Investigation of Topography of the Surface and Distribution of Mechanical Properties Using Scanning Nanoindenter "NanoScan" of the Ca–P Coatings Deposited on Medical Implants by the High-Frequency Magnetron Sputtering Technique[1]

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Abstract – The paper presents the results of investigation of topography of the surface and distribution of mechanical properties of the thin biocompatible Ca–P coatings. Hydroxyapatite (HA) thin films were prepared by the rf-magnetron sputtering technique. The depositions were performed from pure HA target on Si and glassceramic substrates. The procedure of the deposition was following: working gas – Argon, power of radio-frequency generator – 290 W, frequency $\nu = 5.28$ MHz. The topography measurements and the measurement of maps of surface mechanical properties at the same surface area, hardness measurements (indentation and sclerometry tests) and elastic modulus measurements (using the unique spectroscopy technique) of the HA coatings were investigated by Scanning Nanoindenter "NanoScan". The thickness of the coatings was from 0.8 to 3 μm. An average surface roughness of coatings was 12–13 class.

1. Introduction

The thin-film coatings have a wide spectrum of the application in modern technologies. It is used at the production of the medical produces, in particular, for production of implants for the traumatology and the orthopaedy. The requirements to the quality and the physico-mechanical properties of the coatings such a responsible produces as implants, are very high. The elaboration of the methods of forming of a thin biocoatings, optimally combining bioactivity and mechanical strength, and also allowing to produce a precipitation on a substrate in the one cycle with a big use factor of calcium-phosphates is topical problem of the medical science of materials. To choose the methods to forming the coating and materials for production of the implants, is necessary to take into account, theirs application field. The calcium-phosphates coatings are interesting for reconstructive surgery. These coatings raise strength of cohesion of implant with bone tissue and increase a capability for processing of osteoinduction and osteoconduction.

Hydroxyapatite (HA) – $Ca_{10}(PO_4)_6(OH)_2$, which is the main chemical constituent of bone, is nowadays considered a useful biocompatible material. Unfortunately, HA is brittle and the prepared bone implants can provide poor mechanical performance. This drawback was overcome by the development of HA coatings on metals. This takes advantage of the bioactive behavior of the HA ceramic and preserves the mechanical characteristics of the metallic substrate. Metallic materials like Ti, Ti-alloys, alloys based on Co, Cr, Mo, and Ni, special stainless steels, are used as bone implants for many years and their mechanical properties are well known and understood. The experience showed that in the monolithic metallic prostheses, the biological response, especially in long time exploitation, was not satisfactory. The growth of osteoblast cells and their proliferation into the HA film enhanced in case of HA coated metallic implants. The release of metallic elements from the implant slows down or is even stopped by HA coating [1].

Different methods of HA coatings deposition on metallic, including titanic implantates, are exist. At present time, the most perspective methods of the deposition of coatings are the vacuum ion-plasma methods. It is caused, their environmental safely, high cleanest of the engineering procedures and quality of products. Also, it is common knowledge, in ionized or excited state, the atoms and molecules interact with each other better, doing process of deposition more effective. Magnetron sputtering is a frequently used technique to produce structures in form of thin films with good adherence, smoothness and density.

At the disposal of the authors is installation for deposition of the coatings in plasma of the rf-magnetron discharge and NanoScan measurement system for measurement of mechanical properties of surface of thin films.

So, the aim of present work is investigation of surface topography and distribution of mechanical properties using Scanning Nanoindenter "NanoScan" of the Ca–P coatings deposited on medical implants by rf-magnetron sputtering technique.

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2. Materials and methods

The target for sputtering was make from synthetic HA (stochiometric ratio Ca/P = 1.67) with dispersibility of the particles till 80 nm by the following procedure: pressing of the powder at pressure 70 MPa, annealing at the temperature 1100 °C for 1 h in air. An installation type 08RKNO-100T-005 with rf-magnetron source (5.28 MHz) was used to prepare calcium-phosphate coatings [2]. The following parameters were applied in the sputtering process: operation frequency of the rf-generator 5.28 MHz, working gas argon (0.5 Pa), incident power of the rf-generator 290 W.

The topography measurements and the measurement of maps of surface mechanical properties at the same surface area, hardness measurements (indentation and sclerometry tests) and elastic modulus measurements (using the unique spectroscopy technique) of the HA coatings were investigated by Scanning Nanoindenter “NanoScan”.

The main characteristic feature of NanoScan is the use of piezoresonance probe with high bending stiffness of the cantilever ($\approx 5 \cdot 10^4$ N/m). Use of the regime of resonance oscillation permits to perform checking of contact between the probe tip and the surface on two parameters: change of amplitude A and frequency F of the probe oscillations. This makes it possible to discriminate correspondingly viscous and elastic components of the tip-surface interaction, and distinguish an elastic surface and a viscous contamination layer on it, appearing inevitably in an open space, as well as to measure mechanical properties of surfaces. High bending stiffness of the cantilever permits to go through the viscous layer and contact the elastic surface, making an indentation [3].

For hardness measurements and elastic modulus measurements by Scanning Nanoindenter “NanoScan” the samples must have an average surface roughness 12–14 class. Therefore, the samples made from Si and glassceramic (14 class of roughness by R_z) were used as the substrates for Ca-P deposition.

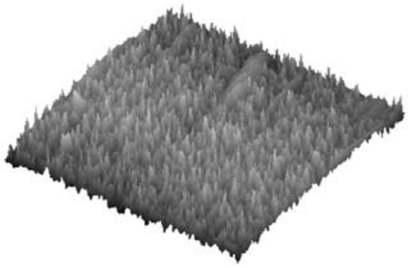
The thickness of the coatings was measured by the profilometer-profilograph “TALYSURF 5”, Taylor–Hobson and was not more 3 μm (Table I).

Table I. The thickness of the Ca–P coatings obtained by the rf-magnetron sputtering technique

Substrate	Time of the sputtering	Thickness, μm
Si	3 h 30 m	0.8
Si	4 h 30 m	1.2
Si	8 h	2.6–3

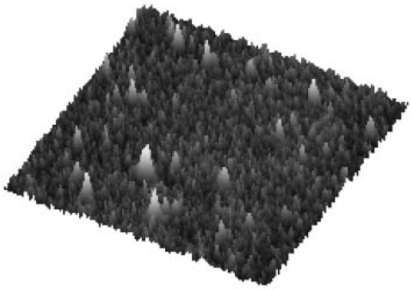
3. Topography of the surface

The Figures 1 and 2 present 3D-images of Ca–P coatings on the substrate Si and glassceramic. Topography of the surface of Ca–P coatings obtained by the rf-magnetron sputtering is rather smooth.



24.00 μm × 24.00 μm × 352.09 nm

Fig. 1. 3D-image of calcium phosphate coating, rf-magnetron sputtering for 30 minutes (R_a = 0.012 μm, R_z = 0.071 μm)



24.00 μm × 24.00 μm × 413.92 nm

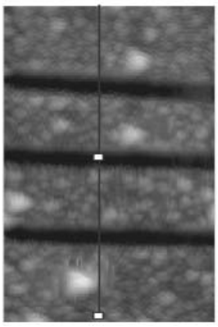
Fig. 2. 3D-image of calcium phosphate coating, rf-magnetron sputtering for 8 hours (R_a = 0.028 μm, R_z = 0.171 μm)

By the way, the roughness increases with increasing the time of deposition.

An average surface roughness of coatings was 12–13 class.

4. Nanohardness

Hardness measurements were done by sclerometry tests. In the mode of scanning probe microscope surface of the sample was studied, and the selected site with a minimum slope and roughness. Then, the scratches were done by needle-indenter on the selected site with varying load (up 2 to 30 mN). The scratching was done by sharp edge of the indenter forward. After that, this site was scanning again. By obtained image was determined the sizes of scratches, which allowed then receive data about nanohardness. Figure 3 shows the image of the scratches with loads 2 and 5 mN on the sample surface of the silicon (rf-magnetron sputtering, 2 h).



10.31 μm × 10.31 μm × 505.91 nm

Fig. 3. The scratches with load 5 mN on the sample surface of the silicon (rf-magnetron sputtering, 2 h)

Figure 4 presents a profile of these scratches. It should be noted that part of the total plastic deformation in case of sclerometry is more than in indentation tests [4]. The value of hardness is

$$H = \kappa P / b^2 , \tag{1}$$

where κ is the coefficient of the form of indentor; P is the load on indentor; b is the width of residual scratch.

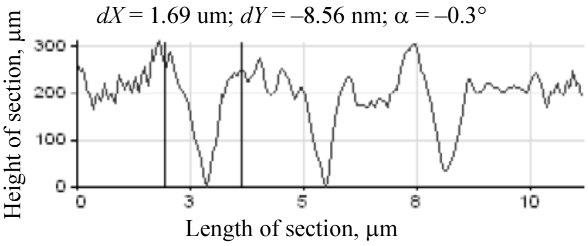


Fig. 4. Section of the scratches with loads 2 and 5 mN on the sample surface of the silicon (rf-magnetron sputtering, 2 h)

According to the paper [4], after the load removal, a depth of the scratch reduces as a result of the elastic recovery. However, the recovery of the width of the scratch is slightly. Thus, using of the sclerometry tests allows avoiding the mistakes caused by elastic recovery of the print after load removal that is particularly important to measure the hardness in nanoscale.

5. Elastic modulus

To determine the elasticity module by NanoScan measurement system is used analysis of the approach curves. On the approach curves is chosen a site of the elastic contact (between the probe touching the surface and the beginning of the plastic deformation). By estimations of authors [3], elastic contact corresponds with immersion of the indenter in the material only 5–15 nm. The area of contact is directly related to a depth immersion of the indenter.

Diameter of contact for "Nanoskan" is estimated [3] as 70–80 nm. Depth of immersion of indenter and size of the print of indenter limits the thickness of coating, whose properties can be measured by this method. The diameter of the contact area should be markedly less than the thickness of measuring film. Otherwise, the contribution of the substrate in the measured properties will exceed the contribution coverage. Consequently, the minimum thickness of the coatings, elasticity module which can be measured by the "Nanoskan" amounts to several hundred nanometers. In our case, the minimum thickness of coating was 0.8 microns (substrate – silicon, rf-magnetron sputtering 3 h 30 min). Physico-mechanical properties studied samples are presented in Table II.

Table II. Physico-mechanical properties of calcium-phosphate coatings measured by Scanning Nanoindenter "NanoScan"

Substrate	Parameters			
	H, GPa	E, GPa	R_a, μm	R_z, μm
Si 0.5 h	9 ± 2	80 ± 4	0.012	0.071
Si 2 h	7 ± 2	121 ± 1	0.033	0.475
Si 3.5 h	10 ± 3	109 ± 6	0.041	0.395
Si 4.5 h	5 ± 2	83 ± 5	0.048	0.207
Si 8 h	7 ± 2	127 ± 9	0.028	0.171

6. Conclusion

The surface topography and physico-mechanical properties of the calcium-phosphate coatings was investigated.

Presented with the using of the ASM "NanoScan" results are consistent with data obtained from standard Nanoindenter NHT CSM Instruments, where for HA coatings H = (9.2 ± 0.5) GPa and E = (111 ± 1) GPa.

The value of nanohardness H does not differ significantly, which allows talk about the homogeneity of coating by thickness.

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