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# Metal Oxide Porous Coatings for Implantant Materials

L. Skatkov[1,*], L. Lyashok[2], V. Gomozov[2], I. Tokareva[2], I. Kolupaev[3] and B. Bayrachniy[2]

[1]*Technical Department, PCB "Argo", 4/23 Shaul ha-Melekh str., 84797 Beer Sheva, Israel*

[2]*Electrochemistry Department, National Technical University "KhPI", 21 Frunze str., 61002 Kharkov, Ukraine*

[3]*Physical – Technical Department, National Technical University "KhPI", 21 Frunzestr. 61002 Kharkov, Ukraine*

**Abstract:** The paper presents the results of survey, dedicated to synthesis of metal oxide coatings on porous materials applied for implant surgery (stainless steel 12X18H9T, titanium alloy and high-purity niobium VT5). This article examines kinetic features of electrochemical formation of anodic oxide coatings on steel, niobium and titanium. It is shown that for steel anodic treatment method does not provide a reliable surface passivation (no current decay, the surface indicates the transition to the passive state).

Analysis of polarization dependences obtained on niobium and titanium in electrolytes with an activator (F-), indicates surface passivation (current slump), and at potentials above 2 on the surface of a transition curves in transpassive state (as evidenced by the current increase). Consequently, it can be concluded that presence of F- results surface activation of titanium and niobium electrode (F- oxide reacts to form water-soluble complexes) that promotes nucleation and formation of pores of the porous structure of the oxide coating.

SEM results verify the presence of self-organized porous oxide film synthesized on titanium and niobium in solutions containing F-.

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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, cobalt – chromium, and niobium and tantalum [1-13].

Materials, claiming to be the implants must meet certain requirements, namely: be corrosion-resistant, possess characteristics similar to the mechanical properties of bone tissue, and do not affect immune system and to integrate with the bone and stimulate bone formation [14].

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 intraosseous parth as a significant effect on osseo integration process, which is most effective at utilization of porous coating materials [14, 15].

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 creating 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 H2SO4 and H2SO4

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[*] Technical Department, PCB "Argo", 4/23 Shaul ha-Melekh str., 84797 Beer Sheva, Israel; Tel/Fax: +97 286 4822 55; E-mail: sf_lskatkov@bezeqint.net

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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.

Polarization measurements were carried out on a potentiostat PI 50-1.1 at scan rate 1 · 10-2 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 (CuKα 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 pores of 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 bepassivized in sulfate solutions wit a pH of 1-3 in the potential range of 0.6-1.4 V. Non-stoichiometric 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.

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

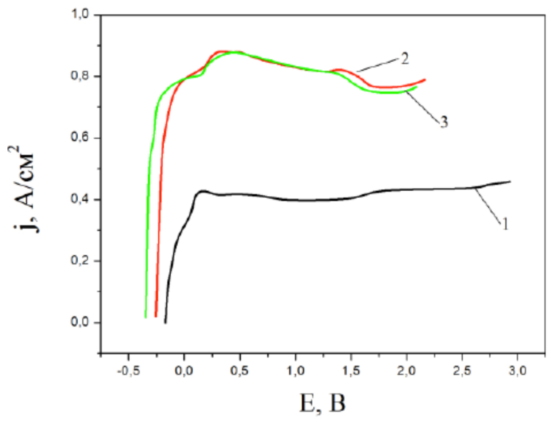


**Figure 1:** Anodic polarization dependencies on steel 12X18H9T insolutions $H_2SO_4$: 1) 1 M; 2) 2 M; 3) 4 M.

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 three-phase structure, which includes intrametallic compounds FeNi and oxides$Fe_2O_3$ and$Ti_3O_5$ (Table **1**).

By means of SEM method data it was carried out a comparison of two steel surface passivation technologies: air-thermal and steam-thermal (Figure **2**).

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 Figures **3**, **4**). On the curves it is observed one maximum current value, which increases with the growth of activator concentration (ion fluoride).

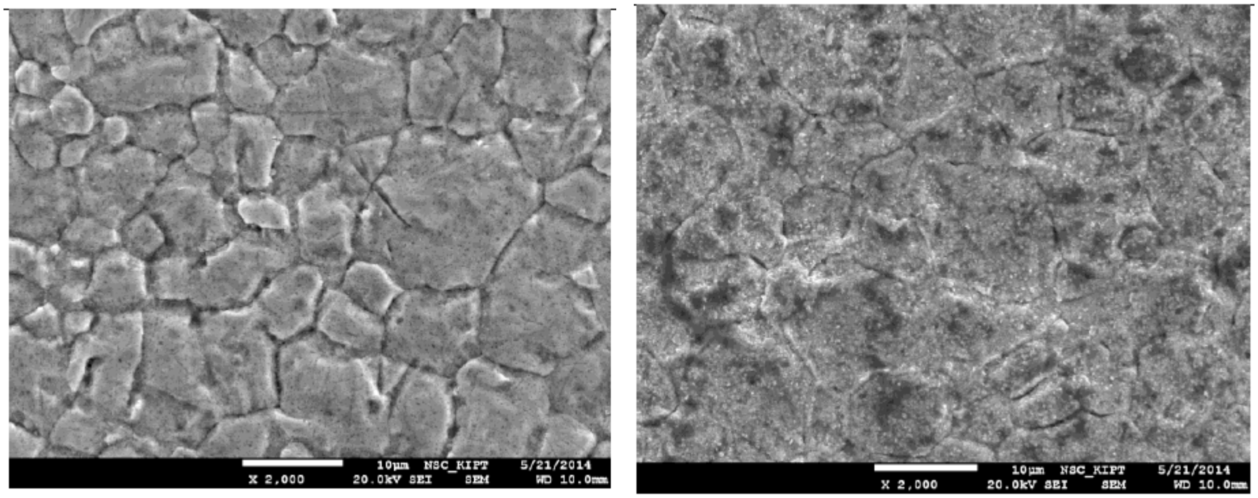
Sharp rise of the anode current and the transition of the system into a passive state are related to formation of oxide monolayer, having the highest oxidation state on the border with the electrolyte. At potential values higher than 1 it is formed multilayer oxide of niobium or titanium. If no activator 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 processes in 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

**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 |



**a** **b**

**Figure 2:** SEM of 12X18H9T steel surface in a result of passivation with two technologies: **a**) air-thermal; **b**) steam-thermal.

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.

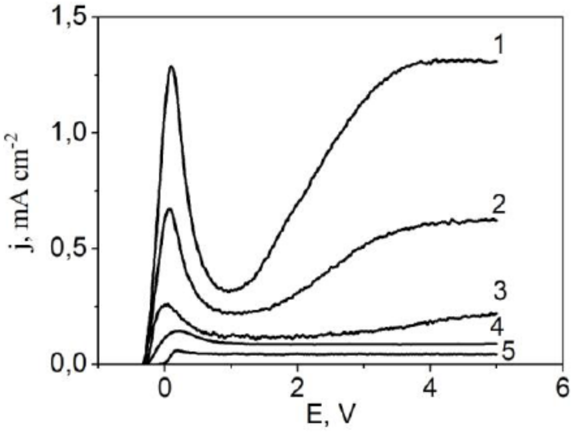


**Figure 3:** Polarization curves of Nb in solutions: 1) 1 M $H_2SO_4$ + 1M HF; 2) 1 M $H_2SO_4$ + 0,5 M HF; 3) 1 M $H_2SO_4$ + 0,25 M HF; 4) 1 M $H_2SO_4$ +0,1 M HF; 5) 1 M $H_2SO_4$.

Figures **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 of HF concentration, aggressiveness of electrolyte is increased, which results in increase of the pore diameter.

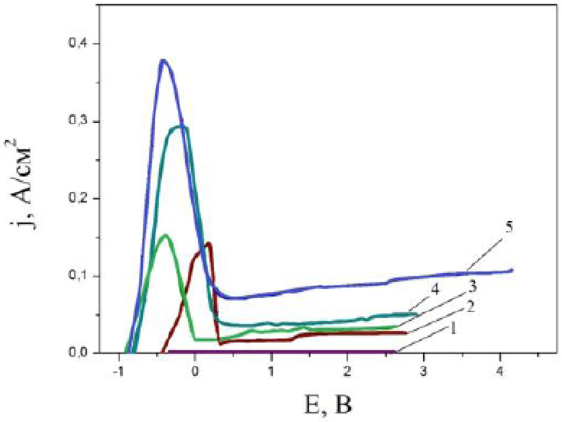
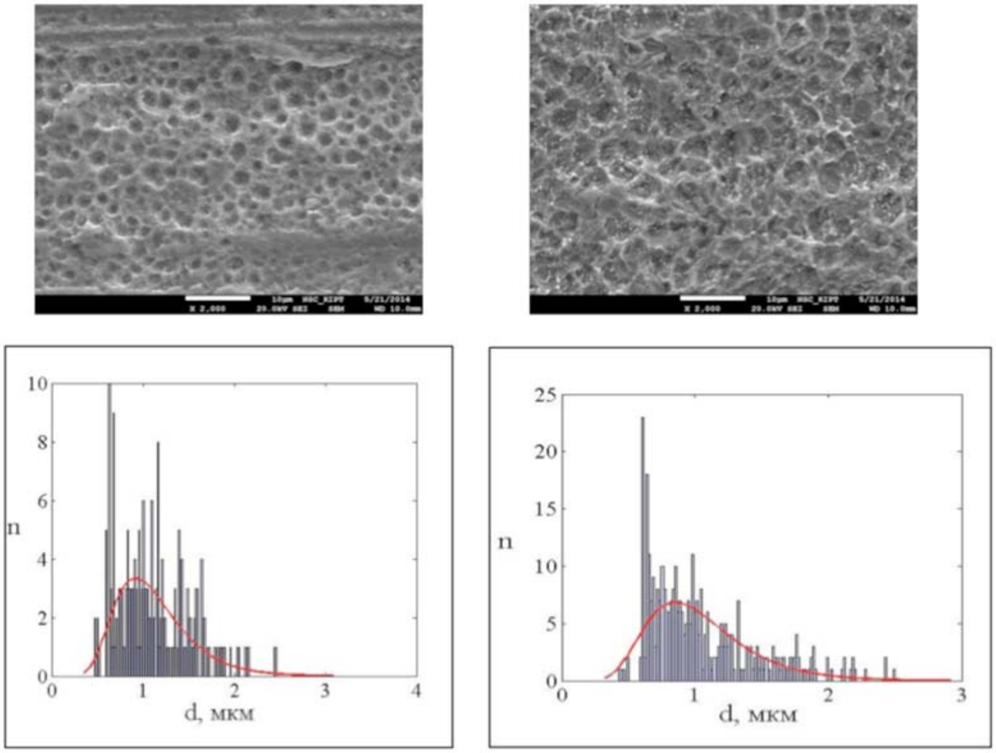


**Figure 4:** Polarizationcurves ofVT5 alloy in solutions: 1) 2M $H_2SO_4$; 2) 2M $H_2SO_4$ + 0,025 MHF; 3) 2M $H_2SO_4$ +0,05 MHF; 4) 2M $H_2SO_4$ + 0,1 MHF; 5) 2M $H_2SO_4$ + 0,5MHF.

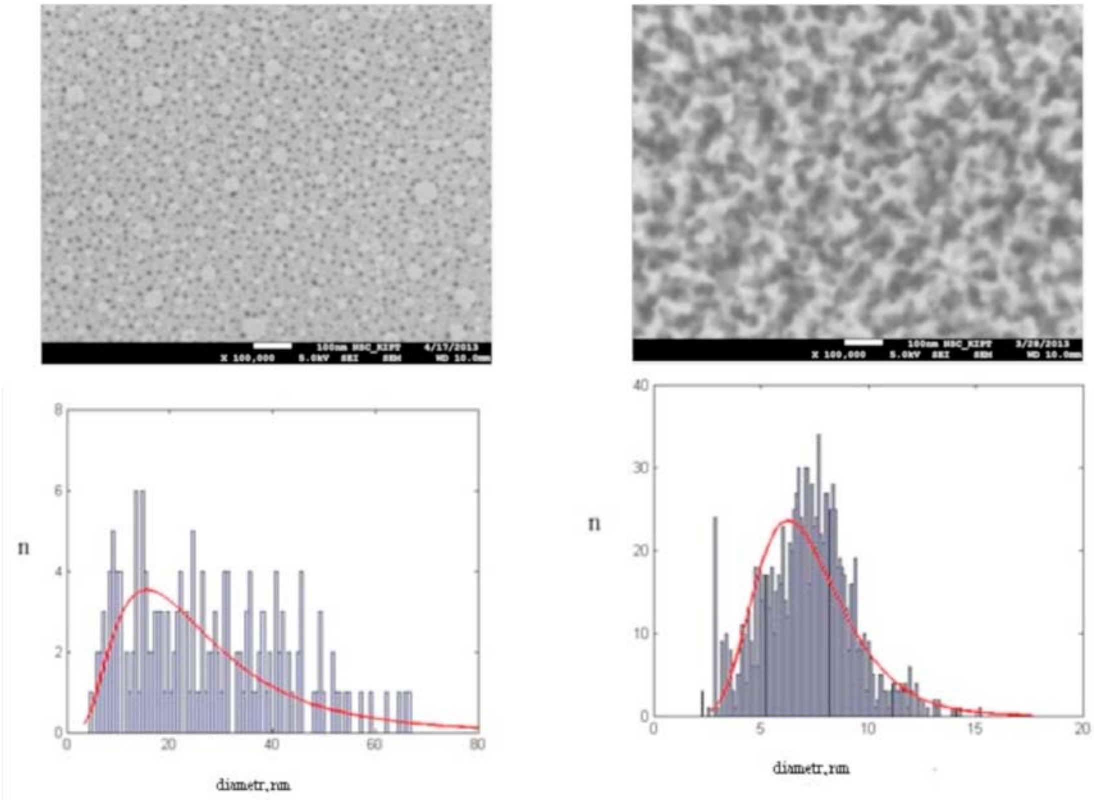
Analysis of corrosivity for steel with coatings received with air-thermal and steam-thermal methods have shown that steam-thermal method gives more positive corrosion potential level and, consequently higher corrosion resistance in the solution (Figure **7**).

Experimental results of AOP corrosivity on VT5 alloy in sulfuric acid with a mixture of activator at two-staged formation of coating have shown, that corrosion potential values are positive (Figure **8**). This verifies improved corrosion stability of such coating in biologically active environments.



**a** **b**

**Figure 5:** SEM of AOP surface on VT5 titaniumalloy, synthesized at 30V within 1,5 h in the solution: **a**) 2M$H_2SO_4$+0,05M HF; **b**) 2M$H_2SO_4$ + 0,5M HF.



**a** **b**

**Figure 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; **b**) 1 M $H_2SO_4$ + 0,5 M HF.

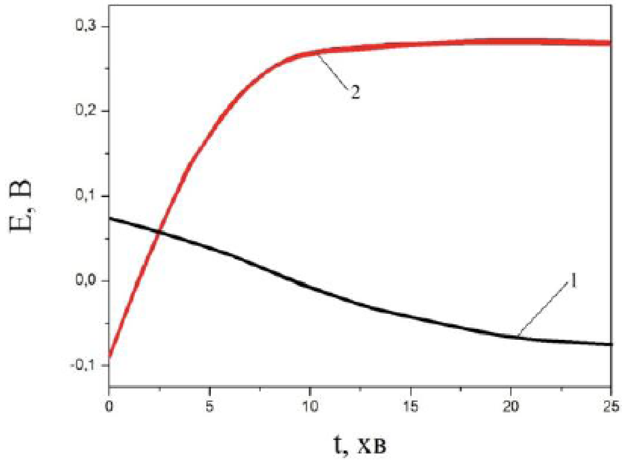


**Figure 7:** Time dependency of corrosion potential of oxide coatings on 12X18H9T steel in 0,9% NaCl solution: 1) air-thermaltreatment; 2) steam-thermaltreatment.

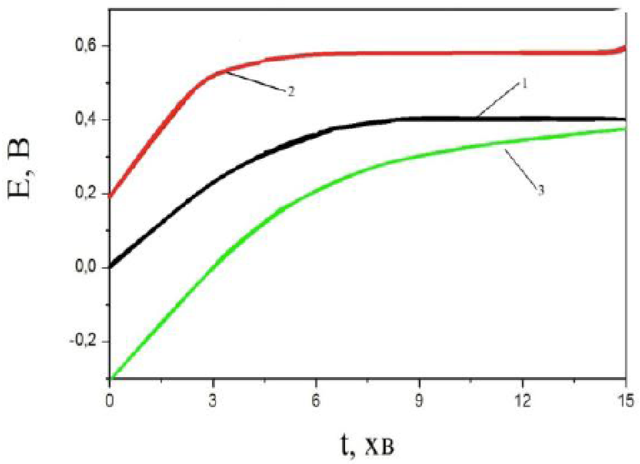


**Figure 8:** Time dependency of corrosion potential of oxide coatings on VT5, in 0,9% NaCl solution: 1) 2M$H_2SO_4$; 2) 2M$H_2SO_4$ + 0,05M HF.

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 the fact that films, synthesized on niobium are thin (200-500 nm), due to which metal substrate nature may be displayed.

## CONCLUSIONS

Thus, based on investigation of synthesized coatings by means of SEM, it has been defined that the surface is developed, contains pores, which presence is favorable for integration of bonet issue and formation of mores olid joint between bone and implant. Pores and roughness on surface of oxide coatings might be filled with different medical substances, for example antibiotics to reduce to greater extent possibility of inflammatory processes. Developed, porous, corrosion-resistant surface of the obtained oxide coatings will contribute to rapid implantation process due to the fact that bonet issue penetrating into the pores of implant surface, activate ososseointegration process.

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