THE MODIFICATION OF POLYTETRAFLUOROETHYLENE SURFACE USING HYDROXYAPATITE COATING DEPOSITED BY RF-MAGNETRON METHOD

T.S. Pryamushko, I.Yu. Grubova, R.O. Banin
Scientific Supervisor: Dr. R.A. Surmenev
Linguistic Advisor: PhD. N.V. Demianenko
Tomsk Polytechnic University, 634050, Russia, Tomsk, Lenin str., 30
E-mail: tatyana.pryamushko@mail.ru

The ossteointegration rate of the polytetrafluoroethylene (PTFE) dental implants is related to their composition and properties of surface. Osteoconductive calcium phosphate coatings promote bone healing and apposition, leading to the rapid biological fixation of implants. The deposition of the hydroxyapatite (HA) coating on the PTFE surface by the RF magnetron sputtering method and the influence of this modification on the wettability, and physicochemical properties are presented in the present work.

Nowadays polymers are widely used in many industries. Polymers have high resistance to abrasion, that enables a high withstand load even in corrosive environments. These characteristics of polymer materials make them attractive to use in certain conditions. One of the most successful polymers used for implants is polytetrafluoroethylene (PTFE) (-C2F4-)n. This material is non-toxic, chemically resistant and has a high biocompatibility with the human body [1-2]. However, PTFE is bioinertness and it weakly affects bone growth in vivo, which is rather important in the initial postoperative period. In order to enhance the rate of implant osseointegration, surface modification was made by applying a thin coating based on hydroxyapatite (HA). This coating has bioactive properties: chemical composition of HA on 90% similar to the composition of human bone. Coatings were formed by high-frequency (rf) magnetron sputtering. RF Magnetron sputtering allows obtaining thin coatings with high adhesion and controlled stoichiometric ratio of elements in the deposited coating.

The aim of this work was the surface modification of PTFE due to using RF magnetron sputtering of HA coating; study of the surface modification effect on wetting angle and surface free energy (SFE) of PTFE .

The starting material was porous PTFE (20x20x1 mm^3) of "Экофлон" which is used to replace bone defects and orbit. This material is chemically inert, clinically tested and already used in medicine.

HA powder – $Ca_{10}(PO_4)_6(NO)_2$, was obtained for the target due to mechanochemical method. Target for sputtering (Ø220 mm, thickness 10 mm) was prepared by ceramic technology: powder pressing was made at a pressure of about 70 MPa, and then annealing at a temperature of 1100°C for 1 hour in air was used. HA coating deposition was carried out in different regimes at a working pressure of 0.4 Pa and a grounded substrate holder (GS) using fully automated installation 08PHO-100T-005 RF-magnetron source (5.28 MHz) (Table 1).

The investigation of wettability and SFE was carried out by EASYDROP equipment (KRUSS) with software DSA1.

IR-spectra of the initial and modified samples were recorded on a Nicolet 5700 firm Thermo Electron Corporation (USA), which allows obtaining absorption spectra, reflection and transmission of molecules in the

infrared spectral region (4000-400cm-1). The results were obtained in the Scientific-Analytical Center of TPU.

Table1.

Labeling of the samples

Processing mode	Lable
The unmodified material	PTFE_1
500W; 120 min	PTFE_5_2_HA
300W; 120 min	PTFE _3_2_HA
300W; 240 min	PTFE _3_4_HA
300W; 360 min	PTFE _3_6_HA

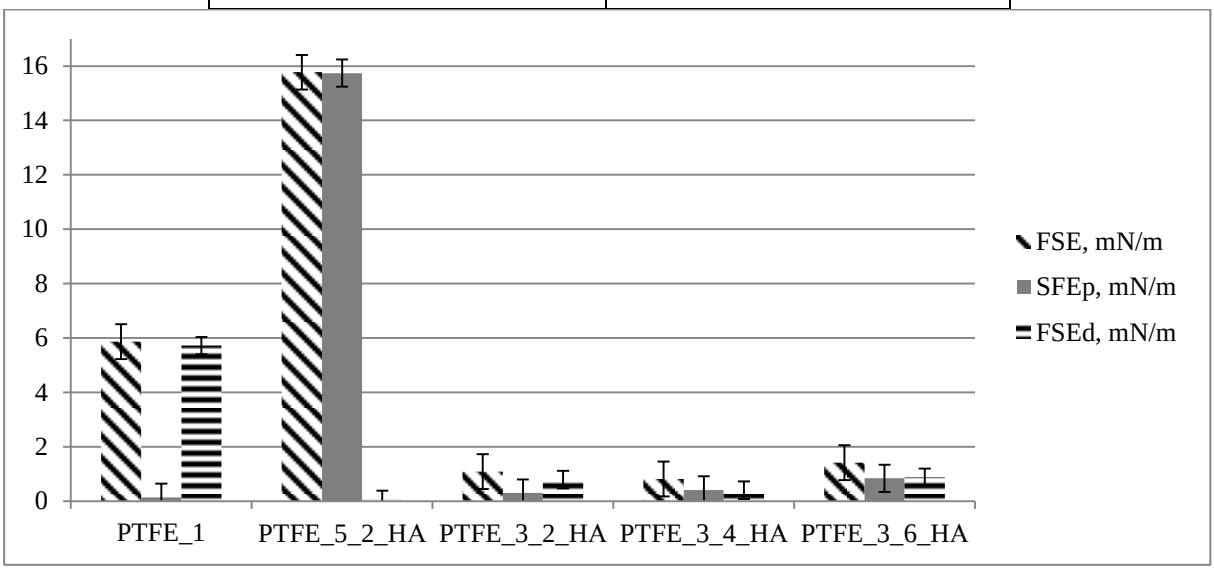

Fig.1. Values of surface free energy of the initial and modified samples

After PTFE modification by HA coating sputtering, sample surface became more hydrophobic in the case of treatment at 300W power for 4 during 6 hours: water contact angle increased on 5-6° (from 139,23° to 144,16° for PTFE_3_4_HA and to 144,53° for PTFE_3_4_HA), SFE data of the samples decreased in 6-times (from 5.86 mN/m to 0.81 mN/m and for PTFE_3_4_HA to 1.41 mN/m for PTFE_3_6_HA), the polar and dispersive components of it are equal for both samples. However, the PTFE_5_2_HA sample has shown more hydrophilic properties: deionized water contact angle of surface decreased on 35,3° compared with the unmodified material and equal to 103,93°. Moreover the SFE of PTFE_5_2_HAsample increased in 3 times (from 5.86 mN/m to 15.77 mN/m) due to its polar component (Figure 1).

Using the contact angle values two curve of dependence between angle and treatment power, angle and treatment time were plotted. Figure 2a represents the dependency of the contact angle and the treatmenttime for the power of 300W - increase in time led to growth of the wetting angle from 132° to 143°, this fact indicates the surface hydrophobicity.

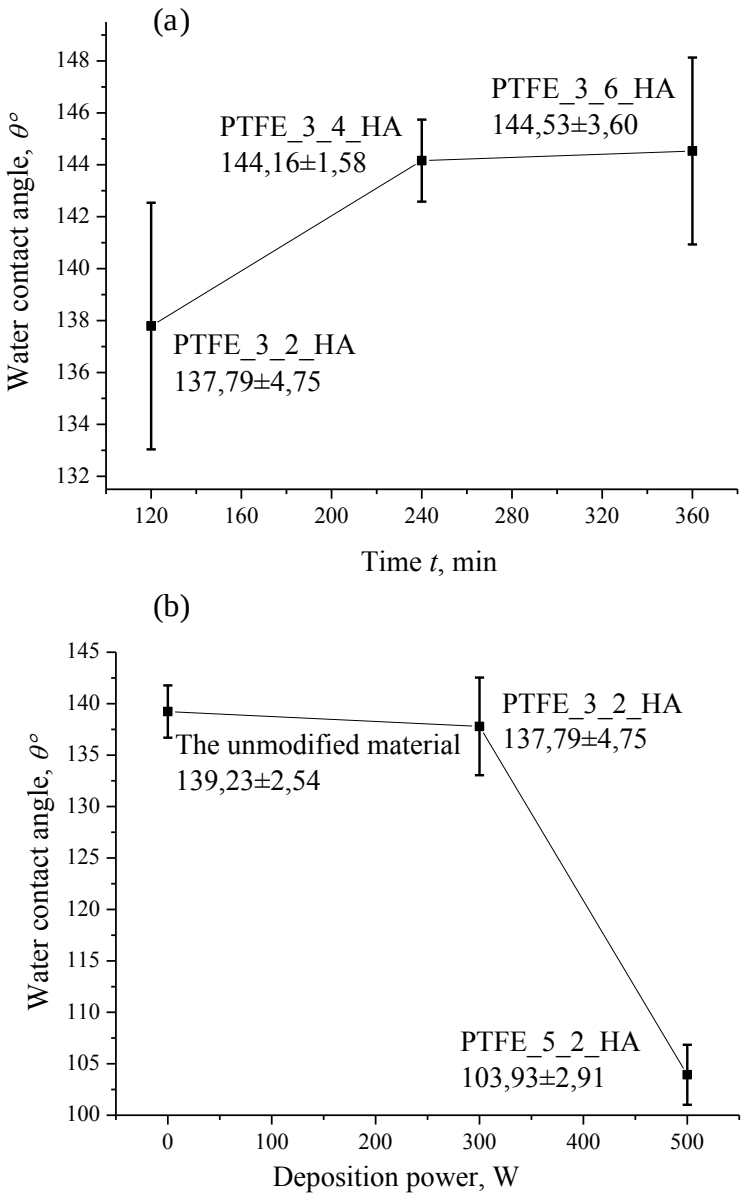

Fig.2. Graphics, depending on the contact angle: a) the time for sample processing power of 300 W and b) the processing power of the samples for time 120 min.

Figure 2b shows the dependence between the contact angle water and depositionpower - the powerincreasing led to the decreasing of the contact angle from 139° to 104°. The highestdecrease of contact angle (on 35,3°) was observed for the sample treated at a power of 500 W for 2 hours. Sample modified at 300 W for 2 hours almost did not change the value of the contact angle (from 139,23 ° to 137,79 °).

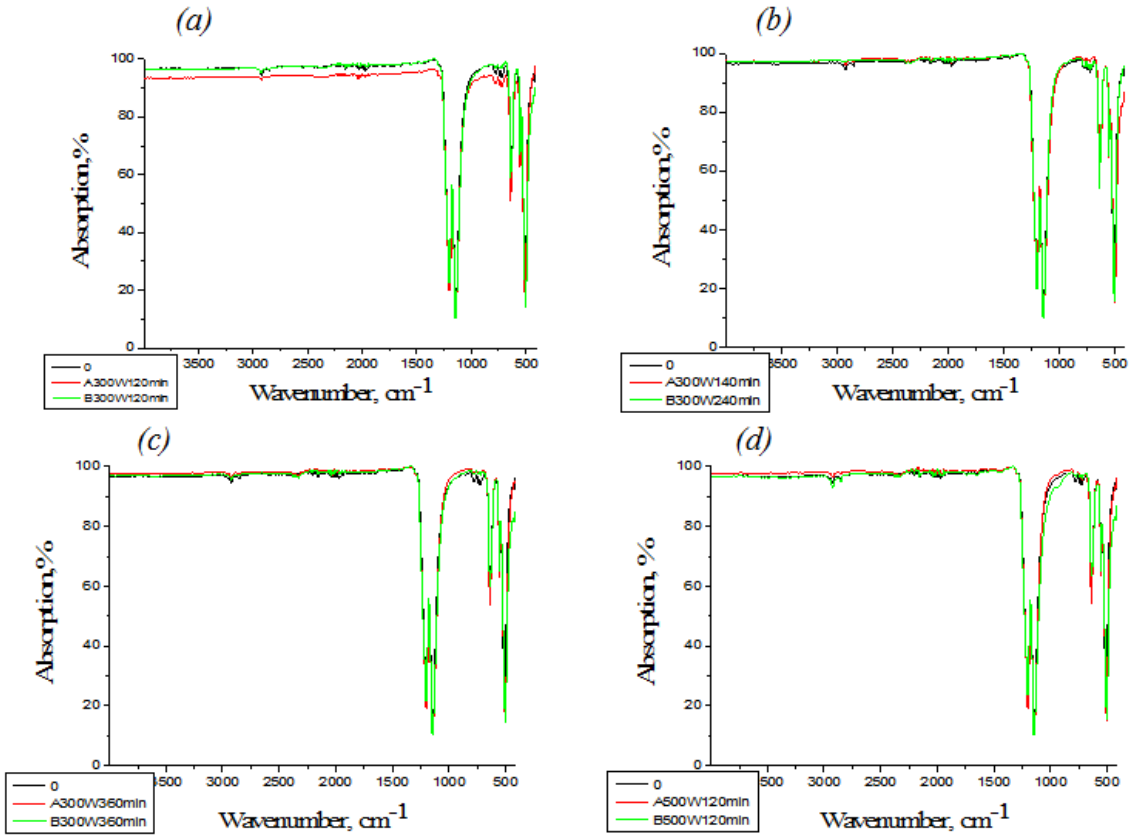

Fig.3. IR spectra of PTFE samples modified in different regimes: a - PTFE _3_2_HA; b - PTFE _3_4_H*A*; c - PTFE _3_6_H*A*; d - PTFE _5_2_H*A*.0 – initial samples, the red line A is uncoated side of modified sample, the green line B is coated side of modified sample.

Fig. 3 shows the most intense bands relate to the stretching vibrations of CF_2 (1200 and 1144 cm^{-1}) and the vibration ν (SS) in the form of inflection at ~ 1233 cm^{-1}. Rolling oscillations γω (CF_2) appeared at 638 cm^{-1}. The bands at 552 and 505 cm^{-1} characterized the deformation of pendulum oscillations CF_2-groups.

Investigation of PTFE surface images after deposition HA coating showed that molecular composition of the surface was not significantly changed, the spectral bands of the typical oscillations of the main structural fragments HA: RO_4^{3-} orthophosphoric groups at 570 cm^{-1}, 601 cm^{-1} and 1031 cm^{-1} was not detected (Fig. 3). The spraying process should lead to partial loss of the OH groups at 631 and 3571 cm^{-1}, which is also not found for all deposition conditions [5].

Thus, the influence of PTFE surface modification using different power and time due to the deposition on final wettability was studied. Analysis of the data has led to the conclusion that to make the surface of PTFE more hydrophilic by RF magnetron sputtering of the HA coating it is necessary to vary the output value of power near 500 W. Moreover, the time of the treatment have to be reduced.

The study was supported by a grant and scholarship of the President of the Russian Federation SP-

6664.2013.4 and MK-485.2014.8, the Russian Foundation for Basic Research (13-08-98082, 14-08-31027 and lightning).

REFERENCES

1. Biomaterials science: an introduction to materials in medicine. 2nd edition / ed. by B.D. Ratner, A.S. Hoffman, F.J. Schoen, J.E. Lemons. San Diego: Elsevier Academic Press, 2004. – 851 p.;
2. Rebinder P.A., Vlodavets I.N., Physicochemical mechanics of porous and fibrous particulate structures. - Riga, 1967. 5 - 40;
3. Shtansky D.V., Bashkova I.A., EA Levashov etc. Multifunctional nanostructured coatings for implants, working under load // Reports of the Academy of Sciences. - 2005. V. 404. - № 2. -. 1-4;
4. Poncin-Epaillard F., Legeay G.. Surface Engineered Polymeric Biomaterials with Improved Biocontact Properties. Journal ofBiomaterials Science Polymer Edition, 2003. – V.14, 1005 p.;
5. M.A. Surmeneva, RA Surmenev, IA Hlusov, VF Pichugin, ME Konischev, M. Epple. Calcium phosphate coating created by rf-magnetron sputtering hydroxyapatite: osteogenic potential in vitro and in vivo. Journal Tomsk Polytechnic University. – 2010. V. 317 - № 2.