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Synthesis of titanium oxide coatings stimulated by electron-beam plasma in argon-oxygen mixture

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Advantages of the electron-beam plasma (EBP) for bio-medical applications were experimentally studied. The bio-active titanium oxide coatings were synthesized in EBP of and argon-oxygen mixture on the surface of plane titanium substrates, and on the titanium nanoparticles with diameter 200 nm. The samples were treated in EBP using the Electron Beam Plasmachemical Reactor (EBPR) described in [1].

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. 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. 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. Plane square-shape titanium samples were inserted into the EBPR reaction zone as it is shown in figure 1. The titanium nanoparticles were treated in EBP using the specially designed rotating devices which was inserted into the working chamber and allowed to mix the powder of nanoparticles during the treatment procedure. The device consisted of a tube, connected to a stepper motor that allows you to rotate the tube in continuous and pulsed modes, to perform reverse and change the speed of rotation.

The oxide layer thickness and its properties were expected to depend on the sample temperature, fluxes of the chemically active EBP particles which reacted with the sample surface. All these parameters were controlled by adjusting the beam current density and the oxygen pressure. The sample temperature was within the range 250-750 ºC. The temperature was optically measured by pyrometer Optris LS (Optris GmbH, Germany) to ensure that the temperature distributions were uniform over the samples. The other experimental conditions were as follows:

- the plasma generating media argon-oxygen mixture (ratio 1 : 1) at the pressure 5 Torr;
- the distance between the injection window and sample surface – 250 mm;
- the EB scanning mode – concentric circles with maximal diameter 130 mm;
- the treatment duration – 5-15 min.

Field-emission scanning electron microscopy (SEM), Fourier transform infrared spectroscopy, Auger spectrometry and X-ray structural phase analysis) were used to characterize morphology, chemical composition, and structure of the synthesized titanium oxide.

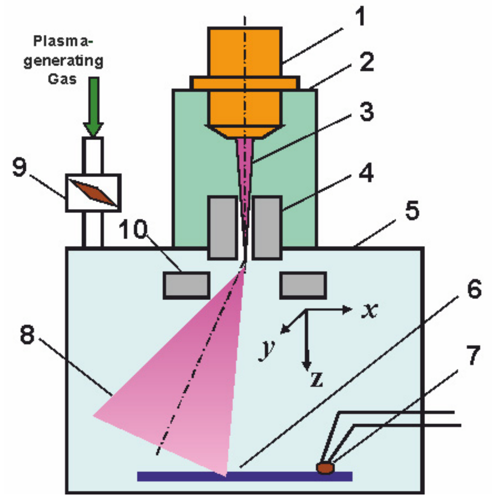


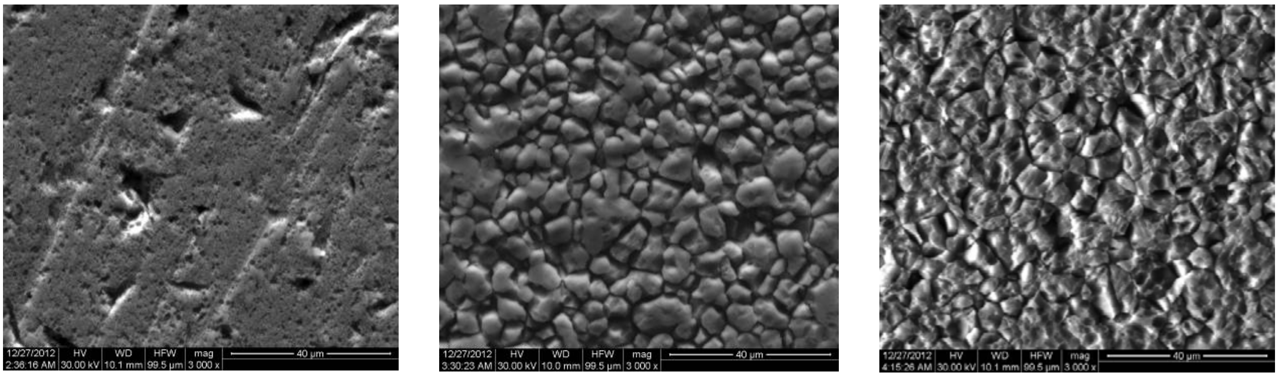
Fig. 1. The design of electron-beam plasmachemical reactor and the treatment procedure of the plane titanium substrates. 1 – electron beam gun; 2 – high vacuum chamber; 3 – EB; 4 – injection window; 5 – working chamber; 6 – titanium substrate; 7 – temperature sensor; 8 – EBP cloud; 9 – gas feeder; 10 – scanning system.

Figure 2 shows the SEM images of plane titanium substrates before and after the EBP-treatment. The EBP treatment resulted in an increase in surface uniformity and surface roughness due to the interactions of heavy plasma particles (especially heavy argon species). The increase of the treatment temperature from 250 ºC to 550 ºC amplified this effect: the surface became more uniform with densely packed grains of smaller size (compare fig. 2b and 2c). The other analyses showed the titanium oxide (IV) in the rutile form to predominate in the coatings composition.

The bioactivity of synthesized TiO_2-coatings was characterized by:

- the water contact angle measurements;
- the ability to precipitate hydroxyapatite (the main inorganic component of bones) from the model solution which simulated the composition of the body fluid.

The studies showed the samples with plasmachemically synthesized TiO_2-coatings were more hydrophilic than untreated titanium. The effect was stable during two weeks and the degradation of the wettability was observed after this period. The EBP-stimulated TiO_2 synthesis improved the hydroxyapatite formation on the surface of plane titanium substrates and the sample treated at higher temperatures being the most bioactive. The EBP-stimulated TiO_2 synthesis is the promising technique to produce bioactive coatings on the surface of titanium medical dental and bone implants.



a) b) c)

Fig. 2. The SEM images of the titanium plane substrates before and after the EBP-treatment in argon-oxygen mixture (magnification ×2000). a) original titanium sample; b) titanium sample treated in the EBP at 250 ºC; c) titanium sample treated in the EBP at 550 ºC. The samples were treated in the EBP at gas pressure 5 Torr, treatment time 15 min

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 sample surface. 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 TiO_2-coatings.

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References

1. *Vasilieva T.* A beam-plasma source for protein modification technology // IEEE Transac. Plasma Sci. – 2010. – V. 38, N 8. – P. 1903–1907.