Metal oxide (Ta-TaOx)-coatings obtained by magnetron sputtering and heat treatment with high-frequency currents

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Abstract. The paper presents the results of obtaining tantalum films with a thickness of 200–900 nm on titanium using DC magnetron sputtering. As a result, a high-strength "Ti-base – Ta-coating" structure with a hardness of at least 2040±150 HV (20.01±1.47 GPa) was produced. The subsequent modification with high-frequency currents provided an increase in hardness to 3694±443 HV (36.23±4.35 GPa), which was associated with the formation of a thin oxide layer of TaO₂ with a tantalum concentration of 74.1–75.2 wt.% and oxygen of about 12.5–13.9 wt.%.

1. Introduction
To improve the functional characteristics of titanium products, including those for medical application, their surface is subjected to a modifying treatment, e.g. plasma spraying and oxidation [1]. Numerous studies showed that some biocompatible metals (titanium, zirconium, tantalum) thermally treated in an oxygen-containing atmosphere had increased hardness and wear resistance [2,3]. It is known that tantalum has the highest biomechanical compatibility among metals and alloys used for medical purposes [4]. This provides its use in the manufacture of individual high-loaded components of implants, as well as functional coatings. In this paper, the possibility of creating a "Ti-base – (Ta-TaOx)-coating" structure due to magnetron sputtering of tantalum on a titanium base and heat treatment with high-frequency currents (HFC) was studied.

2. Methodology
Experimental samples were made in the form of 2 mm thick cp-titanium "Grade 2" disks (D = 14 mm) with central holes. "Ti-base – Ta-coating" structure was produced by magnetron sputtering (DC-mode). After obtaining the layered structure, the heat treatment with HFC in an oxygen-containing atmosphere was conducted. The temperature varied from 600 to 1200 °C at a high-temperature exposure duration of 30 to 300 s.

The surface morphology of the samples was studied using optical and scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDX). To test hardness, the Vickers method (at 10–50 gf) was used.

3. Results
The macrostructure of titanium samples after the tantalum film was formed (through a rectangular mask) was characterized by the presence of a rectangular section with a dark boundary (showed the
difference in height between the base and the film). After heat treatment, titanium and tantalum had characteristic differences in color. The film of an oxidized TaOx tantalum treated with HFC at the temperature of 600–800 °C had a dark gray color (Figure 1a). Thermal treatment under these conditions did not lead to a change in the morphology parameters. The increase in the treatment time to $t = 300$ s at a temperature $T = 800 \pm 15$ °C promoted the formation of microcracks and partial peeling of the metal oxide film.

![Figure 1(a, b).](image)

*Figure 1(a, b).* Titanium disc with TaOx coating obtained by magnetron sputtering of tantalum (0.6 μm film) and subsequent heat treatment with HFC at the temperature $T = 600$ °C and $t = 30$ s (a); a coated sample produced at the temperature above $T = 1000$ °C (b).

At an increase in the treatment duration from 30 to 300 s and the treatment temperature of 1000–1200 °C, there was a more intense oxidation of a titanium base. The resulting scale of titanium spontaneously separated from the surface, but the oxide layer of TaOx was retained (Figure 1b). The areas of a titanium sample, where no tantalum film was observed, were intensively oxidized with the formation of a thick oxide coating of rutile [2]. Thus, the tantalum film had a protective role during the high-temperature oxidation.

The concentration of tantalum after magnetron sputtering reached 94.7–97.5 wt.% (Figure 2a). With a film thickness of about 0.8–0.9 μm, a maximum tantalum concentration of about 98.5–99.0 wt.% was achieved. The presence of titanium in the film was associated with the peculiarity of the EDX method, when the pear-shaped area of characteristic X-radiation (at the accelerating voltage of 20 kV) was about 1 μm.

The surface morphology of titanium samples remained practically unchanged after the deposition of a tantalum layer with a thickness of up to 0.8–0.9 μm. The microchannels remained visible after turning and finishing (Figure 2b). The similar character of the morphology was also observed at a low temperature of heat treatment with HFC. The treatment at a temperature of about 600 °C did not lead to any noticeable changes in the morphology, including the nanoscale range. However, with an increase in the temperature to 800 °C and treatment time to 300 s, nanocrystals of tantalum oxide were formed on the microprotrusions. The dimensional parameters of nanograins of tantalum oxide were difficult to establish.
Figure 2(a, b). Morphology of a titanium sample with a TaOx coating obtained by magnetron sputtering of tantalum (0.6 μm film) and subsequent heat treatment with HFC at the temperature $T = 600$ °C and $t = 30$ s (rectangles show the areas for EDX) (a); a coated sample produced at the temperature above $T = 800$ °C and $t = 30$ s (b).

More distinct grain boundaries were noted at a treatment temperature of about 1000 °C or more. The application of a high-temperature range led to the formation of numerous defects and noticeable cracking (Figure 3a).

Figure 3(a, b). Morphology of a titanium sample with a TaOx coating obtained by magnetron sputtering of tantalum and subsequent heat treatment with HFC at the temperature $T = 800$ °C and $t = 300$ s (a); metal oxide coating fragments (b).
On the fragments of the oxide film, small crystals were observed (Figure 3b). However, this coating structure can not provide high mechanical characteristics and wear resistance, which is due to low adhesion and cracking.

The concentration of tantalum after oxidation by HFC decreased from 94.7–97.5 wt.% to 74.1–75.2 wt.%, while the oxygen concentration reached 12.5–13.9 wt.%. At an oxygen concentration in the metal oxide coating of not more than 13–14 wt.%, no noticeable cracking and failure occurred. Such coatings had high mechanical characteristics, in particular hardness.

The appearance of the TaOx oxide layer was accompanied by an increase in Vickers hardness from 2040±150 HV (20.01±1.47 GPa) to 3694±443 HV (36.23±4.35 GPa). In the course of high-temperature treatment, the above-described cracking occurred and the hardness of the coating decreased noticeably to 550–770 HV (5.39–7.55 GPa), and with a prolonged treatment it approached the hardness of a moderately strengthened commercially pure titanium – about 300–400 HV.

4. Conclusion
Thus, after the deposition of tantalum on the titanium surface and further heat treatment with HFC, the "Ti-base – (Ta-TaOx)-coating" structure was formed. The hardness of metal oxide coatings reached 20–36 GPa, which qualitatively can ensure high wear resistance, provided that the necessary characteristics of the surface morphology are met.

The proposed approach for the modification of the surface of titanium products can ensure an improvement in the quality of medical devices, including implants [2]. The coatings obtained can also find application in the manufacture of electronic components (capacitors), MEMS and sensitive sensors of a wide range of applications [5-10].

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