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Metal Oxide Porous Coatings for Implantant Materials

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Abstract: The paper presents the results of study of synthesis of metal oxide coatings on porous materials used in implant surgery (stainless steel 12X18H9T, titanium alloy and high-purity niobium VT5). It is shown the prospects of electrochemical anodizing method for the purpose of formation of porous, corrosion-resistant and biologically inert coatings, which significantly improve morphological structure of materials.

Keywords: oxidation; anodic film; coating; implantant.

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Introduction

Efficiency the products intended for implantation is mainly caused due to not only the medical and biological requirements, but also the possibilities of modern technologies. Depending on their application purpose, the implants introduced into the body shall comply with the living tissue and to function for a long time. Most of metallic implants currently used in medicine are made of titanium and its alloys, stainless steel, and niobium and tantalum [1 - 3].

Materials, claiming to be the implants must meet certain requirements, namely: be corrosion-resistant, possess characteristics similar to the mechanical properties of bone tissue, do not effect immune system and to integrate with the bone and stimulate bone formation [4].

One of the ways to improve the index of biological functionality and rigidity of bone-implant aggregation is implant covering with functional coatings. At design of dental implants the utmost importance shall be paid to surface morphology, which largely determines not only the strength, corrosion properties, but also conditions for the adsorption of biomolecules and adhesion of tissue cells, which surround the implant. Furthermore, shape and structure of the surface of implant intraosseousparthas a significant affect on osseo integration process, which is most effective at utilization of porous coating materials [4, 5].

Thus, application of new technologies for treatment of medical tools appears to be an urgent task. This work is aimed at identification of the factors that allow to create corrosion-resistant porous oxide coatings on materials: stainless steel 12X18H9T, titanium alloy VT5 niobium and 99.99% used for bone grafts.

2. Experimental

Air-thermal and steam-thermal oxidation was performed on stainless steel sample inside the electric furnace with nichrome heating element and a special insulation at temperatures of 400 ° C and 500 ° C and 0.5 h exposure.

Anodic oxide film (AOP) on steel, alloy and high-purity niobium VT5 were formed in solutions of H_2SO_4 and H_2SO_4 with addition of an activator HF (0,5 - 2 M). Anodizing process was carried out at a room temperature in a volt-static mode. Platinum has served as the counter electrode material.

Polarizationmeasurements were carried out on a potentiostat PI 50-1.1 at scan rate $1 \cdot 10\text{-}2$ V / s in the potentiodynamic mode. Reference electrode - saturated silver chloride. The potentials are given relative to the normal hydrogen electrode.

Corrosion resistance of the synthesized oxide coatings were determined by potentiometric method by measuring of corrosion potentials in 0,9% NaCl solution, simulating the functioning conditions of the exploring materials at fluid conditions.

The phase composition of the coatings was determined by X-ray diffraction method using DRON-2 diffraction metering tool ($CuK\alpha$ radiation). Thickness of the coatings received on VT5 titanium steel was defined with an optical microscope MIM-7.

Morphology of the synthesized coatings was studied using scanning electron microscopy (SEM) method with JSM-7001F microscope. The obtained images were subjected undergo statistical analysis in MATLAB environment, using a specifically developed program. The approach was based on the separation of so-called "areas of interest" in the images, which correspond to the poresof a real structure. As a result it was obtained functions of pores size distribution.

3. Results and Discussion

The process of obtaining of oxide coatings on steel electrodes was carried out by electrochemical oxidation and thermal spraying. Iron is known to be passivized in sulfate solutions wit a pH of 1-3 in the potential range of 0.6-1.4 V. Nonstoichiometric oxide $FeO_{(1,5-x)}$where x varies with pH of solution, depending on the capacity of the film formation, is assumed to be passivation agent.

Fig. 1 shows the anodic polarization dependencies of the inspected steel in a solution of sulfuric acid, having various concentrations.

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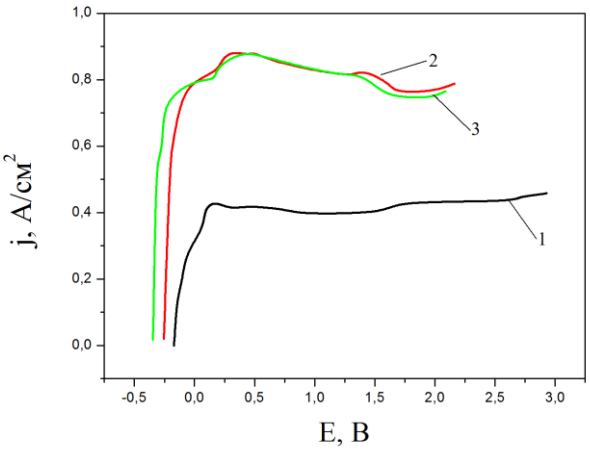


Fig. 1 – Anodic polarization dependencies on steel 12X18H9T insolutionsH_2SO_4: 1) 1 M;2) 2 M; 3) 4 M.

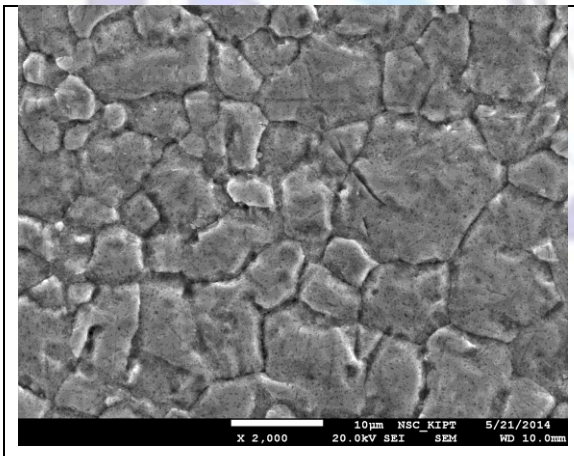
Formation and degradation of oxide film is carried out with diffusion control. At potential levels higher than 0,5 V, current is stabilized, however oxide layer does not provider eliable passivation of the steel layer.

At investigation of properties of the steel samples, received with various methods of gas-thermal oxidation, it has been detected 3-phase structure, which includes intrametallic compounds FeNi and oxides Fe_2O_3 and Ti_3O_5 **(Table 1).**

Table 1

Treatment method	Treatment mode, °C	Properties of coatings		
		Phase composition	Thickness, micron	Corrosion potential, V
Air-thermal	500	FeNi, Fe_2O_3, Ti_3O_5	20–25	–0,075
Steam-thermal	400	FeNi, Fe_3O_4, Ti_3O_5	40–50	0,279

BymeansofSEM method data it was carried out a comparison of two steel surface passivation technologies: air-thermalandsteam-thermal (fig. 2).



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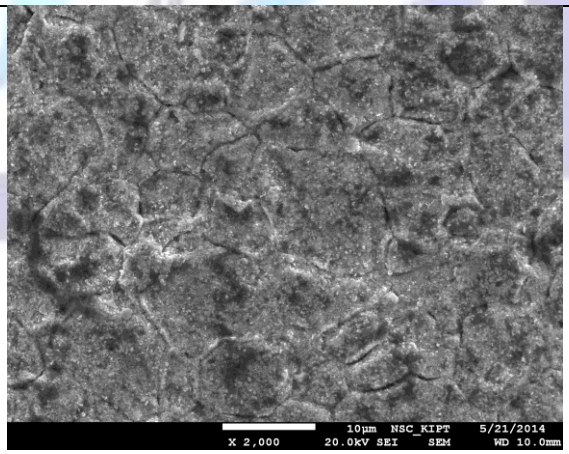

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Fig. 2 – SEM of 12X18H9T steelsurfacein a resultofpassivationwithtwotechnologies: а) air-thermal; б) steam-thermal.

At thermal oxidation of the steel surface it is created a developed coating with heterogeneous surface structure, featured with numerous microscopic roughness, including open pores. Such surface morphology is favorable for penetration of bone cells into microscopic roughness and can provide effective interaction of medical implants with the adjacent bone.

However, particular interest is inclined to biocompatible oxide coatings, which are obtained by electrochemical oxidation of refractory metals such as titanium and niobium. High levels of connection with the bone tissue is achieved by structurally heterogeneous porosity of oxide coating, high degree of sequence in the arrangement of pores and ability to manage variably their size over a wide range of surface morphology and thickness of oxide film.

To identify the factors influencing AOP formation on VT5titanium and niobium alloy, it shall be considered the received polarization dependencies (see Fig. 3, 4). On the curves it is observed one maximum current value, which increases with the growth of activator concentration (ion fluoride).

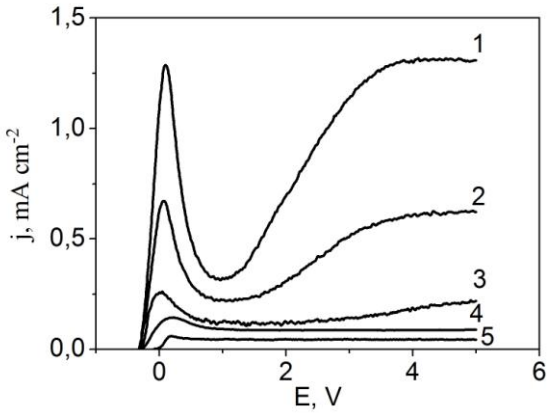

Figure 3. Polarization curves of Nb in solutions: 1) 1 M H_2SO_4 + 1M HF; 2) 1 M H_2SO_4 + 0,5 M HF; 3) 1 M H_2SO_4 + 0,25 M HF;4) 1 M H_2SO_4 +0,1 M HF; 5) 1 M H_2SO_4.

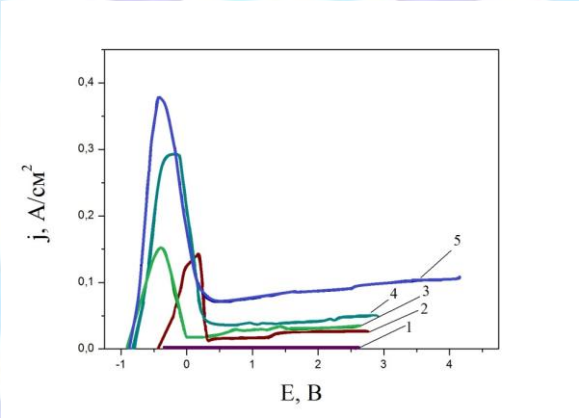

Figure 4.Polarizationcurves ofVT5 alloy in solutions:1) 2M H_2SO_4; 2) 2M H_2SO_4 + 0,025 MHF; 3) 2M H_2SO_4 +0,05 MHF; 4) 2M H_2SO_4 + 0,1 MHF;5) 2M H_2SO_4 + 0,5MHF.

Sharp rise of the anode current and the transition of the system into a passive state are related to formation ofoxide monolayer, having the highest oxidation state on the border with the electrolyte. At potential valueshigher than 1 it is formed multilayer oxide of niobium or titanium. If no activator is presented in solution, current is hardly dependent on the capacity, at the same time non-porous oxide is formed on metal surfaces. At growth of activator (ion fluoride) concentration, current in the system increases as well, while speed of oxide formation and degradation processesin active centers define the geometry of porous AOP on the surface of VT5 and niobium alloy.

Kinetics of niobium anodic oxidation process and the resulting morphology of the received oxide are similar to properties of porous anodic titanium oxide, which shows that these metals have similar anodization patterns.

To increase corrosion resistance ofVT5titanium oxide coatings it was applied two-stage anodizing method. Initially barrier oxide was formed in sulfuric acid solution without activator, and then porous layer was built up in a fluoride electrolyte. Geometric parameters and thickness of pores were determined based on activator concentration, anodization voltage and duration of the process.

Fig. 5 and 6 show SEM data on morphology of AOP, being synthesized on titanium and niobium, and also the function of pore size distribution. It can be noted that concentration HF is a key factor at growth of porous oxide layer. With growth ofHF concentration, aggressiveness of electrolyte is increased, which results in increase of the pore diameter.

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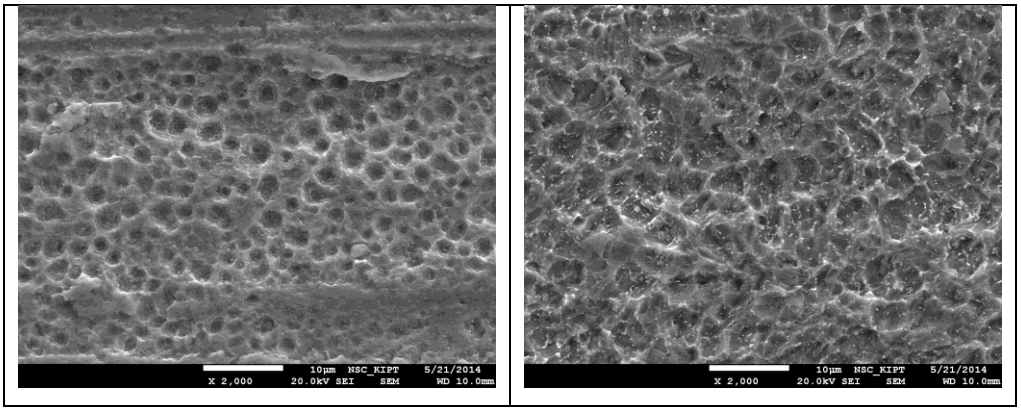


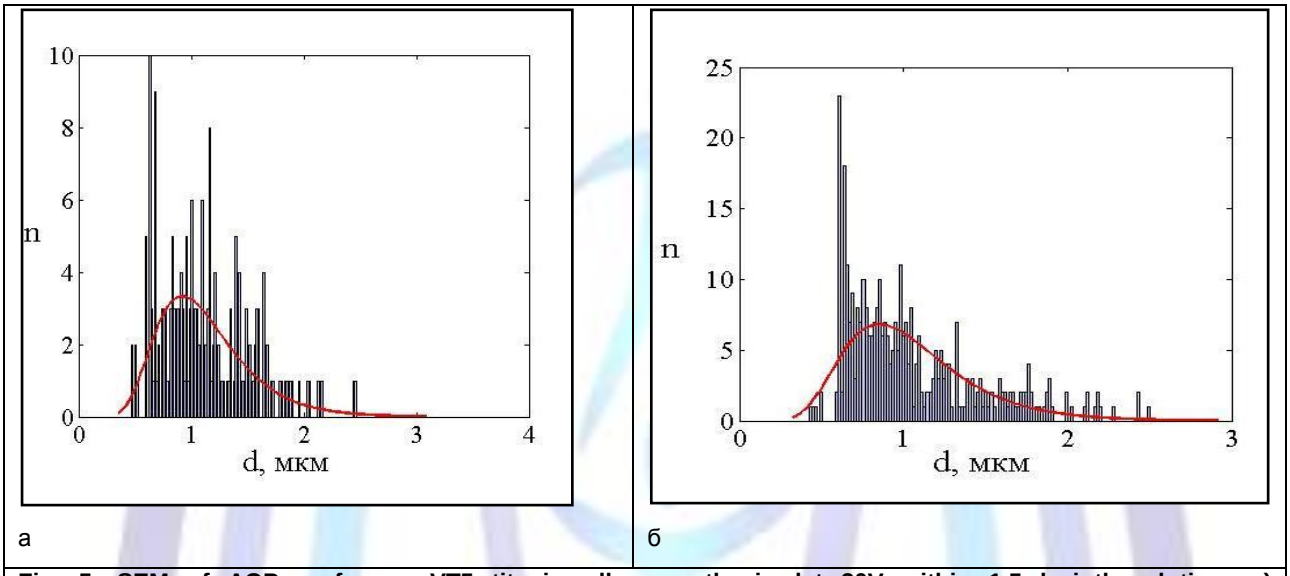
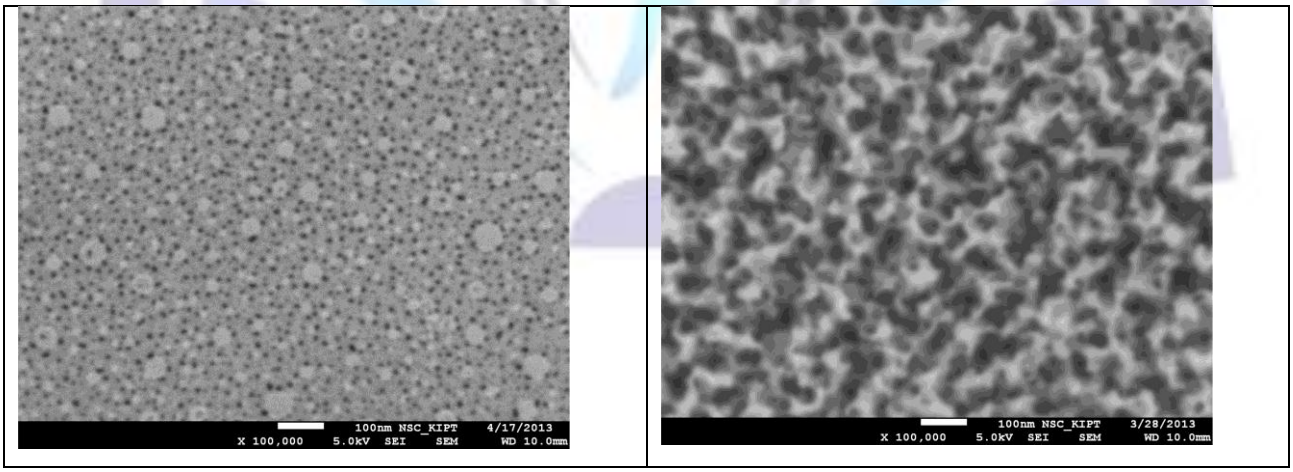


Fig. 5. SEM of AOP surfaceon VT5 titaniumalloy, synthesizedat 30V within 1,5 h inthesolution: а) 2MH_2SO_4+0,05M HF; б) 2MH_2SO_4 + 0,5M HF



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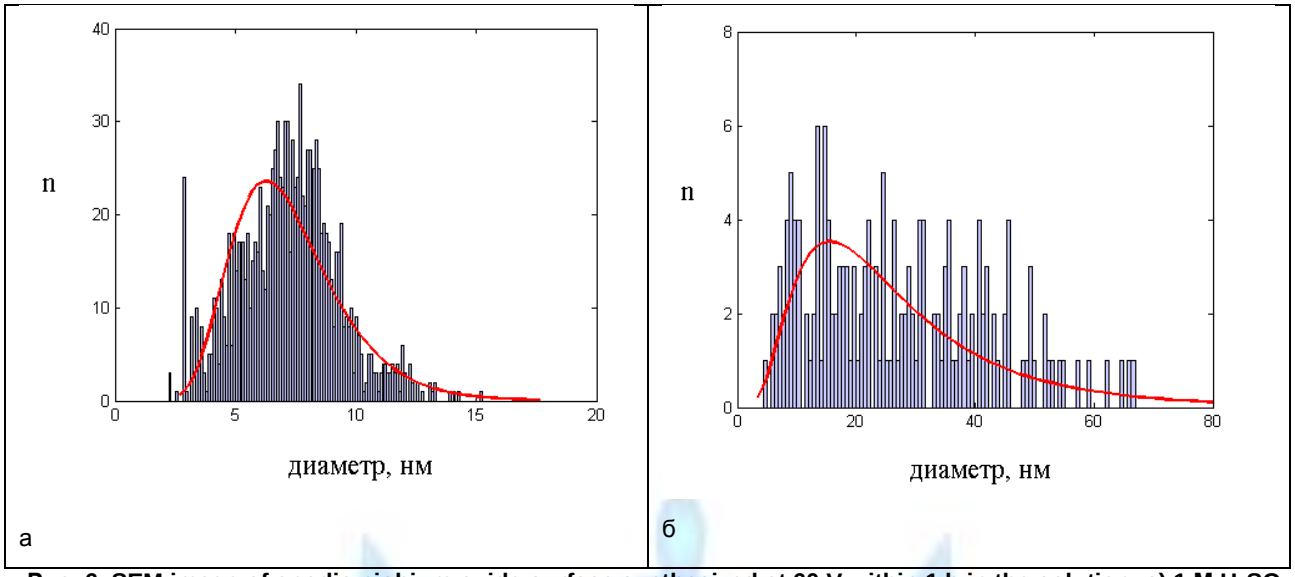

Рис. 6. SEM image of anodic niobium oxide surface synthesized at 60 V within 1 h in the solution: a) 1 M H_2SO_4 + 0,1 M HF;б) 1 M H_2SO_4 + 0,5 M HF.

Analysis of corrosivity for steel with coatings received with air-thermal and steam-thermalmethodshaveshownthatsteam-thermalmethodgivesmorepositivecorrosionpotentialleveland, consequently higher corrosion resistance in the solution (fig. 7).

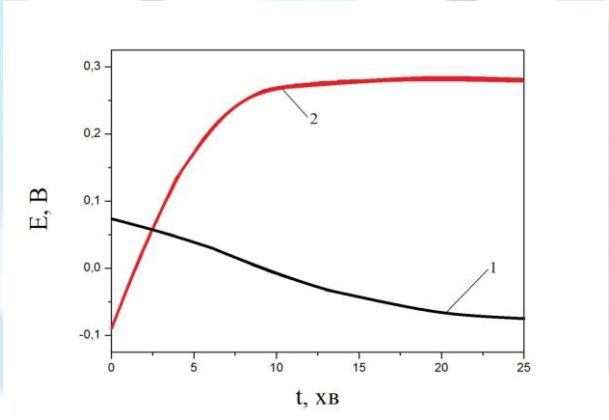

Fig. 7 – Time dependency of corrosion potential of oxide coatings on 12X18H9Tsteel in 0,9% NaCl solution: 1)air-thermaltreatment; 2) steam-thermaltreatment.

Experimental results of AOP corrosivityon VT5 alloyinsulfuricacidwithadmixtureofactivatorat two-staged formation of coating are shown, that corrosion potential values are positive (fig. 8). This verifies improved corrosion stability of such coating in biologically active environments.

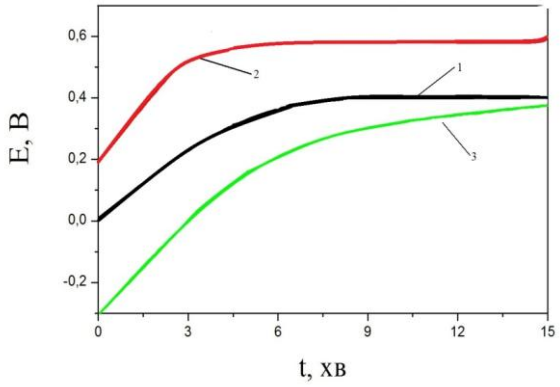

Fig.8. Time dependency of corrosion potential of oxide coatings on VT5, in 0,9% NaCl solution: 1) 2MH_2SO_4; 2) 2MH_2SO_4 + 0,05M HF

Level of AOP corrosion potential on niobium in a solution varies from-0,17 to-0,22 V. Such negative value can possibly be explained with thefact that films, synthesized on niobium are thin (200-500 nm), due to which metal substrate nature may be displayed.

Conclusions

Thus,at investigation of synthesized coatings bymeans of SEM, it has been defined that the surface is developed, contains pores, which presence is favorable for integration of bonetissue and formation of more solid joint between bone and implant. Pores and roughness on surface of oxide coatings might be filled with different medical substances, for example antibiotic storeduce to greater extent possibility of inflammatory processes. Developed, porous, corrosion-resistant surface of the obtained oxide coatings will provide rapid implantation process due to thefact that bonetissue, penetrating into the pores implant surface, activates osseointegration process.

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