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The Study of The Morphology and Structural Properties of Coatings of Implants with Different Shapes of The Developed Surface.

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ABSTRACT

This article describes a technique of uniform film deposition of linear-chain carbon on the developed surface of experimental samples of the implants and prostheses. Were discussed methods of controlling the coating of a linear-chain carbon. Was described a study of the morphology of experimental samples of implants with different shapes of the developed surface on a raster electron microscope and structural properties of experimental coating samples of different areas of the implants using Raman spectroscopy.
Keywords: linear-chain carbon, the prosthesis of the intervertebral disc, endoprosthesis of the hip joint, a dental implant, shoulder implant, Raman spectroscopy, electron microscopy, chemical microanalysis, IR spectoscopy, x-ray analysis.

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INTRODUCTION

Recently, an important challenge was a creating of a technology for the manufacture of biocompatible implants and prostheses due to the formation of the porous structure of their surface [1].

Now scientific studies are also underway the involvement of application of a porous surface of implants and prostheses of various biocompatible coatings.

The conducted studies are related to the formation of coatings on the basis of recombinant bone morphogenetic proteins of human (rhBMP) and inorganic bioinert coating of a linear carbon chain (LCC) [2-5].

In the development of coating technology on the developed surface of implants and prostheses is necessary a uniform film deposition of LCC over the entire developed surface of implants and prostheses.

This requires the study of control methods of remotely controlled (RC) coating LCC, such as Raman spectroscopy, electron microscopy, chemical microanalysis, IR spectroscopy, X-ray analysis [6-9].

Are also needed the solutions of such challenges as the refinement of methods of deposition of films of LCC on the surface of experimental samples, the study of the morphology and structural properties of the formed coating.

Methodology of a uniform application of films of LCC on the developed surface of experimental samples of the implants and prostheses. For the uniform application of films of LCC on the developed surface of experimental samples of implants and prostheses, it is proposed to use a technique based on the deposition of strictly ordered structure of the films RC LCC [10-11].

Films coating of RC LCC was carried out on the entire intraosseous surface of dynamic intervertebral disc prosthesis, total hip endoprosthesis, endoprosthesis of the shoulder joint and dental implants with advanced surface [12] on the experimental «Device for the application of LCC and other heterostructures».

Photograph of the experimental sample of the endoprosthesis of the shoulder joint is shown in figure 1.

Figure 1 – General view of the experimental sample of the endoprosthesis leg of the shoulder joint with a developed surface

In the device was used a carousel for sputtering, providing for the mounting and rotation of the experimental samples relative to the plasma clot. Coating uniformity is ensured by the geometry of the electrodes, by forming of dense plasmoid and by the magnitude of the rotation angle of the experimental samples relative to the plasma clot.

To implement the methods of applying inorganic coatings on bioinert implants and prostheses with a developed surface it is proposed to use a vacuum chamber with a pulsed plasma generator and ion source for the stimulation process. The presence of macropores and micropores makes significant changes to the procedure for the deposition of uniform layers on the entire developed surface. At the same angles of the

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meeting of the plasma stream with the surface of the hole in the form of macropores from the impact of the plasma flow are practically not subjected to spraying.

Figure 2 shows the zones in the form of ellipses that are the most difficult for coating of trapezoidal-shaped macropores that were developed in the previous stages of this research.

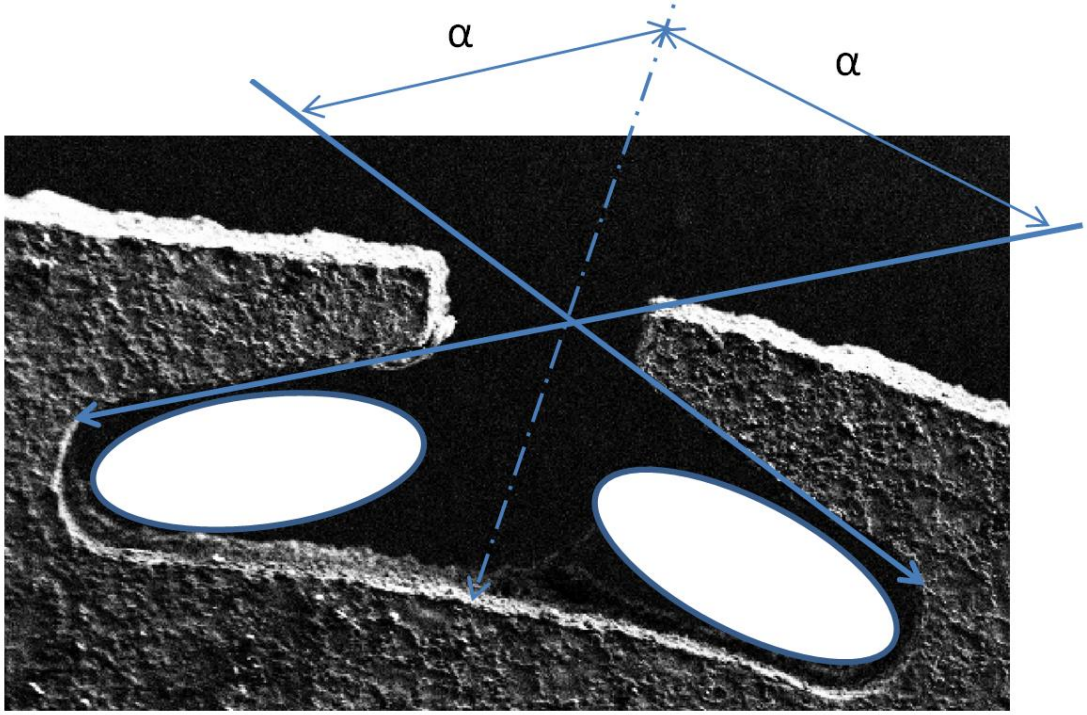

Figure 2 – Ellipse zones that are the most difficult for coating of trapezoidal-shaped macropores

In this regard, were carried out the process of applying LCC films to the experimental samples with the trapezoidal shape of the macropores of the developed surface. It was suggested at the applying of the film (except of the surface rotation) to realize back-and-forth changing the angle α of the meeting of the plasma stream with the surface of the experimental sample. According to the results of the conducted researches it was established that the optimal change of rotation of angles should be considered in the range from -60° to +60°.

The proposed method allows reducing the unevenness of thickness of the formed film due to the increase of a surface, which underway the straight angles of meeting with the plasma flow, both on the surface of implants and prostheses, and inside the macropores.

In works [13-14] on the formation of the structure of the LCC, a significant influence of annealing temperature on the change in the work function and structure of the LCC, as the developed in the present research work the implants and prostheses with a developed surface significantly differ in weight and size characteristics, it becomes obvious the need for optimization of temperature regimes for each of them. The optimal structure of linear chains of carbon is formed at a temperature of 500-600°C. When it increases to 800°C significantly reduces the length of the chains, and at 850°C it causes their graphitization.

Thus, to optimize the structure of linear carbon chains is proposed to stabilize the annealing temperature in the range of 500 to 600°C.

Methods to control the coating of RC LCC on experimental samples. Raman spectroscopy (RS) is an effective method of chemical analysis for studying the composition and structure of substances, based on the phenomenon of inelastic scattering of monochromatic light in the visible, near UV or near IR ranges [6].

Raman spectroscopy has significant advantages compared to other analytical methods. The most important of these are simplicity of sample preparation and a large amount of information received.

Raman spectroscopy - a method based on the scattering of light, so all what is required to for collecting the spectrum is to direct the incident beam exactly on the sample, and then to collect the scattered light.

The thickness of the sample does not cause problems for Raman spectroscopy (in contrast to IR spectroscopy in the analysis of samples in transmission), the surrounding atmosphere also contributes a minor contribution to the RS spectra.

There are no two molecules that have the same Raman spectra, and the intensity of scattered light is related to the amount of the substance. This makes it easy to obtain both quantitative and qualitative information about the sample, gives the opportunity to interpret the spectrum, process the data using computer methods for the quantitative analysis.

Raman spectroscopy is a nondestructive method of analysis. There is no need to dissolve solids, press pellets, compress the sample to the optical elements or otherwise change the physical or chemical structure of the sample. Thus, Raman spectroscopy is widely used to analyze such physical properties as crystallinity, phase transitions and polymorphic condition [7].

With RS you can also explore the natural fiber.

As the equipment you can use a Raman Spectrometer of Horiba Jobin Yvon T64000 [7].
The application area of the spectrometer:

- a determination of the presence of the substance in a mixture of solid and liquid substances;
- registration of changes of the structure of substance, phase transitions in solids at temperatures of 520 - 930 K;
- determination of the purity of the materials;
- characterization of the quality of the synthesis of new substances;
- defining a nonuniform spatial distribution of inclusions, impurity substances in a sample by mapping the distribution of an impurity;
- the study of temporal dynamics of chemical processes;
- express control of the technological industries.

The main characteristics of the spectrometer:

- tripple monochromator. There are two modes: with the addition and subtraction of the dispersion;
- operating frequency range 0.5-8000 cm^{-1} (depends on the wavelength excitation and the quality of the sample);
- the resolution in the subtractive dispersion mode, from 0.2 cm-1 (typical of 2 cm-1) upon excitation 514 nm;
- excitation of Ar+ laser 514 nm - 2.2 W; 488 nm – 1.5 W; 514 nm - 2.7 W; 476 nm – 0.8 W; 458 nm – 0.4 W; 454 nm – 0.1 W; (a different laser use is possible).

In the case of film deposition of two-dimensional ordered linear-chain carbon (LCC DN) samples on the textile products, the most simple and effective method of quality control of the coating is Raman spectroscopy, which uniquely allows the identification of sp communications in the linear-chain carbon.

Electron microscopy – are the research methods of microstructures of solids using the electron microscopes (up to atom-molecular level), their local composition, electric and magnetic fields localized on the surface or in the micro-volumes of bodies [8].

In transmission electron microscope (TEM) electrons with energies from 1 KeV to 5 MeV pass through the object. Were studied the samples in the form of thin films, foils, cuts, etc. with a thickness of 1 nm to 10 μm. Powders, microcrystals, sprays, etc. are possible to study if we apply them before to the substrate - a thin film for studies in PEM or solid substrate for study in the scanning electron microscope (SEM) [8].

Surface and near-surface structure of massive bodies with a thickness substantially greater than 1 μm are studied with the help of REM, reflective and mirror and ion projectors and electronic projectors [8].

The structure of the coating on the objects can be estimated using REM, and rather difficult on practice using a transmission electron microscopy.

In the chemical microanalysis are analyzed the spectra of samples.

Is determined the chemical composition of the sample at various stages of heat treatment of the material, before and after reaction of dehydrohalogenation, and after thermal annealing.

Is estimated a carbon intensity of peaks in the spectra of the sample compared to the intensity of peaks of the other substances (table 1).

For the initial sample are characteristic the absorption peaks at frequencies 615b693 cm^{-1} corresponding to the vibrations of bonds C-Cl 2850-2990 cm^{-1} – vibrations of bonds C-H2. Thus is controlled a carbon receiving frequency [9].

Table 1. Chemical microanalysis of samples [9]

	Content, %			
Sample	C	Cl	K	O
The original fiber	79,4	20,6	-	-
After dehydrohalogenation	97,0	2,0	0,1	0,9
After thermal annealing	99,4	0,4	0,1	0,1

The chemical composition of the samples can be studied by using x-ray microanalysis for chemical analysis by the X-ray analyzer «Oxford technologies».

By IR spectroscopy are analyzed the infrared spectra of the samples. Is determined the chemical composition of the sample at various stages of heat treatment of the material, before and after reaction of dehydrohalogenation, as well as after thermal annealing in vacuum. Is estimated a carbon intensity of peaks in the spectra of the sample compared to the intensity of peaks of other substances. For the initial sample are characteristic the absorption peaks at frequencies 615b693 cm^{-1} corresponding to vibrations of bonds C-Cl, 2850-2990 cm^{-1} – vibrations bonds of C-H2. Table 2 presents the ratio of the intensities of the corresponding absorption peaks of C-Cl and C-H2 - links, the intensity of absorption peak of C-Cl – bond is taken as a unit. Thus, is controlled a frequency of carbon producing by the method of IR - spectroscopy [9].

Table 2. The ratio of peaks of the absorption the bonds C-Cl and C-H2 [9]

	Relative intensity of peaks of the absorption	
Sample	C - Cl	C - H_2
Before processing	1	0,52
After dehydrohalogenation	0,26	0,52
Annealing in vacuum at 400°C	0,09	0,14

IR spectra can be analyzed using Fourier infrared-spectrometer of the firm "Brucker" in the range from 400 to 4000 cm^{-1}.

XRD analyses samples at all stages of the development of the carbon material: after the chemical treatment and all stages of subsequent annealing in air at various temperatures, such as 100, 200°C and 300°C and in vacuum, for example, at 400°C and 500°C. Is analyzed the diffractogram of the sample before and after thermal annealing. Is evaluated the presence of changes in the spectrum that characterize the distance between the chains in the dense hexagonally package of LCC [9].

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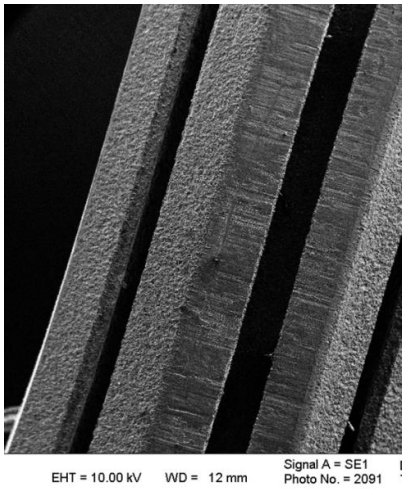
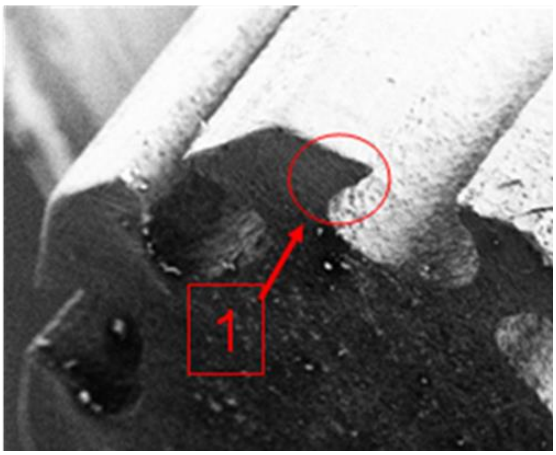
The X-ray diffraction analysis is convenient to perform on a modified X-ray diffractometer "Dron-4" (wavelength L=1,08).

The study of the morphology and structural properties of experimental samples of the coating of implants with different shapes of the developed surface. Determination of the morphology of the samples was carried out on scanning electron microscope LEO 912 Omega AM, and the definition of structural properties, confirming the presence of carbyne connections in the samples on the spectrometer Jobim Yvon Mole Spectrometer with the wavelength of the emitted light at λ = 532nm.

Figure 3 (a) is a view from above of a prototype of a titanium implant with a developed surface in the form of a longitudinal channel with round shape of the macrorelief, on figure 3 (b) is a side view. Figure 3 (c) shows an enlarged surface of the longitudinal channel and the surface of the implant. The drawings are received in a capture mode with the scanning electron microscope at different magnifications.



a)



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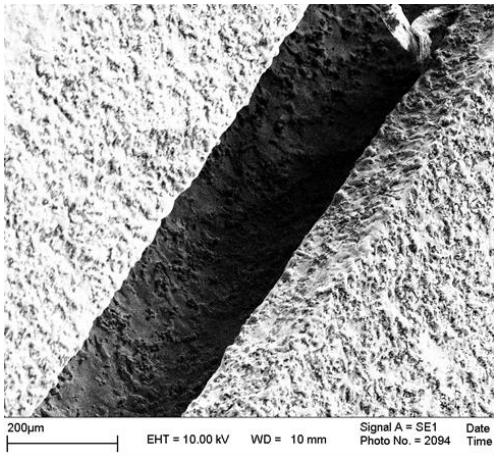

c)

Figure 3 - a) A top view of a prototype of a titanium implant with a developed surface in the form of a longitudinal channel with round shape macro-topography; b) side view of a prototype of a titanium implant with a developed surface in the form of a longitudinal channel with round shape macro topography; c) the increased surface of the longitudinal channel and the surface of the implant.

From the presented figures it is evident that the sample surface is a highly developed structure with a coating on the surface of the implant and within the longitudinal channel. At evaporation was used the technique of the reciprocating rotation axis of the implant. This allows a maximum evenly cover of the entire surface. The proposed method helps the carbon plasma to get inside the channel during the deposition.

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Analysis of film thickness showed that at the bottom of the trough it's larger than in the area of negative angles - 1 figure 12 (b). In these areas the deposition of the coating will occur only at acute angles.

With the aim of determining the structural properties were carried out the studies using the Raman spectroscopy of various sections of samples.

The obtained results of evaporating LCC on the developed surface show that the applied carbyne coating is presented on the entire area of the working surface of the sample, and in the area of negative angles of the implants a decrease in film thickness is observed.

Figure 4 shows portions of the surface of experimental samples generated in the form of holes of cylindrical shape.

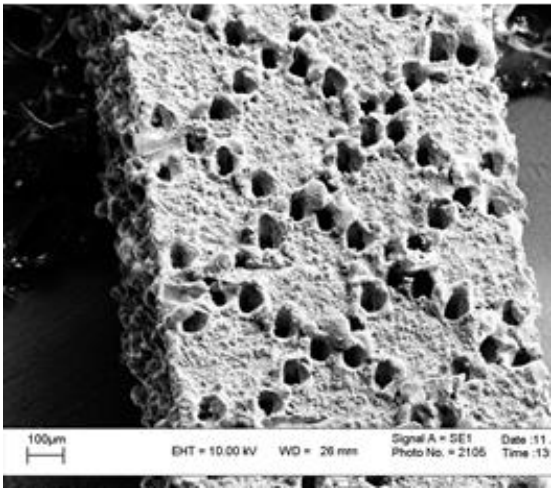

Figure 4 – The surface of area of the experimental sample formed by holes of cylindrical shape

Analysis of the results of electron microscopy shows that the sample is a highly developed structure with periodic cavities on its surface. To estimate the depth of cavities on the sample surface by means of raster electronic microscopy was not possible. It can be assumed that the carbyne coating is deposited inside of these cavities, but it will be significantly thinner than the coating applied to the front part of the samples.

Figure 5 shows a range of the inelastic light scattering from the area of the sample surface, which corresponds to the carbyne type structure and this range can be correlated with the characteristic for RC LCC.

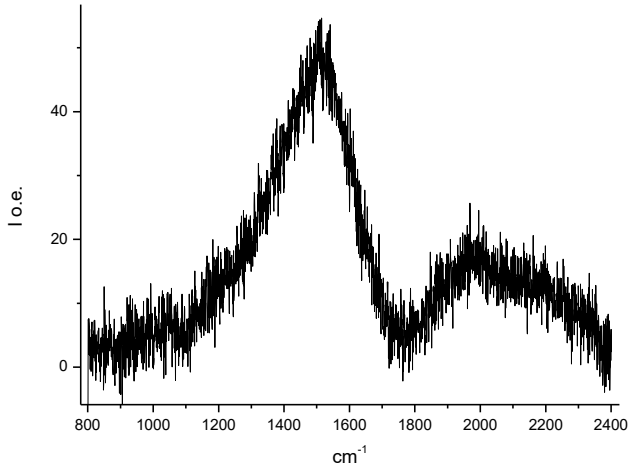

Figure 5 - Range of the inelastic light scattering from the area of the sample surface, which corresponds to the carbyne type structure

Thus, for a series of images of different geometric type were obtained the SEM (scanning electron microscope) images of the surface and the Raman spectra from different areas.

The results of the study found that the carbon film completely repeat the relief of the developed surface of experimental samples with the exception of the regions of the "negative angles" in which the film appears to be sprayed thinner than the main area of the samples.

To improve the quality of coatings and alignment of thicknesses is expected to carry out an additional rotation across the axis of the sample.

The structure of the samples according to the Raman spectroscopy corresponds to the chain carbyne-similar structure, and which can be attributed to the structure of RC LCC.

The total broadening of the main line 1550 cm-1 can be attributed to some disordering of the evaporated film growing on the highly developed surface.

CONCLUSION

The research found that the carbon film perfectly replicate the surface topography of implants and prostheses. With one exception - the regions of "negative angles". A film is deposited there with a thinner layer than in the main area of the samples. To improve the quality of coatings and levelling of thicknesses, it is expected to carry out an additional rotation across the axis of the sample.

The structure of the formed coating for all investigated experimental samples corresponds to the chain carbine similar structure and which can be attributed to the structure of remotely controlled LCC. The increase in the main line 1550 cm-1 can be attributed to some disordering of the evaporated film growing on the highly developed surface.

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