WETTABILITY TEST OF CALCIUM PHOSPHATE-BASED COATINGS DEPOSITED ON TI-40MAS.%NB ALLOY

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ИССЛЕДОВАНИЕ СМАЧИВАЕМОСТИ ПОКРЫТИЙ НА ОСНОВЕ ФОСФАТОВ КАЛЬЦИЯ НА СПЛАВЕ TI-40МАС.%NB

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Аннотация. *В работе было изучено влияние напряжения микродугового оксидирования на физико-химические параметры кальций фосфатных покрытий на поверхности низкомодульного сплава Ti-40мас.%Nb. Были выявлены линейные зависимости роста параметра шероховатости и уменьшения поверхностной энергии от напряжения. Кальций фосфатные покрытия показали высокую гидрофильность, что обусловлено низкими значениями контактных углов и высокой свободной поверхностной энергией. Выявлен диапазон напряжений 200 – 250 В, обеспечивающий формирование покрытий с оптимальными характеристиками: шероховатостью 2,5 – 3,5 мкм и свободной поверхностной энергией 75-85 мН/м.*

Important requirements for metallic biomaterials are the absence of toxicity of alloying elements in the alloy composition and low elasticity modulus comparable to the human bone module. Attractive in part the increased biomechanical compatibility are titanium-niobium alloys, close in properties to the bone properties. To prevent postoperative complications associated with rejection of the active metal it is advisable to form calcium phosphate (CaP) coatings with bioactive and biocompatible properties. The micro arc method is an effective technique to obtain such coatings. At this work the influence of oxidation voltage and duration on the surface morphology, topography and wettability of CaP coatings on low-modulus Ti-40mas.%Nb alloy is investigated.

Ti-40mas.%Nb alloy was chosen to prepare sampling objects. The sample size was 10×10×1 mm^3. In order to form the coatings on the titanium surface the technological complex MicroArc-3.0 was developed. The CaP coatings were deposited in electrolyte aqueous solution of phosphoric acid with hydroxyapatite and calcium carbonate powders in anode regime [1]. The coatings were deposited with pulse mode under the following parameters: pulse time of 100 μs; pulse frequency of 50 Hz; deposition time varies from 5 to 15 min; electrical

voltage varies from 150 to 350 V. The surface morphology was examined by Scanning Electron Microscope (SEM, Jeol JSM-7001F SEM). The surface roughness was defined with Hommel-Etamic T1000 stylus profilometer by the parameter *Ra*. Wettability tests were carried out with Easy Drop goniometer (Kruss) with drop shape analysis software DSA1. To measure the static contact angles of liquids on the solid surface it was used sessile drop method. In tests we used two liquids distilled water as polar and glycerol as a dispersive one. Then we calculated the free surface energy of the coatings in accordance with following Owens-Wendt equation:

$$2\sigma_L(\cos\theta+1)=\sqrt{\sigma_S^P\sigma_L^P}+\sqrt{\sigma_S^D\sigma_L^D} \quad (1)$$

where θ is the contact angle value; $\sigma_L^D, \sigma_S^D, \sigma_L^P, \sigma_S^P$ are dispersive and polar components of the surface energy of the liquids and solids phases, σ_L is the free surface energy of the test liquids.

Fig. 1 shows the SEM images of CaP coatings deposited on Ti-40mas.%Nb alloy surface under different oxidation voltage applied. The main components of structure are spherolytes with pores. The “islands” of porous structure start to form at voltage of 150 V. It corresponds to the initial stage of spherolytes formation. The further increase in the oxidation voltage to 300 V leads to a structural element growth and roughness increase from 2.5 to 6 μm (Fig. 1, 3). However, after 300 V spherolytes started to die. The destruction of spherolytes is connected with current density growth and transformation of the micro arc discharges in arc ones. Therefore the spherolyte and pore sizes depend on the value of micro-plasma discharges in electrolyte.

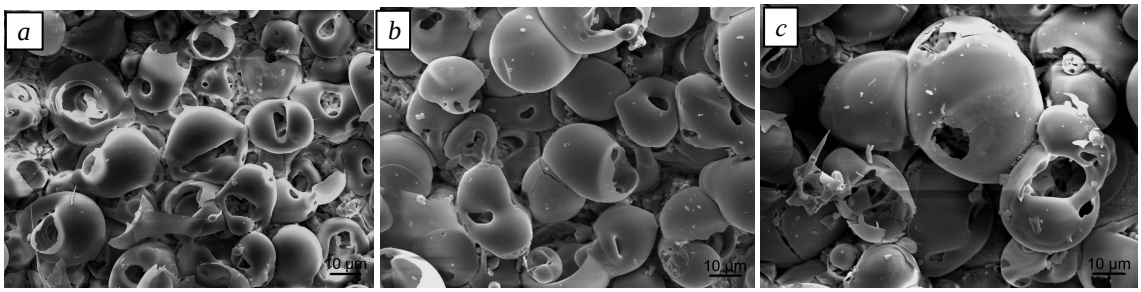

Fig.1. SEM images of CaP coatings deposited under different oxidation voltages, V: 200 (*a*), 250 (*b*), 300 (*c*)

The wettability tests of the CaP coatings showed that the increase of the oxidation voltage and process duration leads to linear decrease of contact angle values with water from 25 to 8º and with glycerol from 50 to 15º, which indicates a high hydrophilicity (Fig. 2). The free surface energy of the coatings consists of two components: the dispersive and polar, with a predominance of polar. It indicates the presence of strong polar chemical bonds (OH-groups, oxides and phosphates) [2]. The increase in voltage leads to a decrease of polar component and increase of dispersive component, because rough surface topography of coatings triggers nonpolar Van-der Waals forces. However, polar bonds keep dominating (Table 1).

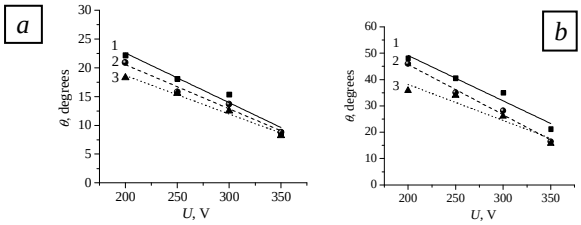

Fig.2. Plots of contact angles of CaP coatings with water (a) and (b) against the oxidation voltage for various time: (1) – 5 min, (2) – 10 min, (3) – 15 min

Table 1

Free surface energy of CaP coatings deposited under different oxidation voltages for various time

***U*, V**	**5 min**			**10 min**			**15 min**		
	σ_S^P, mN/m	σ_S^D, mN/m	σ, mN/m	σ_S^P, mN/m	σ_S^D, mN/m	σ, mN/m	σ_S^P, mN/m	σ_S^D, mN/m	σ, mN/m
200	85.3±0.2	0.8±0.0	86.1±0.2	84.1±0.6	0.9±0.1	85.0±0.7	70.7±0.4	5.5±0.2	76.2±0.6
250	77.5±0.7	3.0±0.2	80.6±0.9	73.3±0.7	4.9±0.2	78.2±0.9	69.2±0.7	6.3±0.2	75.5±1.0
300	73.4±0.7	4.9±0.2	78.3±1.0	65.9±0.9	8.7±0.3	74.6±1.2	64.8±0.3	9.6±0.1	74.4±0.5
350	62.9±0.3	11.4±0.1	74.3±0.4	60.7±0.9	13.3±0.6	74.0±1.5	59.6±0.9	13.8±0.4	73.4±1.3

With voltage and process duration increase the free surface energy linear decreases. Decrease of the surface energy in the coatings depends on surface roughness growth. The attractive forces of the molecules inside the material which accumulate energy on the surface fail as a result of the rough relief. There is a certain roughness value of 4 μm above that the water wetting is absolute, it corresponds to the critical surface energy of the coating equal to the water surface tension of 73 mN/m (Fig. 4, Table 1).

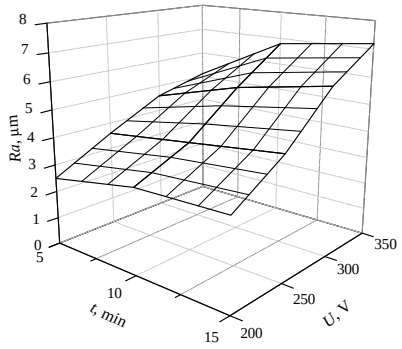

Fig. 3. 3D-Plot of CaP coating roughness against the oxidation voltage and process duration

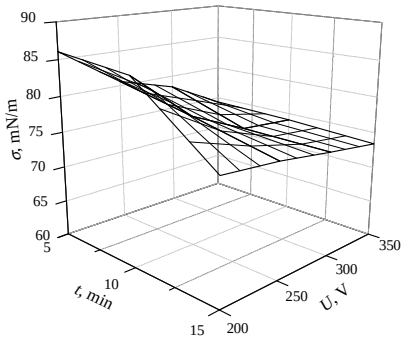

Fig. 4. 3D-Plot of free surface energy of CaP coatings against the oxidation voltage and duration

In conclusion it was shown that the increase of micro arc oxidation voltage and process duration leads to the linear growth of roughness and free surface energy of CaP coatings and the linear decrease of the coating contact angles with liquids. The optimal micro arc oxidation parameters (the electrical voltage of 200-250V and the process duration of 5-10 min) allow to form the CaP coatings with specific characteristics and high hydrophilicity, which promote cell adhesion, proliferation and differentiation on the coating surface [1].

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