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Adhesion of composite carbon/hydroxyapatite coatings on AISI 316L medical steel

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Abstract

In this paper are contains the results of studies concerning the problems associated with increased of hydroxyapatite (HAp) adhesion, manufactured by using Pulse Laser Deposition (PLD) method, to the austenitic steel (AISI 316L) through the coating of carbon interlayer on it. Carbon coating was deposited by Radio Frequency Plasma Assisted Chemical Vapour Deposition (RF PACVD) method.
Test results unequivocally showed that the intermediate carbon layer in a determined manner increase the adhesion of hydroxyapatite to the metallic substrate.
Obtained results give rise to deal with issues of manufacturing composite bilayer – carbon film/HAp – on ready implants, casted from austenitic cast steel by lost-wax process method as well as in gypsum forms.

Keywords: Hydroxyapatite, Carbon coatings, Adhesion, Medical steel

1. Introduction

Specific properties of austenitic steel such as: good corrosion resistance in different environments, good strength parameters, simple plastic working and heat treatment as well as signi-ficantly lower price from titanium and cobalt alloys provides for its wide application in the manufacture of short-term medical implants (ex. marrow bone pins). Use of this steel for long-term implants (ex. hip-joint endoprothesis) is prac-tically impossible because of its toxic effects on the human body. The ability to improve the unsatisfactory properties of mentioned steel, as a material predicted for long-term implants, is still one of the ma-jor challenge of engineering surfaces. Literature data confirm the possibility of modifying the surface of medical steel, so that its toxic effects on the nature of the human body significantly reduce [1÷3, 6÷10, 13, 18]. Such possibility creates manufacturing of carbon/hydroxyapatite bilayer on aus-tenitic steel surface. Carbon layers used in medicine are very interested material for the sake of their biological and mechanical qualities. Such co-verings are characterized by high biocompability degree and ideal bioinertness which result from no immunological replay of organism to implant with carbon layer. They also raise corrosion resistance of metallic implant and create effective barrier for metal ions preventing from its contact with human tissue [1]. Biocomability of metallic im-plants can be increased significantly by thin HAp layer deposited on its surface. Hydroxyapatite (HAp) is a ortho-phosphate of calcium with Ca/P molar ratio equal 1,667 and containing hydroxide (OH^-) groups. Chemical composition of HAp $Ca_{10}(PO_4)_6(OH)_2$ in recalculate on oxygens is as follows [64]: CaO - 55,8 % mas.; P_20_5 - 42,4 % mas.; H_20 - 1,8 % mas. This material is characterized by the chemical and phases composition similar to the composition of bone tissue (table 1). In table 2 compares the mechanical properties of HAp, bone and tooth enamel [11].

Table1.
Comparison of tissue containing calcium in adult humans [14]

Composition	Enamel	Dentin	Bone	HAp
Calcium (% weight)	36,5	35,1	34,8	39,6
Phosphorus (% weight)	17,7	16,9	15,2	18,5
Ca/P (molar ratio)	1,63	1,61	1,71	1,67

Table 2.
Mechanical properties of HAp, bone, tooth enamel

Biomaterial	Compression strenght R_c [MPa]	Bending strenght R_g [MPa]	Ten sile strenght R_z [MPa]	Young modulus E [GPa]	Fracture toughness K_{1c} [MPa*m1/2]
HAp bioceramic	509-917	113-195	38-48	88-100	0,69-1,16
Firm bone, cortical	89-164	130-180	89-114	ok. 16	2,2-4,6
Tooth enamel	270-384	-	10	-	-

Hydroxyapatite ceramic is biological active and indicate the highest biotolerance among all kinds of bioceramics therefore hydroxyapatites are easily resorbable in the human body. HAp coatings are used to promote osteoconductive bonding of metallic implants with bone. Slowly dissolving HAp coat act in addition function of biological barrier between metallic surface and bone [5, 14-17, 19]. Synthetic HAp in the environment of body fluids may be subject to resorbtion. Undergoing of resorbtion, HAp implant is a structural timber for the reconstructing bone tissue because elements included in the implant are penetrating to the tissue structure.

Currently, intensive work on the improvement of adhesion of HAp coatings to the metallic substrate are carried out by manufacture of interlayer between metal-HAp [21, 4, 6-10, 12, 20]. Greatest hope for improving the properties of mentioned HAp layers is associated with appliance of sol-gel and PLD methods.

An interesting solution that improves the HAp layer adhesion to the metallic substrate may apply of the carbon interlayer, what at the same time reduce releasing of metal ions into the human tissue. Connection of the advantages of both methods allow to develop a new technology of materials manufacturing, predicted for long-term implants made of medical steel what is the aim purpose of this work.

It was assumed that the newly manufactured composite, predicted for use on implants, should possess following properties:

- improve biocompability of implant,
- improve adhesion of HAp coating to the substrate,
- prevent human organism from metal ions (after dissolving the bioactive HAp on the surface of the implant remains neutral layer of carbon).

2. Research methodology

Material used for investigation was medical steel – AISI 316L after heat treatment which chemical composition was determined by X-ray spectroscopy and presented in table 3 and microstructure in figure 1. The specified chemical composition correspond to the standard ISO 4967-19769E0.

Carbon layer, with an average thickness 120nm, was fabricated by RF PACVD method. The essence of this method is to excite plasma in methane with nitrogen or other hydrocarbons with nitrogen in an RF electric field at relatively high gas pressure among (20 – 400Pa). General view and scheme of carbon coatings apparatus was presented in figure 2 below.

Table 3.
Chemical composition of sample made of AISI 316L

Chemical composition [%]								
C_{max}	Si_{max}	Mn_{max}	P_{max}	S_{max}	Cr	Ni	Mo	Fe
0.022	0.583	1.669.	0.021	0.022	16.48	13.38	2.49	reszta

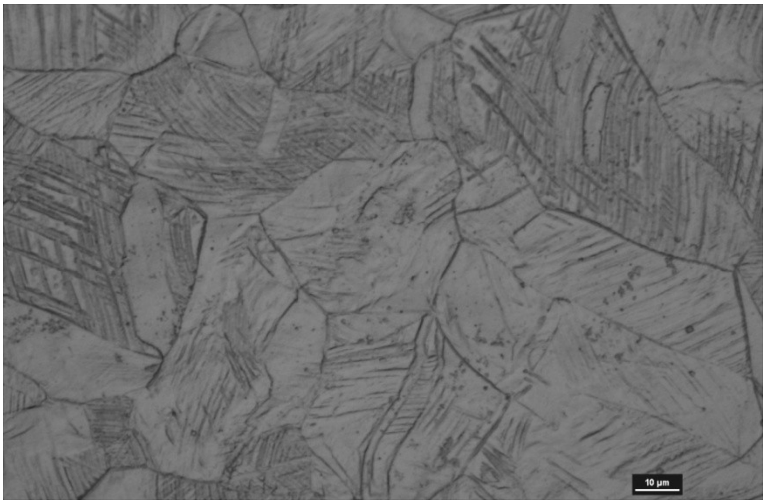


Fig. 1. AISI 316L microstructure after supersaturation (austenite with twins)

a)

b)

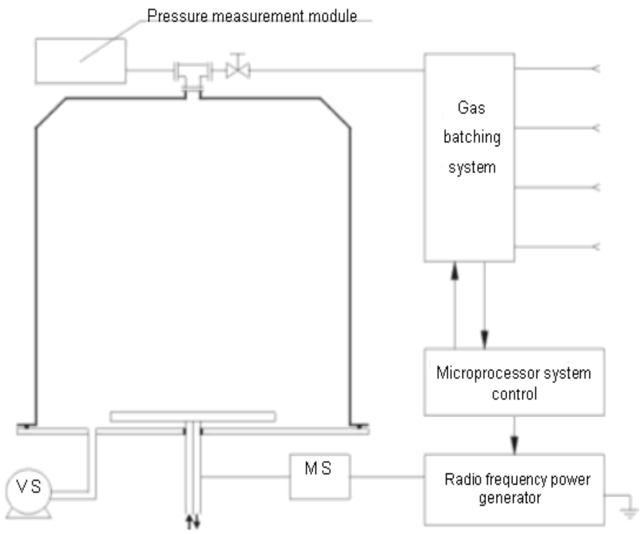


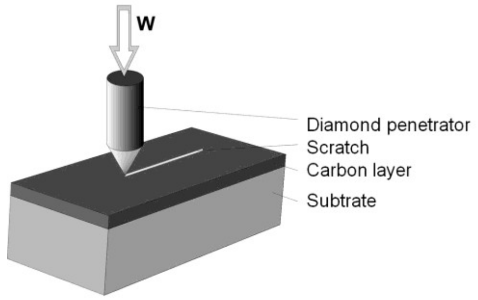
Fig. 2. General view (a) and scheme (b) of carbon coatings apparatus by RF PACVD method

Coating process consist of three stages:

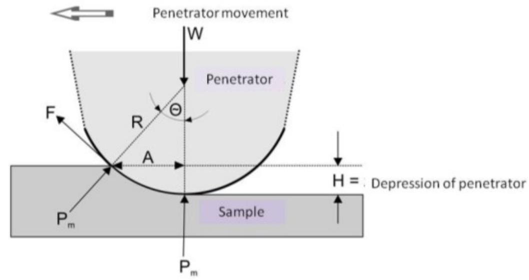
- heating of the sample till 550°C temperature during 15 minutes and potential of 1200V,
- carbon layer deposition during 10 minutes and potential of 900V,
- oxygen termination during 14 minutes

Investigations of adhesion of carbon layers to the substrate were carried out on F-MY MTS Instruments Nano G-200 nano indenter by scratch test method. This method consist in horizontal movement of penetrator ended by diamond cone - vertical angle 87,7°C; radius of the cone 0,91µm – pressing down by axial force to the sample surface with fabricated coating and changing in terms of 0,1÷40mN for measuring length from 0÷500nm (1mN/80nm). Initial load for to designate the initial profile was 0,1mN. Shift speed of penetrator was equal 10µm/sec. (fig. 3). Evaluation of adhesion carry out on the basis of observation in changes of the friction coefficient and then convert by the formula (1) presented below [166].

a)



b)



$$F \equiv P_m \cdot \tan \Theta = \frac{W}{\pi A^2} \cdot \frac{A}{\sqrt{R^2 - A^2}}$$ W – load (1)

c)

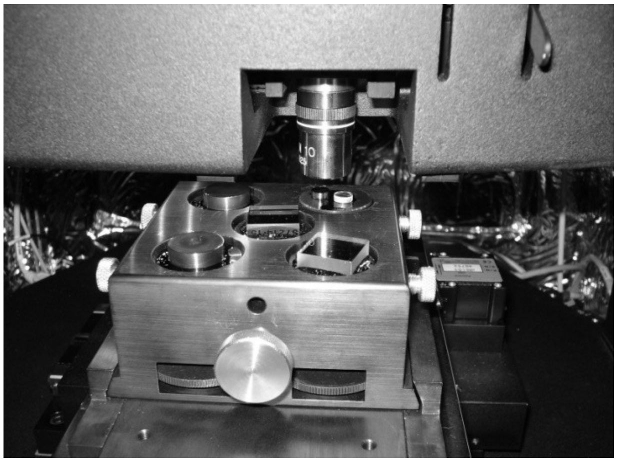


Fig. 3. The principle of layer adhesion measurement by scratch test method on nanoindenter device: scheme (a), way of stresses determine needed for breach of layer (b), view of measurement table (c)

The study was conducted on randomly selected sample covered by carbon layer. On performed sample 5 measurements were made (fig. 4).

As result from figure 4 rapid change in friction coefficient occurred between 70÷100 mN loads, which means in recalculate according to the formula (1) determines the average carbon layer adhesion on 30,5 GPa. This points to the typical diffusive nature of the connection with the ground steel of carbon layer. To confirm this hypothesis, addition investigations on X-ray analyzer, Siemens D-500 Co., with use of characteristic radiation Co K_{α} were carried out. The study was conducted using steps method – $\Delta 2\theta = 0{,}05$deg during counting time – 4 seconds. Current electron beam in the X-ray lamp was 40 mA, voltage 30 kV. Diffraction peaks identification were made using the X-RAYAN software. Results were shown in (fig.5).
From figure 5 results that after carbon layer deposition process on steel substrate, made of AISI 316L steel, peak comes from austenite divide in two towards growth of lattice parameter. Measured microhardness just below carbon film was at an average 450HV. It is significantly higher than in AISI 316L steel core (average 315HV). This provides that manufactured, by RF PACVD method, carbon film possess diffusive nature of the connection with the ground steel.

3. Manufacture of HAp coatings by PLD method

HAP + $CaCO_3$ target was used for laser ablation method. An excimer laser system type ArF (λ=193nm) operating at a pulse duration of 15÷20ns and pulse frequency of 20Hz was used (fig. 6). The films were deposited at the temperature of 450°C.

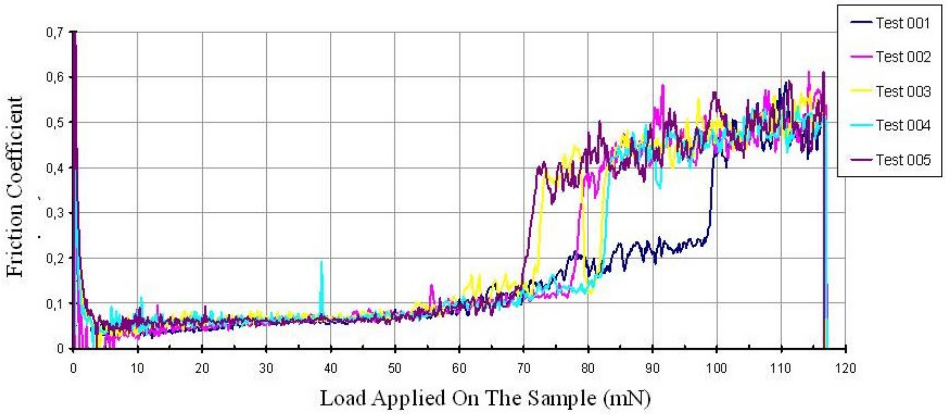


Fig. 4. Results of carbon coatings adhesion to the AISI 316L substrate

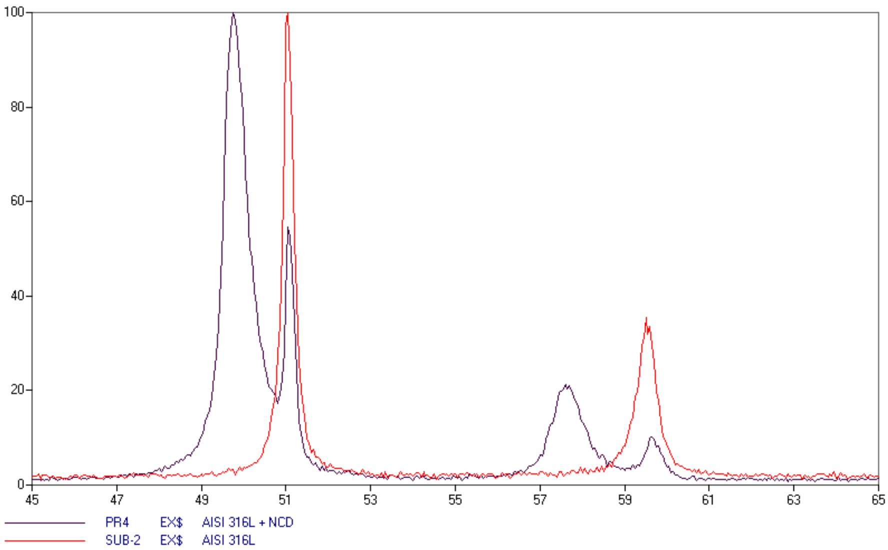


Fig. 5. Diffraction pattern of AISI 316L steel before and after carbon layer deposition

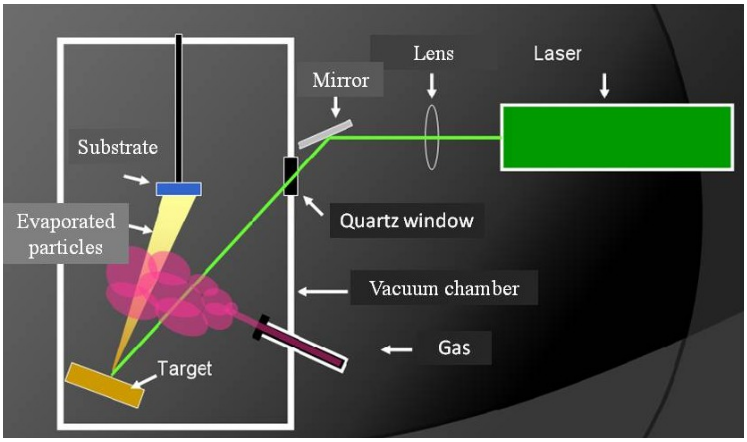
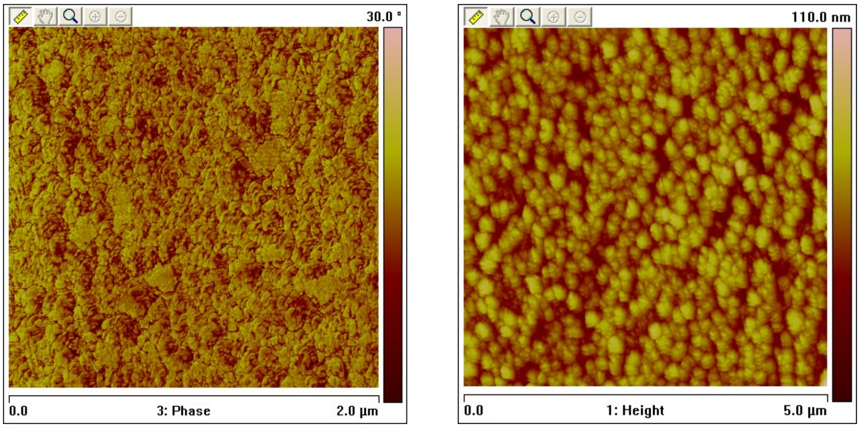


Fig .6. An excimer laser system for HAp deposition

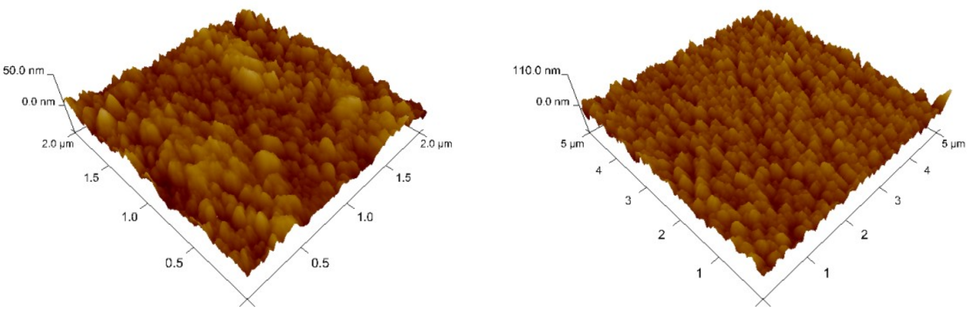
Due to the fact that during HAp manufacture process, by PLD method, the damage of the carbon layer may exist caused by laser beam, decided to create hydroxyapatite with thickness no more than 500nm to minimize the impact time of laser beam on the carbon layer.

Topography investigations of as fabricated coatings were carried out by using AFM (Atomic Force Microscope) method of Vecco Multimode with NanoScoper controller Company. AFM structural analysis of the HAp coating, with deposited carbon film as an interface, clearly demonstrate its homogenity, good adhesion to the surface and lack of cracks. AFM images, of as-fabricated layers, indicate that C/HAp coatings are continuous and coherent. Roughness of surface layer was define by Ra parameter (fig.7).

a)



b)



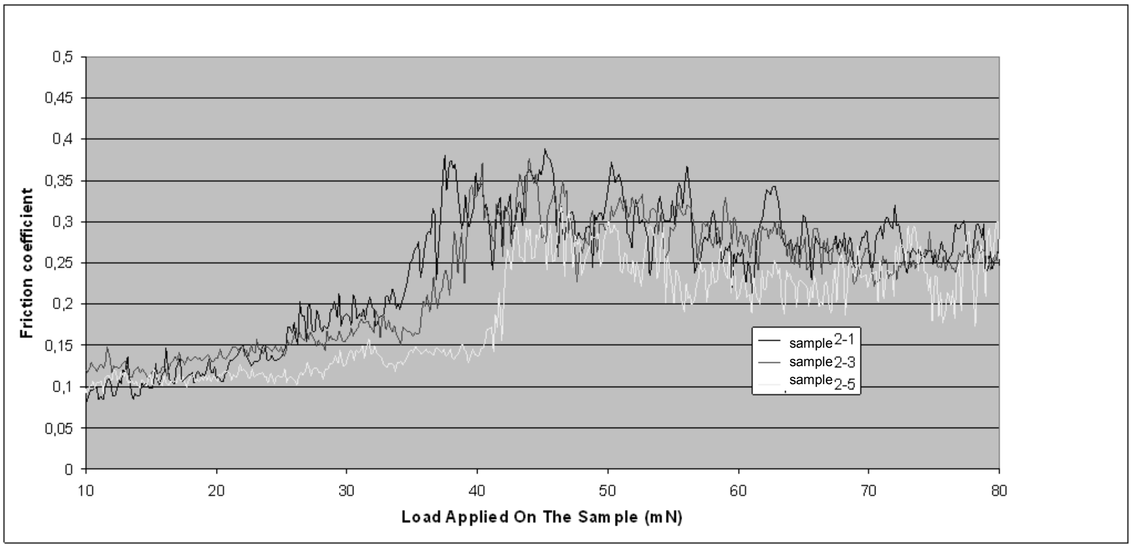
Ra = 13.70 nm

Fig. 7. AFM image of the C/HAp coatings deposited by PLD method

Adhesion investigations of as fabricated HAp layers carried out in a similar way as in the case of carbon layer. The study was conducted on randomly selected samples, three measurements per each. Results were presented in figure 8.

As result from figure (8a) rapid change in friction coefficient occurred between 30 ÷ 40 mN loads. Taking into consideration the average power 35mN set of adhesion by formula (1) on 22,3GPa. Significantly higher adhesion to the surface is characterize by HAp coating deposited on mentioned steel with carbon interlayer (fig.8b). It shows the average adhesion of 38,3GPa. Characteristic is that in the chart occurs second “change” of friction coefficient in range of 70÷80mN. This demonstrates the rupture of the carbon layer with the steel substrate simultaneously the lack of diffusion of connection between hydroxyapatite and carbon layer.

a)



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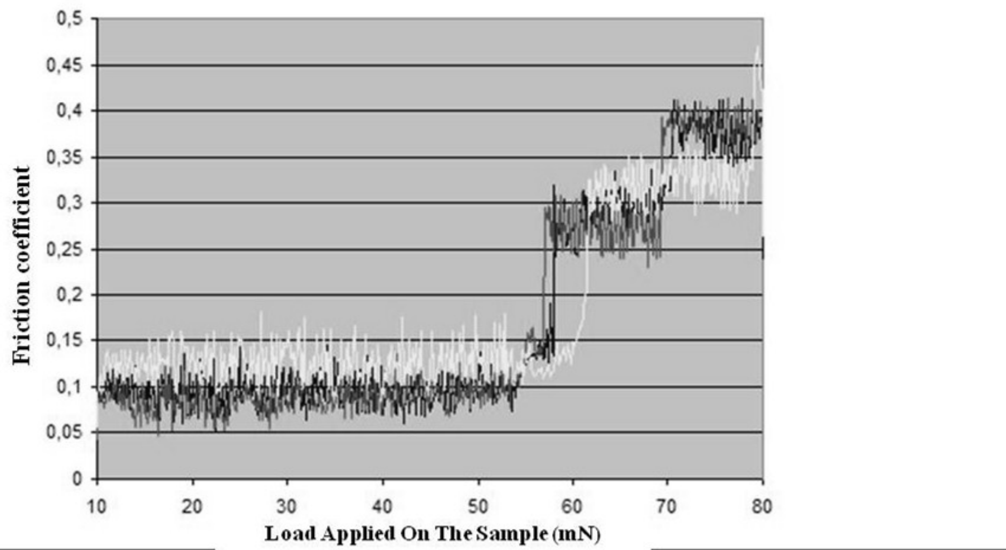

Fig. 8. Results of HAp adhesion to the AISI 316L substrate: without carbon film (a), with carbon film (b)

4. Conclusions

Deposited on AISI 316L steel by RF PACVD method carbon layer possess average thickness – 120nm. Its characterized by an uniform and compact structure with an average roughness – 5nm. Adhesion of the carbon film to the metallic substrate possess diffusion character. It is testified by nanoindenter examination and X-ray diffraction analysis. An average adhesion value of carbon layer to the metallic substrate is 30,5GPa.

Manufactured by PLD method, with an average thickness 500nm, HAp layer possess undersized and high homogeneus nanocrystalline structure consisted of clusters in diameter of tens nanometers and average roughness – 13,7nm.

Adhesion of hydroxyapatite layer, deposited directly on metallic substrate is almost twice lower (equals 22,3GPa) than in case of composite layer – carbon film/HAp (equals 38,3GPa). Characteristic is that HAp layer is not diffusion bounded with carbon layer and during higher stresses comes to their separation.

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