СЕКЦИЯ 9. MODERN ISSUES OF SCIENCE AND TECHNOLOGIES

(РАБОЧИЙ ЯЗЫК СЕЦИИ: АНГЛИЙСКИЙ)

STUDY OF CALCIUM-PHOSPHATE FILMS OBTAINED BY PULSED-LASER DEPOSITION

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Modern medical technologies allow reconstructing organs in a human’s body fully or partly. To make such an operation implants are widely used. Polymers are considered to be perspective for such purposes because their use in implants production allows forming different composite structures.

It is required that the surface of an implant should regenerate the organic tissue, to integrate with the organic tissue, to be vivid (rough, porous) and biocompatible. Calcium-phosphates are coated on the surface of an implant in order to improve its bio acceptability with the bone tissue [1].

Laser ablation was chosen as a method of formation of calcium-phosphate coatings on the surface of the polymer. The information on influence of the target’s composition on structure and properties of a coating formed by laser ablation provided by available literature sources is not enough. So the aim of this work was the study of influence of the chemical composition of the sputtered target on the morphology and the composition of the formed coatings.

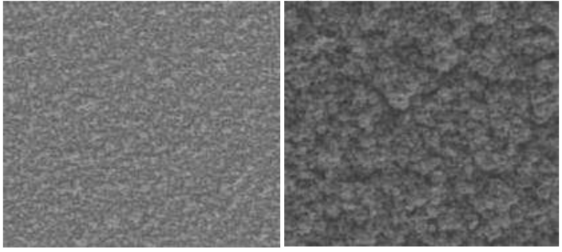
Materials. Copolymer tetrafluoroethylene with vinylidene fluoride (TFE/VDF) was deposited on the 20×20 mm glass plate. Thin polymer 2%mass coating was formed on one of the sides of the glass plate in the solution of organic dissolvents in %mass: acetone 20, ethyl acetate 20, cyclohexanone 40, butyl acetate 20. The copolymer solution TFE/VDF was formed in hermetic reactor at 50°C with constant mixing it until receiving a transparent homogenous solution. Then the solution was cooled at room temperature and was deposited on the glass plate by airstream atomization. Then the samples were put into a box furnace where the final polymer coating formation was carried in the regimes: heating up to 35°C with the rate 1 grad per minute, holding for 4 hours at 70°C, heating up to 200°C with the rate 1 grad per minute, holding for 2 hours at 200°C. To modify the obtained materials surface the method of laser ablation was used. The sputtering targets: hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) - target 1 and dibasic calcium-phosphate ($CaHPO_4$) - target 2.

The modification was carried with Lotis TII pulse-periodic laser. The general view of the set is in the figure 1. The laser emits pulses with frequency ν=15 Hz, the duration of an impulse was τ=7 ns, laser wavelength was λ=1.064 mkm, energy of an impulse wass E_0=170 mJ, laser power density was W=2.7 W/cm^2.

Figure 1. The general view of the experimental set. 1-monometr, 2-laser set, 3-lens, 4-box furnace, 5-power meter

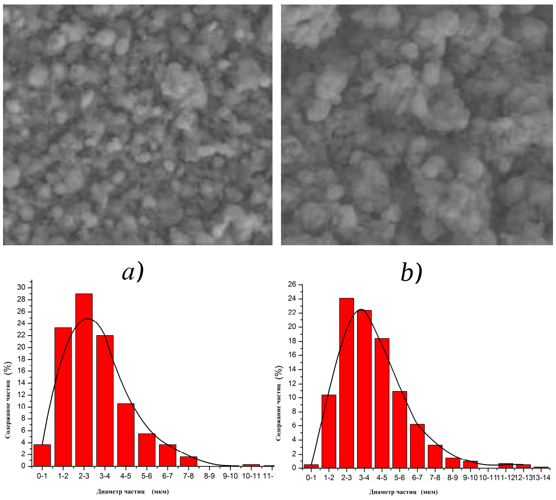
Methods. The study of the surface morphology and elemental composition of the samples was carried by scanning electron microscopy on ESEM Quanta 400 FEG microscope with in-built EDS-analyzer in a low vacuum regime without using conductor coatings in order to exclude the deformation of coatings morphology.

In the figure 2 there are images of the coatings at 1000×. From these images we can see that formed coatings have homogeneous, vivid, granular structure. There are also images at 5000× from scanning electron microscope. Using this images histogram on linear size distribution (grain diameters) was built (figure 3c). From figure 3 it is obvious that the grains distribution graph of the coating formed using hydroxyapatite target has a wide maximum between 2 mkm and 3 mkm which allows to evaluate the average diameter of the grain in the coating is in this interval. The average diameter of the coating formed using dibasic calcium-phosphate target is between 3 mkm and 4 mkm (figure 3d). To sum up, the difference in the average grain sizes of these two coatings is insignificant. Taking into account the SEM images analysis a conclusion that the morphologies of two coatings are similar may be suggested.



a) b)

Figure 2. SEM images of the coatings at 1000×, a) target 1, b) target 2

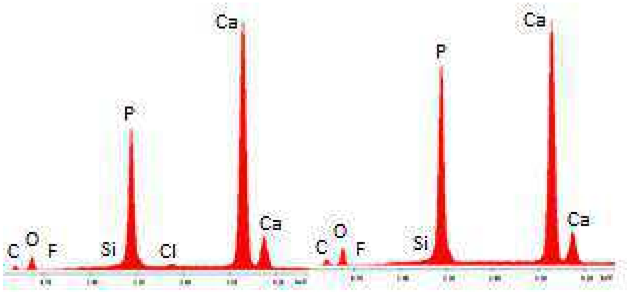


a) *b)*

c) *d)*

Figure 3. SEM images of the coatings at 5000× and histograms on linear size distribution a, c) target 1, b, d) target 2

EDS-spectra of the coatings are shown in figure 4. Peaks of such chemical elements as C, O, F, Cl in the spectra correspond to polymer layer deposited on the plate. Therefore these peaks have small intensity or they are absent while studying the coating. Peaks of Ca, P correspond to the calcium-phosphate coating, that's why in the coating zone they have very high intensity. The percentage of chemical elements in the coating according to EDS-analysis is shown in the table 1. The presence of Si peak could be explained by using the glass plate as a substrate. EDS-analysis has shown that modification of polymer's surface by laser ablation using different calcium-phosphate targets allows varying elemental composition of a forming coating. Also for both coatings the ratio Ca/P was calculated. They were 2.17 for the coatings from hydroxyapatite and 1.52 for the coatings from dibasic calcium-phosphate which is close to stoichiometric ratio 1.67.



a) *b)*

Figure 4. EDS-spectra of the coatings made from a) target 1, b) target 2

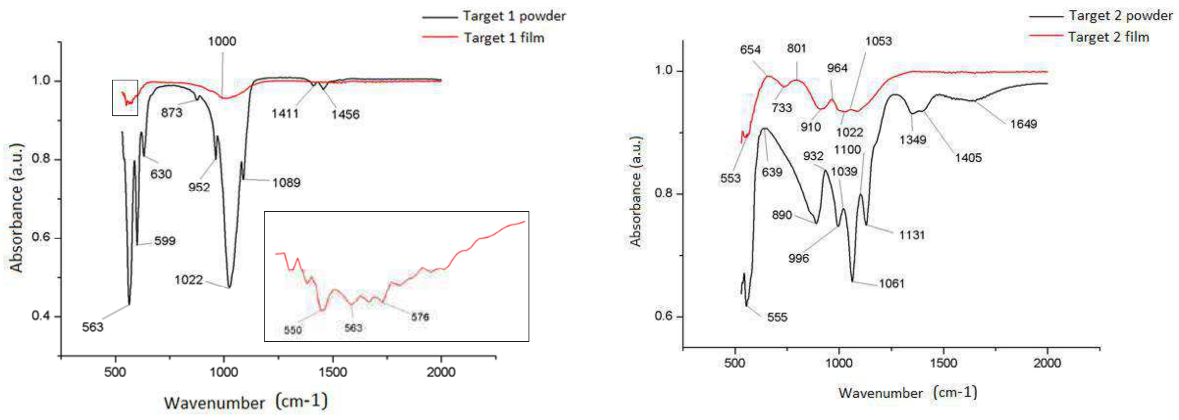
Table 1

Chemical composition of the calcium-phosphate coatings

Target	At, mass%					Ca/P
	Ca	P	C	O	F	-
Target 1	43.91	20.20	12.96	22.67	0	2.17
Target 2	36.11	23.81	16.54	23.14	0.13	1.52

The chemical composition of samples was analyzed by the infrared spectroscopy (Nicolet 6700 (ThermoScientific)) at a spectral resolution of 2 cm^{-1}. First, FTIR analysis of the used targets was performed (figure 5).

The presence of typical hydroxyapatite peaks were detected. Target 1 powder: 563 cm^{-1} is assigned to P–O modes [2], 1022 cm^{-1} – anti-symmetric P–O stretching *v*3 [3]. Target 1 film: 563 cm^{-1} – P–O modes [2], 1000 cm^{-1} - asymmetric stretching mode of PO_4^{3-} [4] (figure 5a). Target 2 powder: 555 cm^{-1} - anti-symmetric P–O bending v4 [3], 1061 cm^{-1} – v3 asymmetric stretching mode of PO_4^{3-} [5]. Target 2 film: 553 cm^{-1} – anti-symmetric P–O bending v4 [3], 1053 cm^{-1} – v3 asymmetric stretching mode of PO_4^{3-} [5] (figure 5b).



a)

b)

Figure 5. FTIR-spectra of calcium-phosphate powders and films, a) target 1, b) target 2

FTIR-analysis showed that chemical composition of the coating in both cases is the same as the chemical composition of the target and confirmed that using different targets allows varying the elemental composition.

Results. The modification of the polymer layer was carried by laser ablation with the use of two different by composition calcium-phosphate targets. It was shown that the formed coatings have vivid, grained, homogeneous surface and the average diameters are close to each other by value so their morphology differs insignificantly. It was shown that the chemical composition contain all the elements of the initial target when using laser ablation. It was also found out that forming calcium-phosphate coatings by laser ablation with the use of different targets allows varying elemental composition of forming coatings.

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