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LETTERS TO THE EDITOR

Characteristics of the Synthesis of TiO_2 Films on a Titanium Surface by the Sol-Gel Technique

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Examination of a possibility of the formation of a chemical bond between an artificial implant surface, for example titanium, and a bone tissue is one of the major characteristics of modern biocompatible materials intended for orthopedics, reconstruction surgery, and dentistry. The important problem of the chemical materials technology is the creation of a dental implant surface ability to create rational conditions for a contact bone formation (formation and evolution of a bone tissue), which is the optimal mechanism for the formation of an organotypic osteal material on an implant surface. It was shown earlier that the elemental composition of an implant surface and a relief pattern of a titanium surface play an important role in formation of osteoblasts (young osteal cells) and in rise of their osteocompatibility [1]. It is fair to say that qualitative and quantitative characteristics of osteointegration directly depend on surface topography of titanium implants, including nanostructured implants, and on their chemical composition [2, 3]. Therefore the important direction for the evolution of medical materials technology is the development of surface modification methods, which shall make it possible to increase osteocompatibility of metal implants and organism tissues.

The aim of the present work was to deposit TiO_2-based porous coatings on titanium and silicon by a sol-gel technique and to study topography of the surface of resulting oxide films.

The creation of continuous transparent films on supports is described in the literature [1, 2], the attention being usually focused on the optimization of conditions for synthesizing continuous faultless films [2]. Our task was to synthesize a film having a microcrack network penetrating the whole film volume using a dip coating thechnique in conditions of a high thermal gradient. Such a coating texture can strengthen adhesion between cells and titanium surface.

We used KDB-10 Si (100) plates and Grade-4 titanium rods (l 1 cm, d 1 cm) as supports. Silicon and titanium preliminarily passed a stage of standardizetion. Silicon plates were purified in H_2SO_4 and H_2O_2 solutions, and further in an HF solution (5%) to remove natural oxide SiO_2, with the subsequent treatment by deionized water to remove fluoride ions, and then the samples were heated by dried gas helium at 100°C. Titanium rods were preliminarily washed by isopropanol (special-purity grade) in an ultrasonic bath at 50°C and then in ultrapure water. Various compositions of inorganic acids were used for further etching. The quantitative compositions of electrolytes and the duration and conditions of etching were chosen experimentally to fit two characteristics: formed microrelief should attain 2–3 μm and the wetting angle determined by water, from 0° up to 5°. The developed microrelief of a titanium surface with a roughness factor Ra ~ 1.4–1.7 μm was reached by sequential etching in HF (3%) and then in H_2SO_4 (10%).

The first stage of the work was the development of the procedure for the synthesis of the initial titanium oxide sol. As a result we have selected the procedure described in [4] based on the tetraisopropyl titanate hydrolysis in isopropanol in the presence of diethanolamine. This choice was based on a high stability of the sol and a fast cross-linking to form a strong gel in destabilization conditions. It is not characteristic for stable aqueous sols, which are more favorable to coagulation with the formation of unstable point contacts. The experiments have shown that the slightest deviation from the stoichiometry results in coagulation of titanium oxide particles. As a result we used the final molar ratio $Ti(Oi\text{-}Pr)_4$: diethanolamine : *i*-PrOH : H_2O = 1 : 2 : 12 : 2 for the synthesis of sols.

The following stage of the work was the development of conditions for depositing a film on a model support: the single-crystal polished silicon or titanium. Originally a support was washed by water with surfactants, then etched by concentrated nitric acid, and again washed by deionized distillate. After that the plate was immersed in sol on a Shimadzu AG-50kNXD installation and drawn out with various rates. As a result we have obtained films of various thickness. The control of films thickness uniformity has shown that large inhomogeneity have formed perpendicularly to the axes of drawing on rates below 10 mm/min. At rates above 250 mm/min local disruptions of film arose, which probably was connected not so much with a rheology, as with the presence of mechanical impurities appearing from an ambient atmosphere. As a result we have chosen the rate of 100 mm/min for further experiments. According to the electron-microscopy of the film cleavage surface, at this rate the films had a thickness from 110 up to 200 nm.

After that we studied a possibility of creating a film possessing a network of microcracks. To solve this problem, we have prepared films in conditions of a significant thermal gradient and a fast drying of the deposited gel. According to the electron-microscopy data, cracks passed through the whole thickness of the oxide layer under a near-right angle, their width was from 0.3 up to 2 μm, all cracks being joined in a uniform network. After depositing films the samples were washed free from the organic component by boiling in a distillate and calcination at 400°C. Scanning electron microscopy has shown that the coating homogeneity decreases only slightly as a result of this treatment.

The examination of the osteocompatibility of the obtained samples with a TiO_2 layer was carried out in comparison with proper (real) titanium oxide. The last-named sample simulated a subject with a smooth surface of titanium.

As a result of a fortnight test the coating area of sections under study differentiated from that of reference samples by 15%, which points to a high degree of osteocompatibility of TiO_2 coating in comparison with a surface of a real titanium oxide film on a metal titanium surface.

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