Pulsed High Power Action and Technology of Nanostructural Bioceramic Coatings

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The pulsed high power action on electrode electrolyte interface with microplasma discharges is the advanced method for obtaining nanostructural bioceramic coatings on titanium and titanium based alloys for stomatology and orthopedy. The coating formation process can be control with registration of cyclic voltammetry characteristics during each pulse using the original measuring equipment and construct the bioceramic coating with the given properties.

The high power microplasma technologies in electrolytic solutions are the most advanced method for obtaining nanostructural bioactive ceramic coatings on titanium implants containing hydroxyapatite [1]. These coatings have strong adhesion, high corrosion protection and wear resistance [2].

The high-density current flow through electrode/electrolyte interface initiates electro-chemical reactions, microplasma discharges and current-sheet charging. A topical problem is to research the mechanism of the fast proceeding pulsed microplasma processes, and mechanism of the bioceramic coating formation. For achievement of this purpose, it is necessary to develop the original equipment allowing record the voltammetry characteristics of these processes. The voltammetry characteristics are a source of the information about a nature and composition of the treatment material surface and the kinetics of the electrode processes and they allow control the contribution of the electrochemical and microplasma processes.

Developed the advanced equipment of a second generation new equipment – the Computer Aided Measurement System (CAMS) allows to measure shot current pulse duration (30–300 mks) and high current density (7–10 A/cm^2) and to control the high-voltage and high current signals of the microplasma coating formation and can be used for investigation the process of bioceramic coatings formation on titanium surface by pulsed microplasma processes [3]. CAMS improved technical and metrological characteristics.

It was shown from the experimental research the voltammetry characteristic shape depends from a nature of electrode, of an electrolyte composition, a time of process, an amplitude and pulsed duration of voltage polarization. New equipment allows record the voltammetry characteristics of the pulsed microplasma processes in electrolytic solutions keeping as soluble and an unsoluble component such as hadroxyapatite and calcium phosphate.

It is possible to supervise thickness, porosity, pore size, roughness, structure, composition and properties of the bioceramic coatings using the voltammetry characteristics.

The bioactive ceramic coatings were tested on hardness, adhesion, roughness, which were tested with help Nano Hardness Tester" NHT-S-AX-000X, Micro-Scratch Tester MST-S-AX-0000, and Micro Measure 3D station.

The cyclic voltammetry dependencies of the microplasma processes formation of the bioceramic coatings by the pulsed potentiostatic condition at various values of voltage were investigated. The voltammetry dependencies in electrolytic solutions with the different adds of chemical composition of calcium differ from each other.

The cyclic voltammetry characteristics depend on both nature of electrolyte and polarization voltage amplitude. The developed equipment for obtaining the bioceramic coatings on titanium and titanium-based alloys by the pulsed microplasma process is capable to treat the surface up to 50 dm^2 in area. The deposition rate is 2–3 μm/min.

The analysis of the voltammetry dependencies shows, that dynamic of voltammetry dependencies changes allows to supervise the process of bioceramic coatings formation and to construct bioceramic coatings with given properties.

Nano- and microporous bioceramic coatings obtained in the electrolytic solutions have different composition in dependence of titanium alloy and composition and component concentration of electrolyte.

Both the pore size and porosity coatings depend from the amplitude and pulse duration of the polarization voltage. With increasing the voltage amplitude the coating porosity grows passing through maximal value. Due to the microplasma process regimes, we can obtain the nanopores bioactive ceramic coatings with nanocrystalline structure.

Hydroxyapatite (HAp) and HAp/yttria-stabilized zirconium (YSZ) nanopowders were coated on Ti-

6Al-4V alloys using an electrochemical method, microplasma oxidation [4]. Both the HAp and HAp/YSZ films were uniformly coated with ~ 8–20 μm thickness on the alloys. X-ray diffraction (XRD) analysis results show that HAp film is XRD amorphous and HAp/YSZ is nanocrystalline with a rutile phase. Scanning electron microscopy (SEM) analyses on the films show uniform microporous structures, and these pores are observed as closed ones. Transmission electron microscopy (TEM) analyses reveal that HAp films are almost amorphous, containing anatase nanocrystals with ~ 30–40 nm size. TEM analyses on the HAp/YSZ films show formation of rutile nanocrystals with ~ 200–300 nm size as well as antase nanocrystals of ~ 20–30 nm size.

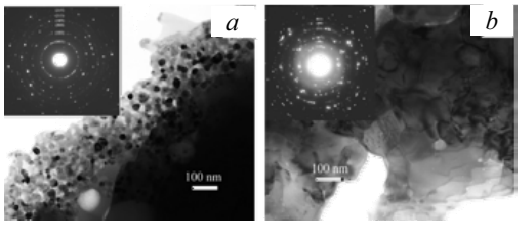

Fig. 1. Transmission electron microscopy (TEM) image of HAp coated Ti-6Al-4V alloy (*a*); its blown-up TEM image and selected area electron diffraction (SAED) pattern showing formation of nanocrystalline anatase. Transmission electron microscopy (TEM) image of HAp/YSZ coated Ti-6Al-4 V alloy (*b*); its blown-up TEM images and selected area electron diffraction (SAED) patterns showing formation of nanocrystalline anatase and rutile, respectively

Such coatings can be uniformly put both on a smooth surface, and on rough surfaces of implants, having the complex form and geometry. It is especially important, as now the different kinds of the implants are used in the orthopedic with the various function characteristics having as the smooth surface for knee joint and the rough surface for merging of bones.

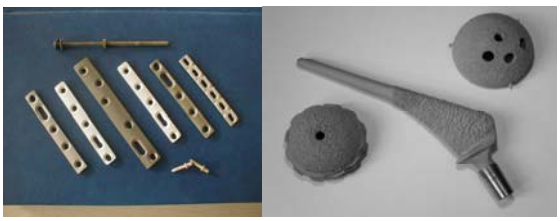

Fig. 2. Stomatologic and orthopedic implants with nanocrystalline bioceramic coatings

Due to high temperature produced during the microplasma discharges, the boiceramic coatings in fused state are deposited on metal surface immersed in an electrolytic solution. The process exhibits strong adhesion between the coated layer and the based material. Moreover, this technology makes it possible to apply nanoporous or microporous coatings by bridging large pores. It should be emphasized that coatings can be custom made for particular function and include a nonporous, dense surface and porous patches.

The composition of the coated layers their thickness, porosity, roughness, and hence physical-mechanical properties are determined by the mode of the microplasma processes and electrolyte used.

The nanoporous bioactive ceramic coatings with nanocrystalline structure of hydroxyapatite and titanium oxides has the high values of nano- and microhardness, strength adhesion, low roughness

For the first time new measuring equipment - the Computer Aided Measurement System was developed for recording the cyclic voltammetry characteristics of the high current pulsed microplasma process in high-voltage electrochemistry.

The cyclic voltammetry characteristic depends on the electrolyte and electrode composition, and the microplasma process regimes such as the shape, amplitude and the pulse duration of the polarization voltage, the process time.

The using of this equipment and the recording of the cyclic voltammetry characteristics open a new possibility of scientific research of kinetics and mechanism of bioceramic coatings formation.

The cyclic voltammetry characteristic is reflecting the influence of various factors at the given moment of the coating formation: the microplasma process regimes, the electrolyte and electrode material composition. The cyclic voltammetry characteristic and equipment, which allows them to record – CAMS and the research physical-chemical laws of the various factors influence on the voltammetry characteristics, that is a new instrument for the bioceramic coating construct with the given properties.

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