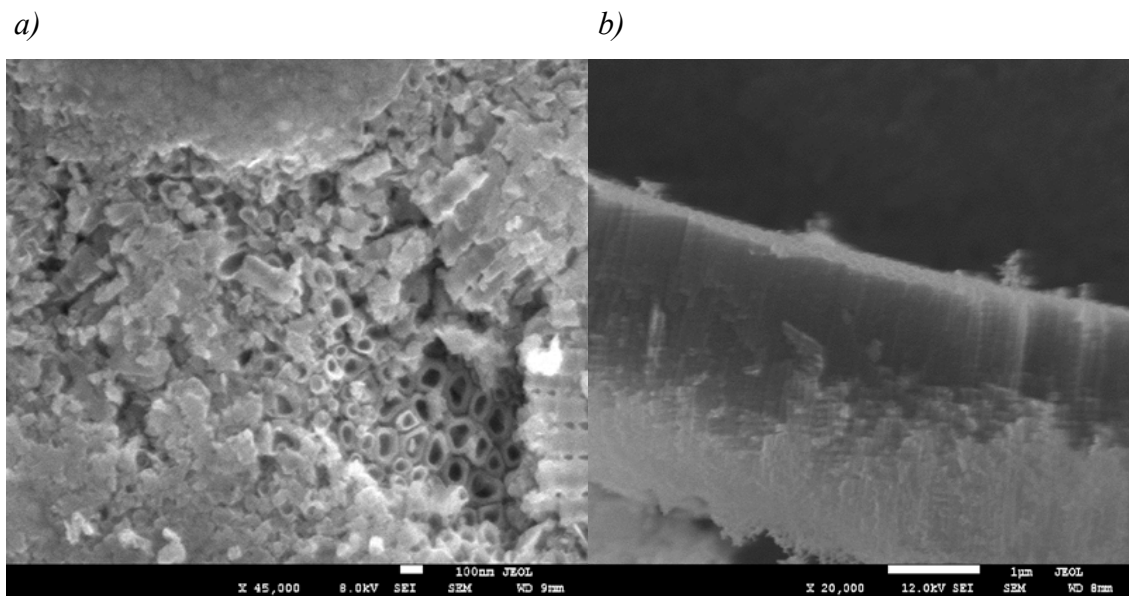
- Initial barrier layer formation – there is an exponential decrease in anodic current density until it reaches the steady state. A current drop is due to the formation of the compact oxide film that increases the resistance thus reducing the current density [17].
- Formation of uniformly distributed pores – chemical dissolution of barrier oxide layer and increase of current density. During this stage, nanopores are formed by random local dissolution of TiO<sub>2</sub> surface, as often indicated [18]. Beranek suggests that pore formation at the beginning takes place at random locations and self-organization of pores is the effect of completion of simultaneous processes (1) and (2). Raja *et al.* [19] suggest that pore's ordering is an effect of local surface perturbations, where the strain energy increases, causing the migration of F<sup>-</sup> ions to regions of higher strain energy and of hydrogen ions, in order to maintain electrical neutrality, and leading to the appearance of Ti<sup>4+</sup> ions.
- Separation of interconnected pores into nanotubes – the current density again stabilizes. The nanotubes formation is the result of the simultaneous growth of voids (regions between pores which are susceptible to field-assisted oxidation/dissolution) and pores as suggested by Mor *et al.* [20]. In contrast, Raja *et al.* [19] claim that separation of pores into individual nanotubes may be a result of the repulsive force between cation vacancies. After 1 h nanotubes are grown, as also confirmed by Crawford [16].

Based on the previous research the growth mechanism of titania nanotube arrays, the nanotube formation can be schematically represented by Fig. 2 [20].



**Fig. 2.** Schematic diagram of the evolution of titania nanotubes in anodization: (a) oxide layer formation; (b) pore formation on the oxide layer; (c) chimbs formation between pores; (d) growth of the pores and the chimbs; (e) fully developed titania nanotube arrays [20]

The results of microscopic examinations of the anodized specimen are presented in Fig. 3.



**Fig. 3.** Surface of nanotubular oxide layer formed in 1M H<sub>3</sub>PO<sub>4</sub> + 0.3% HF, at temperature 20°C for 30 min; a) top view, b) cross-section

The obtained results are evidence that this ternary and two-phase porous alloy can be successfully oxidized electrochemically with appearing nanotubular structure. The length of nanotubes can be adjusted by the mainly change in time. The drastic change in voltage may result in a disappearance of nanotubular structure, and change in temperature – in the increase

in porosity or decrease in crystallinity. The colonies of nanotubes may vary depending on the phase composition of the substrate, but this effect seems relatively small.

The presence of nanotubes with an internal diameter ranging from 20 to 100 nm is observed. The resulting nanotubes have dimensions able to facilitate an adhesion of hydroxyapatite. The calcium phosphate coating formed on nanotubular oxide layer is shown in Fig. 4.

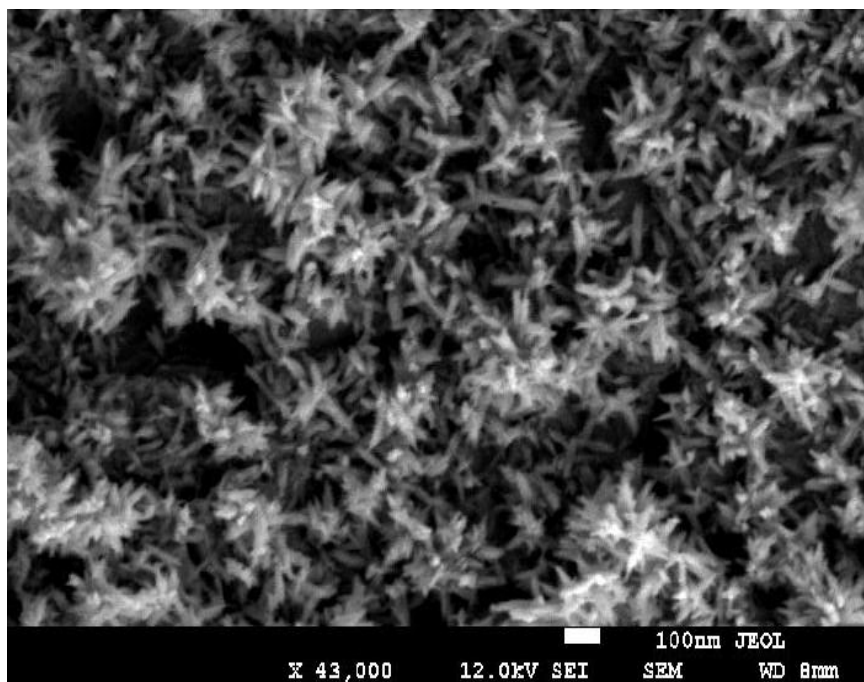


Fig. 4. Surface top view of the calcium phosphate coating formed by the ECAD technique

## CONCLUSIONS

The conducted research is one of the few which concern on surface modification porous titanium implants made by SLM. The results confirm the expected results :

- The porous titanium alloy Ti13Zr13Nb may be successfully electrochemically oxidized, that results in an appearance of fine nanotubular surface oxide layer.
- The oxide nanotubes possess internal diameter ranging from 20 to 100 nm, able to facilitate an adhesion of hydroxyapatite.
- Colonies of the nanotubes may vary depending on the local phase composition of the substrate.
- The nanotubular oxide layer may be covered with hydroxyapatite coating also with porous titanium alloy as a substrate.
- The formed hydroxyapatite coatings are dense and well adjacent to the base, enhancing the bioactivity of the metallic material.

The discussed surface modification indicates the possibility of its widespread use in the field of surface engineering of titanium implants.

## ACKNOWLEDGMENTS

The research was made under the project entitled “Fabrication technologies of bioactive coatings on porous titanium alloy” and financed by the National Science Centre (decision No. DEC-2012/05/N/ST8/02909) .

## REFERENCES

1. Huang J., Zhang X., Yan W., Chen Z., Shuai X., Wang A., Wang Y.: Nanotubular topography enhances the bioactivity of titanium implants. *Nanomed. Nanotech. Biol. and Med.* 13 (2017) 1913–1923.
2. Liu X., Chu P.K., Ding C.: Surface modification of titanium, titanium alloys, and related materials for biomedical applications. *Mater. Sci. Eng. R.* 47 (2004) 49–121.
3. Sarraf M., Zalnezhad E., Bushroa A.R., Hamoud A.M.S., Rafieerad A.R., Nasiri-Tabrizi B.: Effect of microstructural evolution on wettability and tribological behavior of TiO<sub>2</sub> nanotubular arrays coated on Ti-6Al-4V. *Ceram. Int.* 41 (2015) 7952-7962.
4. Briggs E.P., Wapole A.R., Wilshaw P.R., Karlsson M., Palsgard E.: Formation of highly adherent nano-porous alumina on Ti-based substrates: A novel bone implant coating. *J. Mater. Sc. Mat. Med.* 15 (2004) 1021-1029.
5. Yang J., Zhang K., Que K., Hou S., Chen Z., Li Y., Wang Y., Song Y., Guam B., Zhang W., Zhu D., Li Ch., Wang D., Geng P.: Surface modification of titanium with hydroxyapatite layer induced by phase-transited lysozyme coating. *Mater. Sci. Eng. C* 92 (2018) 206-215.
6. Seramak T., Serbiński W., Zieliński A.: Formation of porous structure of the metallic materials used on bone implants. *Solid State Phenom.* 183 (2012) 155-162.
7. Jakubowicz J.: Formation of porous TiO<sub>x</sub> biomaterials in H<sub>3</sub>PO<sub>4</sub> electrolytes. *Electrochem. Comm.* 10 (2008) 735-739.
8. Long M., Rack H.J.: Titanium alloys in total joint replacement - a materials science perspective. *Biomater.* 19 (1998) 1621-1639
9. Świczko-Żurek B., Bartmański M.: Investigations of titanium implants covered with hydroxyapatite layer. *Adv. Mater. Sci.* 16 (2016) 78-86.
10. Ossowska A., Sobieszcyk S., Supernak M., Zielinski A.: Morphology and properties of nanotubular oxide layer on the Ti-13Nb-13Zr alloy. *Surf. Coat. Techn.* 258 (2014) 1239-1248.
11. Krupa D., Baszkiewicz J., Sobczak J.W., Bliński A., Barcz A.: Modifying the properties of titanium surface with the aim of improving its bioactivity and corrosion resistance. *J. Mater. Proc. Techn.* 143-144 (2003) 158-163.
12. Vanzillotta P.S., Sader M.S., Bastos I.N., de Almeida Soares G.: Improvement on in vitro titanium bioactivity by three different surface treatments. *Dental Mater.* 22 (2006) 275-282.
13. Lewandowska M., Roguska A., Pisarek M., Polk B., Janik-Czachor M., Kurzydłowski K.J.: Morphology and chemical characterization on Ti surface modified for biomedical applications. *Biomolec. Eng.* 24 (2007) 438-444.
14. Zieliński A., Sobieszcyk S., Seramak T., Serbiński W., Świczko-Żurek B., Ossowska A.: Biocompatibility and bioactivity of load-bearing metallic implants. *Adv. Mater. Sci.* 10 (2010) 21-3.

15. Jażdżewska M., Majkowska-Marzec B.: Hydroxyapatite deposition on the laser modified Ti13Nb13Zr alloy. *Adv. Mater. Sci.* 17 (2017) 5-13.
16. Crawford G., Chawla N., Das K., Bose S., Bandyopadhyay A.: Microstructure and deformation behavior of biocompatible TiO<sub>2</sub> nanotubes on titanium substrate. *Acta Biomater.* 3 (2007) 359-367.
17. Prida V.M., Manova E., Vega V., Hernandez-Velez M., Aranda P., Pirola K.R., Vazquez M., Ruiz-Hitzky E.: Temperature influence on the anodic growth of self-aligned titanium dioxide nanotubes arrays. *J. Magn. Magn. Mater.* 316 (2007) 110-113.
18. Beranek R., Hildebrand H., Schmuki P.: Self-organized porous titanium prepared in H<sub>2</sub>SO<sub>4</sub>/HF electrolytes. *Electrochem. Solid State Lett.* 6 (2003) B12-B14.
19. Raja K.S., Misra M., Paramaguru K.: Formation of self-ordered nano-tubular structure of anodic oxide layer on titanium. *Electrochim. Acta* 51 (2005) 154-165.
20. Mor G.K., Varghese O.K., Paulose M., Mukherjee N., Grimes C.A.: Fabrication of tapered conical-shaped titanium nanotubes. *J. Mater. Res.* 18 (2003) 2588-2593.

