Production of nano-ceramic coatings on titanium implants

A A Fomin¹, I V Rodionov¹, M A Fomina¹, N V Petrova²

¹ Yuri Gagarin State Technical University of Saratov, Saratov, Russia
² Saratov State University, Saratov, Russia

E-mail: afominalex@rambler.ru

Abstract. Composite titania coatings modified with hydroxyapatite nanoparticles were obtained on intraosseous implants fabricated from commercially pure titanium and titanium alloy Ti-2.5Al-5Mo-5V. The present study aims to identify consistency changes of morphological characteristics and physico-mechanical properties of titanium items coatings obtained by oxidation during induction heat treatment and modification with colloidal hydroxyapatite nanoparticles. The influence of temperature between 600 and 1200 ºC and duration of thermal modification from 1 to 300 s was studied. It was established that high hardness about 6.7±1.9 GPa for nanocrystalline TiO₂ coatings and 19.2±0.6 GPa for nano-ceramic “TiO₂+HAp” coatings is reached at 1000 ºC and 120 s.

1. Introduction

In medical practice, metals, particularly titanium and its medical alloys (Ti-2.5Al-5Mo-5V, Ti-4Al-6V, etc.), are widely used when endoprostheses and dental implants are manufactured [1]. It is especially important to produce biocompatible materials and coatings in order to improve osseointegration on the surface of these medical items [2]. The metal substrate of such implants has resistance to mechanical loads of distributed type. When installed with an interference fit into the prepared bone bed there is significant shear force causing coating delamination and biocompatibility reduction. Under 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 morphological heterogeneity of the microstructure, combined with the homogeneity of nanostructure [3, 4].

The surface structural modification is usually performed by plasma spraying, sol-gel deposition, oxidation, etc. [5, 6]. A characteristic feature of these methods is high energy consumption and cost of materials, complex technological sequence, relatively long production of the required phase state, lower mechanical strength combined with high porosity, limited or lacking possible formation of nanoscale elements. It is an important problem of obtaining of mechanically strong functional coatings having high biocompatibility on the surface of metallic materials.

Electrical equipment that generates high frequency eddy currents is used to ensure the necessary physico-chemical effects on the well-conductive materials and various composites. Hence the aim of this work is to develop a technology enabling to produce on titanium biocompatible mechanically durable oxide coatings with increased morphology of micro- and nanostructure using a new method of induction heat treatment (IHT) and surface modification by nano-ceramic bioactive materials, such as hydroxyapatite (HAp) nanoparticles.
2. Methodology

2.1. Preparation of coatings
Titanium samples are cylinders fabricated from commercially pure (CP) titanium and titanium alloy Ti-2.5Al-5Mo-5V. Their surface is subjected to machining and micro-texturizing treatment comprising abrasive air-blasting by corundum abrasive with dispersion of 200...300 μm. Titanium samples are subjected to ultrasonic cleaning in aqueous surfactants and ethanol.

The surface of the prepared samples was oxidized by IHT in an oxygen-containing environment. An IHT thermal cycle comprises intensive heating up to the required temperature, exposition at the same temperature from 1 to 300 s and still air cooling.

The next stage included modification with colloidal HAp nanoparticles and final IHT of composite structure for less than 300 s. Using atomization the microdroplets of colloid solution are entered into the air stream and further this mixture is directed onto the surface of the sample with an oxide matrix coating.

The IHT effect at 600...1200 °C on the performance of micro- and nanostructure of the coatings and mechanical properties was defined. IHT regimes were given double numbers: the first number indicated the temperature of titanium substrate, the second one marked the heat treatment duration in seconds. For example, IHT regime “1000-001” designates the temperature of 1000 °C and the exposure duration of 1 s (transition to stationary thermal treatment).

2.2. Coating characterization
To analyze the surface morphology of the coatings scanning electron microscopy (SEM) was applied. SEM of the coatings is performed on MIRA II LMU (HV: 30 kV). The microstructure of coatings was studied at magnification from ×1000 to ×20000 and nanostructure – from ×100000 to ×200000.

Hardness of the coatings were analyzed by nanoindentation using a mechanical properties tester Nanovea Ergonomic Workstation with low (100 mN) load applied to Berkovich indenter.

3. Results and discussion

3.1. Surface morphology
The structure of the titania (TiO₂, rutile [3]) coatings is determined by intensive oxidation due to thermophysical effect of high-frequency currents in titanium substrate (Figure 1a).

![Figure 1. Microstructure of titania (a) and nano-ceramic (b) coatings (×1000).](image-url)
The shape of rutile nanocrystals is associated with the IHT temperature, so at 600…800 °C rounded, needle-like and plate oxide structures are formed [4]. On the surface of titanium alloy Ti-2.5Al-5Mo-5V mainly rounded crystals are formed (Figure 2a). When the IHT temperature reaches 800 °C, the crystals grow as well (Figure 2b). When IHT exceeds 1000 °C and 150...180 s the number of coating defects increases causing plate splitting and the formation of prismatic crystals. When the temperature and IHT duration increase the crystals grow to 150…300 nm. At the temperature above 1000 °C and exposure duration more than 120 s the oxide coating becomes quite thick as there appear numerous fractures and its spontaneous destruction is observed.

![Figure 2. Nanostructure of titania coatings obtained on IHT regime: a – “800-120” on titanium alloy Ti-2.5Al-5Mo-5V (×133000); b – “800-030” on CP-Ti (×100000).](image)

The matrix of this composite structure is formed by titania crystals with the relief elements uniformly modified with a thin layer of HAp nanoparticles having an average size of 30...70 nm (Figure 1b, 3).

![Figure 3. Porous structure of nano-ceramic TiO₂+HAp coatings obtained on IHT regime: a – “1000-030” (microstructure, ×20000); b – “600-120” (nanostructure, ×200000).](image)
At this modification HAp nanoparticles can penetrate into pores, micro- or nanochannels, and fractures. Changing the saturation of oxide matrix with the filler mechanical properties of the coatings, hardness in particular, and other biocompatibility qualities can be controlled.

3.2. Hardness

Oxide TiO\(_2\) and nano-ceramic TiO\(_2\)+HAp coatings are characterized by enhanced hardness (Figure 4). In general, the required hardness values characterize these coatings as high strength, and the margin of hardness compared to cortical bone is 8...12 times higher [3]. This parameter completely ensures the integrity of biocompatible coating during the installation with the interference fit into the prepared bone bed and further functioning under the physiologically normal loads.

![Figure 4. Hardness of nanocrystalline TiO\(_2\) and TiO\(_2\)+HAp coatings.](image)

The hardness of coatings modified with HAp nanoparticles at IHT of 600 °C is characterized by triple increase to 6 GPa compared to the titanium substrate. When the IHT temperature increases to 800...1200 °C the hardness value is highest and equals 15.0...19.2 GPa. Highest hardness is reached at the chosen duration of thermal treatment about 120 s.

4. Conclusions

The surface structure of titanium and titanium alloy Ti-2.5Al-5Mo-5V after IHT is characterized by high morphological heterogeneity and mechanical properties. Titania coatings are formed of rounded, needle-like, plate, and prismatic nanocrystals. The optimal combination of nanostructure parameters and high hardness 4.9...9.5 GPa of thin-coatings is achieved at IHT regimes “800-030” and “800-120”. To obtain a thick-layer coating (≥ 10 μm) with high hardness on the implant surface it is required to form a porous structure of prismatic crystals at IHT regimes “1000-120”, “1200-030” and “1200-120”.

Oxidation at IHT and subsequent modification with HAp provide the formation of mechanically strong composite structure consisting of porous titania matrix and nanocrystalline bioceramic filler. It was established that porous titania coatings modified with HAp nanoparticles and formed by heating from 800 to 1200 °C and holding for at least 30 s have high bioactivity and hardness of 15.0...19.2 GPa.
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References
[1] Paital S and Dahotre N 2009 Mater. Sci. Eng. R 66 1
[2] Dorozhkin S V 2010 Biomaterials 31 1465
[3] Fomin A A, Steinhauer A B, Rodionov I V, Fomina M A, Zakharevich A M, Skaptsov A A, Gribov A N and Karsakova Ya D 2014 J. Fric. Wear 35 32
[4] Fomin A A, Steinhauer A B, Rodionov I V, Fomina M A and Zakharevich A M 2013 Tech. Phys. Lett. 39 969
[5] Sung Y-M, Shin Y-K and Ryu J-J 2007 Nanotechnology 18 065602
[6] Lee B-H and Koshizaki N 2008 Nanotechnology 19 415303