Microstructure and composition of zirconium coatings obtained by electro-spark alloying

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Abstract. The study focuses on electro-spark alloying of titanium surface and formation of a porous zirconium coating. The coating morphology was formed as a result of melt drop transfer, heat treatment, and partially oxidation. The study establishes the influence of technological regimes of alloying on the surface morphological and chemical composition.

1. Introduction
Some zirconium alloys have found application in medicine along with titanium [1,2]. Much attention is paid to the surface morphology of materials used for the production of intraosseous implants. For example, the surface of dental implants should have the required open porosity to ensure the osseointegration [3-9].

Electro-spark alloying (ESA) is an effective method for the production of porous coatings. This method ensures the formation of highly porous coatings on the surface of biocompatible metals, e.g. tantalum coatings on titanium [10-12]. In this paper, the morphology of the surface and the elemental composition of the coatings produced by ESA with zirconium on the surface of titanium at DC and AC operating current were studied.

2. Methodology
Samples of VT1-0 commercially pure (cp) titanium were subjected to ESA with zirconium grade "E110" (Zr – balance, Nb – 0.9–1.1 wt.%). ESA was conducted in the pulse mode at the following parameters: pulse duration within 10–100 ms, current amplitude of 0.8–2.5 A, and pulse energy ranging within 0.01–0.1 J [2]. In this work, the effect of 3 direct current values was studied: 0.8, 1.5 and 2.5 A. The morphology and elemental composition of the coatings formed at the constant current were compared to the analogous parameters for the layers obtained at AC operating current I = 1.75 A.

The surface morphology of the samples was studied using scanning electron microscopy (SEM). SEM combined with energy-dispersive X-ray analysis (EDX) of chemical composition of samples was performed on "MIRA II LMU" with "INCA PentaFETx3" detector. Changes in titanium, zirconium and oxygen concentrations (at.%) were studied. Hardness of the coatings was evaluated by microindentation using "PMT-3M" (at the load of 100 gf).

3. Results
The resulting zirconium coatings on titanium were characterised by heterogeneous surface morphology, and their microstructure resembled the morphology of sprayed coatings [5]. When a DC operating current equaled 0.8 A the zirconium coating consisted of large microparticles that were unevenly distributed over the surface (Figure 1a). Analysis of the chemical composition of the coating surface showed the presence of zirconium – about 24.57 at.%, titanium – about 49.03 at.% and oxygen
– 26.09 at.%. Thus, an intensive transfer of the alloying element was observed, as well as the simultaneous oxidation of the base (Ti) and coating (Zr) materials. At the operating current of 1.5 A, a more homogeneous transfer of zirconium micro-drops of a smaller size was observed (Figure 1b).

The amount of zirconium in the surface did not exceed 16.21 at.%, whereas the amount of oxygen was much less – about 5.16 at.%. Areas with a high oxygen content of up to 25 at.% were locally observed.

The increase in direct current during ESA to 2.5 A led to a decrease in the surface heterogeneity. Cracks appeared on the coating (Figure 2a). The transfer of zirconium micro-drops decreased sharply, the amount of zirconium did not exceed 2.33 at.% (Figure 2a). The amount of oxygen reached a maximum of about 37.17 at.%. Thus, the reduction in the amount of zirconium can be explained by the accelerated oxidation of the electrode-tool and titanium base materials, as well as by the formation of microparticles with low adhesion.

The surface of the coating formed by ESA with AC operating current $I = 1.75$ A had cracks and a smoother relief (Figure 2b). The content of zirconium was 21.93 at.%, oxygen – about 39.7 at.%, titanium – balance. While analyzing the chemical composition of the coating, it can be assumed that during ESA under AC operating current the oxidation of the coating material occurred. Thus, when using AC mode for ESA, the metal transfer was carried out more intensively than with a constant current.

There were differences in the morphology of the coatings formed by ESA with DC and AC operating current. Metal drops transferred during crystallization on the titanium base acquired an irregular shape in the course of ESA at the constant current (Figure 3a). The average size of the structural elements (particles) was 8.0 μm. The open pore size was 8.1 μm with a total porosity of 54%.

When ESA with the alternating current was conducted, zirconium formed spherical structural elements with the size of 7.5 μm (Figure 3b). The open pore size was significantly less compared to that when the treatment by direct current was performed and it amounted to 4.7 μm. The coatings formed due to ESA with the alternating current were characterized by a low porosity of about 48%.

It should also be noted the formation of nano-sized structural elements (particles) in the form of individual crystals with a size of not less than 60 nm was observed (Figure 3b).
Figure 2(a, b). Morphology of the zirconia coating after ESA at 2.5 A (DC mode) (a); after ESA at 1.75 A (AC mode) (b).

Preliminary data on hardness showed that as a result of ESA, the coatings with a hardness of 10.4±2.0 GPa were formed at the current values I = 2.5 A (DC mode) and 1.75 A (AC mode). High hardness values supported the assumption of the possible oxidation of the base and coating materials in the course of ESA. Probably, nano-sized structural elements formed after ESA at 1.75 A (AC mode) can be oxide crystals phase (Figure 3b).

Figure 3(a, b). Morphology of the zirconium coating after ESA at 1.5 A (DC mode) (a); after ESA at 1.75 A (AC mode) (b).
4. Conclusion
The surface morphology of titanium samples after ESA with zirconium was characterized by the formation of the coatings of Ti-Zr-O system. These functional coatings were formed of micro-sized drops (not exceeding 30–50 μm). The most pronounced structure was formed at the operating current of 1.5 A, the concentration of zirconium was about 16.21 at.% and oxygen – at least 5.16 at.%.

The enhanced transfer of the electrode metal occurred when the average operating current of 1.75 A (AC mode) was applied. The resulting coating consisted of zirconium – 39.7 at.%, oxygen and titanium – 21.93 at.%.

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