Hybrid Calcium Phosphate Coatings for Titanium Implants

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Abstract. Hybrid multilayer coatings were obtained on titanium substrates by the combination of two methods: the micro-arc oxidation in phosphoric acid solution with the addition of calcium compounds to high supersaturated state and RF magnetron sputtering of the target made of synthetic hydroxyapatite. 16 different groups of coatings were formed on titanium substrates and in vitro studies were conducted in accordance with ISO 23317 in the solution simulating body fluid. The studies using SEM, XRD of the coatings of the samples before and after exposure to SBF were performed. The features of morphology, chemical and phase composition of the studied coatings are shown.

1. Introduction

Implants must be compatible with living tissues. Modern medical materials science aims at improving the implant survival. It can be achieved by forming biocompatible and bioactive coatings. The implants made on the base of Titanium and its alloys capable of surviving under mechanical loads in the recovery process find a wide application in traumatology. To reduce the duration of treatment different biocoatings are formed on the titanium surface. These coatings in particular calcium phosphate coatings on the base of hydroxyapatite must combine bioactivity and high mechanical strength. A number of technologies have been applied in industry. The calcium phosphate coatings on titanium implant materials formed using the techniques developed at Tomsk Polytechnic University are shown in Fig.1.

The electrochemical method is the simplest, widely used and effective method of forming coatings. MAO allows us to form the coatings with the thickness to 30 μm and high adhesion with substrate surface. However, this method has some limitations: MAO coating can be formed only on the valve group materials, their chemical composition of are poorly controlled, and they have low elasticity.

One of the promising methods for the formation of calcium phosphate coating is a method RFMS of target. Using this method the dense coatings with high adhesion can be formed on complex shapes surfaces maintaining stoichiometric composition of a sputtered target and controlled chemical composition. Method RFMS of target has the following features: low rate of coating growth and low porosity of coatings.

The combination of MAO and RFMS methods allows us to use the advantages of each method, masking their shortcomings.

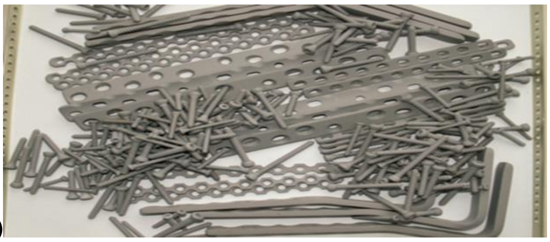
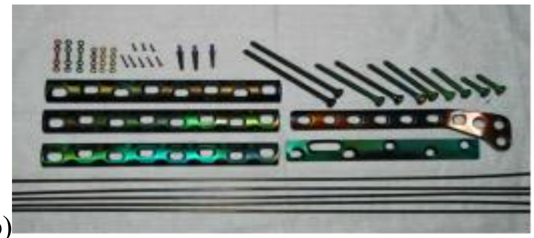
a)  b) 

Fig.1. Implants with calcium phosphate coatings. a) micro-arc oxidation (MAO), b) high-frequency magnetron sputtering (RFMS) of target

2. Experimental part

For the study the samples were made of titanium plate (BT1-0) of the following size:10×10×2,8 mm^3. Preparation of samples before forming coatings included sandblasting and chemical cleaning in an ultrasonic bath with distilled water.

Formation of calcium phosphate coatings by the micro-arc oxidation method was performed in a saturated solution of CaO in 10% H3PO4 with the addition of phase dispersion of hydroxyapatite with particle size of 70 microns.

The following technological conditions of formation of MAO coatings were used: dense coatings were formed at constant voltage of about 150 V for 15 minutes, the porous - 170 V, 30 minutes. The pore size of the dense coatings is 1 - 2 µm, porous coatings of 5 - 7 µm.

The formation of calcium phosphate coatings by RF magnetron sputtering target of hydroxyapatite was produced using the setup developed at Tomsk Polytechnic University (see Fig. 2.), under the following technological conditions: preliminary pressure of chamber is $7 \cdot 10^{-3}$ Pa, operating pressure of Ar is $5 \cdot 10^{-1}$ Pa, RF power is 2 kW, deposition duration is 8 hours, distance between the target and samples is 35 mm.

Fig.2 Setup of RFMS developed in Tomsk Polytechnic University

Using the combination of MAO and RFMS methods, 16 different types of coatings were formed.

Crystallization of calcium phosphate coatings was carried out at temperature 730-770° C.

Roughness of the coatings was determined by the profilometer "Talysurf 5-120". The morphology of the coating surface and elemental analysis were examined by scanning electron microscopy “JEOL-6000”.

In vitro evaluation for apatite-forming ability of implant materials was carried out according to ISO 23317 [1].

3. Results and discussion

Using the data of evaluation for apatite-forming ability of implant materials the best coating from 16 kinds was chosen for studies in vivo. For obtaining this coating it is necessary to carry out the following sequential technological operations: MAO-annealing-RFMS of target- annealing. [2]

According to the energy dispersive analysis of MAO coatings, the coatings have calcium-deficient composition. In contrast, RFMS coating has a calcium-rich composition. Thus, using a combination of these methods it is possible to obtain balanced chemical composition of the coating.

Fig. 3 shows SEM images of surface of the hybrid coating made after exposure to SBF solution. The analysis of images shows that apatite crystallites form on the titanium surface. The apatite crystallites are supposed to contribute to osseointegration of implant.

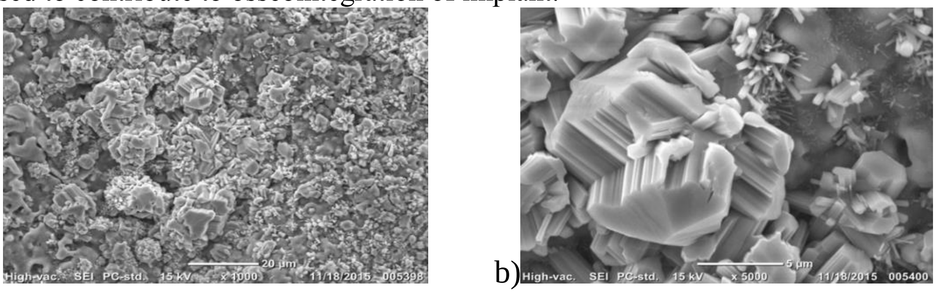
a) 
b)

Fig.3 SEM of hybrid calcium phosphate coating after exposure of samples to SBF solution with magnifying a -1000; b -5000

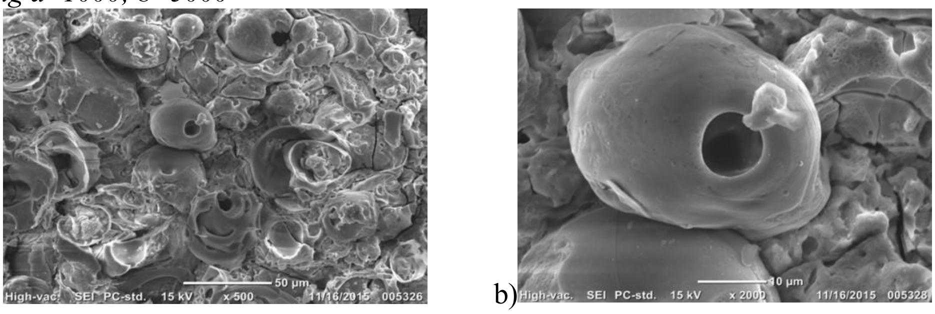
a) 
b)

Fig.4 SEM of calcium phosphate coating obtained using MAO after exposure of samples to SBF solution with magnifying a -500; b -2000

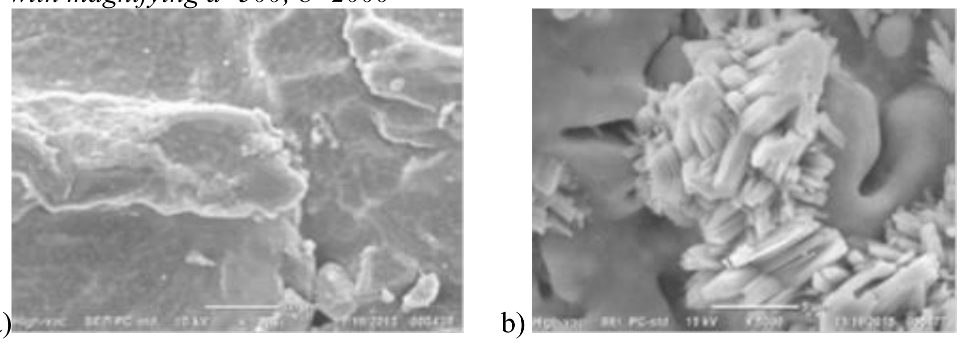
a) 
b)

Fig.5 *SEM of calcium phosphate coating obtained using RFMS after exposure of samples to SBF solution with magnifying a -1000; b -5000*

This conclusion was confirmed by the results of the energy dispersion analysis of surfaces of titanium samples with hybrid coatings samples before and after exposure to SBF, (Table 1). After exposure to SBF the content of P, O increase and content of Ca, Ti decrease. Thus, exposure of samples in SBF allows us to bring the value of calcium to phosphorus ratio to normal in vivo.

Table 1. Chemical content of hybrid CaP coating after exposure of samples to SBF according energy dispersion analysis

	Ca, at.%	P,at.%	Ca/P	O, at.%	Ti, at.%
Before SBF	32.43	5.52	5.87	36.89	25.16
After SBF	25.81	16.61	1.55	42.10	15.49

Table 2. Chemical content of CaP coating obtained using MAO after exposure of samples to SBF according energy dispersion analysis

	Ca, at.%	P,at.%	Ca/P	O, at.%	Ti, at.%
Before SBF	8.07	21.9	0.36	46.94	23.09
After SBF	10.26	23.53	0.43	47.19	19.02

Table 3. Chemical content of CaP coating obtained using RFMS after exposure of samples to SBF according energy dispersion analysis

	Ca, at.%	P, at.%	Ca/P	O, at.%	Ti, at.%
Before SBF	35.33	14.86	2.37	39.91	9.80
After SBF	34.69	14.47	2.39	39.87	10.97

The proposed method of forming calcium phosphate coatings allows us to form multilayer coatings on titanium implants, consisting of a combination of two methods- micro-arc oxidation and RF magnetron sputtering target. The chemical composition of the coating is the compound of calcium, phosphorus, titanium, and their oxide compounds. The composite structure of the coating allows combining the high mechanical properties of titanium with high bioactivity of calcium phosphate layer. At present, the most optimal type of coating produced by applying the combination of MAO and RFMS of target with double annealing is studied in vivo using large laboratory animals.

Acknowledgement
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References
[1] ISO 23317. Implants for surgery — In vitro evaluation for apatite-forming ability of implant materials Another reference
[2] Kharapudchenko E. Hybrid calcium phosphate coatings for titanium implants/ E. Kharapudchenko, N. Bogomolova, V. Ignatov, S. Jakimov, S. Tverdokhlebov – Journal of Biotechnology and Biomaterials, 2016 – 69 p.