Advanced Materials Research Vol. 787 (2013) pp 376-381
Online available since 2013/Sep/04 at www.scientific.net

doi:10.4028/www.scientific.net/AMR.787.376

Structure of Composite Biocompatible Titania Coatings Modified with Hydroxyapatite Nanoparticles

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Keywords: Titania, Hydroxyapatite, Biocompatible coating, Induction heat treatment, Oxidation, Intraosseous implant

Abstract. The article describes prospective composite biocompatible titania coatings modified with hydroxyapatite nanoparticles and obtained on intraosseous implants fabricated from commercially pure titanium. Consistency changes of morphological characteristics and crystalline structure, mechanical properties and biocompatibility of experimental titanium implant coatings obtained by the combination of oxidation and surface modification with hydroxyapatite during induction heat treatment are defined.

Introduction

In medical practice, metals, particularly titanium and its alloys, are widely used when prosthetic components, joint endoprostheses and intraosseous dental implants are fabricated [1]. It is especially important to obtain biocompatible coatings that improve osseointegration on the surface of these medical devices. The metal base of such implants has resistance to mechanical loads of distributed type. When installed with an interference fit in the prepared bone bed there is significant shear force causing delamination and biocompatibility reduction. In such extreme conditions, the surface layer mechanical characteristics (a combination of hardness and sufficient elasticity) require special attention. Moreover the biocompatible coating should have high porosity and morphological heterogeneity of the microstructure, as well as the homogeneity of nanostructures [2].

The surface structural modification is usually made by arc-plasma spraying, vacuum-condensation methods of deposition (PVD, CVD) and oxidation [3]. A characteristic feature of these methods is high energy consumption and cost of materials, coating material low efficiency, complex technological sequence, relatively long duration of obtaining the required phase-structural state, decreased mechanical strength and fracture toughness at high porosity, and limited or lack of possible formation of nanometer structure elements.

Theoretical and experimental studies of the oxidation of titanium and its alloys by P. Kofstad, D. Liner, as well as more recent studies are well-known [4]. However, it is an important problem of obtaining mechanically strong functional coatings having bioactivity on the surface of metallic biocompatible materials. Considering the above mentioned the aim of this work is to develop a technology enabling to obtain on titanium biocompatible mechanically durable coatings with increased morphology of micro- and nanostructure by using a new method of induction heat treatment (IHT) and modification of hydroxyapatite (HA) nanoparticles.

Materials and methods

The samples are 2 mm thick plates of commercially pure titanium VT1-00, the surface of which was subjected to sandblasting and ultrasonic cleaning. The surface of the prepared samples is oxidized using induction heating technique in an oxygen-containing environment, e.g. air at atmospheric pressure. Next is the modification with colloidal HA nanoparticles and final induction heat treatment (IHT) of 30…300 s. The IHT effect in the temperature range of 600...1200 °C on the performance of micro- and nanostructure of the coatings and mechanical properties was defined. Regimes of the coating samples were assigned to double numbers: the first number corresponded to the temperature of titanium base IHT (06 – 600 °C, ... , 12 – 1200 °C), the second marked the heat treatment duration measured in seconds. For example, IHT regime 06-120 designates the temperature of 600 °C and the exposure duration of 120 s.

To study the phase-structural state of coatings X-ray diffraction analysis (XRD; Gemini/Xcalibur; CuKα, $\lambda = 1{,}541874$ Å) and scanning electron microscopy (SEM; MIRA II LMU) were applied.

Mechanical properties were evaluated by nanoindentation studying thin-layer coatings with low (10 mN) load applied to the Berkovich indenter (NANOVEA Ergonomic Workstation; ISO 14577, ASTM E 2546).

Biocompatibility testing of coating samples was carried out *in vitro*. Human dermal fibroblasts separated by adult donor normal skin fragment migration were used.

Results and discussion

The oxide coatings on the titanium surface are titania TiO_2 – rutile (Fig. 1). Percentage of coating phase depends on the IHT temperature and duration. The results of phase composition of coating samples obtained at IHT of 1000 °C are shown in Table 1.

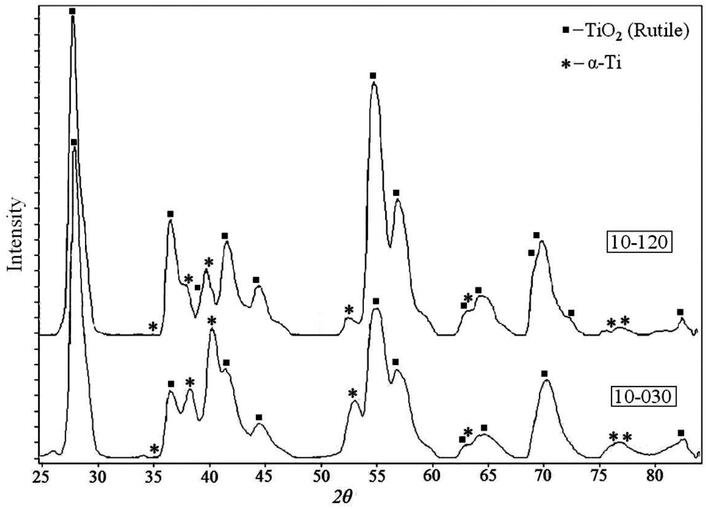

Fig. 1. XRD analysis of experimental coatings obtained at regimes 10-030 and 10-120

Table 1. Phase composition of oxide coatings obtained using IHT of titanium VT1-00

Sample	Processing conditions		Phase composition of the coatings, %	
	Temperature, °C	Duration, s	α-Ti	TiO_2 (rutile)
10-030	1000	30	29	71
10-120		120	17	83
10-300		300	0	100

The structure of the oxide matrix layer coatings is defined by intensive oxidation due to thermophysical effect of high-frequency (hf) currents. Rutile crystals form depends mainly on the IHT temperature, so at 600 °C rounded and plate oxide structures are formed. With the increase of the IHT temperature to 800 °C needle-like crystals having the width of 30...80 nm and the length of 600...1300 nm are formed (Fig. 2a). When the IHT duration exceeds 150...180 s defects in the coating increase which leads to split plate and prismatic crystal forms of 200...400 nm (Fig. 2b).

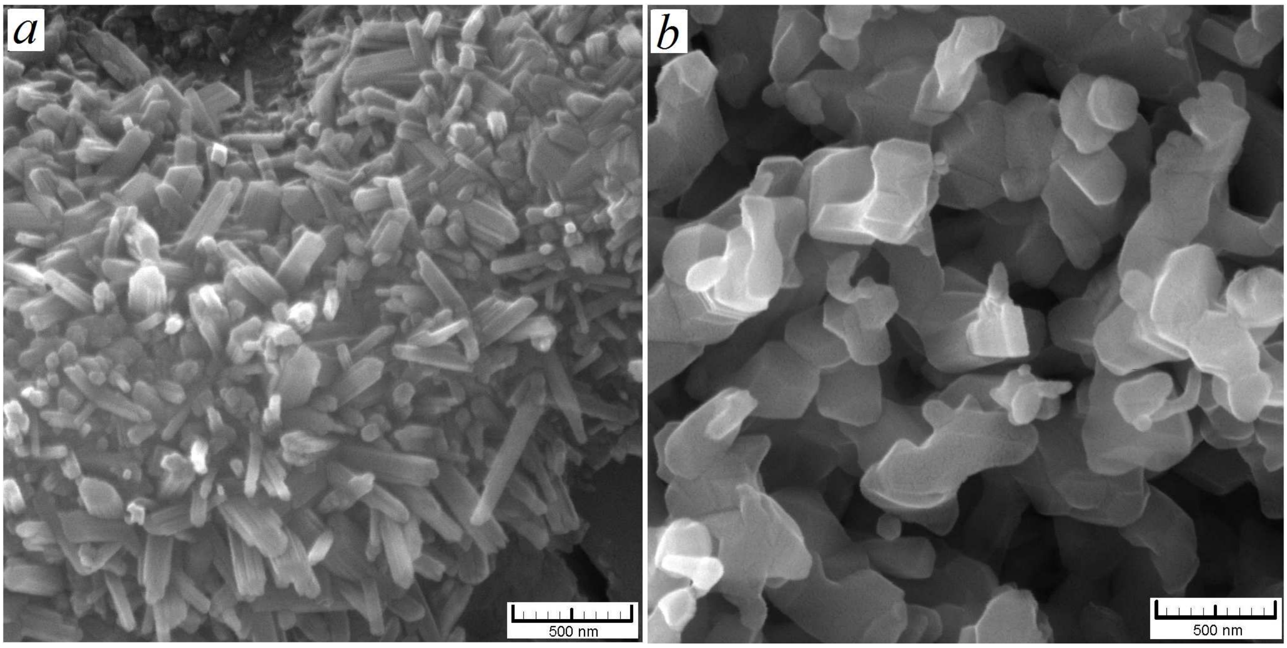

Fig. 2. SEM of surface morphology of titania coatings:
a – needle-like nanocrystals (IHT 08-030); *b* – prismatic submicron crystals (IHT 12-120)

SEM of surface morphology of composite coatings has shown the porous structure consisting of an oxide TiO_2 matrix which is modified with HA nanoparticles (Fig. 3).

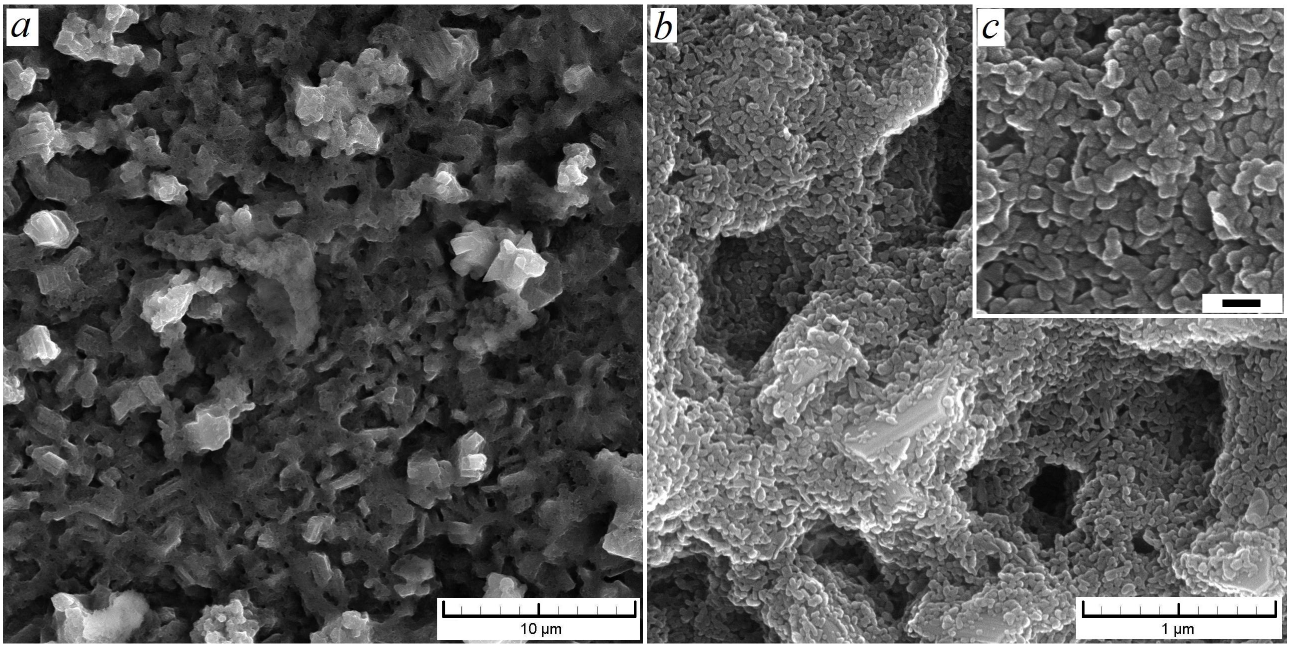

Fig. 3. SEM of surface morphology of composite titania coatings modified with HA nanoparticles:
a, *b* – microstructure; *c* – nanostructure (mark = 100 nm)

The surface microstructure is a relief of the original metal base mechanically processed and oxidized (Fig. 3a). The nanometer scale research reveals the fine structure presented by rounded grains, their agglomerates and the smallest pores (Fig. 3b). The matrix of this structure is formed by an oxide TiO_2 with the relief elements (ridges, open pores) which are uniformly modified with a thin layer of HA nanoparticles having an average size of 30...50 nm (Fig. 3c).

The uniformity of the obtained bioactive ceramic layer is confirmed by XRD analysis. Modifying HA nanoparticles agent remains in sufficient quantity and the decomposition phases (e.g. tetracalcium phosphate, tricalcium phosphate) having accelerated resorption in this range of the IHT temperature and duration were not revealed (Fig. 4). Thus, modification with bioactive ceramic HA nanoparticles improves morphological and geometric characteristics of the intraosseous implant surface layer.

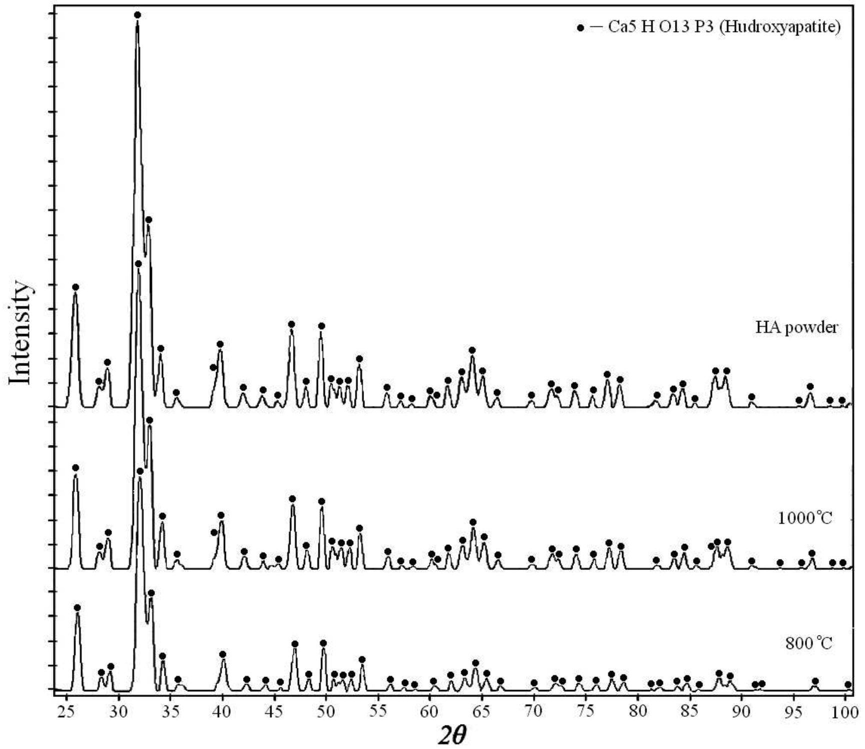

Fig. 4. XRD analysis of thick-layer nanocrystalline HA coatings obtained on the surface of titanium samples at the IHT temperatures: 800 °C (lower spectrum), 1000 °C (middle spectrum) and synthetic powder (upper spectrum)

Titania coatings and its composition with HA nanoparticles are characterized by high hardness and elastic modulus (Table 2).

Table 2. Mechanical properties of biocompatible coatings defined by nanoindentation

Sample	Hardness, GPa	Vickers hardness, HV	Elastic modulus, GPa
VT1-00	2,27 ± 0,41	215 ± 39	119 ± 4
06-120*	7,14 ± 3,04	675 ± 287	158 ± 123
08-120*	4,87 ± 3,17	460 ± 300	122 ± 119
12-120*	9,46 ± 2,38	894 ± 225	260 ± 80
06-120	5,69 ± 1,56	538 ± 147	95 ± 20
08-120	16,38 ± 0,70	1548 ± 66	173 ± 18
12-120	14,98 ± 0,28	1416 ± 27	234 ± 55

* – oxide coatings without HA nanoparticles

The titania coating hardness is described by a parabolic dependence on the IHT temperature. Local minimum corresponds to the range of 840...870 °C which may be caused by the changes in the titanium base crystal structure (phase transition α-Ti ↔ β-Ti). Further increase in hardness is ensured by limited access of oxygen, otherwise the coating hardness decreases sharply and the coating separates spontaneously. In general, the obtained hardness characterizes these coatings as high-strength and the margin of mechanical properties compared to the cortical bone tissue is 8…12 times higher.

The hardness of coatings modified with HA nanoparticles at IHT of 600 °C is characterized by triple increase up to 6 GPa compared to the titanium base. With the further increase in IHT temperature up to 800...1200 °C the hardness is highest and equals 15...16 GPa which is 7.5 times higher than the hardness of titanium VT1-00. Elastic modulus of coatings obtained by IHT at 600 °C is slightly lower than that of titanium but at 800 °C and 1200 °C it increases to 173...234 GPa.

In vitro biocompatibility testing of titania coatings showed that the high morphological heterogeneity of the surface structure ensures stable fibroblast adhesion (Fig. 5).

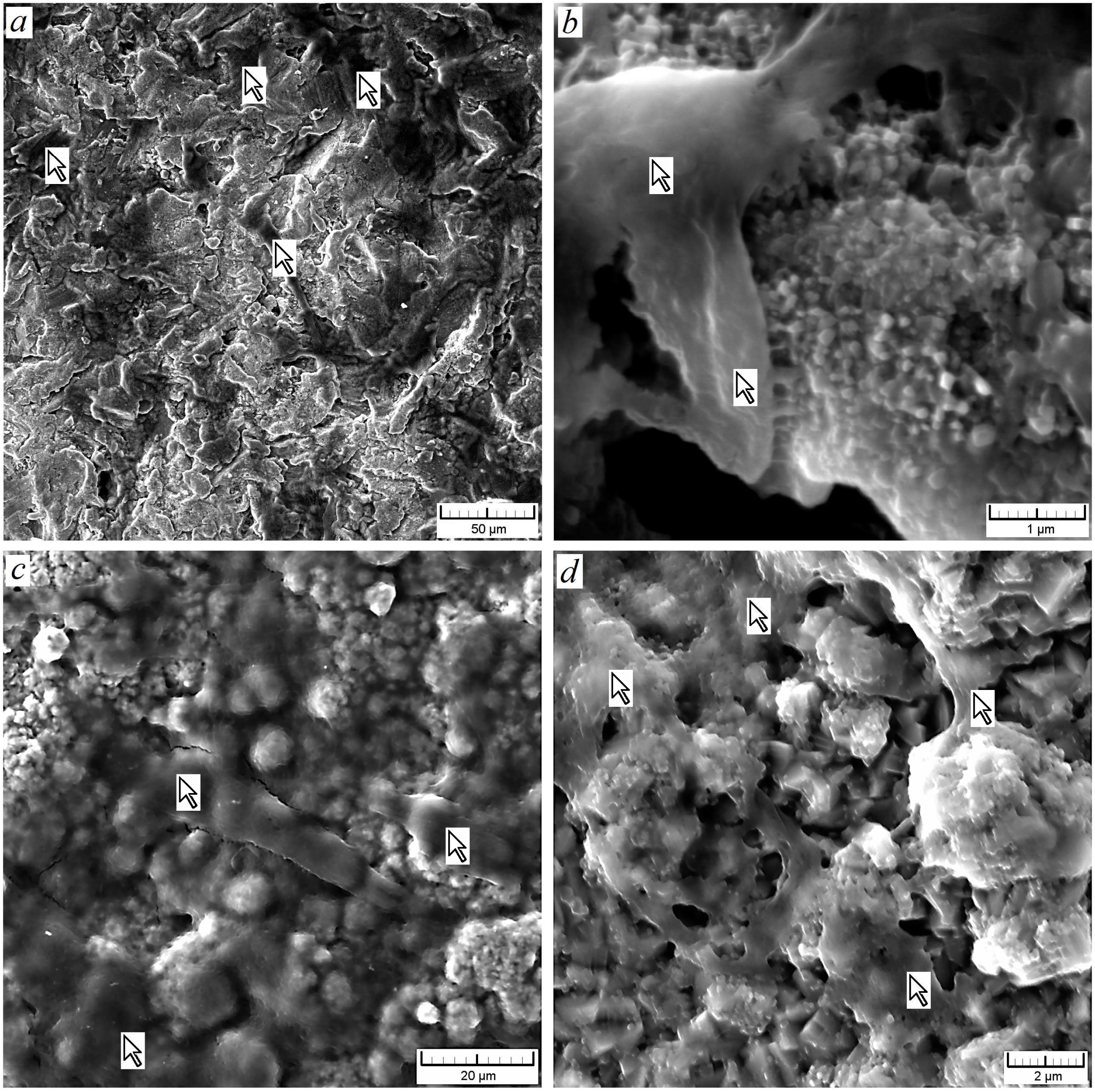

Fig. 5. SEM of surface morphology micro- (*a*, *c*) and nanostructure (*b*, *d*) of biocompatible coatings after *in vitro* testing: *a*, *b* – titania coating obtained at IHT regime 08-120; *c*, *d* – titania coating with HA nanoparticles obtained at IHT regime 10-120 (arrows show fibroblasts)

It was defined that the increased morphological heterogeneity of needle-like titania structure coatings stimulates the formation of a single complex «biocompatible coating – biological structure». Numerous nanopores facilitate cell adhesion (Fig. 5 *b*, 5 *d*). SEM images show cells as dark scattering objects (shown by arrows). Fibroblasts are fixed mainly in micropores having an average size of about 5...15 µm. In this case, cell adhesion is best stimulated in the presence of submicron and nanometer crystals. Thus, we can state that the titania coatings have high biomechanical compatibility, especially geometric bioactivity combined with high hardness.

Modification of titania coatings with HA nanoparticles enhances cell adhesion. Increased bioactivity of HA nanocrystalline phase and morphological heterogeneity of the composite porous structure lead to rapid formation of the cell monolayer, in-depth penetration of porous structure and minimize the area without fixed cells (Fig. 5 *c*). Analysis of hardness measurement results suggests that the composite porous titania coatings modified with HA nanoparticles are the most highly promising functional element of the biotechnical system «intraosseous implant – biological tissue».

Conclusions

The surface structure of commercially pure titanium after IHT is characterized by high morphological heterogeneity and mechanical properties. Titania coatings are formed of plate, needle-like and prismatic nanocrystals. The optimal parameters of morphology and high hardness are achieved at IHT regimes 06-120 and 12-120 (at limited access of oxygen). Thus, the thin-layer titania coating with needle-like crystal nanostructure is highly biocompatible, that is established by *in vitro* testing. To obtain a thick-layer coating (about 5...10 μm) with high hardness on titanium implants it is necessary to form a porous crystalline structure consisting of submicron prismatic crystals.

Oxidation at IHT and the subsequent modification with HA nanoparticles provide the formation of mechanically strong composite structure consisting of a porous titania matrix (rutile) and nanocrystalline bioactive ceramic filler. It was established that thin-layer porous titania coatings modified with HA nanoparticles and formed by heating from 800 to 1200 °C and holding of at least 30 s have high bioactivity and hardness of 15...16 GPa.

Acknowledgments

The research was carried out with partial financial support: grant RFBR 13-03-00898, № 13-03-00248, grant of the President of the Russian Federation MD-97.2013.8, SP-1051.2012.4, as well as Russian Ministry of Education, with the support of the Federal Target Program «Research and scientific-pedagogical personnel of innovative Russia» for 2009-2013, contract 14.B37.21.0571.

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Advanced Materials Researches, Engineering and Manufacturing Technologies in Industry
10.4028/www.scientific.net/AMR.787

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