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INVESTIGATION OF SURFACE FREE ENERGY OF THE GLASS-CERAMIC COATINGS ON TITANIUM FOR MEDICAL PURPOSES

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Abstract. Biocompatible calcium silicophosphate glass-ceramic coatings for titanium on the base of glasses in R_2O–RO–RO_2–R_2O_3–P_2O_5–SiO_2 system have been obtained. The influence of crystallization ability and roughness of experimental coatings on their surface free energy has been established. The use of titanium implants with applied apatite-containing glass-ceramic coating will significantly increase biocompatibility of the prosthetic implant and will reduce the time of its union with the bone.

Keywords: glass-ceramic coating on titanium, roughness, surface free energy.

1. Introduction

Contemporary advances in the science of medical materials are aimed at the creation of the new biocompatible materials, among which the most prospective are the implants with physically modified [1], especially protective biocompatible coating on titanium. Direct contact of such coatings with human body tissues determines the necessity of compliance of the coatings to stringent requirements to their phase and elemental composition, mechanical, chemical and biological properties.

Important factor of the successful adaptation of biocompatible glass materials *in vivo* is the simulation of the structure and chemical composition close to the natural bone by the coating in order to form a bone tissue on its surface [2]. Composite materials on the base of titanium and its alloys with applied ceramic apatite-containing coating are currently well known. However, prolonged use of implants on the base of such composite materials in human body may lead to peeling of ceramic coating from the base due to its poor adhesion with titanium alloys resulting from the unconformity of their temperature coefficients of linear expansion. High performance properties of biocompatible materials are possible with application of glass-ceramic materials based on calcium silicophosphate glasses onto titanium alloys. These coatings have the certain level of solubility and fine volume crystallization of calcium phosphates, in particular of calcium hydroxyapatite (HAP), responsible for the biocompatibility. Being an analog of the main component of the bone mineral base, HAP has pronounced osteoconductive properties, provides adhesion of proteins and bone tissue cells, is actively involved in the ionic exchange and metabolism of the bone matrix, and supports ionic and covalent bonds with the bone minerals [3].

From the thermodynamic point of view, in order to support the osseointegration, the metal surface must provide spontaneous protein adsorption, which, along with other factors (Table 1), substantially depends on the surface free energy (SFE).

Table 1

Properties of the biomaterial layer controlling protein adsorption [4]

Properties of the biomaterial surface	Protein properties
Chemical composition	Number of bonds
Surface morphology	Quarternary, tertiary and secondary structure
Free energy	General hydrophobicity
Charge	Charge
Acid-base properties	Isoelectric point
Cleanliness of the surface	Specific interaction of residues

Table 2

Surface free energy of biocompatible materials

Biocompatible material	SFE, mJ/m^2			Reference
	Polar component	Dispersive component	Total value	
Ti6Al4V	8.59	30.14	38.73	[6]
Ti (etched)	8.88	32.97	41.85	
ZrO_2 (ceramics)	7.55	34.46	42.01	
Ti (polished)	15.97	31.05	47.01	
Ti (oxidized)	–	–	40	[4]
TEMPAX borosilicate glass	33	21.1	54.1	[3]
BIOVERIT glass ceramics	58.4	8.0	66.4	

According to the data of Table 1, the composite effect formed by the surface free energy, the chemical composition of the coating and its surface morphology control the results of the osseous integration both in general, and within its stages: precipitation, migration, proliferation and differentiation of cells [5]. Moreover, the dominant factor of the bone cell adhesion is SFE [6], as the wetting of the surface, which controls the degree of contact with physiological medium, significantly depends on surface energy [1]. Surface free energy determines work of the new phase formation on the interface and the free activation energy of phase transition process [7]. It is considered that in order to carry out absorption, SFE of biocompatible material has to range between 60.0 and 120.0 mJ/m^2 [3]. Among the known biocompatible materials, the highest SFE values are characteristic to glass ceramics, which is caused by their chemical composition and structure (Table 2).

Ensuring the range of biocompatible coatings microroughness between 1.0 and 10.0 μm with the purpose of maximal bond provision between a bone and implant surface [1] imparts these coatings with a higher surface energy, wettability and can act as an additional initiating agent of tissue growth. This is explained by attaching and proliferating of osteogenic cells on the coating surface and corresponding increase of the of osseous integration area [8]. Bioactivity extremum points for calcium silicophosphate coating have been established at microroughness of 2.0–3.0 μm [9] and at ≥ 3.5 μm [6]. The force of bone-implant interaction will not increase with the continuous increase of surface roughness [1].

Development of biocompatible glass-ceramic coating on titanium with optimal SFE and microroughness values will provide the solution to the relevant problem of creation of the prosthetic implants with advanced osteoinductive properties.

2. Experimental

2.1. Aim and Methods of the Research

The aim of this work was the development of glass-ceramic coatings on titanium and investigation of the influence of their volume and surface structure and chemical composition on the surface free energy. Presence of crystalline phase was determined with X-ray diffraction analysis (XRD), which has been carried out on DRON-3 diffractometer. Petrographic analysis was conducted on the optical microscope NU-2E. Surface microrelief was studied with Surtronic3 + profilometer. Arithmetical mean value of the profile irregularities (R_a) has been determined according to the standard.

Values of the surface free energy for solids cannot be assessed directly from the value of surface tension, because there is no movement of the molecules on their surface [10]. Assessment of the surface free energy of the experimental coatings has been carried out by indirect method, put forward by Owens, Wendt, Rabel and Kaelble (OWRK), according to which the surface energy of a solid includes two components: dispersive and polar ones. Dispersive component includes Van der Waals force and other nonspecific interactions, and polar component includes strong interactions and hydrogen bonds. The following equation has been derived on the basis of these ideas [11]:

$$\frac{s_L \cdot (\cos q + 1)}{\sqrt[2]{s_L^D}} = \frac{\sqrt{s_S^P} \cdot \sqrt{s_L^P}}{\sqrt{s_L^D}} + \sqrt{s_S^D} \quad (1)$$

where cosθ – a cosine of contact angle between a liquid and a solid surface; σ_L^D – dispersive component of the surface tension of a liquid, mN/m; σ_L^P – polar component of the surface tension of a liquid, mN/m; σ_L – general value of the surface tension of a liquid, mN/m; σ_S^D – dispersive component of a solid surface free energy, mJ/m^2; σ_S^P – polar component of a solid surface free energy, mJ/m^2.

According to the OWRK method, the surface free energy of the material has been calculated on the basis of contact angle between its surface and different liquids with the following calculation of the two surface free energy components with the Mathcad computer software [10]. In order to increase the accuracy of obtained values of the above property, more than two liquids with known polar and nonpolar surface tension components have been used [12]. Dispersive component of the surface tension is predominant in nonpolar liquids (Table 3), while polar – in polar ones [13].

Contact angle has been measured by the static method and calculated by the sitting-drop method. Liquid drop on the tested horizontal surface was projected on the screen and photographed. The angle between a line tangent to the drop in the point of the contact of three phases (solid, liquid and gaseous) and a surface of the specimen has been determined on the photograph. Accuracy of such determination is assessed to be 1.0–5.0 degrees [13].

2.2. Selection of Criteria for the Development of Biocompatible Glass-Ceramic Coatings

Synthesis of biocompatible glass-ceramic coatings is carried out on the basis of calcium silicophosphate glasses with high reactivity, their bioactivity is determined by:

- solubility level at $f_{Si} < 0.32$ [15];
- occurrence of fine volume crystallization of HAP with the size of crystals ranging from 1.0 to 3.0 μm and the CaO : P_2O_5 ratio of 1.0–4.0 in the compositions of glasses [16].

Determinant factors of biocompatibility manifestation for glass-ceramic coatings are:

- ensuring SFE values of ≥ 60 mJ/m^2 for protein adsorption [3];
- surface crystallization process in the coating with the formation of HAP crystals having 1.0–10.0 μm in size [1] to ensure respective microhardness of 2.0–3.5 μm with the purpose of maximal manifestation of bioactivity [6, 9].

2.3. Selection of the System, Development of Model Glasses and Coating on their Base

R_2O–RO–RO_2–R_2O_3–P_2O_5–SiO_2 system has been selected for the synthesis of glasses, which were the bases for biocompatible glass-ceramic coatings on titanium, where R_2O – Na_2O, K_2O; RO – CaO, ZnO, MgO, SrO; RO_2 – TiO_2, ZrO_2; R_2O_3 – Al_2O_3, B_2O_3 with amounts (mas %): SiO_2 45.0–50.0; P_2O_5 0.0–10.0; Na_2O 3.3–10.0; K_2O 0.0–5.0; CaO 10.0–20.0; ZnO 0.0–3.0; MgO 0.0–13.8; SrO 0.0–8.0; TiO_2 0.0–5.0; ZrO_2 0.0–5.0; B_2O_3 0.0–7.0; Al_2O_3 0.0–5.0; CaF_2 4.0–6.0 and CaO:P_2O_5 ratio of 1.5–3.3 to ensure calcium phosphate crystallization during thermal treatment of the coatings. Structural factor f_{Si} and CaO:P_2O_5 ratio of model glasses are given in Table 4.

10 model glass compositions marked with “T” letter have been synthesized in the selected system and projected to the pseudo-ternary system: R_b – resorption component (R_2O) – R_z – resistive component (SiO_2, R_2O_3) – F – phase-forming component (P_2O_5, RO, RO_2, CaF_2). Their post-melting crystallization ability has been studied. All model glasses have been melted under similar conditions at the temperatures of 1573–1753 K in corundum crucibles followed by the quenching on a metal sheet. By the visual assessment of the crystalline phase the model glasses can be divided into opacified – T2, T4, T7, T8, T9, T10; opalescent – T1, T5, T6 and opalescent glass with macroliquation – T3 (Fig.1).

Glass-ceramic coatings on titanium alloy VT5 have been obtained by the slip technology, dried at the temperature of 353–393 K and fired at 1023–1323 K for 1.0–1.5 min. Coating markings correspond to the markings of glasses, which where the bases for their obtaining.

Table 3

Surface tension of test liquids on the liquid-air interface at 293 K [13, 14]

Test liquid	Surface tension, mN/m		
	Polar component	Dispersive component	General value
Distilled water	50.8	21.8	72.6
Benzyl alcohol	10.3	26.85	37.17
Toluene	0.0	28.4	28.4
Glycerol	24.4	37.0	63.4
Ethylene glycol	19.0	29.3	48.3
Formamide	19.0	39.0	58.0

Table 4

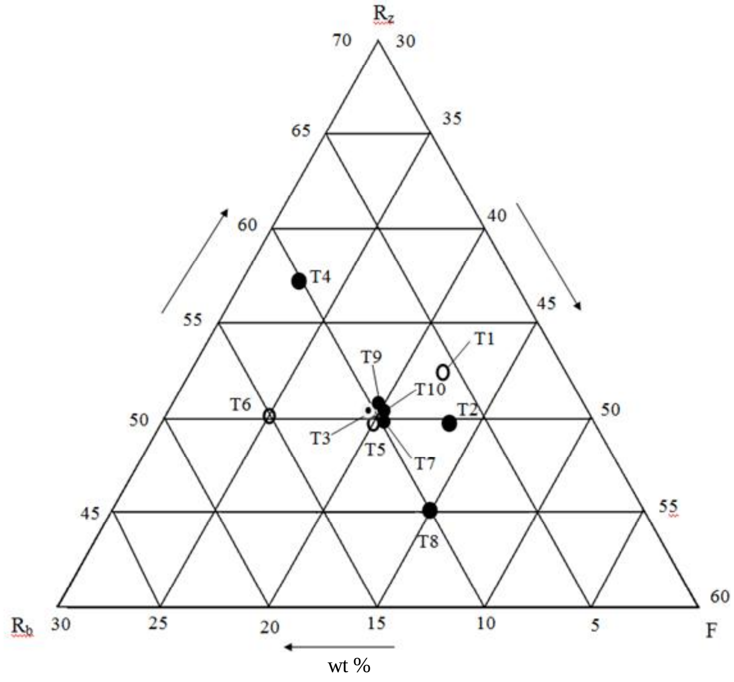
Structural factor f_{Si} and CaO:P_2O_5 ratio for model glasses

Parameter	Model glass									
	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
f_{Si}	0.30	0.31	0.28	0.27	0.27	0.28	0.29	0.28	0.32	0.28
CaO:P_2O_5	3.3	2.5	2.0	2.0	2.0	1.5	2.0	2.0	2.0	2.0

Table 5

Characteristics of crystalline phase and roughness parameter R_a for experimental coatings

Characteristics of crystalline phase and roughness parameter Ra	Marking									
	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
	After glass melting									
Amount, vol %	15.0	18.0	16.0	20.0	11.0	12.0	23.0	25.0	20.0	27.0
Size, μm	1.0	1.0	1.0	1.0	1.0	1.0	5.0	5.0	3.0	5.0
	After thermal treatment of the coatings									
Amount, vol %	30.0	37.0	33.0	40.0	23.0	26.0	47.0	55.0	43.0	50.0
Size, μm	2.0	2.0	1.0–3.0	1.0–3.0	1.0	1.0	8.0	5.0	3.0–5.0	8.0
Rougness parameter R_a	2.2	2.4	3.4	3.2	1.2	1.8	8.2	5.4	4.8	10.0



● – opacified glasses;

○ – opalescent glasses;

◉ – opalescent glass with macroiquation

Fig. 1. Experimental system resorption component (R_b) – resistive component (R_z) – phase-forming component (F) wt%

3. Results and Discussion

3.1. Investigation of Crystallization Ability of Glass-Ceramic Coating and Roughness of their Surface

Peculiarity of model glasses after melting is the presence of data crystal HAP phase in them, established with XRD analysis. Character of the crystallization is determined by CaO:P_2O_5 ratio and by the presence of crystallization catalysts, TiO_2 and ZrO_2. For all experimental coatings, volume fine crystallization with the formation of HAP crystal phase and insignificant formation of renanite for T6 and quartz for T3 glasses is observed after thermal treatment. Gradual formation of HAP crystals during cooling of experimental glasses is a determining factor of HAP crystallization, its quantity and size after thermal treatment of the coatings. According to the data of petrographic analysis it has been established that HAP in the amount of 23.0–55.0 vol % with the crystal size about 1.0–8.0 μm (Table 5) is characteristic for experimental coatings after thermal treatment.

On the basis of the results of surface morphology investigation it has been established that microroughness of experimental coatings ranges from 1.2 to 10.0 μm with the thickness of the layer being 100–150 μm.

In compliance with mentioned requirements and study of the crystallization ability and roughness, the coatings T3 and T4, which are characterized by crystallization of HAP with crystal size of 1.0–3.0 μm and roughness parameter R_a = 3.2–3.4 μm, and, for comparison, T1 and T2 coatings, have been selected for measuring of SFE.

3.2. Influence of Surface Structure of Experimental Coatings on the Value of their Surface Free Energy

Main characteristics of adsorbing surface is its energetic (in a simple case, level of hydrophobicity or hydrophility) and electrochemical properties. Surface charge leads to the electrostatic interaction between charged surface and charged sections of a protein molecule. However, proteins are adsorbed on the most surfaces with hydrophobic sections even if there an electrostatic repulsion between the surface and protein exists. This is explained by bipolarity of proteins. This is attributable by bipolarity of proteins, which have maximal affinity (thermodynamic characteristic, quantitative description of the interaction force between substances) to the surface with intermediate polarity [17].

With the purpose of stimulating the protein adsorption process on the surface of biocompatible glass-ceramic coatings on titanium the computational values of f_{Si} = 0.27–0.28 have been ensured for the model glasses T3 and T4, which allow the increase of the surface SFE *via* the increase of electrostatic portion of chemical bonds in glasses.

By measuring contact angles of each of the test liquids on experimental coatings and by substituting them into Eq. (1) components of SFE have been calculated using Mathcad software (Table 6).

As is evident from the data of Table 6, the values of SFE dispersive component of all experimental coatings differ insignificantly, unlike polar component, which is an important factor of biological interaction [6]. SFE polar component values of all experimental coatings are greater than the values of dispersive component. This is caused by the increase of the contribution of polar interactions as a result of surface hydrophobisation.

According to the Tables 4-6, the highest SFE values of 60.0–61.0 mJ/m^2 are characteristic of the coatings with relatively low connectedness level of silicon-oxygen network of the initial glass, f_{Si} = 0.27–0.28 and microroughness values in the range of 3.2–3.4 μm. Lower values of SFE = 47.0–51.0 mJ/m^2 are characteristic of the coatings with relatively high connectedness values of silicon-oxygen network of initial glass, f_{Si} = 0.30–0.31 and microroughness of 2.2–2.4 μm.

Adsorption of the components of blood plasma consisting of water, inorganic (Na^+, Ca^{2+}, K^+, Mg^{2+}, Cl^-, HPO_4^{2-}, HCO_3^-) and organic (proteins: albumin, globulin and fibrinogen) constituents is very important for hydrophilic materials used as bioactive bone implants.

To establish the possibility of inorganic constituent adsorption of the plasma experimental coatings T3 and T4 have been exposed during 6 months to Simulated Body Fluid (SBF), which models human blood plasma. After exposure to SBF (ISO 23317:2014), the increase of polar component of the coatings surface free energies has been noted,with retention of the value of total SFE in the range of 61.0–62.0 mJ/m^2 respectively, which is associated with precipitation of components of the medium during formation of apatite-like layer on their surface.

In order to establish the possibility of organic constituents adsorption of the human plasma, experimental coatings T3, T4 have been exposed for 7 and 14 days to 10 % albumin solution, which, unlike other proteins, has a significant number of hydrophilic groups –OH, –COOH, –NH_2. It has been established that during the exposure the components of the solution have precipitated on the coating surface, which has led to the increase of total SFE in the range of 61.0–64.0 mJ/m^2 (Table 7). Obduction of the material surface areas can be explained by formation of protein layer on the surface of the implant due to protein metabolism reaction between albumin and the implant [17]. Conducted researches show high biological activity of considered materials and feasibility of their application as the coating for bone implants.

Table 6

Surface free energy, correlation coefficient of each linear dependence

Coating	SFE, mJ/m^2			Coefficient of linear correlation
	Polar component	Dispersive component	Total value	R^2
T1	27.028	20.058	51.158	0.792
T2	31.694	19.464	47.087	0.808
T3	41.090	18.657	60.000	0.881
T4	41.685	19.470	61.155	0.899

Table 7

Surface free energy and correlation coefficients after exposure to albumin

Coating	SFE, mJ/m^2			Coefficient of linear correlation
	Polar component	Dispersive component	Total value	R^2
Exposure for 7 days				
T3	42.90	18.169	61.069	0.892
T4	43.829	19.105	62.934	0.902
Exposure for 14 days				
T3	43.60	19.392	62.992	0.901
T4	44.468	19.434	63.902	0.902

4. Conclusions

On the basis of $R_2O–RO–RO_2–R_2O_3–P_2O_5–SiO_2$ system the calcium silicophosphate glasses have been synthesized and glass-ceramic coatings on titanium have been obtained on their base. Conditions of ensuring surface free energy of 60.0 mJ/m^2 have been established: $f_{Si} = 0.28$, fine surface crystallization with the size of hydroxyapatite crystals of 1.0–3.0 μm and $R_a = 3.4$ μm.

Implementation of such biocompatible coatings will allow increasing of protein adsorption to their surface and shorten the binding terms of biomaterial to a bone. These materials are recommended for obtaining implants of bone tissue sections under static loads, in particular the stem of hip prosthesis.

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ДОСЛІДЖЕННЯ ВІЛЬНОЇ ЕНЕРГІЇ ПОВЕРХНІ СКЛОКРИСТАЛІЧНИХ ПОКРИТТІВ ПО ТИТАНУ МЕДИЧНОГО ПРИЗНАЧЕННЯ

Анотація. *Одержано біосумісні кальційсилікофосфатні склокристалічні покриття по титану на основі стекол системи* $R_2O – RO – RO_2 – R_2O_3 – P_2O_5 – SiO_2$. *Встановлено вплив кристалізаційної здатності та шорсткості отриманих покриттів на вільну енергію їх поверхні. Встановлено, що використання титанових імплантатів з нанесеним на нього апатитвмісним склокристалічним покриттям суттєво підвищує біосумісність ендопротезу та дає можливість скоротити термін зрощування його з кісткою.*

Ключові слова: *склокристалічні покриття по титану, шорсткість, вільна енергія поверхні.*