Formation of a combined bioceramics layer on titanium implants

P A Tsygankov¹,², A S Skryabin¹, A A Krikorov¹, R I Chelmodeev¹, V R Vesnin¹, and F F Parada-Becerra²
¹ Bauman Moscow State Technical University, Moscow, Russia
² Universidad Industrial de Santander, Bucaramanga, Colombia

E-mail: piotrtsy@mail.ru

Abstract. Titanium and its alloys are currently the main materials for prosthetics, despite the fact that they, like other metals, have significant drawbacks: they cause metallosis, can provoke the formation of fibrous tissues and bone resorption in the contact zone, are toxic and, in some cases, allergenically dangerous. The novel trend in implant technology is the prevention of direct contact of living tissues with the metal surface. For this reason, various types of protective coatings are used, usually on the base of ceramics or carbon. It is known that in the contact zone it is preferable to create a well-developed or even porous surface with osteointegrative properties. This paper discusses the combined technology of modification of titanium. Implant surface treatment includes two main stages: 1) growing a porous protective layer of titanium dioxide deep into the material surface and 2) filling the pores formed on the surface of titanium dioxide with hydroxyapatite to ensure high osseointegrative properties. The formation of a layer of titanium dioxide is provided by microarc oxidation processing with controllable density of pulsed current; then the pores are filled with crystalline hydroxyapatite by detonation spraying. The results of studying the structure and surface properties of the modified titanium samples are presented and discussed.

1. Introduction

Despite the increasingly active introduction of carbon-based materials into medical practice [1,2], today titanium and its alloys remain the main materials in the medical prosthetics industry, as they provide good performance characteristics of products, especially those experiencing high mechanical stresses, such as implants, anchors, clamps and fasteners threaded items. The ability of titanium to form a protective amorphous oxide film under atmospheric conditions, a low corrosivity and its bioinertness contribute to osseointegration, which in some cases, unfortunately, is insufficient. This fact makes look for new opportunities to improve the osseointegrative properties of titanium products.

Possible solutions can be very roughly divided into three distinct areas: the formation of a special structure of the titanium surface (for example, the use of porous or granular structures, the formation of a well-developed surface) (1); growing or deposition of protective (as a rule, ceramics) layers in the zone of contact with bone tissues that prevent the emission of metal or impurities into the body (2); the use of bioactive coatings that stimulate bone growth (3).

It is obvious that it is impossible to find any single technology that would implement all possible options at a reasonable price for industry. In our opinion, the combination of microarc oxidation (MAO) surface treatment of titanium with the subsequent deposition of hydroxyapatite (HA) by detonation spray method provides a coating with potentially high osseointegration properties and good
prospects for industrial applications. Next, we describe the features of the implementation of this combination of high-performance technologies.

2. Description of methods

When developing the coating, it was supposed to create a titanium dioxide layer on the surface of the titanium implant with good adhesion to the substrate and a thickness sufficient to act as a barrier to the penetration of metal particles into the tissues of the body. It is desirable to have a well-developed and/or porous ceramic surface also. The layer of hydroxyapatite with high crystallinity deposited on the layer of titanium dioxide should act as a bioactive layer. The adhesion of the outer layer of HA is ensured both by the porosity of the ceramic substrate and the technology of applying this layer.

A reliable isolation of the surface of the titanium implant from direct contact with body tissues is provided by a titanium dioxide film of noticeably greater thickness (more than 1 μm) than that formed in natural atmospheric conditions. Known methods of titanium dioxide film formation, such as physical vapor deposition (PVD) in a reactive gas environment [3] or potentiostatic anodizing [4,5], are either relatively expensive or require long processing times.

Microarc oxidation has long been used in aerospace, oil, automotive, electrical industries as a technology for modifying the surface of valve-type metals including titanium [6]. A remarkable feature of this technology is that, in an aqueous electrolyte solution, micro discharges transform the surface layers of a metal into oxide compounds of this metal. Moreover, the growth of oxide phases goes deep into the surface of the metal, practically without changing the external dimensions of the product. This means that this technology can be the finish for most titanium implants and fixing elements, while maintaining the necessary sharpness of the working edges and overall dimensions of the product, but at the same time convert the metal surface into ceramics.

Titanium dioxide exists in the form of several crystalline modifications: with tetragonal syngony (anatase, rutile) and rhombic syngony (brookite). In [7], it is argued that the anatase phase of titanium dioxide is the preferred phase for stimulating of the osseointegration.

The source of material for the hydroxyapatite coating is usually the powder phase, and the material is deposited to the substrate by PVD technologies [3], jet spraying [8] or electrochemical and electrophoretic methods [9,10]. Moreover, the stoichiometric composition is usually guaranteed only by electrochemical methods, since in other technologies the HA exposed to complex high energy effects in plasma or high enthalpy gas flows. As a result, the initial HA is decomposed in the deposition process into components that have significantly different evaporation enthalpy temperatures and depletion of one of the components occurs (usually phosphorus compounds). In addition, HA coatings with a high degree of crystallinity are preferred, since amorphized layers dissolve rather quickly in the body and there is no improvement in the osseointegration properties of implants.

Vacuum PVD methods, having a high cost and low productivity, form layers with poorly pronounced crystallinity and lean composition. Jet spraying methods (cold spraying, plasma jet, high velocity oxygen fuel) are widely used in the medical device industry because of the high productivity of these methods and the relative simplicity of the organization of the process. But in this case it is necessary to ensure good adhesion of the sprayed layer, which for this class of technologies is associated with the processes of thermal formation of the interface between the substrate and the coating by converting the enthalpy of the high speed flow with the powder into thermal energy.

With significant heat loads on HA particles and large times (~10⁻²...5·10⁻² s) of staying particles in the high-temperature region of flow, the pyrolysis of apatite makes it necessary to correct the ratio of the components of the original powder, and in some cases can lead to significant deviations in stoichiometry through coating thickness.

The detonation spray method which is used in this work is inherently a pulsed process and makes it possible to fine-tune the ratio between the average power and the kinetic energy of the powder fed to the substrate. This, in turn, provides not only the maintenance of HA stoichiometry in the coating, but also enables control over the degree of crystallinity of the coating.
3. Experimental results
Since the MAO process by its nature, is the process of spark breakdown of a dielectric film on a metal, the surface obtained after processing is characterized by porosity, which is avoided under normal conditions by choosing technological modes that reduce the discharge current density to a level not exceeding 50 A/dm² to achieve low porosity over the entire surface. In this paper, we take the opposite approach, using the increased energy of the microarc and the corresponding current densities of up to 150 A/dm² we form a well-developed porous ceramic surface with a total thickness of about 30±3 μm. In order to understand how the treatment at forced current mode changes the characteristics of the oxidized layer, a comparative analysis of the titanium alloy samples processed in these two modes was performed.

The X-ray diffraction (XRD) pattern of Ti-6V-4Al titanium alloy sample which was treated at a standard current density is presented at Figure 1, while Figure 2 shows the XRD pattern for a sample processed at an increased current density. These Figures demonstrate also the lattice interplanar distances of the titanium and titanium oxide. The corresponding phases are designated as: (Ti)-titanium, (Rt)-rutile, (Ant)-anatase. All XRD studies discussed in this work were performed on a DRON-3M X-ray diffractometer equipped with a CuKα copper anode. It can be seen that in the Figure 2 a peaks at an angles of 2θ=25.25° and 2θ=48.1° which correspond to the bioactive phase of titanium dioxide – anatase, are clearly recorded. It should be noted that the total processing time at high current density is also reduced in several times.

Microhardness measurements and adhesion testing of treated samples were performed by Nanovea Scratch Tester M1 equipment. Microhardness was measured in accordance with recommendations of ISO 6507 standard [11]. The scratch test was carried out with a 0.2 mm diamond indenter at a load of up to 60 N. Surface roughness was evaluated with a Form Talusurf PG420 profilometer according to ISO 468 standard [12]. A sample treated by MAO at the standard current densities has a dense surface with a microhardness of HV0.5<sub>15</sub> 330±20 MPa with a roughness of R<sub>a</sub> = 0.44 μm, a sample processed at
elevated current densities has a slightly higher roughness of $R_a = 0.48 \, \mu m$, a noticeably lower microhardness $HV_{0.5/15} = 290 \pm 6 \, MPa$ and loose coarse surface. However, after removing the upper loose layer and polishing the microhardness of both samples became close, the microhardness of the latter increased to $HV_{0.5/15} = 340 \pm 11 \, MPa$, and the roughness for both samples was $Ra = 0.20 \, \mu m$. The scratch test showed the adhesion of the modified layer for both samples above 50 N. Good adhesions for both samples is explained by the same mechanism of growth of the modified layer deep into the titanium surface.

The HA coating was sprayed using the installation described earlier in [13,14]. The distance from the muzzle to the substrate was 14 cm. The ratio of volume concentrations of oxygen and fuel (acetylene) was 2.1. As the initial HA, a powder ("Biteka", Ltd.) with an average dispersion of $\approx 30 \, \mu m$ was used. The Figure 3 shows the XRD pattern of HA coating sprayed on modified by MAO surface of a titanium sample Ti-6Al-4V. The Figure 4 demonstrates the XRD pattern of the initial powder. Interplanar distances of the HA lattice are indicated in both Figure 3 and Figure 4. It can be seen that the initial crystal structure of HA (interplanar distance) is reproduced quite well in the coating.

![Figure 3. XRD pattern of the HA coating.](image1)

![Figure 4. XRD pattern of the initial powder of HA.](image2)

Nicolet-380 equipment with Centaurus microscope was used to analyze the degree of crystallinity of the HA coating by Fourier-transform infrared spectroscopy (FTIR). The results are presented in Figure 5, which shows the dependencies for the initial powder (curve 1) and coatings obtained in different regimes (curves 2 and 3) of detonation spraying on the treated by MAO surface of Ti-6Al-4V samples. It can be seen that the degree of crystallinity of the coating can be controlled by changing the processing modes. The presence of crystalline apatite is indicated by a line of about $3570 \, cm^{-1}$, characteristic of carbonate-apatite, while the absence of narrow distinct spectral lines in the region of 1300-2300 $cm^{-1}$ indicates the degree of amorphization of HA in the coating.
4. Conclusion
Thus, the proposed treatment method, which includes an MAO treatment of a titanium implant followed by detonation spraying of HA, allows to obtain coatings satisfying the basic requirements: a titanium dioxide film with a developed surface, good adhesion, and a significant fraction of the bioactive phase - anatase is formed; the outer sprayed layer of hydroxyapatite has a high degree of crystallinity and reproduces the stoichiometry of the original HA powder.

Acknowledgments
The authors are grateful to Dr. Pavlov A. Yu. for important scientific advices and to Dr. Krylov I. E. and Barzinsky O. V. for the materials and equipment provided.

References
[1] Mironov S P, Shevtsov V L, Kononovich N A, Stepanov M A, Gorbach E N, Golubev G Sh, Sergeev K S, Arkhipenko V I, Grin’ A A, Skryabin V L, Reznik L B, Shatokhin V D, Baimuratov A A 2015 Carbonic nano-structural grafts - innovation product for traumatology and orthopaedics. Part 1: Experimental study results Bulletin of Traumatology and Orthopedics 3 46
[2] Borzunov D Yu, Shevtsov V I, Stogov M V, Ovchinnikov E N 2016 Analysis of the experience of use of carbon nanostructured implants in traumatology and orthopaedics Bulletin of Traumatology and Orthopedics 2 77
[3] Mattox Donald M 2010 Handbook of Physical Vapor Deposition (PVD) Processing 2nd Edition (Netherlands: Elsevier Inc.)
[4] Macak J M, Schmuki P 2006 Anodic growth of self-organized anodic TiO2 nanotubes in viscous electrolytes Electrochimica Acta 52(3) 1258
[5] Ghicov A, Tsuchiya H, Macak J M, Schmuki P 2005 Titanium oxide nanotubes prepared in phosphate electrolytes Electrochemistry Communication 7 505
[6] Suminov I V 2011 Plasma electrolytic modification of metal and alloy surfaces (Moscow: Technosphere)
[7] Kim H-M, Himeno T, Kokubo T, Nakamura T 2005 Process and kinetics of bonelike apatite formation on sintered hydroxyapatite in a simulated body fluid Biomaterials 26 4366

[8] Zhitomirsky I, Gal-Or L 1997 Electrophoretic deposition of hydroxyapatite Journal of Materials Science: Materials in medicine 8 213

[9] Zhitomirsky I 2000 Ceramic films using cathodic electrodeposition JOM-e 52(1) 1

[10] Davis J R 2004 Handbook of thermal spray technology (USA: ASM International)

[11] International Organization for Standardization (ISO) 2018 Metallic materials. Vickers hardness test, ISO 6507 (Switzerland: International Organization for Standardization)

[12] International Organization for Standardization (ISO) 1982 Surface roughness-Parameters, their values and general rules for specifying requirements, ISO 468 (Switzerland: International Organization for Standardization)

[13] Tsygankov P A, Skriabin A S, Loktionov E Yu, Telekh V D, Chelmodeev R I 2017 On using of gas detonation for spraying of biocompatible films onto the carbon nanocomposites Journal of Physics: Conference Series 815 012031

[14] Tsygankov P A, Skriabin A S, Telekh V D, Loktionov E Yu, Chelmodeev R I 2018 Interaction between dusty shock waves and three-dimensional scaffolds of carbon nanocomposites upon the deposition of biocompatible coatings Bulletin of the Russian Academy of Science: Physics 82 380