Structure and mechanical properties of a composite based on titanium and a bioactive coating with a two-level surface relief

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Abstract. To develop bone implants using Ti materials, the issue of creating bioactive coatings that ensure their rapid engraftment to the bone is acute. The rate of fusion of Ti implants with bone tissue is significantly influenced by the degree of modification of the coating surface based on changes in the relief, chemical composition of the surface layer and mechanical characteristics of the implant. The structure and mechanical properties of a Ti-based composite with TiO_2/Ag/HAp coating of an island-like type were investigated, which showed high bioactive properties of the sample. The paper shows that the application of an island-like coating on the Ti surface with a height difference of 0.7 microns does not lead to a deterioration in the mechanical characteristics of the Ti implant, and the hardness increases by 15%.

1. Introduction

In recent years, much attention has been paid to the use of Ti-based materials in the biomedicine, since they are very reliable in terms of mechanical characteristics, non-toxic and often have good biocompatibility [1–3]. Ti and its alloys are of great interest as implantable materials because of their excellent corrosion resistance, good mechanical properties and excellent biocompatibility compared to other competing materials [3–5]. The high corrosion resistance of Ti and its alloys is due to the strong and dense protective TiO_2 film on their surface. However, it has been found that in some aggressive media, such as human body fluids, the destruction of the natural oxide film occurs [6, 7]. Moreover, the native TiO_2 film does not have a pronounced bioactivity for bone osseointegration, which, together with the human factor, can lead to bone damage and subsequent implant loss. To improve the mechanical, corrosion and biomedical properties of Ti implants, their surface is modified depending on the product nature and the purpose of use [8].

By artificially increasing the TiO_2 film thickness, the chemical and mechanical stability of the coating can be achieved. Also, some methods of obtaining TiO_2 films allow changing the implant surface morphology at both the micron and nanometer levels. In a number of works it is noted that the cumulative presence of surface relief irregularities as on nano- and micro level it contributes to a better and faster implant engraftment [9, 10]. Thus, a porous structure is formed that provides interlocking areas and a biomimetic microenvironment that promotes adhesion of osteoblast cells during the initial period of cell growth [11, 12]. To facilitate osseointegration at the border with the surrounding tissues, the surface is additionally modified with substances chemically similar to the mineral part of the bone tissue. Apatites and hydroxyapatites are most often used as such substances, since they have a chemical and crystallographic structure very similar to the human bone structure, which eliminates biocompatibility problems [13, 14]. The above factors correlate significantly with the rate of new bone growth and the rate of recovery, which underlines the importance of careful design of coatings for osteointegrated implants.

In this work, we investigated the structure and mechanical properties of a Ti-based composite with TiO_2/Ag/HAp coating with a controlled composition and surface relief at the micro- and nanoscale. The coating was developed by us [15] using a combined sol-gel synthesis and electrochemical deposition from solution and showed high bioactive properties. The mechanical characteristics of the coating and the coated implant also affect the rate of bone tissue engraftment to the implant surface.

2. Methods

The structure and morphology of the coating were studied using a Merlin scanning electron microscope (Carl Zeiss Microscopy), the EDS prefix for the Zeiss Merlin scanning microscope was used to construct element maps. Rigaku "MiniFlex II" X-ray diffractometer was used for X-ray phase analysis.

Atomic force microscopy (AFM) using a scanning probe microscope Solver P47 Pro in semi-contact mode (tapping mode) in air was used to study the relief of the Ti surface and coating.

The strength characteristics of nanotitanium were certified on the Instron 5882 universal testing machine at room temperature with a traverse movement speed of 1 mm/min.

The measurements were carried out on a TV-5214-10 Tochline hardness tester at a load of 10 kgf, the exposure time was 10 seconds, allowing a stepwise load from 250 mN to 20 N. The Vickers method of the recovered print was used. The indenter was a regular four-sided diamond pyramid with an angle of 136° between opposite faces.

The adhesive strength of the coating was determined in the process of its destruction by applying force. The NanoScan-3D nanohardometer was used with a variable controlled load on the Berkovich diamond indenter in the form of a triangular pyramid from 130 microns to 20 mN along the path length (scratch length) of no more than 100 microns. The movement speed of the indenter is 1 micron/sec. The radius of rounding of the indenter tip is not more than 100 nm. The indenter is positioned face forward when scratching. Three scratches were applied to each sample. The load of the first cracks appearance was determined from the dependence of the indenter insertion depth on displacement. F is the load of the appearance of the first cracks or detachments.

3. Results and discussions

3.1. TiO_2/Ag/HAp composite coating structure

The coating was obtained by template electrochemical synthesis on the Ti plates surface. The template was a porous TiO_2 coating with micro- and nano-roughness. The resulting template structure was analyzed by SEM. Figure 1 shows micrographs of the synthesized TiO_2 oxide coating (template), the morphology of which is characterized by the presence of micro- and nano-roughnesses. Two-level relief hierarchy significantly increases the bioactivity of the implant surface [15].

An island-like system of Ag and hydroxyapatite (/Ag/HAp) with micron roughness was deposited on the TiO_2 template surface.

Micrographs of the sample were obtained using SEM, and elemental maps of the surface were compiled by X-ray spectral microanalysis with an electron probe (figure 2).

Micrographs and elemental maps show that it is possible to achieve a high level of Ag, Ca, and P (hydroxyapatite) structures localization on Ti. The structures repeat the template geometry, forming a micron-sized star-shaped island system. Between the HAp islands is a

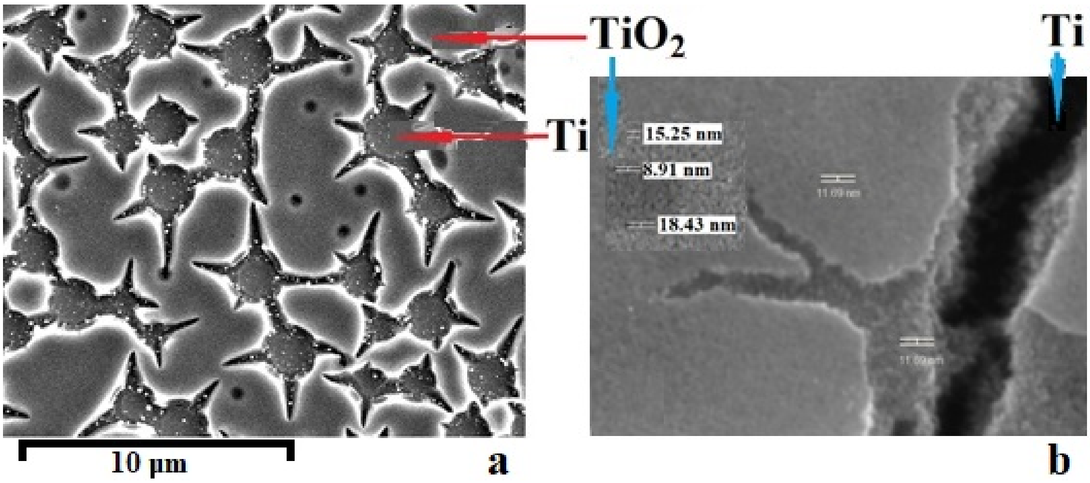

Figure 1. Micrographs of the TiO_2 film: surface micro-roughness (*a*), surface nano-roughness (*b*).

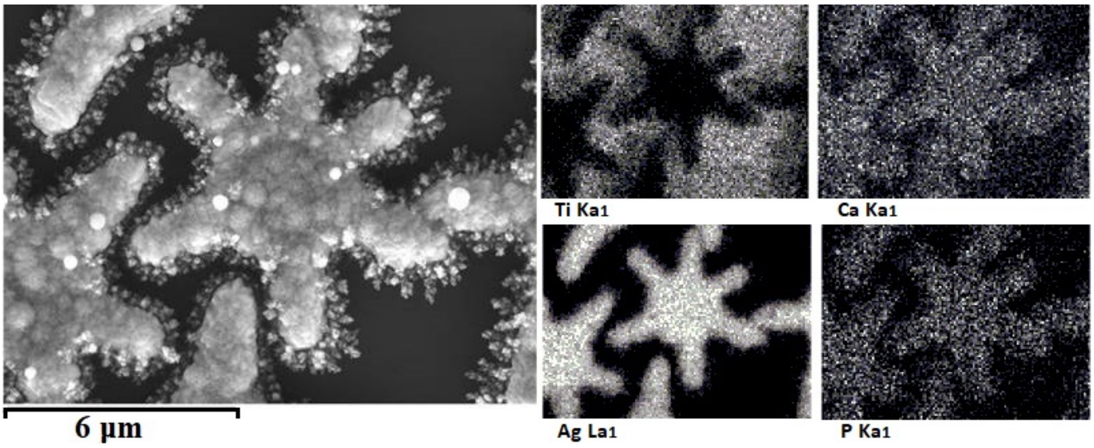

Figure 2. Micrographs and element maps of TiO_2/Ag/HAp composite coating.

TiO_2 coating. The resulting coatings have a developed relief consisting of micro- and nano-irregularities. Due to this the implant bioactivity increases, since it contributes to the accelerated osteoblast differentiation.

We confirmed the crystal structure of the synthesized coating using an X-ray phase analysis. The diffractogram contains reflexes of the Ti substrate, Ag microparticles, thereby forming a dense structure of TiO_2 and hydroxyapatite.

Atomic force microscopy (AFM) was used to study the surface relief (roughness) of Ti with TiO_2/Ag/HAp coating. The sample has a strong roughness (figure 3*a*). The height difference between the islands of Ag/HAp and Ti is 0.7 microns. Height difference within one island of the Ag/Ag coating is 40 nm (figure 3*b*).

3.2. Strength characteristics of Ti samples coated with TiO_2 and TiO_2/Ag/HAp

The chemical effect of reagents on the material surface in the temperature range 200–400°C can change the mechanical characteristics of Ti (titanium with high strength characteristics), and can lead to deterioration of the strength properties of the implant. Despite the fact that the Ti mechanical properties have been studied in detail to date, information on the effect of the

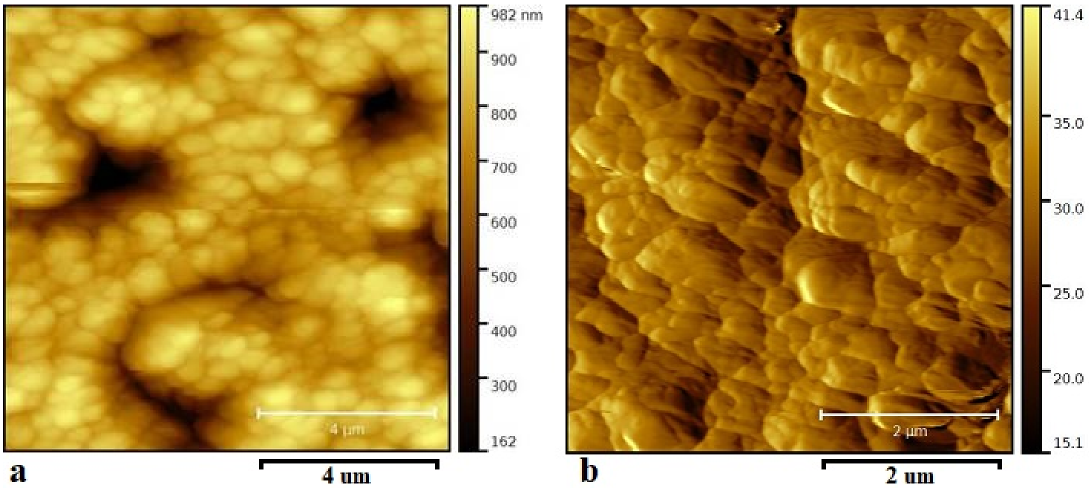

Figure 3. AFM surface reconstruction: Ti sample with Ag/HAp island coating (*a*), within one Ag/HAp island (*b*).

coatings obtained by chemical methods at elevated temperatures on the mechanical properties and Ti structure is not provided.

To determine the results convergence, 5 samples of the same series were mechanically tested. The total loading error during the test did not exceed ±3% at $f = 50\,\mathrm{Hz}$.

In general, for the coated and non-coated samples, the average tensile strength and elongation were $\sigma_\mathrm{b} = 900\,\mathrm{MPa}$ and $\delta = 10.9\%$. Fatigue durability tests of hardened Ti demonstrated that the samples withstood 1×10^6 cycles at a load of 390 MPa and did not collapse.

If we consider the mechanical behavior of Ti samples with surface coatings, it did not differ from the behavior of non-coated Ti samples. In all samples, we observed hardening at the initial deformation stage, reaching the maximum flow stress value, then subsequent softening and destruction of the sample. The sol-gel and electrochemical coatings application on the Ti surface does not lead to the mechanical characteristics deterioration of pure and hardened Ti.

3.3. Microhardness of Ti samples coated with TiO_2 and TiO_2/Ag/HAp

Hardness values in accordance with the standards are given in conventional HV units, the implied physical dimension is [kgf/mm^2]. For each material, the values of 8 hardness determinations on 2 separate samples were averaged, indentation was carried out near the geometric center of the grinds with the 10 seconds load application.

The initial Ti had a hardness of 190 HV. In Ti coated with TiO_2/Ag/HAp, the average hardness value of the sample increased to 220 HV. Since the coating consists of micron-sized islands of Ag/HAp composition and sections of Ti coated with TiO_2, the coating had different hardness at different points of the surface. The increase in the microhardness is due to the Ag/HAp islands.

This conclusion is indirectly confirmed by measurements obtained using a nanoindenter on an AFM microscope. If we compare different sample surface points, they differ in amplitude and resonance frequency depending on the sample hardness at the measurement point (figure 4).

Thus, a lighter contrast spot with a larger amplitude corresponds to more rigid areas of the sample surface consisting of an insular coating (Ag/HAp). The dark areas of the sample consisting of TiO_2 on Ti with a smaller amplitude correspond to a lower stiffness. The brightness difference is 2 times different. The amplitudes of the Ti sample without island coating are 6–11 nA, and the amplitude of the coated Ti sample is 11–28 nA.

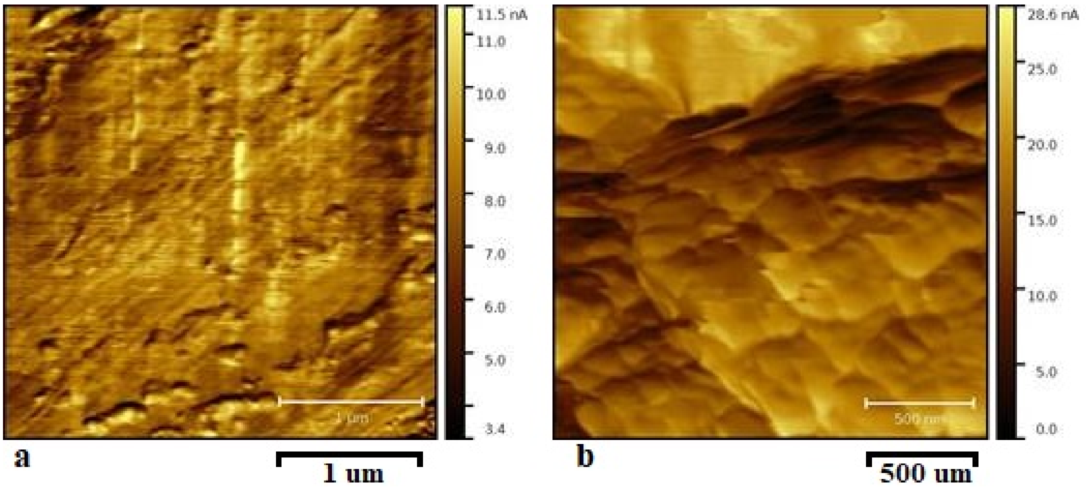

Figure 4. Variation of the oscillation amplitude (nA) of the nanoindent on samples: Ti without coating (*a*), Ti with TiO_2/Ag/HAp coating (*b*).

Table 1. Results of measurements of the adhesion strength of coatings to the substrate.

Sample	Sample 1	Sample 2	Sample 3
Sample composition	TiO_2 on BT 6 Ti	Composite TiO_2/Ag coating on BT 6 Ti	Composite TiO_2/Ag/HAp coating on BT 6 Ti
Coating thickness, nm	150	350	700
F, mN	5.2 ± 0.3	11.0 ± 2.8	9.0 ± 0.8

3.4. The bonding strength of TiO_2, TiO_2/Ag, and TiO_2/Ag/HAp coatings with the Ti surface

The adhesive strength of coatings was determined during their destruction by applying force to the diamond indenter. The load of the first cracks appearance was determined from the dependence of the indenter insertion depth from displacement.

The coating destruction and its integrity violation occurs due to elastic–plastic deformations from indentation, friction during contact of the diamond with the coating and substrate, residual internal stresses present in the coating. The loads (F) at which the first cracks appear are presented in table 1.

It was revealed that the maximum destruction load of the Ag- and hydroxyapatite-based insular coatings (TiO_2/Ag and TiO_2/Ag/HAp) is twice as high as that of TiO_2 coating. The increased coating adhesion is due to the micron roughness of the surface. The height difference between Ti and TiO_2/Ag/HAp island coating reaches 0.7 microns.

Conclusions

The resulting coatings have a developed surface relief consisting of micro- and nano-irregularities, and due to this the bioactivity of the implant increases, since it contributes to the accelerated osteoblast differentiation [15].

Micrographs of the surface and its elemental maps show that a high localization level of Ca and P has been achieved, and the deposited hydroxyapatite repeats the island type geometry of the TiO_2 template (micron surface roughness). If we consider the mechanical behavior of Ti samples with surface coatings, it did not differ from the behavior of non-coated Ti samples.

Sol-gel and electrochemical application of coatings to the Ti surface does not lead to deterioration of the mechanical characteristics of Ti and hardened Ti. Ti with TiO_2/Ag/HAp coating has an average hardness value increased by 15% compared to the original uncoated Ti. The observed hardness value increase is due to the micron island coating. This conclusion is indirectly confirmed by measurements obtained using a nanoindenter on an AFM microscope. The study of the coatings strength showed that the maximum load of insular coating destruction (the height difference between the Ag/HAp islands is 0.7 microns) is twice as high as that of the TiO_2 coating and does not lead to chipping of the coating from the Ti surface. This increases the rate of bone tissue engraftment to the implant surface.

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