Development of a technology for producing thin-film structures based on TiO$_2$ and ZrO$_2$ oxides by gas thermal oxidation

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Abstract.
A new highly efficient method for gas-thermal oxidation of VT6 bioinert titanium alloy with a dosed feed of ultrafine TiO$_2$/ZrO$_2$ particles into the treatment zone has been developed. A physical model for the formation of thin-film oxide heterostructures modified with TiO$_2$/ZrO$_2$ powders has been developed. A set of physicomechanical properties and surface characteristics of oxidized titanium samples was experimentally studied. Electron microscopic studies and microhardness measurements of the synthesized film coatings were performed. A high-tech electric furnace device has been developed for the implementation of gas thermal oxidation with the simultaneous dosed supply of fine powder materials into the working chamber of the furnace.

1. Introduction
Among the promising directions for the creation of high-quality medical devices is gas thermal oxidation, which allows using mechanically strong, corrosion-resistant, and biocompatible thermoxide coatings on the functional surface of metal implantable structures without the use of additional expensive materials, sophisticated equipment, and accessories [1-10].

Thin-film oxide coatings of intraosseous implants, created by electrochemical and gas-thermal oxidation, protect the metal base from the corrosive effects of body fluids (blood, lymph, tissue fluid). Oxidized implants do not cause prolonged allergic reactions of the body and do not have a toxicological effect on the surrounding biostructures. This refers to the main indicators of biocompatibility of implantable structures [11-15].

High strength of the fixation of oxidized implants in the bone is ensured by the creation of oxide coatings with the ability to effectively physico-mechanical adhesion to the surrounding biological tissue. This ability is due to the presence of pronounced roughness and morphological heterogeneity in the coatings. The structurally heterogeneous, microporous surface of the coatings provides better contact bone growth with more intense tissue reactions compared to a surface having a smooth, uniform microrelief. Therefore, the developed oxidized surface promotes, firstly, the active growth of bone cell structures into the pores and depressions of the oxide layer with the course of the implant bio-integration, and secondly, directed bone regeneration and accelerated osteogenesis.

2. Methodology
Samples for the preparation of thin-film oxide coatings were rectangular plates with a working surface area of 2 cm$^2$ and a thickness of 2 mm. Samples were made from bioinert titanium alloy VT6. The surface of the plates was sandblasted with Al$_2$O$_3$ corundum abrasive particles with a dispersion of 250 μm at a pressure of an air-abrasive jet of 0.67 MPa for 30 seconds to create the initial
microroughness. After preliminary sandblasting, the samples were ultrasonically cleaned in an alcoholic washing solution at a frequency of ultrasonic vibrations of 22 kHz for 3 minutes to remove any greasy contaminants. Then, on the surface of titanium samples, a thin-film oxide coating was synthesized by gas thermal oxidation in an electric furnace with an air atmosphere.

During gas-thermal oxidation of metal products, the formation of a coating occurs due to the physicochemical interaction of the metal matrix with oxygen in the reaction medium. As a result of this reaction interaction, cermet oxide compounds are formed on the surface to be treated, which give it a complex of enhanced physicochemical and mechanical properties different from those of the base metal. There is also diffusion hardening of the modified surface layers of the product while maintaining the chemical composition of the main metal matrix.

The oxidation mode provided for thermal modification of the surface at temperatures in the furnace 400-500 °C with a shutter speed of 0.5-1.5 hours at each temperature. In the process of oxidation, nanosized and ultrafine powders of biocompatible and corrosion-resistant oxides were metered into the furnace. In the first experiment, TiO$_2$ oxide particles with a dispersion of the order of 25 nm were supplied. In the second experiment, ZrO$_2$ oxide powder with a dispersion of 20–30 μm was dosed. After gas thermal synthesis of thin-film ultrafine films with distributed TiO$_2$ or ZrO$_2$ particles, the surface of the modified titanium plates was studied by scanning electron microscopy, profilometry, X-ray phase analysis, and microhardness and thickness measurements.

The morphology of coatings was studied by scanning electron microscopy (SEM) at various magnifications using analytical equipment such as MIRA II LMU, Tescan. X-ray phase analysis (XRD) of the resulting coatings was carried out on a DRON-4 diffractometer in CuKα radiation at a scanning speed of the Bragg angle of 2 deg/min. Microhardness was measured using a PMT-3M instrument with an indenter load of 0.49035 N (ISO 6507-1: 2005). The roughness and microrelief of the treated surface were studied by the profilometric method of measuring the parameters of microroughnesses $R_a$, $R_z$, $R_{zmax}$, Sm along ten base lines, followed by mathematical processing of the measurement results using a Mitutoyo high-precision digital profiler SurfTes SJ-410.

3. Results

A physical model of the structure formation of thin-film oxide coatings was developed under the conditions of the reaction interaction of titanium samples with an oxygen-containing medium and during the spraying of oxide fine powders (Figure 1).

Powder material (TiO$_2$ or ZrO$_2$) is fed into the oxidation chamber through a metering device. Heated particles of the powder material are deposited and fixed on the thermally activated surface of the samples due to thermal diffusion processes. As a result, the oxidizable surface is modified and acquires enhanced physical and mechanical characteristics and protective properties. The thickness of such composite structures is 4-30 microns.

Modification of oxide coatings by nano- and ultrafine particles of TiO$_2$/ZrO$_2$ during coating formation leads to the formation of oxide heterostructures (composites) with a matrix microstructure and a filler of nanoparticles of a powder material. Using the developed method, it is possible to simultaneously supply an oxidizing gas medium and powder materials. This makes it possible to obtain multifunctional metal oxide coatings in various reaction media (air atmosphere, superheated water vapor, argon-oxygen mixtures). The coatings created are characterized by a certain heterogeneity of the structure, the dimension of the elements of which is in the ultrafine and nanoscale ranges. It was experimentally established that coatings with distributed particles of TiO$_2$/ZrO$_2$ modifying powder can significantly increase the biological compatibility of the surface of titanium intraosseous implants.
Figure 1. A model for the formation of a composite structure with a dosed supply of nanosized oxide powders in the process of gas thermal oxidation:
I - gas thermal oxidation at a dosed feed of nanoparticles of modifying powder; II - the formation and growth of thermoxides; III - formed thermal spray composite coating with a matrix oxide microstructure filled with nanoparticles of powder material.

To conduct thermal oxidation, a specialized electric furnace was developed with the possibility of a metered supply of modifying powder materials (TiO$_2$/ZrO$_2$) into the furnace (Figure 2) [patent]. The technological modes of the VT6 titanium oxidation process were experimentally established: $t = 400-450$ °C, $\tau = 1.0-1.5$ hours, dispersion of modifying particles of powder material $d \leq 25$nm.
Figure 2. A device for gas-thermal oxidation of metal products with a system for simultaneously supplying an oxidizing gas medium and powder materials to the oxidation chamber: 1 - a cylindrical chamber, 2, 3 - covers, 4 - a thermocouple, 5 - a heating element, 6 - current-insulated electrical leads of a power source, 7 - a casing with gaskets made of heat-insulating material, 8 - a fitting for supplying an oxidizing gas medium, 9 - a fitting for supplying a protective gas for cooling products, 10 - a gas outlet, 11 - cooling circuits, 12 - latch, 13 - hopper, 14 - mixing chamber, 15 - fitting for connection to a gas cylinder, 16 - outlet, 17 - adapter.

Thermoxide coatings 24–53 μm thick were obtained on the surface of the samples. The profile of the obtained thermoxide oxide rough surfaces of titanium samples has a different character depending on the regimes of hardening gas-thermal treatment and is due to different density values of the existing microprotrusions. With increasing temperature from t = 400 °C to t = 500 °C and the duration of oxidation from τ = 0.5 h to τ = 1.5 h, the density of microprotrusions increases, which leads to the formation of a microheterogeneous structure of oxide coatings.

The obtained profilograms of the microrelief of the thermally oxidized surface are characterized by a combination of many protrusions and depressions of different configurations located in different directions relative to each other and relative to the baseline of the profile (Figure 3).

Figure 3. Profilograms of the microrelief of the surface of VT6 titanium with an oxide coating obtained at t = 450 °C and various oxidation times.

Microstructural analysis of titanium samples with the obtained thermoxide coating modified with ultrafine particles of TiO₂/ZrO₂ powders showed uniform distribution of the modifying particles, high morphological uniformity, and the same size of the structural components (Figure 4.).
Figure 4. The structure of the ceramic-metal oxide coating modified by particles of titanium oxide powder obtained on the surface of titanium samples at $t = 450^\circ$C and $\tau = 1.5$ h (according to SEM).

A morphologically developed coating is capable of exhibiting high bioadhesiveness with the possibility of strong intergrowth of the ceramic-metal oxide coating with bone tissue.

X-ray phase studies showed that during the oxidation of samples from VT6 titanium, the values of interplanar spacing for different intensities of diffraction lines correspond to the presence in the resulting coating of the largest number of phases of titanium and its dioxide TiO$_2$ with a very low content of lower oxides Ti$_2$O$_3$ and Ti$_3$O$_5$, ZrO$_2$.

The obtained phase composition of the coatings includes bioinert oxide compounds of titanium and zirconium, which, forming a mechanically strong matrix structure, can be used with high efficiency as functional surface layers of intraosseous titanium implants.

As a result of the experimental work, the requirements for thermoxide coatings of medical devices were formulated (Table 1).

| Table 1. Basic requirements for oxide coatings |
|----------------------------------------------|
| Requirements                  | Indicators for medical devices                                      |
| Phase Composition             | characterized by high homogeneity, includes its own bioinert metal   |
|                               | oxide compounds with a small permissible content of other phases     |
| Coating thickness             | $h = 2-80$ microns; affects the mechanical strength, roughness and    |
|                               | nature of the morphology of oxides                                    |
| Microhardness                 | HV = 7-10 GPa                                                        |
| Total open porosity           | $\leq 60\%$                                                          |
| Dead current corrosion potential| $E_{corr} = 0.4-0.5$ V (in liquid biological media)                  |
| Special properties            | biocompatibility, the factors of which are the chemical composition  |
|                               | of the base material and the coating material, total open porosity,   |
|                               | current-free corrosion potential                                      |

4. Conclusions

A new method for the synthesis of thin-film heterostructured oxide systems based on VT6 medical titanium alloy has been developed, which provides for thermal oxidation in air with a dosed supply of ultrafine TiO$_2$/ZrO$_2$ powders. Specialized electric furnace equipment has been created for gas thermal oxidation of titanium medical implants with the possibility of dosed supply of modifying powder materials into the furnace.

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