Correlation Between Structural and Bioactive Properties of Titanium Dioxide Formed by Atomic Layer Deposition

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Abstract—Bioactive materials are of great interest due to a strong bond between bioactive surface and bone material. Materials and techniques, used for pretreatment of implant surfaces, have a number of considerable disadvantages. Bioactive thin films, grown by Atomic Layer Deposition, can solve a number of problems of pretreatment, increase the quality and lifetime of implant. The article describes a structural approach to theoretical prediction of bioactive materials as well as experiments performed on new bioactive TiO$_2$ surfaces with a different crystalline structure.

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INTRODUCTION

Biocompatible materials have been the object of intensive research over the past decades. Osteointegration is a key factor which guarantees a strong bond between an implanted device and bone [1]. This term was introduced into medicine after the discovery of formation of a strong bond between a class of materials and human bone, avoiding soft tissue formation. This property allows replacing different parts of human skeleton. The key objective of medical material engineering—formulation theoretical criteria which allow previously evaluate osteointegration properties of a material. Capability of osteointegration is detected experimentally, but research materials need a set of biological test that require money and time. In this article, we suggest a selection of criteria for an a-priory estimation of biocompatibility properties of thin films based on comparison crystallography bond tissue and covering implantable object.

Titanium is a material which is broadly used in implantation medicine along with stainless steel and Co/Cr alloy [1]. The fact is that titanium is one of the key materials in this field due to a very good compromise between strength, wear resistance and neutral reaction from mammal body cells and tissue. Metals in implantation medicine are often called bioinert. This means that a strong bond between an implant and human bone is formed rather slowly [1]. Due to this formation of bioactivity covering allows accelerating the process of osteointegration. Currently the main method to modify a surface includes acid etch, grit sand blasting and covering implants of synthetic hydroxyapatite (HA)—analogous to a bond tissue.

This method aims at developing of a surface, achieving optimal asperity and improving bioactivity properties of implant. Each method has the same clinical problem and may lead to some complications.

The work aims to create an experiment test of a structured approach to choose a covering material.

THEORETICAL BACKGROUND AND METHOD

Research studies of biocompatible materials usually involve long in vivo studies and cell experiments. However, at early stages of development fast experiments are needed greatly. Over the past 3 decades in vitro tests such as soaking in Simulated Body Fluid (SBF) have emerged. Authors of the review article [2] show a strong correlation between SBF test and in vivo studies, supporting them with a solid number of experimental materials. Hereby, SBF-soaking is a test which allows evaluating the biocompatibility of materials at early stages of development. Structures, observed on the surface of material after soaking in SBF, are bone-like hydroxyapatite (HA) and apatite-like calcium and phosphate structures. Nevertheless this test allows us to obtain only quality value of bioactivity properties. Often there’s a more important quantitative characteristic of osteointegration—the beginning of formation hydroxyapatite and the growth rate of a bond tissue on surface implants. In this article we are making an attempt to go from quality value to quantitative estimate.

A new method to modify surface applied in this research is an atomic layer deposition (ALD). ALD using self-saturating surface reactions is a unique technique that allows growing coatings with monolayer accuracy, high thickness uniformity on large-area sub-
substrates and with very high covering conformability of substrates with a highly profiled surface [4]. Coating the surface of the implanted structure of thin films of metal oxides (about 20 nm) can provide a significant improvement in the properties of the implant surface in two directions [1, 3]. Firstly, conformal thin film protects the patient from harmful effects on the development of surface treatment, secondly, transition metal oxides creates positive environment for rapid bone formation on the surface inside the human body. One of the most perspective materials is TiO₂ [1, 3]. Works on biocompatible properties of TiO₂ in anatase phase grown by ALD exist [3]. However, several works discuss the possibility of using another crystalline phase of TiO₂, rutile as a possible biocompatible material. Some of the works detect both crystalline modifications of TiO₂ to be biocompatible and compare them due to structural similarities between both structures and hydroxyapatite, which is the basis of bone [5, 6].

Some authors [5–7] have developed a method to estimate osteointegration capabilities of materials to analyze crystallographic characteristics. This method can predict bioactivity properties of materials. It is known that the basis of human bone tissue material is hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) in the hexagonal crystallographic modification. The crystal lattice of transition metals with similar interplane distances, especially tetragonal, are potential candidates for the rapid formation of bone tissue in the environment of human body. Actually, if grille anatase TiO₂ in the plane (110) superimpose with a lattice of hydroxyapatite in the plane (0001) may be noted the almost complete compliance (Fig. 1/ left). Other modification of titanium dioxide rutile in plane (101) shows less bioactivity, but there is a significant correlation with structural HA. These properties are confirmed by theoretical research into deposition on the surface of rutile [8]. It should also be noted that in the first case, the important groups of atoms are the same as in the second — there is a difference of about 3% [5] despite the similarity distances in lattices (central OH-group apatite less coincides with the oxygen atom rutile) (Fig. 1).

Thus, in the context of a structural factor both crystal modification of titanium dioxide must show bioactivity properties. Further tests will be conducted experiment to examine our estimates for definition difference.

**EXPERIMENTAL**

Deposition of thin TiO₂ films was performed using hot wall low pressure ALD Picosun Sunale R-150 reactor with titanium ethoxide (Ti(OC₂H₅)₄) and water as precursors. Titanium grade 4 plates (26 × 15 × 2 mm) and Si (100 mm) plates were used as substrates. Nitrogen with purity of 99.999% was used as purge gas. Reactor temperature was 300°C, pulses of metal precursor, and water were both 0.1 s with 4.0 s purge of nitrogen.

TiO₂ anatase phase is anticipated in ALD process in this range of temperatures with more than 300 reaction cycles as shown earlier. Rutile is a high temperature crystalline phase and in this research it was obtained with rapid thermal annealing (RTA) at 650°C of resulting ALD films in a nitrogen atmosphere. Titanium plates with 500 cycles of TiO₂ were annealed in a nitrogen atmosphere for 30 seconds.

Hereby, with ALD and subsequent annealing, two crystalline modifications of TiO₂ coatings were achieved. Titanium plates with both types of coatings were soaked in SBF for 3, 6, 9 and 12 days. During these experiments, the dynamics of hydroxyapatite formation was controlled with the mass alteration of the samples. After soaking, samples were washed in deionized water and dried in a nitrogen atmosphere for 2 hours. Three series of samples with both types of films were examined, recurrence of data of mass alteration was observed with inaccuracy of 5%.

**RESULTS AND DISCUSSION**

Crystalline phase of resulting thin oxide films was examined with X-Ray Diffraction (XRD) with ARL X'TRA (Thermo Scientific) tool. Scanning was performed in theta-theta mode in the range of angle 20–60 deg. In Fig. 2 the XRD pattern of deposited (18 nm) TiO₂ coatings of anatase (2) and rutile phase (3) after RTA are presented. Peak at 25.3 degrees refers to anatase (101). Peak at 27.4 degrees refers to rutile (110) plane.

The detection of hydroxyapatite on soaked in SBF Ti plates with TiO₂ coatings was performed using Scanning Electron Microscopy (SEM) with element analyses (EPMA) with FEI Quanta 200 tool. On both types ofstructures continuous paving surface was observed. Peaks which are presented in the spectra of the elemental analysis refer to the elements Ca, P, O,