High Current Microplasma Processes for Modification of Titanium Alloys by Bioactive Ceramic Nanoporous Coatings

V.A. Mamaeva, A.I. Mamaev, T.I. Dorofeeva, Yu.Yu. Bydnitskaia, A.A. Makarov

Institute of Strength Physics and Materials Science, SB of RAS, Tomsk, Russia
634070 Tomsk, av.Academicheskii 8/2, phone 3822-492091, fax3822-492576,
E-mail: vam-tomsk@rambler.ru

Abstract – The high-current pulsed microplasma process is the advanced method for obtaining bioceramic coatings on titanium and titanium based alloys. For the first time the cyclyc voltammetry characteristics of the microplasma processes in alkaline, neutral and acid electrolytic solutions were recorded using the new equipment – Computer Aided Measurement System.

1. Introduction

It is well known, that amorphous hydroxyapatite, obtained on titanium surface by plasma-spraing method quickly solves in a human organism and does not protect an implant from corrosion. Therefore, it is necessary to form hydroxyapatite coating in the crystalline structure.

The microplasma processes in electrolytic solutions are the most advanced method for obtaining bioactive ceramic coatings containing hydroxyapatite or calcium phosphate combinations on titanium implants. The bioactive ceramic coatings formed by microplasma processes in electrolytic solutions have nano- and micropores structure. These coatings have strong adhesion, high corrosion protection and wear resistance.

Developed the new equipment – the Computer Aided Measurement System (CAMS) allows to measure shot current pulse duration (30–300 μs) and high current density (7–10 A/cm^2) and to control the high-voltage and high current signals of the microplasma processes.

The high-density current flow through electrode/electrolyte interface initiates electro-chemical reactions, microplasma discharges and current-sheet charging. Using the measuring and data-processing system [1] and the parametric model [2] the parameters of microplasma high-current pulsed processes, the specific resistance of the electrode/electrolyte interface and specific capacity for titanium and titanium-based alloys in electrolytes of varying composition have been described [3]. The results of investigations allow the regularities underlying the influence of the parameters of microplasma processes on the properties of bioceramic coatings to be established.

A topical problem is the research of the mechanism of the fast proceeding pulsed microplasma processes, and the mechanism of the bioceramic coating formation. For achievement of this purpose it is necessary to develop the original equipment allowing to record the voltammetry characteristics of these processes.

The voltammetry characteristics are a source of the information about a nature of the kinetics of the electrode processes at electrochemistry and they allow control the contribution of the electrochemical and microplasma processes.

It is interesting to know, how the form of the voltammetry characteristic depends from a nature of electrode, of an electrolyte composition, a time of process, an amplitude and pulsed duration of polarization voltage. Whether reflect the form voltammetry characteristic influence of the various factors on the process formation the bioceramic coatings by the high current pulsed microplasma processes.

Whether it is possible to supervise thickness, porosity, pore size, roughness, structure, composition and properties of the bioceramic coatings using the voltammetry characteristics. To answer these questions is the purpose of the given work.

2. Experimental

Titanium and Ti-based alloy samples with a size $10 \cdot 20$ mm were used as the substrate material and were treated by the pulsed microplasma processes using high polarization voltage about 200–500 V and the high density current.

The advanced equipment of a second generation – Computer Aided Measurement System was developed and can be used for investigation the process of the formation bioceramic coatings on titanium surface by pulsed microplasma processes. New equipment allows to record the voltammetry characteristics of the pulsed microplasma processes in electrolytic solutions keeping as solvable and an unsolvable component such as hadroxyapatite and calcium phosphate.

CAMS improved technical and metrological characteristics. This equipment allows to record the voltammetry dependences of the pulsed microplasma processes using the voltage amplitude up to 3000 V, the rate of change voltage up 10^8 V/s, the currents up to 100 A, and to control the voltage and current signals with step-type behaviour 25 mV and 1 mA accordingly. CAMS allows to record cyclic voltammetric dependences using the original trapezoid form of the polarizatuion pulsed voltage.

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

3. Results and Discussion

The voltammetry dependencies in alkaline solutions with the different adds of chemical composition of calcium differ from each other and are presented in Fig. 1.

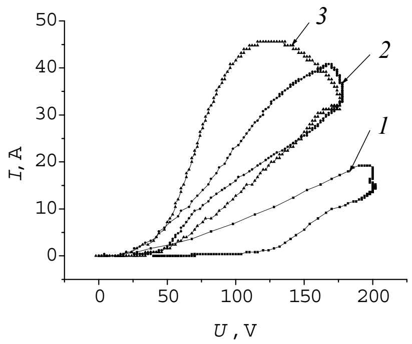


Fig. 1. The cyclic voltammetry dependencies at the polarisation potential $U = 300$ V in KOH solution with the adds of chemical composition of calcium: *1* – hydroxyapatite (HA); *2* – fluorate; *3* – phosphate

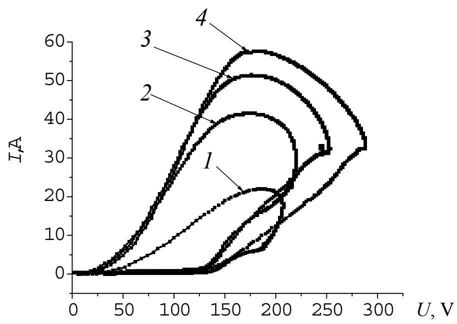


Fig. 2. The ciclic voltammetry dependencies in KOH electrolyte with calcium fluorate after ten minutes of carrying out of the pulsed microplasma process at various potential, V: *1* – 200; *2* – 250; *3* – 300; *4* – 350

The ciclyc voltammetry dependencies of the microplasma processes formation of the bioceramic coatings by the pulsed potentiostatic condition at various values of voltage were investigated. The cyclic voltammetry characteristics depend both of a nature of electrolyte, and the polarisation voltage amplitude, Figs. 1–2.

The cyclic voltammetry characteristic form differ in acidic and alkaline electrolytes as shown at Figs. 1–4.

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.

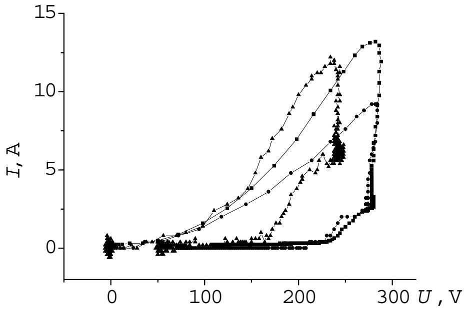


Fig. 3. The cyclic voltammetry dependencies at the polarisation voltage $U = 300$ V in acidic solution with the adds of chemical composition of calcium: *1* – gluconate; *2* – HA; *3* – phosphate.

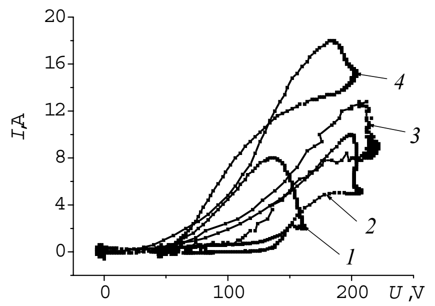


Fig. 4. The cyclic voltammetry dependencies in acid H_3PO_4 electrolyte with $Ca_3(PO_4)_2$ after ten minutes of carrying out of the pulsed microplasma process at the different polarization voltage amplitude, V: *1* – 200; *2* – 250; *3* – 300; *4* – 350

To increase the process time the active resistance of interface electrode/electrolyte increases with the coating thickness increasing and that is the cause of active part of current I_A decreasing, and capacitor part of current I_C increasing, Fig. 5.

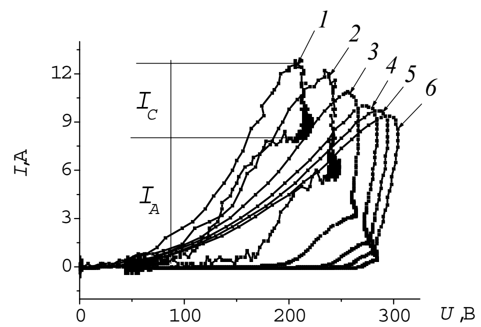
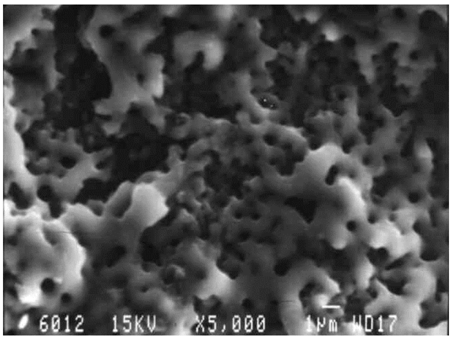


Fig. 5. The ciclyc voltammetry characteristics of acidic electrolyte in the dependence on the time of coating, min: *1* – 0; *2* – 1; *3* – 3; *4* – 5; *5* – 7; *6* – 10

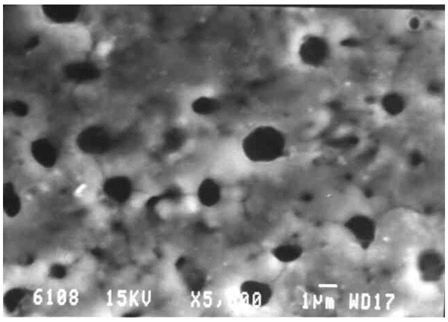
The cyclic voltammetry characteristic is reflecting the influence of various factors at the given moment of the coating formation: the microplasma process regimes, the electrolyte and electrode material composition. The cyclic voltammetry characteristic and equipment, which allows them to record – CAMS 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.

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

Nano and microporous bioceramic coatings obtained in the electrolytic solutions having different composition are presented in Fig. 6.



a



b

Fig. 6. Morfology of the bioceramic coatings obtained in acidic (a) and alkaline electrolytes (b). $U = 300$ V, the process time is 10 min. Magnification is 5000

Both the pore size and porosity coatings depend from the amplitude and pulse duration of the polarisation voltage. With augmentation 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. 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 orthopaedic with the various function characteristics having as the smooth surface for knee joint and also the rough surface for merging of bones.

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 micro-hardness, strength adhesion, low 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.

4. Conclusion

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

The cyclic voltammetry characteristic forms depend on the electrolyte and electrode composition, and the microplasma process regimes such as the form, 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 and it is the new instrument for the constructing of the bioceramic coatings with the given properties.

References

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