Electrical Potential and Topography of the Surface of a Calcium-Phosphate Coating Deposited with RF-Magnetron Discharge

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Abstract—Research into the correlations of the surface electric potential of electret calcium-phosphate coatings formed by RF-magnetron sputtering and the surface topography are performed. It is determined that the electric potential over the coating surface has irregular distribution. The highest value of the potential is localized in the region near structural elements (vertices) with a higher peak sharpness value. The spots on the coating surface having a maximum potential within the range of 670–900 mV correspond to a profile of points with heights in the range of 77–326 nm. The higher values of the electron work function of the surface of the coating as compared to a titanium surface without the coating correspond to enhancement of the adhesion effect of osteoblasts and osteoclasts to the surface of the calcium-phosphate coatings.

INTRODUCTION

The creation of biocompatible materials for the long-term restoration and substitution of human bone tissue is one of the prime objectives of medical materials science. Until now, more widespread and widely used metallic materials have been considered for this purpose due to their high strength properties and relatively low cost. Surface modification of the implants is performed by the formation of coatings including those based on calcium phosphate [1] for imparting biocompatibility, i.e., chemical-biological similarity to bone tissue to them and controlling their properties. There are a number of methods which allow such coatings to be obtained: the microarc or the plasma electrolytic oxidation, laser ablation, the sol-gel method, RF-magnetron sputtering, etc. [2]. The last one is distinct from others in terms of the capability of controlling the coating thickness in the nanometer range and creating a predetermined periodic structure, for example, by using deposition masks [3], and high surface adhesion to the substrate.

In studies performed earlier, an important and essential requirement to intraosseous implants was found: the implant surface must be rough and/or microporous [4], first and foremost to enhance the properties of surface adhesion to a substrate [5, 6]. The optimal surface characteristics for improving biological processes are still being discussed. However, it is determined that surface roughness unambiguously improves bone-implant healing and prevents its failure [7]. In paper [8] it was shown that the optimal surface roughness of the implant is R_a 2.5–4.0 μm.

One more important property of biocoatings in the composition of implants introduced into a musculoskeletal system is their electrical compatibility at all organization levels of living systems (molecular, cellular, organ tissue) [9]. As was shown experimentally in papers [10–15], electrically polarized hydroxyapatite enhances the effect of bone-tissue growth on a surface, which is important in relation to monitoring the vital activity of electroexcitable and unexcitable cells.

Nowadays there are a lot of papers related to the electrical polarization of surfaces based on hydroxyap-

atite (HA) [16−19]. Moreover, it is determined according to the results of a literature review that the effect of the polarization of thin RF-magnetron coatings based on hydroxyapatite and its dependence on the surface morphology are barely studied. Mathematical representations on the distribution of electric charge on the surface of hydroxyapatite particles are developed in studies of V.S. Bystrov [20, 21]. It is shown, that the density of the surface positive electric charge of HA nanoparticles increases with a decrease in their size. Therefore, it is to be expected that structural elements of the surface with a larger sharpness will make a big contribution to the total positive charge of the surfaces. Thus, by changing the topography of a metal substrate under a coating and thus surface topology, we can obtain the required electric-charge distribution and surface electric potential. However, we did not find such an approach in publications.

The aim of this research is to estimate the relationships between the surface electric potential and the surface roughness of a thin electret calcium-phosphate coating formed on the titanium substrates by the RF-magnetron sputtering of a hydroxyapatite target.

EXPERIMENTAL

Titanium samples of the BT1-0 brand, in the form of disks 10 mm diameter, were used as substrates. Surface processing of the titanium substrates was performed using abrasive paper of the P150, P320, P400, P600, P1000, P1500, and P2000 brands. Polishing was performed with diamond paste, whose abrasive ability was 28−20, 20−18, and 14−10 μm. Before the coating process, the substrate surface cleaning of impurities was performed by deoiling of the samples in an ultrasound bath with saponifying solutions and organic dissolutions with subsequent drying in air.

Deposition of the calcium-phosphate coatings was performed by RF-magnetron sputtering of the target made of HA powder using a "Yakhont-2M" machine with the source frequency 13.56 MHz [22]. HA synthesized by heterophase synthesis with mechanochemical activation is used (Bizneslink, Moscow). Target forming in the shape of disks 110−120 mm diameter and 3−6 mm thickness was performed by uniaxial pressing of the mold powders at room temperature in a steel press-form using a hydrostatic press MIS-6000.4K (Armavir, Russia). The mold powders were prepared using an aqueous solution of polyvinyl alcohol of higher-grade PVA-16/1 brand manufactured by OOO "Khelat" (Moscow, Russia); firing of the blanks after pressing was performed in a programable chamber electric furnace ITM 12.1200 in air. The maximum firing temperature was 1000°C, timing cycle of heating up to the maximum temperature was 4 h, and cooling, more than 30 h.

A vacuum machine with a magnetron-sputtering system and source of ion cleaning was used in the study. The construction of the machine provides ion cleaning of the sample surface and coating deposition from a fixed magnetron inside of the working chamber. Before target sputtering, the surface of the substrate, being in the vacuum chamber, was activated by an ion source of free closed electron drift at the energy 1.5−2.9 eV, current 10−30 mA and a pressure in the chamber of 1 Pa. The time of ion activation was 15 min.

Sputtering was performed using argon as the working gas whereas the pressure of the working gas was 0.2 Pa, the sputtering time was 2 h, and the high-frequency discharge power was 250 W. The thickness of the obtained calcium-phosphate coatings did not exceed 650 nm. Measuring the thickness of the coating was performed on witness samples of polished single-crystal silicon by spectral ellipsometry using an Ellipse-1891 SAG system (Novosibirsk, Russia). The surface roughness of the metal samples before coating deposition and coating surface after their deposition was measured by the "Profilometer-296" over R_a (*GOST* (State Standard) *2789-73*).

A Philips SEM 515 scanning electron microscope with an EDAX ECON IV (USA) microanalyzer was used for titanium-sample surface imaging after processing.

Investigation of the topology of the coating surface on samples was performed using the measuring system INTEGRA (NT-MDI, Russia). The Calvin probe method in an atomic-force microscope (AFM) was used to measure the contact-potential difference between the probe and sample and for characterization of the relationship between the surface electric potential and the substrate-surface geometry. The Calvin probe method is based on a two-pass technique. During the first pass, the surface relief of the sample is determined using the semi-contact mode (cantilever oscillations being excited mechanically). During the second pass, this relief is traced upon passing over the sample at some height for determining the surface electric potential. This distribution is like the contact-potential difference distribution [23], if constant bias is not applied to the probe.

Photoelectron spectroscopy was used to determine the work function and make a correlation with the charge state of the surface of metal samples and samples with a coating. The equipment was developed and manufactured in a laboratory of the Institute of Biomedical Engineering and Nanotechnologies at Riga Technical University (Latvia). The photoelectron spectroscopy installation includes a vacuum chamber with a substrate holder and a window, transmitting light from the photostimulator, and a system for recording transmitted electrons (electron detector). The mechanical rotor pump and the diffusion pump allow a pressure in the chamber of about 10^{-4} Pa to be reached.
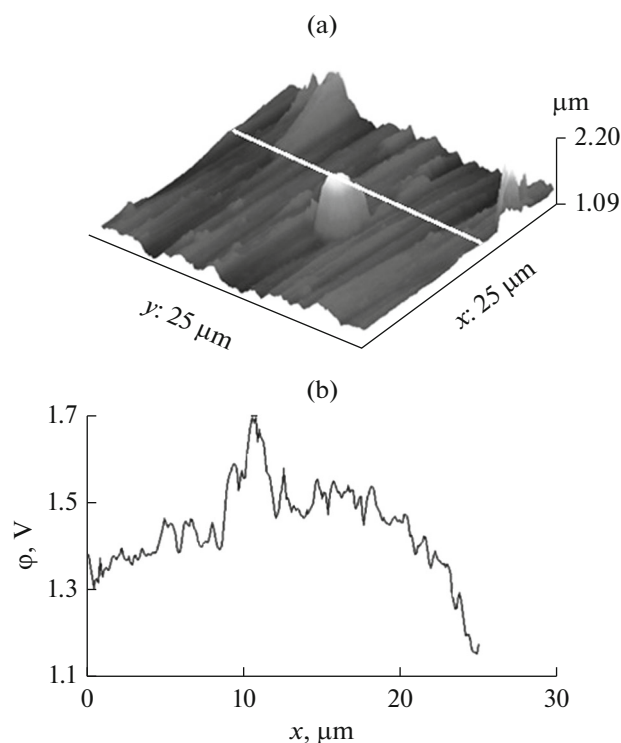
(a)

(b)

Fig. 1. Image of the RF-magnetron calcium-phosphate coating on a titanium substrate (a), the white line shows the scanning path; the distribution profile of the electric potential over the scanning surface (b).

The substrate holder is oriented at an angle of 45° to the light beam. Photostimulation of the samples was performed using a deuterium lamp with a power of 30 W radiating a continuous light spectrum with photon energies from 3.1 to 6.2 eV ($\pm 2\%$). The light beam was focused by a quartz lens on a grating monochromator for selecting the required wavelength and then, the light beam was focused on the sample, the diameter of the spot is no more than 1 mm. The secondary emission multiplier was used as a system for recording electron emission from the sample surface. The dark current from the electron detector is 0.1 pulses per second; therefore, the detector is capable of recording up to 105 pulses per second. The electron-detector diaphragm (diameter is 8 mm) is enough to identify a great number of electrons, what is more, it excludes foreign electrons. The current of emitted particles was measured by a secondary-emission multiplier working in the single-electron counting mode.

RESULTS AND DISCUSSION

The measured roughness by R_a was 0.7 μm on the substrate surface and 0.6 μm on the coating surface. It is known that coatings formed by RF-magnetron sputtering due to their small thickness repeat the substrate surface and fill also discontinuities in the form of sur-face pores, cavities and others that in some cases may result in a negligible increase in the roughness due to the small thickness of a coating [24]. We performed a similar study of the phase composition and surface morphology of calcium-phosphate coatings formed by HA target sputtering earlier in paper [25]. It was shown that a coating, represented mainly by $Ca_{10}(PO_4)_6(OH)_2$(hex) phase, is formed and its morphology is formed in the shape of hemispheres. The coatings are continuous and homogeneous, microdefects on the substrate surface without a coating were not found. The coating is electret because it bears an electric charge which is retained for a long time: the charge state is retained for at least six months. Measuring of the potential for a longer time was not performed.

A fragment of the AFM image of the coating surface, obtained from a scan region 25 × 25 μm (Fig. 1a), and a profile of the electric-potential distribution (Fig. 1b) along a line, obtained using the Calvin probe technique, are shown in Fig. 1. A fragment of the image, containing the structural unit at the center of the scan area, whose height was far above the average height of nearby units, was selected for better visualization of the results.

Figure 1a shows that the electric potential is distributed unequally on the surface, its maximum is localized near the peak structural unit. The maximum potential near this unit is 1.7 V, which exceeds the average potential along the potential scanning line, equal to 1.25 V. Also, it is seen from the distribution profile that the electric potential correlates with the surface roughness.

Electric potential distributions obtained using AFM are shown in Fig. 2. Calvin-probe method was used for the two-pass technique, scanning region being 50 × 50 μm. An average roughness, determined during scanning in this area, equals $R_a = 0.5$ μm. The results of measuring the contact-potential difference $\Delta\varphi$ (CPD) on the scanning line are presented in Fig. 2d. The measurements show that the distribution of the electric charge on the surface correlates with the surface topology; it is seen especially evident from the drastic transitions from the "peaks" to the "cavities". Moreover, a structural unit with a height of 1.5 μm, which has a high CPD equal to 1.2 V, is clearly seen in Figs. 2d and 2e.

During the investigation, multifold surface scanning of the samples with a coating was performed to determine the dependence of the average electric potential on the surface roughness by R_a. A significant linear correlation between the surface roughness of the substrate with the coating and the average electric potential was found (Pearson correlation coefficient $R = 0.74$ [26] when the critical parameter was equal to 0.54 (Fig. 3)). The average electric potential for surfaces with a larger average roughness is higher. Thus,
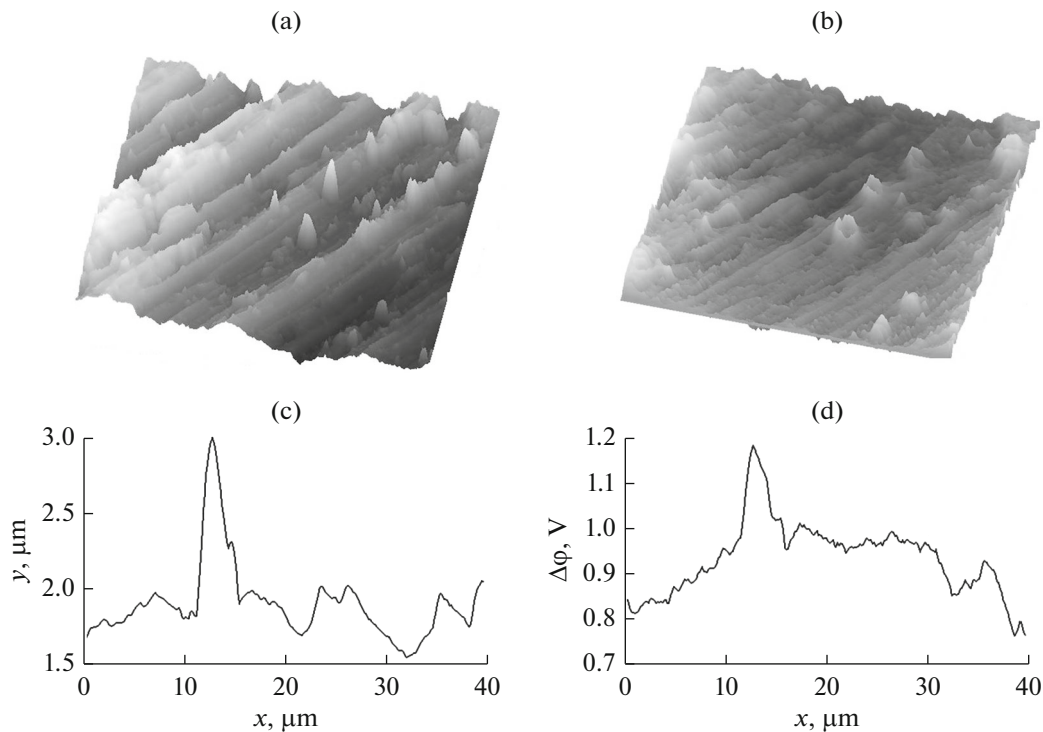
(a)

(b)

(c)

(d)

Fig. 2. Topography (a) and distributions of the contact-potential difference (CPD) over a surface (b), and topography profile (c) and CPD ($\Delta\varphi$, V) of a surface (d), formed on titanium by the RF-magnetron sputtering.

surfaces with an average roughness of $R_a = 67.5$ nm have an average electric potential $\varphi_{av} = 0.850 \pm 0.002$ V, and a surface with the average roughness $R_a = 196.6$ nm has the average electric potential $\varphi_{av} = 0.94 \pm 0.012$ V.

It is known that calcium-phosphate coatings are applied in medicine for osteointegration enhancement [1, 2]. The reason for the enhanced bonding between the coating and bone is the high adhesion of osteoblasts and osteoclasts to the calcium-phosphate coating. Enhanced adhesion is due to a set of reasons

Fig. 3. Dependence of the average electric potential φ_{av} on the roughness parameter R_a of a surface.

including the surface electric charge and its electric potential.

Figure 4 shows the spectra of the photoelectric emission current as a function of the photon energy from the metallic surface of the titanium sample without a coating and with a coating formed by RF-magnetron sputtering on a titanium substrate. According to measurements of the spectra, the electronic work function characterizing the surface-charge density was estimated.

In contrast to AFM with a Calvin probe, this type of measurement provides data on the work function at the millimeter scale, as the excitation-spot diameter of electrons from the sample surface is 2 mm. The electronic work function of the surface of titanium according to the measurements is 4.65 ± 0.05 V, which is in accordance with the tabulated data on the work function of the TiO_2 surface [27]. According to calculations, the values of the work function of the coating surface is 5.02 ± 0.05 eV, which is higher than from that of titanium. During measurements the correlations between the roughness and the electronic work function of a coating surface were not found, the work function of HA was equal to 5.02 ± 0.05 eV, which corresponds to data published by other research groups [21, 28].
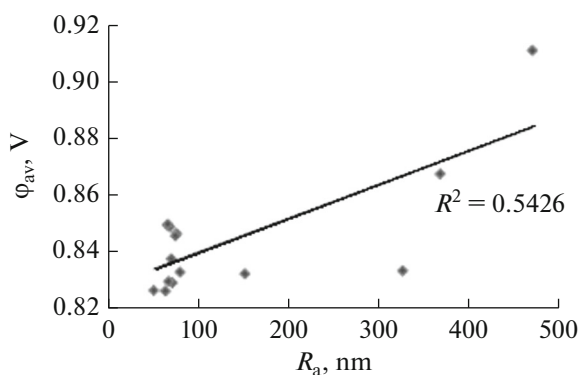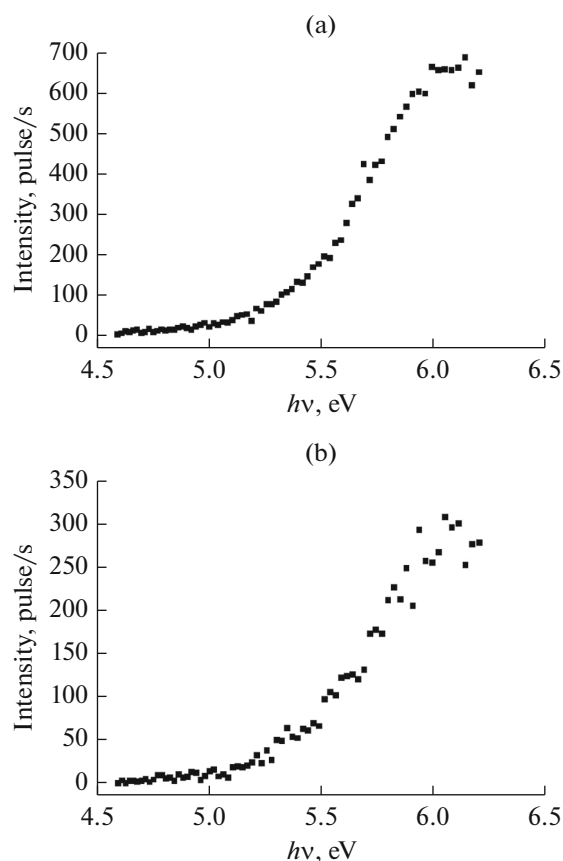
Fig. 4. Intensity of electron emission on the radiation energy from a titanium surface (a) and a calcium-phosphate coating, formed on titanium by RF-magnetron sputtering (b).

cient, the average electric potential was obtained for several random peaks located in different regions of the scanned image. The obtained dependence of the a coefficient on the electric potential, measured for the peaks of surface structural units is shown in Fig. 6.

For determination of the surface roughness affecting the potential slightly, measurements of the potentials and heights of corresponding coating surface points were performed with a surface scanning step in directions orthogonal to each other.

A 3D histogram was constructed (Fig. 7) in accordance with surface scanning by a Calvin probe with the scanning step $\Delta x = \Delta y = 5$ μm, where the X axis corresponds to the heights of surface points (h), the Y axis corresponds to the surface potential (φ) at these points, and $n = f(\varphi, h)$ designates the number of surface points possessing predetermined values of φ and h.

By analyzing the histogram form in the plane (φ, h) (Fig. 8, top view), we can select an area of elliptical shape, described by the equation:

$$\frac{h^2}{A^2} + \frac{\varphi^2}{B^2} = 1,$$

where A and B are the values of the semi-axes of an ellipse, equal to 0.23 μm and 0.06 V, respectively. Thus, the equation will be as follows:

$$\frac{h^2}{0.05} + \frac{\varphi^2}{0.36} = 1.$$

Within the ellipse, the histogram has a sharp maximum, localized at the point with coordinates ~0.25 μm and ~0.8 V.

Thus, a correlation between the surface potential and the heights of surface points (roughness) of the RF-magnetron calcium-phosphate coating is observed. The maximal number of coating surface points possess a potential, in the range 0.67−0.90 V, while the height of these points equals 77−326 nm, and the histogram has one sharp maximum.

For estimation of the relationship between the peak sharpness of the coating surface and the surface electric potential, approximation by a cuspidal function $f(x) = ax^2 + bx + c$ was performed, where coefficient a characterizes the peak sharpness. Figure 5 shows an example of applying this approach for describing one of the typical profiles. For calculation of the a coeffi-

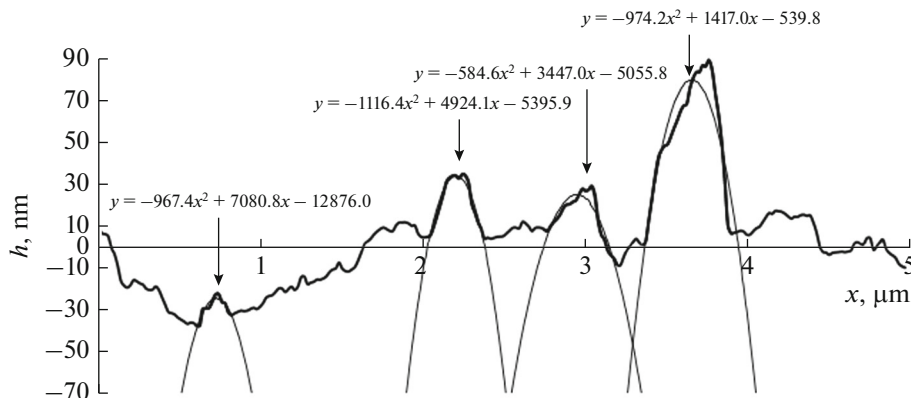**Fig. 5.** Surface profile of substrate with a coating, described by a cuspidal function, H—peak height, x—peak coordinate (μm).
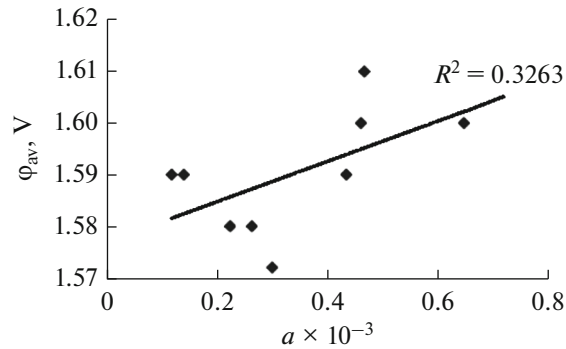
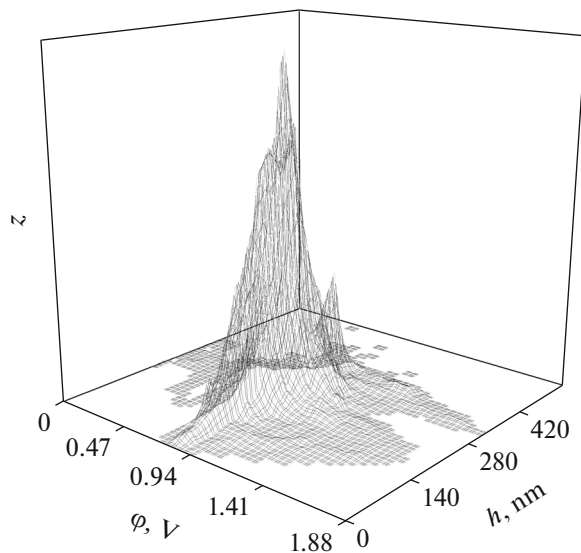**Fig. 6.** Dependence of the *a* coefficient on the average electric potential.

Fig. 7. Histogram of the distribution of surface points of the calcium-phosphate coating over the values of the potentials and heights.
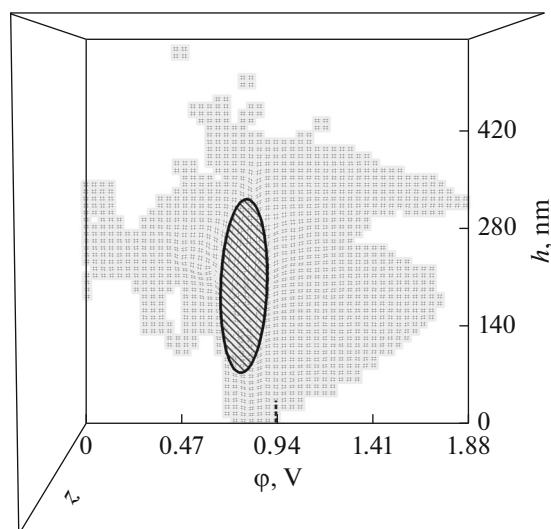

Fig. 8. Top view of a histogram of distribution of coating surface points by height and the corresponding potential with a selected area in the shape of ellipse, where the distribution maximum is localized.

CONCLUSION

A calcium-phosphate coating, obtained on substrates of "pure" titanium by the RF-magnetron sputtering of a HA solid-phase target, is electret, i.e., bears an electric charge. The electric-potential distribution on the coating surface has an inhomogeneous pattern: its maximum is localized near structural units (peaks) of the coating surface with higher peak sharpness. There is a correlation between the surface potential and surface roughness. The 3D histogram of the surface-point distribution over potentials and heights has a sharp maximum, localized at the point with the coordinates ~0.8 V and ~0.25 μm, respectively. Preliminary surface preparation with the creation of a relief with a point height in the range of 77−326 nm leads to a potential increase in the range 670−900 mV. The obtained electronic work function of the calcium-phosphate coating surface is higher than those from a surface without a coating (5.02 ± 0.05 and 4.65 ± 0.05, respectively). Higher work function values are accompanied by adhesion-effect enhancement of bone tissue cells to the coating surface in comparison to the titanium-substrate surface. Thus, implant osteointegration with a calcium-phosphate electret coating, introduced into bone tissue, is improved.

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Translated by E. Linnik