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Nanostructure of Composite Bioactive Titania Coatings Modified with Hydroxyapatite in Medical Titanium Implants

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The nanostructure of composite bioactive titania coatings modified with hydroxyapatite was studied in VT1-00 medical titanium implants. The morphology parameters as well as nanometric crystalline parameters, mechanical properties, and biological compatibility of titania coatings were studied using induction treatment.

Various metals (e.g. titanium VT1-00, VT-0, and its alloys VT6 and VT16) are widely used in medical practice for manufacture of implants [1]. Titanium-based biocompatible coatings are of significant interest. Such coating improves osteointegration (healing). The metal structure improves the mechanical properties of the implants. The surface layer should meet particular requirements (hardness and elasticity). Biocompatible coating should have specific morphology (porosity and heterogeneity) and homogeneous micro- and macro-nanostructure [2, 3].

The surface layer is modified using gas–thermal, vacuum, and oxidation methods. These methods require energy and material expenses, as well as sophisticated technology. The duration of the coating process is rather long, this making it difficult to obtain nanostructures.

The experiments and theoretical research of Kofstad, Lainer, and Voitovich into oxidation of hard-melting metals (e.g. titanium) are well-known. Recently, similar research was performed by Solntsev, Korshunov, et al. These studies were devoted to kinetics of oxide coating under isothermic conditions [4, 5]. The problem of mechanically strong biocompatible interface coating of the bone-implant structure is insufficiently understood. The goal of this work was to develop a technology providing the required nanostructure of composite bioactive titania coatings modified with hydroxyapatite in medical titanium implants using the methods of induction-thermal treatment (ITT) and modification of hydroxyapatite (HA) with nanoparticles.

Materials and Methods

The experimental samples were 2-mm thick titanium VT1-00 plates treated with corundum abrasive, 1.5 M HF + 1.5 M HNO_3, and ultrasonic cleaning. The surface of the sample was oxidized by high-frequency electric current (HFEC). The resulting samples were modified using HA colloid nanoparticles and 300-sec induction treatment within the temperature range 600-1200°C. This treatment modifies the mechanical properties of the samples. The treatment mode is classified as follows: the first number in the classification indicates the temperature of titanium induction treatment (06 – 600°C, ..., 12 – 1200°C); the second number, the treatment time (e.g., mode 06-120 implies temperature 600°C for 120 sec; mode 12-030 implies temperature 1200°C for 30 sec, etc.).

The coating structure was examined using a MIRA II LMU raster electron microscope. The surface images were processed using AGPM-6M software. The mechanical parameters of the coating were tested using special methods for low (10 mN) load implemented in a Bercovich indenter NANOVEA Ergonomic Workstation (ISO 14577, ASTM E 2546). Biological compatibility was tested *in vitro*. Adult human dermal fibroblasts were used. The fibroblasts were cultivated for 14-28 days. The coating-cell samples were studied using raster electron microscopy.

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Results and Discussion

Metal-oxide surface structure is determined by oxidation processes induced by HFEC. There are several types of morphology of crystalline structure. TiO_2 (rutile) crystal structure depends on induction treatment temperature; for instance, at 600°C the crystals have the shape of rounded and planar oxide structures. At 800°C the crystal size is 70 ± 10 nm. At induction treatment time 150-180 sec, the crystal structure is needle-shaped, planar, and prismatic. At induction treatment temperature 1000°C, the oxide crystal size is 70 nm. However, if the induction treatment time is 3-5 sec, the crystal elements are destroyed. At induction treatment temperature 1200°C, the oxide layer is separated.

Sand-jet treatment of TiO_2 layer modifies the coating structure within the sub-micrometer range. Additional mechanical activation results in formation of the following crystals:

1) needle nanocrystals (Fig. 1);

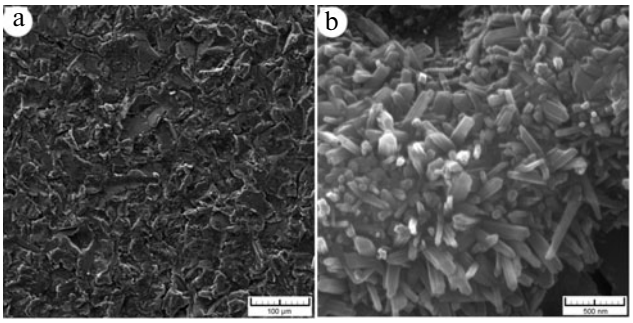

Fig. 1. Morphology of TiO_2 coating obtained in induction treatment mode 600-30: a) microstructure; b) nanostructure.

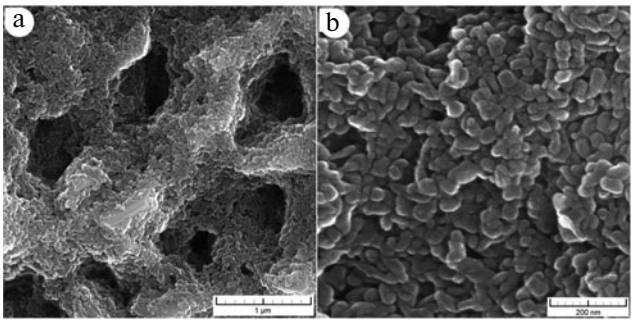

Fig. 2. Morphology of (a) microstructure and (b) nanostructure of coatings obtained at induction treatment temperature 800°C and treatment time 120 sec.

TABLE 1. Mechanical Properties of Biologically Active Coatings

Sample No.	Hardness, HPa	Wickers hardness, HV	Elastic modulus, HPa
VT1-00	2.27 ± 0.41	215 ± 39	119 ± 4
06*	7.14 ± 3.04	675 ± 287	158 ± 123
08*	4.87 ± 3.17	460 ± 300	122 ± 119
12*	9.46 ± 2.38	894 ± 225	260 ± 80
06	5.69 ± 1.56	538 ± 147	95 ± 20
08	16.38 ± 0.70	1548 ± 66	173 ± 18
12	14.98 ± 0.28	1416 ± 27	234 ± 55

* Metal oxide coating without HA nanoparticles.

2) planar sub-micrometer crystals;

3) prismatic crystals resulting in strong frame.

The growth of a TiO_2 coating on a heterogeneous surface results in transformation of needle crystals (thickness, 30-80 nm; length, 0.6-1.3 μm) into typical plane structures (size, 1-2 μm). Metal oxide coating applied to a plane surface at 1000°C is converted to a 0.2-0.4-μm layer. At induction temperature >800°C and induction time >120 sec, the morphological heterogeneity decreases by 30-50%. Therefore, the induction treatment parameters 600-800°C and 30-120 sec are recommended.

The raster electron microscopy of the coating surface revealed porous structure of TiO_2 modified by nanoparticles (Fig. 2).

The coating surface relief is formed after oxidation. Nanometric structure is represented by rounded grains, their agglomerates, and fine pores. The frame of the structure is a metal oxide matrix with structure relief modified by HA nanoparticles 30-50 nm in size (Fig. 2b). Induction temperature increase results in formation of layered structure (pore size, 50-500 nm).

The mechanical properties of titania coating (nanometric hardness) are given in Table 1.

Titania coating hardness depends parabolically on induction treatment temperature. A local minimum is observed within the temperature range 840-870°C. This fact is interpreted as being due to crystal structure modification (phase transition α-Ti ⇔ α-Ti) or coalescence of needle crystals observed microscopically. Further hardness increase is observed under limited oxygen supply. Otherwise, the coating hardness decreases. Thus, planar structure is characterized by decreased mechanical hardness. In general, the hardness of the coating is high enough (8-12 times harder than bone tissue).

The hardness of the coating modified with HA nanoparticles at induction treatment temperature 600°C is

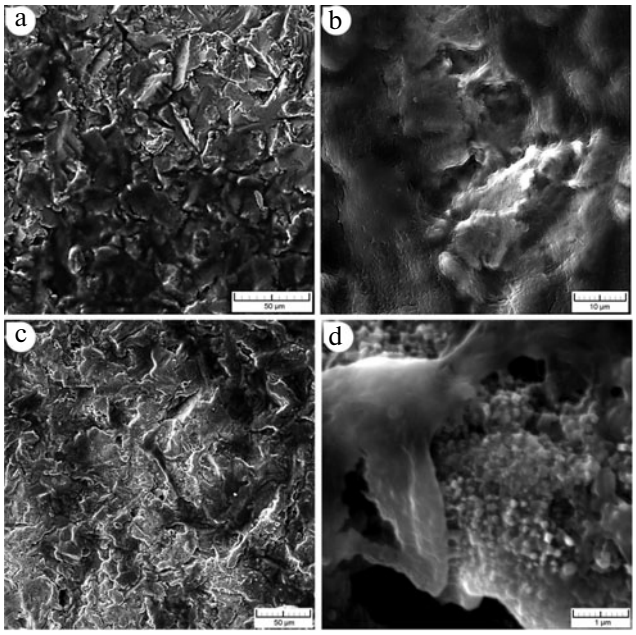

Fig. 3. Morphology of titanium (a, b) and TiO_2 coating obtained at induction treatment temperature 800°C and treatment time 120 sec (c, d) after *in vitro* tests for 14 days.

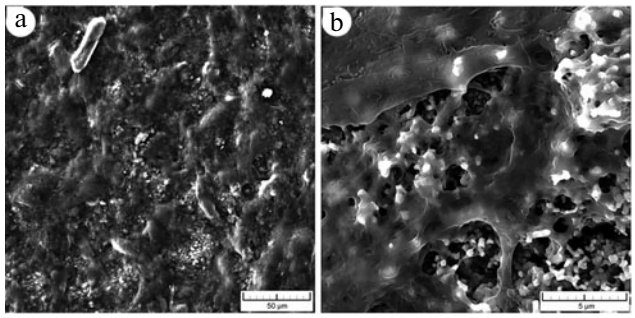

Fig. 4. Morphology of TiO_2 coating obtained at induction treatment temperature 800°C after *in vitro* tests for 14 (a) and 28 (b) days.

6 HPa, which is three times larger than the hardness of titania substrate. At induction treatment temperature 800-1200°C, the nanohardness is maximal (15-16 HPa), where it is 7.5-fold higher than the hardness of titanium VT1-00. The elastic modulus of the coating at induction treatment temperature 600°C is lower than that value for titanium. At induction treatment temperature 800-1200°C, the elastic modulus of the coating reaches 173-234 HPa.

The biological compatibility of the TiO_2 coating *in vitro* provides attachment of fibroblasts (Fig. 3). A titanium VT1-00 sample treated with sand-wheel blasting was used as a control (Fig. 3, a and b).

The morphology of the needle crystals of the TiO_2 coating provides for the formation of complexes of biologically compatible coating and biological tissue. Nanopores provide cell adhesion (Fig. 3d). In microphotographs, the cells are shown as dark scattering objects. The electron detector allows the cell size and distribution over the surface to be estimated. The heterogeneity of the elemental composition is shown in the photographs as dark segments (Fig. 3, a and c). Analysis of the photographs demonstrates that cells are attached to 5-15-μm pores. Sub-micrometric and nanometric crystals facilitate adhesion. Thus, the TiO_2 coating provides biological compatibility in combination with mechanical hardness.

Modification of TiO_2 coating with HA nanoparticles stabilizes cell adhesion. Biological activity of complexes of TiO_2 with HA allows formation of a cell monolayer (Fig. 4). Hardness analysis of porous TiO_2 layers modified with HA nanoparticles demonstrates that such structures are the most promising for use in implant–bone tissue complexes.

Conclusions

The surface structure of titanium after induction treatment is morphologically heterogeneous and provides improved mechanical properties. The crystal structure of titania coating is needle-shaped, planar, and prismatic. The best parameters of morphology and mechanical hardness are observed after induction treatment 600-120 and 1200-120 and limited oxygen supply. Thus, thin-layer TiO_2 coatings with needle nanostructure provide biological compatibility *in vitro*. A thick-layer (5-10 μm) coating with increased mechanical hardness can be obtained on a titanium implant surface if necessary. The porous structure of the coating includes prismatic sub-micrometer crystals.

HFEC treatment combined with induction treatment forms mechanically strong composites of porous metal oxide matrix and HA nanoparticles. Thin-layer TiO_2 coatings with needle crystals modified with HA nanoparticles obtained at temperature 800-1200°C for 30 sec provide biological compatibility and mechanical hardness 15-16 HPa.

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