Synthesis of bio-active titanium oxide coatings stimulated by electron-beam plasma

Abstract: Advantages of the electron-beam plasma (EBP) for production of bioactive titanium oxide coatings were experimentally studied. The coatings were synthesized in EBP of oxygen on the surface of plane titanium substrates. A number of analytical techniques were used to characterize morphology, chemical composition, and structure of the synthesized titanium oxide. The analysis showed the titanium oxide (IV) in the rutile form to predominate in the coatings composition.

The samples with plasmachemically synthesized TiO₂-coatings were more hydrophilic than untreated titanium. The effect was stable during two weeks and then the degradation of the wettability began. The EBP-stimulated TiO₂ synthesis improved the hydroxyapatite formation on the surface of plane titanium substrates. The EBP-stimulated TiO₂ synthesis is promising technique to produce bioactive coatings on the surface of titanium medical dental and bone implants.

The computer simulation of plasma-surface interaction was carried out to predict the plasma composition, to find the spatial distribution of the sample temperature, and to calculate the flows of the chemically active plasma particles bombarding the tube wall. The flows of atomic and singlet oxygen were found to be the most intensive and, therefore, these particles are likely to be responsible for the formation of the biocompatible TiO₂-coatings.

Keywords: Titanium oxide (IV); rutile; hydroxyapatite; oxygen species; computer simulation

1 Introduction

Titanium and titanium alloys are widely used in the production of dental and orthopedic implants because of their superior mechanical properties, such as tensile strength, yield strength, and lightness (with specific gravity of 4.5 g cm⁻³) [1]. Though the metallic titanium implant is covered by a thin native oxide film which stimulates osseointegration, it may corrode away and be separated from the bone by fibrous tissue with immune reactions when the implant is introduced into a bone [2]. Moreover, usually metallic surfaces are not adequately bioactive, and surface treatment is needed to enhance the bioactivity to improve osseointegration of the implant with the bone tissues.

A number of techniques have been developed to improve roughness, topography, and composition of titanium implants surface, and to increase the thickness of TiO₂ layer and therefore its biocompatibility. These techniques include blasting with hard particles, etching in an acidic solution, and coating with bioactive substances by sol-gel technologies, chemical or physical vapor deposition, high-temperature pressing, etc. [3-5].

A variety of plasma-assisted techniques have been developed to obtain bioactive titanium surfaces, including powder, suspension or liquid plasma spraying [6], radio-frequency magnetron sputtering [7], direct current magnetron sputtering [8], pulsed laser deposition [9] or combination of different techniques [10]. Furthermore, there are various ion beam techniques, including ion implantation [11], ion beam sputtering [12], ion beam dynamic mixing [13], and ion-beam-assisted deposition [14].

In the present study, the titanium oxide layer was synthesized using the electron-beam plasma (EBP), generated by injection of an electron beam into oxygen media. Principles of EBP generation, its properties, and fundamentals of applications are described in detail in reference [15].

The objectives of the present study were as follows:

- to experimentally study the plasma-stimulated synthesis of titanium oxides in strongly non-equilibrium low temperature EBP at the surface of the plane substrates;
to characterize the morphology and the chemical composition of the formed titanium oxide coatings; and
- to prove the bioactivity of the formed titanium oxides coatings.

2 Experimental procedure

2.1 Titanium samples

The EBP-stimulated synthesis of titanium oxides was studied at the surface of the plane substrates (size 20×20 mm). All samples were made of titanium alloy VT1-00 and contained 99.6% of titanium. The other elements were Fe (~0.15%), C (~0.05%), Si (~0.08%), N (~0.04%), O (~0.08%).

The samples were mechanically polished and then successively cleaned with acetone, isopropyl alcohol (for 10 min with each reagent) and deionized water (three times for 10 min) in an ultrasonic bath. To make the roughness and topography uniform, the samples were etched with the mixture of HCl and H$_2$SO$_4$ (1:3) for 30 min at room temperature and washed again with deionized water (three times for 10 min) before the EBP-treatment. The acid etching results in micro pits on the titanium surface and has been shown to greatly enhance osseointegration [4].

Both clean polished and acid etched titanium substrates were used as control samples for the characterization of samples surface properties and bioactivity.

2.2 Characterization of the samples’ surface

The surface morphologies and elemental composition of the control samples, the EBP-treated samples and the coatings formed after soaking in simulated body fluid solution (SBF) were examined by field-emission scanning electron microscopy (SEM) using FEI Quanta 200 (FEI Company, USA). The studied samples were placed in the Quanta 200 chamber without any prior treatment. Three different fields within each sample were randomly chosen, and 3 images of each field were taken at the magnifications ×300, 600, 2000, 3000, 6000, 30 000. The measurements were carried out at the accelerating voltage 5 kV. Energy-dispersive X-ray spectroscopy (EDS) was also performed.

The crystalline structure of synthesized titanium oxide and the compositions of functional groups in thin films formed on the surfaces of the titanium substrates were analyzed using Fourier transform infrared (FT-IR) spectroscopy and Raman spectroscopy.

IR spectral measurements in the wavenumber range 450-4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ were carried out using a Perkin-Elmer Spectrum 100 FT-IR spectrometer (PerkinElmer, USA) equipped with a PIKE Technologies specula VeeMAX™ reflectance accessory and a wire grid polarizer. The reflection-absorption method [16,17] at the incidence of p-polarized IR radiation at the angle of 70° on a Ti-substrate surface was used. The reflection-absorption spectroscopy is one of the most sensitive optical methods of IR analysis of thin films on plane metal surfaces and makes it possible to study the components of vibrational transition moments of coating films that are normal to the metal surface [16,17]. The spectra were measured with respect to the reflectance of a referent original Ti-substrate that was not subjected to acidic, EBP or SBF treatments. The absorption bands of the coating films on metal substrates are revealed as selective decreases of the reflectance. Identification of the absorption bands was carried out in accordance with [18-22].

The wettability of the plane titanium samples before and after the EBP-treatment was characterized by static water contact angles. The contact angle $\theta$ was measured by the sessile drop method using an optical contact angle-measuring device CAM 101 (KSV Instruments, Finland). Measurements were made at room temperature and 45% relative humidity. The deionized water droplets of approximately 3 µl were then placed on the substrate using a threaded plunger microsyringe (Hamilton, USA). The contact angle of sessile drops was determined on the left-hand and right-hand sides of the drop contour using an image analysis program with the inaccuracy ±0.1 degrees. The contact angles were determined at intervals of 0.2-1 min, depending on the rate of change of droplet size and shape. Independent measurements were made for 3 droplets on each plane substrate, and the final mean value was evaluated. The contact angle measurements were performed after EBP treatment and then the wettability degradation was studied after 24 and 48 hours and 1, 2 and 3 weeks. To avoid the adsorption of organic impurities, each sample was kept in a separate clean glass container with ground glass stopper and partially filled with silica gel before and between contact angle measurements. The experimental data were statistically analyzed by Student’s test, $p$-values smaller than 0.05 were considered as reliable.
2.3 Bioactivity characterization of the EBP-treated samples

Bioactivity or the bone bonding capacity of implant surfaces is frequently quantified by the ability to form bone-like hydroxyapatite (the main inorganic component of bones) in vitro [23]. To characterize their bioactivities, the plane EBP-treated samples were soaked in simulated body fluid solution. The ion concentrations of the SBF are nearly equal to those of human blood plasma, as shown in reference [24]. The SBF was prepared by dissolving reagent grade NaCl, NaHCO$_3$, KCl, K$_2$HPO$_4$•3H$_2$O, MgCl$_2$•6H$_2$O, CaCl$_2$•3H$_2$O, and Na$_2$SO$_4$ (Sigma, Germany) in distilled water, and buffered at pH 7.40 at 37°C with tris-hydroxymethylaminomethane [(CH$_2$OH)$_3$CNH$_2$] and 1 M hydrochloric acid. After soaking in SBF for two weeks, the samples were taken out, rinsed with deionized water and dried at room temperature. The formed hydroxyapatite coating was studied using various analytical methods (see “Characterization of the samples surface” section).

2.4 Treatment procedure

For the controllable titanium oxides synthesis the Electron Beam Plasmachemical Reactor (EBPR) described in detail in [25] was used. Fig. 1 illustrates the treatment procedure. The focused continuous electron beam (EB) (3) generated by the electron-beam gun (1) which is located in the high vacuum chamber (2) is injected into the working chamber (5) filled with the plasma-generating gas through the injection window (4) [26]. In passing through the gas, the EB is scattered in elastic collisions and the energy of fast electrons gradually diminishes during various inelastic interactions with the medium (ionization, excitation, dissociation). As a result, the cloud of the EBP (8) is generated, with all plasma parameters being functions of \(x, y, \) and \(z\) coordinates ( \(z\) is the axis of the EB injection).

The electromagnetic scanning system (10), which is placed inside the working chamber near the injection window, is able to deflect the injected EB axis in \(x\) and \(y\) directions and thereby control the spatial distribution of the plasma particles over the plasma bulk. The working chamber is preliminary evacuated to pressure \(~1\) Pa and then filled with the plasma-generating media (the chemically pure oxygen was used as plasma-generating gas). The oxygen pressure in the working chamber was \(10^2\) - \(10^3\) Pa.

The plane titanium samples pretreated as described above were inserted into the EBPR reaction zone as shown in Fig. 1. The distance between the injection window and the titanium substrate, \(z_0\), depended on the gas pressure in the working chamber and was optimized experimentally.

A miniature thermo-sensor (7) was inserted into the center of the plane substrate to monitor the material temperature \(T_s\) during the treatment. The temperature was also controlled by non-contact infrared pyrometer Optris LS (Optris GmbH, Germany). All samples were processed within the range \(T_s = 330-550\) °C. The temperature control was carried out by selecting the EB current \(I_b\) ( \(1 < I_b < 100\) mA). The optimal treatment time \(\tau\) was found experimentally and varied from 5 to 15 min.

3 Results and discussion

3.1 The structure and the chemical composition of oxide layer synthesized in EBP

Fig. 2 shows the SEM images of plane titanium substrates before and after the EBP treatment. The surface of original untreated titanium sample had numerous scratches even after mechanical polishing and was coated by the oxide due to the contact with air. This oxide layer was porous with a characteristic pore size of \(~1\) µm.

The EBP treatment resulted in an increase in surface uniformity and surface roughness due to simultaneous
interactions of heavy plasma particles with the oxide layer formation. The mechanisms responsible for the plasma-stimulated surface cleaning which provides the reproducible starting conditions for further particle adsorption onto the sample surface and their subsequent reactions of the oxides synthesis are given in references [27, 28]. The SEM studies of the surface layer which was synthesized in the oxygen EBP showed the layer to consist of titanium oxide grains with typical size ~10 µm separated by ~1 µm cracks. The oxide coating formed in the oxygen EBP on the surfaces pretreated in acidic solution was the most uniform and was composed of tightly packed grains with the same typical size of ~10 µm.

The peaks corresponding to titanium and oxygen were observed in the EDS spectra of all studied samples. The oxygen peak was the most significant in the titanium sample treated in the EBP of oxygen with preliminary acidic etching (Fig. 3), which assumes the oxide layer on this sample to be the thickest. The traces of carbon and aluminium revealed in the EDS spectra were attributed to the abrasive paste applied for mechanical polishing.

The reflectance spectra of the studied Ti substrates exposed to different treatments are shown in Fig. 4. The absorption band at 826 cm\(^{-1}\) observed for curves 2, 3 and 4 in Fig. 4 could be related to titanium dioxide (TiO\(_2\)) in the rutile crystalline structure [16, 18]. Note that the maximal intensity of the band at 826 cm\(^{-1}\) is observed for the Ti sample exposed only to EBP treatment (curve 3 in Fig. 4), whereas this band is absent in the spectrum of the Ti substrate exposed to the acidic etching only (curve 1 in Fig. 4). These results make it possible to conclude that the electron beam plasma treatment produces a film of titanium (IV) oxide of rutile crystalline structure.

For the Ti substrates exposed to the acidic etching (curves 1, 2, 4 in Fig. 4), the baseline reflectance is considerably lower than for the sample without acidic etching (curve 3 in Fig. 4). This effect can be related to a considerably lower surface roughness of the sample without acidic etching as compared to that of the samples exposed to acidic etching, due to IR radiation angular scattering at the surface roughness. This conclusion correlates with the results obtained using scanning electron microscopy (see Fig. 2).

### 3.2 The contact angles measurements

Measurements of the water contact angle on plane titanium samples before and after the EBP treatment are shown in Table 1. The measurements showed that the water contact angle of the original titanium sample was 66.0±2.5 degrees. According to [29], the original samples were slightly hydrophilic, and the EBP treatment was expected to improve their wettability and, as a result, biocompatibility.
The studies showed that samples after acidic etching and samples with plasmachemically synthesized TiO$_2$-coatings were more hydrophilic than untreated titanium. No time dependence of the contact angle was observed after 48 hours for all treated samples. The slight wettability degradation of the samples with plasmachemically synthesized TiO$_2$ was observed after this period, whereas the wettability of acidic etched samples became equal to that of the untreated titanium substrate. Thus, the titanium oxide coating with high and stable wettability can be obtained using the EBP-stimulated TiO$_2$ synthesis.

### 3.3 Bioactivity characterization of the EBP-treated samples

The morphology of hydroxyapatite formed after the incubation of titanium samples in SBF is shown in Fig. 5. All studied samples precipitated hydroxyapatite from SBF at their surfaces. The hydroxyapatite at the original titanium sample produced discrete clusters, whereas the EBP-stimulated TiO$_2$ synthesis improved the uniformity of the hydroxyapatite formation. The sample treated in EBP at 550°C was the most bioactive. The precipitated hydroxyapatite produced macroporous scaffolds of elongated shape and diameter ~50 – 100 nm. The majority of the hydroxyapatite particles tended to agglomeration and formed aggregates with diameter of ~3 μm.

The samples were preliminary etched in acid mixture, treated in EBP of oxygen at pressure 670 Pa for 15 min and then soaked in SBF for two weeks at 37°C.

In the IR reflection-absorption spectrum of the SBF-treated sample (curve 4 in Fig. 4) a number of characteristic absorption bands of various hydroxyapatite functional groups is observed in the wavenumber ranges 400 - 600 cm$^{-1}$ (a) and their fragments in the range of 500-1800 cm$^{-1}$ (b).

#### Table 1: Water contact angle for untreated titanium substrate and titanium substrates after acidic etching and EBP treatment.

| Time after treatment, days | Sample | Acidic etching | Acidic etching and EBP treatment at 550°C | EBP treatment at 550°C without acidic etching |
|---------------------------|--------|----------------|------------------------------------------|---------------------------------------------|
| 0                         | Original titanium | 66.0 ± 2.5 | 21.1 ± 7.6* | 6.9 ± 1.2* | 8.8 ± 1.6* |
| 1                         | Acidic etching | 69.8 ± 2.1 | 19.3 ± 4.2* | 9.0 ± 1.5* | 15.7 ± 1.9* |
| 2                         | Acidic etching | 67.8 ± 1.5 | 20.3 ± 5.3* | 17.5 ± 2.3* | 16.4 ± 2.1* |
| 7                         | Acidic etching | 70.0 ± 2.7 | 29.2 ± 4.9* | 22.8 ± 0.5* | 18.0 ± 1.5* |
| 21                        | Acidic etching | 66.7 ± 1.8 | 59.3 ± 2.4 | 32.5 ± 4.2* ,** | 20.9 ± 1.5* ,** |

All data are expressed as mean ± S.D.

* $p < 0.05$ vs. original titanium sample

** $p < 0.05$ vs. acidic etched titanium sample
and 900 - 1200 cm$^{-1}$. The bands with reflectance minima at 468, 487, 502, 548, 594, 982, 1030, 1054, 1088 and 1155 cm$^{-1}$ can be related to stretching and deformational vibrations of PO$_4^{3-}$ groups of hydroxyapatite. The bands at 655 and 660 cm$^{-1}$ can be attributed to the vibrations of OH$^-$ groups in hydroxyapatite. The bands at 1292, 1396, 1460, 1624 cm$^{-1}$ can be related to the vibrations of CO$_3^{2-}$ groups.

3.4. Discussion: physical-chemical mechanisms of titanium oxide synthesis stimulated by EBP

The computer simulation of plasma-surface interaction was carried out to predict the plasma composition, and to calculate the flows of the chemically active plasma particles falling on the sample surface.

To simulate the EBP composition, a simple kinetic scheme that takes into account the processes involving only non-excited oxygen atoms and molecules of O$_2$ and O$_3$ (Table 2) was used. The comparison of the simulation results obtained by means of this and more complicated kinetic schemes showed that the simple scheme is able to calculate concentrations of the main neutral EBP components with sufficient accuracy [30,31].

Computer simulation of the oxygen EBP generation near a plane surface and plasma-surface interaction was carried out using the approach described in [31,32]. Fig. 6 illustrates the simulation results and presents radial distributions of the fluxes of selected active species (electrons, positive ions, O atoms and O$_2$(a'X$_g$) molecules) falling on the sample surface. Under typical conditions of titanium oxide synthesis, the fluxes of the neutral particles were more intense than those of the charged particles. The dominant active species were O atoms. The flux of O$_2$(a'X$_g$) molecules was less intense than that of O atoms by a factor of three, whereas the fluxes of charged particles were an order of magnitude weaker. Therefore, the reactions of atomic and excited oxygen with titanium surface are significantly responsible for the oxide layer formation.

Precise calculation of the intensities of the plasma particles fluxes demands more complicated kinetic models that take into account not only plasmachemical reactions in a gas but the heterogeneous recombination of plasma particles on the solid surface [33]. This approach could clarify concentrations of plasma particles, and the concentration of O-atoms among them, near the surface to be treated, but it is unlikely to modify the conclusions that O- and O$_3$-fluxes dominate and that these particles are mainly responsible for the titanium oxidation in the EBP.

The fluxes shown in Fig. 6 slightly diminish in the radial direction because they were calculated assuming that the electromagnetic system (10) (see Fig. 1) was switched off, i.e., the injected EB was supposed to be non-scanned. Special calculations showed that the uniform fluxes of chemically active plasma particles can be generated by adjusting frequencies of the EBP-cloud oscillations over the sample surface. Uniform distributions of the surface

---

**Figure 5:** SEM images (magnification ×3000) of the hydroxyapatite formation on TiO$_2$ coatings synthesized in EBP: control sample (a), sample treated in EBP at 330°C (b), sample treated in EBP at 550°C (c).

**Table 2:** Kinetic scheme used for the calculation of the neutral particles concentration in oxygen EBP.

| Reaction                          | The energy (eV (*) or the rate constant (cm$^3$ s$^{-1}$ or cm$^3$ s$^{-1}$ (**)) |
|----------------------------------|--------------------------------------------------------------------------------|
| $e_b + O_2 \rightarrow e_b + O + O$ | 20.2 (*)                                                                      |
| $O + 2O_2 \rightarrow O_3 + O_2$  | $6.9 \times 10^{-10} (300/T)^{-25}$ (**)                                       |
| $O + O_3 \rightarrow O_2 + O_2$   | $2 \times 10^{-4} \exp(-2300/T)$ (**)                                          |
| $O + O + O_2 \rightarrow 2O_2$   | $6.7 \times 10^{-11} (300/T)^{-65}$ (**)                                       |
| $O_3 + O_2 \rightarrow O + 2O_2$  | $1.65 \times 10^{-6} \exp(-11400/T)$ (**)                                     |
temperature are obtained in the same manner, and therefore, sufficiently large-size samples can be treated uniformly by scanning the EBP cloud.

4 Conclusions

1. The EBP-stimulated synthesis of titanium oxides was experimentally supported. The technique was successfully used to obtain titanium oxide coatings at the surface of the plane substrates.

2. A number of analytical techniques were used to characterize morphology, chemical composition, and structure of the synthesized titanium oxide. The analysis showed that titanium oxide (IV) in rutile form predominates the composition of the coatings. The optimal micro-relief of the surface could be preliminarily formed by means of conventional techniques (e.g., etching in the acidic mixture) but EBP treatment was able to improve the surface significantly. The oxide coatings synthesized in the oxygen EBP on the surfaces pretreated in acidic solution were the most uniform and were composed of tightly packed grains with typical size ~10 µm.

3. The bioactivity of synthesized TiO₂ coatings was characterized by water contact angle measurements and the ability to precipitate hydroxyapatite from the model solution, which simulated the composition of the body fluid. These studies showed that the samples with plasmachemically-synthesized TiO₂ coatings were more hydrophilic than untreated titanium. Higher hydrophilicity was observed for two weeks and after this period the degradation of the wettability began. The EBP-stimulated TiO₂ synthesis improved the hydroxyapatite formation on the surface of plane titanium substrates, with the sample treated at 550°C being the most bioactive. Thus, the EBP-stimulated TiO₂ synthesis is a promising technique to produce bioactive coatings on the surface of titanium medical dental and bone implants.

4. Computer simulation of plasma-surface interaction was carried out 1) to predict the plasma composition near the surface to be treated, 2) to find the temperature distribution on the sample surface, and 3) to calculate the flows of the chemically active plasma particles falling on the sample wall. The fluxes of atomic and singlet oxygen were found to be the most intense, and therefore these particles are likely to be responsible for the formation of biocompatible TiO₂ coatings.

Acknowledgements: This work was supported by RFBR, grants 12-08-31246-mol_a, and 12-08-90019-Bel_a.

References

[1] Park J.B., Lakes R.S., Biomaterials an Introduction, Plenum Press, New York, 1992
[2] Lin F.H., Hsu Y.S., Lin S.H., Chen T.M., Mater. Chem. Phys., 2004, 87, 24
[3] Massaro C., Rotolo P., De Riccardis F., Milella E., Napoli A., Wieland M., et al., J. Mater. Sci. Mater. Med., 2002, 13, 535
[4] Kim H.W., Kim H.E., Salih V., Knowles J.C., J. Biomed. Mater. Res. B Appl. Biomater., 2004, 72B, 1
[5] Park J.B., Kim Y.S., Lee G., Yun B.G., Kim C.H., J. Tissue. Eng. Regen. Med., 2013, 10, 115
[6] Dudek A., Arch. Metall. Mater., 2011, 56, 135
[7] Boyd A.R., Burke G.A., Duffy H., Holmberg M., O’Kane C., Meenan B.J., Kingshott P., J. Mater. Sci. Mater. Med., 2011, 22, 71
[8] Shtansky D.V., Kiryukhantsen-Korneev P.V., Bashkova I.A., Sheveiko A.N., Levashov E.A., Int. J. Refract. Met. Hard Mater., 2010, 28, 32
[9] Katayama H., Katto M., Nakayama T., Surf. Coat. Technol., 2009, 204, 135
[10] Roy M., Balla V.K., Bandayopadhyay A., Bose S., Acta Biomater., 2011, 7, 866
[11] Rautray T.R., Narayanan R., Kwon T.Y., Kim K.H., Thin Solid Films, 2010, 518, 3160
[12] Sobieszczuk S., Zieliński A., Adv. Mater. Sci., 2008, 8, 35
[13] Yoshinari M., Watanabe Y., Ohtsuka Y., Derand T., Surf. Coat. Technol., 1997, 76, 1485
[14] Bai X., More K., Rouleau C.M., Rabiei A., Acta Biomater., 2010, 6, 2264
[15] Vasiliev M.N., In: Fortov V.E. (Ed.), Encyclopedia of low-temperature plasma, Nauka, Moscow, 2001, V IX 436
[16] Greenler R.G., J. Chem. Phys., 1969, 50, 1963
[17] Transferetti B.C., Davanzo C.U., Zoppi R.A., Cruz N.C., Moraes M.A.B., Phys. Rev. B., 2001, 64, 125404
[18] Zhang J.Y., Boyd I.W., O’Sullivan B.J., Hurly P.K., Kelly P.V., Senator J.P., J. Non-Sryst. Solids, 2002, 303, 134

Figure 6: The steady-state axial flow distributions (q) of electrons, oxygen atoms, O₂⁺ ions, and singlet oxygen as the function of the distance from the center of the sample (r). The treatment conditions: P = 670 Pa, E₀ = 30 kV, I₀ = 10 mA, z₀ = 150 mm.
[19] Bellamy L.J., The infrared spectra of complex molecules, Methuen & Co., London, 1954
[20] Van der Houwen J.A.M., Cressy G., Cressy B.A., Valsami-Jones E., J. Cryst. Growth, 2003, 96, 249
[21] Rapacz-Kmita A., Elosarzcyk A., Paszkiewicz Z.C., Paluszkiewicz C., J. Mol. Struct., 2004, 65, 704
[22] Berzina-Cimdina L., Borodajenko N., In: T. Theophanides (Ed.), Infrared spectroscopy – Materials science, engineering and technology, 2012, 123
[23] Sato K., Kumagai Y., Tanaka J., J. Biomed. Mater. Res., 2000, 50, 16
[24] Kokubo T., Ito S., Huang Z.T., Hatashi T., Sakka S., Kitsugi T., Yamamuro T., J. Biomed. Mater. Res., 1990, 24, 331
[25] Vasilieva T.M., IEEE Transac. Plasma Sci., 2010, 38, 1903
[26] Vasilieva T.M., Bayandina D.V., Instr. Exp. Tech., 2010, 53, 289
[27] Thull R., Grant D., In: Brunette D.M. (Ed.), Titanium in Medicine: Material Science, Surface Science, Engineering, Biological Responses and Medical Applications, Springer-Verlag, Berlin and Heidelberg, 2001, 283
[28] Handbook of Deposition Technologies for Film and Coatings, 2nd edition, Noyes, Park Ridge, NJ, 1994
[29] Yuan Y., Lee T.R., In: Bracco G., Holst B. (Eds.), Surface Science Techniques, Springer-Verlag, Berlin and Heidelberg, 2013, 3
[30] Aleksandrov N.L., Vasiliev M.N., Lysenko S.L., Negodaev S.S., In: 4-th European Conference for Aerospace Sciences, 4-8 July 2011, S-Petersburg, Russia
[31] Aleksandrov N.L., Konovalov V.P., Son E.E., In: Son E.E. (Ed.), Encyclopedia of low-temperature plasma, Yanus-K, Moscow, 2010, Ser. B. V III-3, 265
[32] Aleksandrov N.L., Vasiliev M.N., Lysenko S.L., Mahir A.Kh., Plasma Physics Reports, 2005, 31, 425
[33] Kutasi K., Sa P.A., Guerra V., J. Phys. D: Appl. Phys., 2012, 45, 19205