Deposition of Biocompatible Calcium-Phosphate Coatings by High Power Ion Beam Ablation Plasma[1]

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Abstract – Biocompatible calcium phosphate (CaP) coatings are widely used in stomatology and traumatic surgery. This material is very appropriate for the medical areas, due to it provides connection hardness of metal implants with bone tissue. Different techniques of CaP coating deposition are used: sol-gel method, physical and electro chemical vapor deposition, laser evaporation and etc. All these technologies form the coatings which possess by different drawbacks: low crystallinity, secondary phase presence, low adhesion and mechanical characteristics, restricted time service of coatings and others. These drawbacks are explained by small range control of coating characteristics during deposition process. Method of coating deposition from ablation plasma, which is generated during interaction of CaP target and high-power pulsed ion beams (HPPIB), has very promising potential. Our researches show that HPPIB technique allows produce nano-sized, multilayer coatings of any kind of materials: metals, alloys and ceramics. Structure of such coatings is interchange of nano-sized layers, in turn growth and size of formed phases are restricted by thickness of depositing layer. As a results of these, the coating formed with nano-sized phases have low intrinsic tensions and possess good mechanical characteristics. The results of experimental research of mechanical and tribological characteristics of calcium phosphate coatings, deposited by means of HPPIB are presented in this work.

1. Introduction

Biocompatible calcium phosphate (CaP) coatings deposited on the metal substrates have an increasing growth of applications in orthopedic surgery and stomatology [1]. Hydroxyapatite (HAP) belong to group of calcium phosphate materials $Ca_{10}(PO_4)_6(OH)_2$ and it is widely used as original structure for medical material production. GAP is main part of bony matrix with stoichiometric ratio Ca/P = 1.67. This property provides high biocompatibility of GAP [2]. Many different technologies are used to deposit calcium phosphate coatings: RF magnetron sputtering [3, 4], laser deposition [5], physical vapour deposition [6], sol-gel method [7], electrophoresis [8] and others. Main drawbacks of all these methods are following: imbalance of main chemical elements, secondary phases presence [$Ca_4P_2O_9$, $Ca_3(PO_4)_2$], low crystallinity of coating (amorphous phase presence up to 100%), imperfective structure of coating and poor mechanical characteristics. All abovementioned drawbacks lead to deteriorated biocompatibility of calcium-phosphate coating to human tissues. Moreover, these disadvantages spoil performance requirements of implants and strongly restrict their application range. So conventional equilibrium plasma technologies cannot meet even present day requirements for medical coatings. We propose plasma technology which is based on essentially non-equilibrium plasma generated by high-power pulsed ion beam.

All these disadvantages are result of fact that current technologies do not allow changing deposition conditions in appropriate range. We propose deposition technique based on synthesis in ablation plasma, which is generated as result of interaction of high power pulsed ion beam with hydroxyapatite target. As following from our results [9, 10], this high power pulsed ion beam method (HPPIB method) has broad range of possibilities to produce coatings with specified properties. Requirements to these coatings are high enough so as it is planned to use then as material of human implants. Structure of these coatings is an alternation of nanosized layers. Growth and size of nanostructural phases is limited by thickness of deposited layer only. This leads to coating deposition which consists of nanosized phases with extremely small inner tensions. This allows increase a crack growth resistance of coatings and improve mechanical, tribological and biocompatible characteristics.

Adhesion of coatings deposited by HPPIB method is higher than in all other techniques. Laser vapor deposition is similar technology to HPPIB method. However, coefficient of beam energy using at the HPPIB method is much higher. It allows diminish power inputs (in 2–10 times) and increase coating deposition rate up to 0.01÷10 cm/s, which in $10–10^3$ higher than at the laser deposition.

[1] This work was supported by RFBR (Project No. 08-02-99020-р-офи).

In the article results of experimental research of mechanical and tribological characteristics of hydroxyapatite coatings $Ca_{10}(PO_4)_6(OH)_2$, which were deposited by means of HPPIB method are described and discussed.

2. Experimental setup

Deposition process was carried out on the TEMP-2 facility with following parameters: 70% H^+, 30% C^+ beam composition; 350 keV energy, 60 ns pulse duration, up to 5.5 J/cm^2 energy density, diode with cylindrical (linear) focusing, ~ 2.5×4.0 cm^2 beam size at a target.

The scheme of coating deposition is given in Fig. 1.

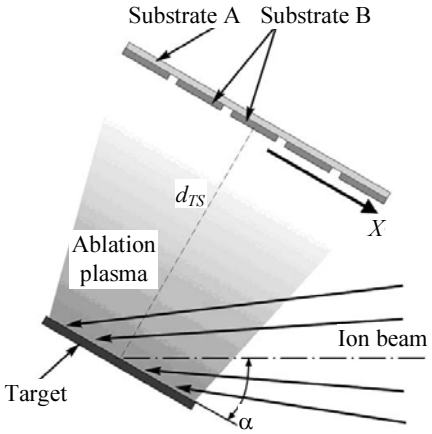

Fig. 1. Scheme of coating deposition. Substrate A – glass; substrate B – silicon; d_{TS} – target-substrate distance

Target was prepared by means of ceramic technology using powder of natural hydroxyapatite $Ca(PO_4)_6(OH)_2$ (with ratio Ca/P = 1.67), and particle dispersion up to 80 nm. This technology includes following steps: compressing of hydroxyapatite powder at the pressure 70 MPa, annealing of received GAP form at the 1100 °C during 1 h at the air atmosphere. Accelerated high-power pulsed ion beam comes to target, which is placed in vacuum chamber ($5 \cdot 10^{-6}$ Torr). Ablation plasma is generated as result of interaction of high power pulsed ion beam with target material and deposited on the substrate. Substrate is monocrystalline silicon. Coating thickness was determined by number of ion current pulses and was measured by Linnik interferometer. Elemental composition of coating was determined by Auger spectroscopy method. Nano-hardness and Young's modulus were measured by nano-hardness meter NHT-S-AX-00H at the diamond indenter loading 25 milli-Newtons. Oliver–Harra method was used to determine nano-hardness [11] in 1o points with next averaging. Adhesion was defined by using MST-SAX-0000 device, as critical load on diamond indenter when flaking of coating from substrate started and rapid increasing of acoustic emission signal took place. Microscopic imagine of scratch was used for adhesion diagnostic also. Friction coefficient and roughness were measure. Non-contact 3D profilometry method was used to obtain three-dimensional images of coating surface. Loading-unloading curves (Fig. 2) were used the elastic restoration by means of the equation

$$R(\%) = \frac{H_m - H_0}{H_m} \cdot 100\%, \qquad (1)$$

where H_m is the maximum depth of indenter implementation; H_0 is the depth of residual impress.

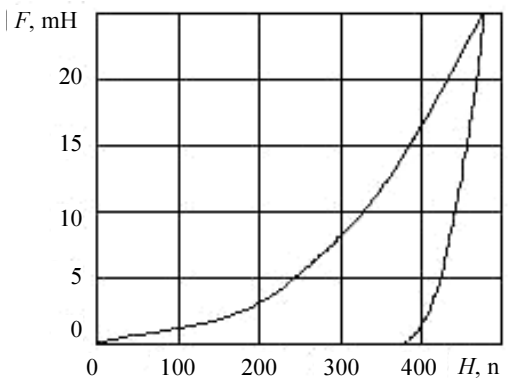

Fig. 2. Loading-unloading curves: H_m = 474.61 nm; H_0 = 384.42 nm

3. Results and discussions

Main characteristics of deposited coatings are given in Table 1.

Table 1. Characteristics of coatings

Thickness, nm	Nano-hardness, GPa	Young's modulus, GPa	Elastic recovery, %	Adhesion, F_{cr}, N	Constant of friction	Roughness, nm
148	3.95	129	22.6	0.23	0.1	137

During 40 pulses of ion current coating thickness reaches a value 1.48 microns, which corresponds to deposition speed 3.7 nm per pulse, that a little bit higher than typical deposition speed 1–2 nm per pulse for good quality of coating [9]. It is necessary to determine the term "deposition speed". Deposition speed is mean thickness of coating, which is deposited during one ion current pulse. Ratio of element concentrations Ca/P is about 1.56, which is very much approaching to conventional meaning for natural hydroxyapatite – 1.67.

As it is seen from Table 1, coating has high nano-hardness and high density. High enough Young's modulus value is evidence of high mechanical strength and good elastic properties of coatings. On the other hand, relatively low value of elastic recovery means that coating is plastic. Dependences of acoustic emis-

sion value (*1*) and friction coefficient (*2*) versus loading force on the diamond indenter (radius is 20 microns) are shown in the Fig. 3.

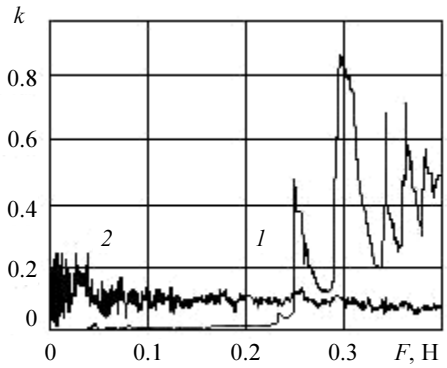

Fig. 3. Acoustic emission (*1*) and the friction constant (*2*) versus loading force

Critical load which corresponds to acoustic emission signal increasing is $F_{critical} = 0.23$ Newton. Friction coefficient meaning on the diamond indenter at the low loads is not too high and is about 0.1. At the same time, roughness (parameter $R_a = 137$ nm on the Fig. 4) is high enough from the separate stretched granules of column structure of coating (Fig. 5). It is could be explained by too fast deposition speed.

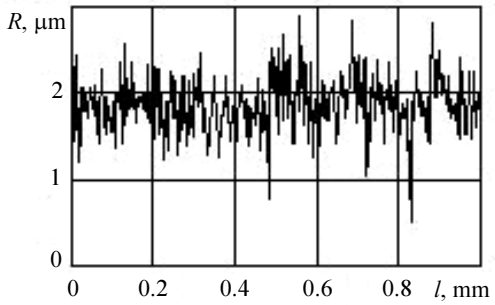

Fig. 4. Profile of the hydroxyapatite coating surface

4. Conclusion

Calcium-phosphate coatings deposited by ablation plasma, which, in turn, was generated as result of interaction of high-power pulsed ion beams with natural hydroxyapatite target have high nano-hardness, good elastic and plastic properties. Adhesion of coating is high enough. Coatings have low friction coefficient.

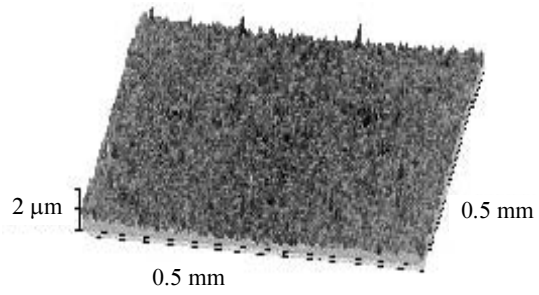

Fig. 5. 3D image of the hydroxyapatite coating surface

Roughness of coatings is high, which is connected with too fast deposition speed. Mechanical and tribological characteristics of deposited coatings allow to consider an ablation plasma of high power pulsed ion beams as very promising methods of biocompatible calcium-phosphate coatings production for reconstructive surgery of bony tissues.

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