Electron Beam Plasma Application for Synthesis of Bioactive Titanium Oxide Coatings

T M Vasilieva¹, I V Sokolov² and K V Balakin¹

¹ Moscow Institute of Physics and Technology, Dolgoprudny, Moscow region, 141700, Russia

² Keldysh Research Centre, Moscow, 125438, Russia

E-mail: tmvasilieva@gmail.com

Abstract. Prospective bio-medical applications of the electron-beam plasma (EBP) were experimentally studied. The EBP-treated titanium samples were investigated from the point of view of their bio-compatibility.

The titanium oxide coatings were synthesized in the EBP of oxygen on the surface of plane titanium substrates and on the inner surface of the titanium tubes. The EBB-treatment was able to significantly improve the surface uniformity and roughness. Titanium oxide TiO₂ (IV) in the rutile form predominated in the coatings composition.

The bioactivity of synthesized TiO₂-coatings was characterized by the water contact angle measurements and by the ability to precipitate hydroxyapatite from the model solution which simulated the composition of the body fluid. The studies showed the samples with plasma-chemically synthesized TiO₂-coatings to be more hydrophilic than untreated titanium and to precipitate hydroxyapatite on their surface effectively.

1. Introduction

Titanium and titanium alloys are widely used for dental and orthopedic implants production because of their superior mechanical properties such as tensile strength, yield strength, and lightness [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 by improving osseointegration of the implant with the bone tissues.

A variety of plasma-assisted techniques have been developed to obtain bioactive titanium surfaces [3-6]. In the present study the titanium oxide layer was synthesized using the electron-beam plasma (EBP), generated by the injection of the electron beam into oxygen media. Under typical conditions of the EBP generation (medium pressure 0.1 < P_m < 10 kPa and moderate EB power N_b < 1 kW) the plasma is strongly non-equilibrium and cold. Being injected into a gas the EB ionizes the gas, excites the gas molecules and is able to cause molecule dissociation. As a result, the EBP composition is complicated and there are a lot of chemically active particles that do not exist under equilibrium conditions. The main advantage of the beam-plasma technologies with respect to the approaches mentioned above are:

- the possibility of the uniform treatment of large-size substrates and bodies with complicated shape;
- shorter treatment time;
- power saving due to the higher gas pressures (in comparison with conventionally used plasmas) at which the EBP-treatment is performed.

The aims 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 titanium substrates;
• to characterize the morphology and the chemical composition of the formed titanium oxide coatings;
• to prove the bioactivity of the titanium oxides coatings characterizing (in vitro) the samples ability to form bone-like hydroxyapatite (the main inorganic component of bones) by its precipitation from a solution which simulate the body fluid.

2. Materials and methods

2.1. Materials
The EBP-stimulated synthesis of titanium oxides was studied at the surface of the plane substrates (size 20x20 mm) and on the inner surface of the thin titanium tube with diameter 15 mm and length 100 mm. The samples were mechanically polished and cleaned with acetone, isopropyl alcohol and deionized water in ultrasonic bath. To uniform the roughness and topography the samples were etched with the mixture of HCl and H$_2$SO$_4$ for 30 min at room temperature and washed again with deionized water before the EBP-treatment.

2.2. Characterisation of EBP-treated titanium samples
2.2.1. Field-emission scanning electron microscopy (SEM). The surface morphologies were examined using FEI Quanta 200 (FEI Company, USA). The measurements were carried out at the accelerating voltage 5 kV. Three different fields within each sample were randomly chosen, and 3 images of each field were taken at the magnifications x300, 600, 2000, 3000, 6000, 30 000.

2.2.2. Raman spectroscopy. The Raman spectra were recorded using a T64000 - HORIBA Jobin Yvon (Horiba Jobin Yvon IBH Ltd., Japan) equipped with a liquid N$_2$-cooled CCD detector. The laser excitation line used was the 488 nm of an argon laser. The power of the incident laser beam was about 50 mW on the sample’s surface. For focusing of laser spot an X100 objective was used. Typical spectra line width was 0.5 cm$^{-1}$ while the recorded spectra were the average of 3 scans.

2.2.2. X-ray diffraction (XRD). XRD was carried out by the sliding beam method using ARL X'TRA powder diffractometer (Thermo Fisher Scientific, USA) equipped with CoK$_\alpha$ radiation source. The conditions were as follows: the angle of incidence of the primary X-ray beam 5°, accelerating voltage 30 kV, and anode current 10 mA. The XRD pattern was recorded in the range of scattering angles 2$\theta$ = 10-130°, scanning intervals 0.1°. The resolution of the interplanar spacing measurements was ±0.0001 nm.

2.2.3. Contact angle measurements. The wettability of the plane titanium samples before and after the EBP-treatment was characterized by water static contact angles. The contact angle was measured by the sessile drop method using an optical contact angle-measuring device CAM 101 (KSV Instruments, Finland). The contact angle measurements were performed after the EBP-treatment and then the wettability degradation was studied after 24, 48 hours and 1, 2 and 3 weeks.

2.3. Bioactivity characterization of the EBP-treated titanium samples
Bioactivity or the bone bonding capacity of titanium surfaces was quantified by their ability to form bone-like hydroxyapatite (the main inorganic component of bones) in vitro [7]. To characterize their bioactivities the EBP-treated samples were soaked in a simulated body fluid solution (SBF) [8] for two weeks.

3. Treatment procedure
For the controllable titanium oxides synthesis the Electron Beam Plasmachemical Reactor (EBPR) described in detail in [9] was used. Figure 1 illustrates the treatment procedure. The focused continuous electron beam (EB) 3 generated by the electron-beam gun 1 that was located in the high vacuum chamber 2 was injected into the working chamber 5 filled with the plasma-generating gas through the injection window 4 [10]. In passing EB through the gas the cloud 8 of the EBP was generated and the sample 6 was inserted into the plasma cloud to be treated. Since all plasma parameters are functions not only of \( P_m \) and \( N_b \) but of \( x \), \( y \), and \( z \) coordinates (\( z \) is the axis of the EB injection) the plasma cloud control was required to treat the sample uniformly. The electromagnetic scanning system 10, which is placed inside the working chamber near the injection window, was able to deflect the axis of scattered EB in \( x \) and \( y \) directions forming a rectangular raster. Varying frequencies and amplitudes of scanning the sample...
treatment was controlled. To estimate intensities of the fluxes of plasma particles falling on the sample surface the computer simulation of the EBP was carried out for real treatment conditions using the specially developed method [11].

Plane square-shape titanium samples 20x20 mm in size and 2 mm in depth, h, were inserted into the EBPR reaction zone as it is shown in Figure 1a. Each sample had a number of longitudinal and transversal narrow grooves about (3/4)h in depth which notched the entire sample on a set of smaller square segments. The sample was held in the reaction chamber by thin stainless steel wires to minimize the heat leakage from the sample. After treatment the sample was broken along grooves onto separate pieces for further study. Each piece was kept in separate clean glass container with ground glass stopper partially filled with silica gel to prevent the adsorption of organic impurities during storage.

Before treatment the titanium tube was placed inside a cylindrical holder which tightly covered the tube’s external surface and also acted as a heat protecting cover. This unit was located in the reaction chamber so that the tube axis coincided with the axis z of the injected EB (figure 1b). The tube was cut on segments immediately after treatment; each segment was kept as described above.

To separate the effect of the plasma-assisted oxidation from the conventional oxide synthesis due to the titanium heating in rarefied oxygen atmosphere special experiment were carried out: the heat-protecting envelope was removed and the water-cooled diaphragm 11 was located in front of the tube localizing the plasma cloud inside the tube only. Properties of inner and outer surfaces of the samples were then studied and compared.

The miniature thermo-sensor 7 was fixed at a certain point (usually at the centre) of the plane substrate to measure the material temperature. A set of thermo-sensors were placed into the tube’s holder to monitor the temperature distribution along the tube during the treatment. The local temperatures at various points of both plane and tube samples could be also optically measured by pyrometer Optris LS (Optris GmbH, Germany) to ensure that the temperature distributions were uniform over the samples.

All samples were processed within the temperature range $T_s = 250-750 \, ^\circ C$. The temperature control was carried out by adjusting the EB current $I_b$ within the range 1 < $I_b$ < 100 mA at a constant oxygen pressure that was 670 Pa in the described series of the experiments. The optimal treatment time $\tau$ was found experimentally and varied from 5 to 15 min depending of the $T_s$-value that was automatically kept constant during the treatment.

![Figure 1](image-url)

**Figure 1.** The design of electron-beam plasmachemical reactor and the treatment procedure of the plane titanium substrates (a) and titanium tube (b).

1 – electron beam gun; 2 – high vacuum chamber; 3 – EB; 4 – injection window; 5 – working chamber; 6 – plane titanium substrate or titanium tube with heat protecting holder; 7 – temperature sensor(s); 8 – EBP cloud; 9 – gas feeder; 10 – scanning system; 11 – water-cooled diaphragm.

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

Figure 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 the characteristic pore size ~1 µm and the surface had non-ordered structure (figure 2a). Acid etching improved the surface and formed large-size grains (~ 15 µm in characteristic size) having rigid facets (figure 2b).

The treatment in the oxygen EBP was expected to result in:
the increase in surface uniformity and improvement of the surface roughness due to the action of fast electrons and heavy plasma particles [12, 13];
- simultaneous synthesis of the titanium oxide layer.

Studies showed that titanium oxide films that were plasmachemically synthesized without any pretreatment in acid consisted of grains with typical size ~10 µm separated by ~1 µm cracks; no pores were observed. The oxide coatings formed in the oxygen EBP on the surfaces pretreated in acidic solution were more uniform in comparison with the above case but they were composed of tightly packed grains of the same typical size ~10 µm and the grain facets became smoother (figures 2c and 2d). The treatment temperature rises from 330 ºC to 550 ºC amplified this effect: the surface became more uniform with densely packed grains of smaller size (compare figures 2c and 2d).

Figure 2. The SEM images of the titanium plane substrates before and after the EBP-treatment (magnification ×2000): a) orginal titanium sample; b) titanium sample after acidic etching; c) tutanuim sample treated in the EBP of oxygen at 330 ºC after preliminary acidic etching; d) tutanium sample treated in the EBP of oxygen 550 ºC after preliminary acidic etching.

The samples were treated in EBP at gas pressure 670 Pa, treatment time 15 min

The results of XRD analysis of the inner surface of the titanium tube treated in the oxygen EBP are presented in figure 3. The analysis showed the titanium oxide (IV) in the rutile isoform predominates in the coatings composition. The XRD analysis revealed that the diffraction patterns of two samples treated in the EBP for 5 min at the same oxygen pressure and accelerating voltage at $I_b = 18$ mA ($T_s = 415$ ºC) and 9 mA ($T_s = 275$ ºC) were not qualitatively different but titanium dioxide content was lower in the second sample. This distinction indicates that the thinner oxide layer was synthesized at lower temperature $T_s$ and, therefore, the oxide layer thickness could be controlled by the temperature of the EBP-stimulated synthesis.

Figure 3. The XRD-analysis of the titanium tube treated in the EBP of oxygen.
Treatment conditions: gas pressure 670 Pa, EB current 9 mA, temperature $275±5$ ºC, treatment time 5 min

4. The contact angles measurements and bioactivity characterization of the EBP-treated samples

The measurements showed that the water contact angle of the original titanium samples was only 66.0±2.5 degrees, which is not sufficient to expect high biocompatibility of oxidized surfaces and only samples with specially improved wettability are likely to be more biocompatible. The samples after conventional acidic etching and, especially, the samples with plasmachemically synthesized TiO$_2$-coatings acquired higher hydrophilicity than untreated titanium (table 1). For all treated samples no time dependence of the contact angle was observed for 48 hours storage but after this period only slight
wettability degradation of the plasmachemically treated samples was observed, whereas the wettability of acidic etched samples (without plasmachemical treatment) became equal to that of the original titanium substrate.

**Table 1.** Water contact angle for untreated titanium substrate and titanium substrates after acidic etching and the EBP-treatment.

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

The morphology of hydroxyapatite deposited on various titanium samples after their incubation in the SBF is shown in figure 4. All studied samples precipitated hydroxyapatite from SBF at their surfaces to a greater or lesser extent. The hydroxyapatite deposited at the original titanium sample in a form of discrete clusters (figure 4a). The plasmachemically synthesized TiO$_2$ improved the hydroxyapatite layer formation at the surface: the layer was more uniform and dense (figure 4b and 4c). The precipitated hydroxyapatite produced the 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 and the hydroxyapatite layer uniformity turned out to improve when the temperature of the preliminary plasmachemical treatment of titanium was higher (compare figure 4b and 4c).

**Figure 4.** The SEM images of the hydroxyapatite formed on titanium plane substrates (magnification ×3000): a) control sample; b) sample treated in the EBP at 330 °C; c) sample treated in the EBP at 550 °C. The samples a) and b) were preliminary etched in acid mixture, treated in the EBP of oxygen at pressure 670 Pa for 15 min. All samples were soaked in SBF for two weeks at 37 °C.

4. Conclusions

- The EBP-stimulated oxides synthesis of titanium alloys was experimentally proved. The technique was successfully used to obtain titanium oxide coatings on both plane surfaces and inner surfaces of tubes.

- EBB-treatment was able to improve the surface uniformity and roughness significantly. The oxide coatings synthesized in the oxygen EBP on the surfaces pretreated in acidic solution were the most uniform and composed of tightly packed grains with typical size ~10 μm. Titanium oxide (IV) in the rutile form predominated in the coatings composition.

- The samples with plasmachemically synthesized TiO$_2$-coatings were more hydrophilic than untreated titanium and effectively precipitated hydroxyapatite on their surface. Thus, the EBP-
stimulated TiO₂ synthesis is the promising technique to produce bioactive coatings on the surface of titanium medical dental and bone implants.

References

[1] Park J B and Lakes R S 1992 Biomaterials an Introduction (New York: Plenum Press)
[2] Lin F H, Hsu Y S, Lin S H and Chen T M 2004 Mater. Chem. Phys. 87 24-30
[3] Dudek A 2011 Arch. Metall. Mater. 56 135-140
[4] Boyd A R, Burke G A, Duffy H, Holmberg M, O’Kane C, Meenan B J and Kingshott P 2011 Mater. Sci. Mater. Med. 22 71-84
[5] Katayama H, Katto M and Nakayama T 2009 Surf. Coat. Technol. 204 135-140
[6] Roy M, Balla V K, Bandypadhyay A and Bose S 2011 Acta Biomater. 7 866-873
[7] Sato K, Kumagai Y and Tanaka J 2000 J. Biomed. Mater. Res. 50 16-20
[8] Kokubo T, Ito S, Huang Z.T, Hatashi T, Sakka S, Kitsugi T and Yamamuro T 1990 J. Biomed. Mater. Res. 24 331-343
[9] Vasilieva T 2010 IEEE Transac. Plasma Sci. 38 1903-1907
[10] Vasilieva T M and Bayandina D V 2010 Instr. Exp. Tech. 53 289-296
[11] Aleksandrov N L, Vasiliev M N, Lysenko N L and Negodaev S S 2011 Electron-beam plasma technologies for simulation of envirionmental effects on satelite surface 4-th European Conference for Aerospace Sciences 4-8 July 2011 S-Peterburg Russia (9 pages on CD)
[12] Aleksandrov N L, Konovalov V P and Son E E 2010 Encyclopedia of low-temperature plasma ed E E Son (Moscow: Yanus-K) volume III pp 265-273
[13] Aleksandrov N L, Vasiliev M N, Lysenko N L and A Kh Mahir 2005 Plasma Physics Reports 31 425-435