Microstructure, mechanical and hydrophilic properties of two-layer nanostructured TaN/Ta$_2$O$_5$ coatings

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Abstract. The microstructure, mechanical and hydrophilic properties of two-layer TaN/Ta$_2$O$_5$ coatings on stainless steel and silicon wafers were studied using atomic force microscopy (AFM), nanoindentation (NI) and sessile drop method. It was found that the two-layer films are characterized by a granular structure with low roughness values. The average values of the elastic modulus and microhardness for TaN/Ta$_2$O$_5$ were 130 GPa and 8.7 GPa, respectively. The contact angles for the two-layer coatings were 95.1$^\circ$ and 90.0$^\circ$ on the steel and silicon substrates, respectively.

1. Introduction

In biomedical devices, metals and their alloys are used due to their inertness and structural function. Metal implants are widely used in orthopedic surgery (artificial joints for hips, knees, shoulders, ankles, etc.), in maxillofacial and cardiovascular (endoprostheses, stents) surgery and as dental materials [1, 2]. Although a large number of metals and their alloys are used in medical devices, the most common are stainless steels [3–5], titanium and its alloys [3, 6–8], tantalum [3–7] and alloys based on cobalt [3, 8].

Currently, researches are being held to create new designs of prostheses and biomaterials with unique properties in order to increase their service life and reduce the need for repeated operations. The most serious complication are limited the life of the prosthesis is loosening due to an inflammatory reaction to wear products. Unfavorable reactions of tissue, such as tumor formation, are common complications after surgery [9]. Solving these problems is possible by mechanical and hydrophilic properties increasing of the prostheses surface. One of the most effective method of biomechanical and tribocorrosive characteristics increasing is the application of ceramic, compositional and nanostructured coatings with different compositions on the working prostheses and stent surfaces using modern ion-plasma methods [10]. The modification by nanostructured coatings on the prostheses surface also leads to a change in the superficial and structural characteristics of the material, such as roughness, topography, and wettability [11]. Therefore, the study of the structural, mechanical and hydrophilic properties of such coatings at the nanoscale is an important task for both materials science and medicine.
The aim of this work is to investigate microstructure, mechanical and hydrophilic properties of one- and two-layer nanostructured films of tantalum compounds on steel and silicon substrates by AFM, NI and sessile drop methods.

2. Materials and methods
Nanostructured coatings based on Ta were deposited by magnetron sputtering. Pre-cleaned samples of polished stainless steel (AISI 321) and silicon wafers were used as substrates. The tantalum target with a diameter of 170 mm and a thickness of 8 mm was used. The magnetron discharge power was 4-5 kW. ICP source for oxygen activation with RF power up to 1 kW was applied. The main parameters of the process were the following: gas pressure $P_{Ar} = 2.3\cdot10^{-1}$ Pa, oxygen mass flow rate $q = 35$ sccm, nitrogen mass flow rate $q = 27$ sccm, magnetron voltage $U_{m} = 500$-580 V, magnetron current $I_{m} = 4.3$-7.6 A, total pressure $P = 2.8$-$3.0\cdot10^1$ Pa, film thickness 0.8-$1.5$ μm.

The microstructure of the obtained films was studied by AFM method on Dimension FastScan microscope (Bruker, USA) in the PeakForce QNM mode. Standard silicon cantilevers NSC 11 A (MikroMasch, Estonia) with a tip radius of 10.0 nm and a console stiffness of 4.11 N/m were used. The values of the root mean square roughness $R_q$ of the nanostructured coatings were calculated by the obtained AFM images (scan area is 5x5 μm) with using NanoScope Analysis. The contact angle and surface free energy of the coatings were determined by the sessile drop method on DSA 100 E device (KRUSS, Germany). Two test liquids were used - water and diiodomethane. The surface free energy was calculated using the Owens, Wendt, Rabel and Kaelble (OWRK) method [12]. The microhardness (H) and elastic modulus (E) were measured by Hysitron 750 Ubi nanoindenter (USA). The radius of diamond indenter of Berkovich type was 60 nm. Three curves were obtained for each sample with a constant increase in load from 100 to 10000 μN with partial unloading at each point for 30 cycles.

3. Results and discussion
Based on the obtained AFM images, it was found that the tantalum oxide film on the silicon substrates is characterized by a fine-grained structure with a minimum roughness $R_q = 1.1$ nm (figure A1). The grain sizes were 12-18 nm. After the tantalum nitride film deposition, a homogeneous granular structure consisting of grains with a diameter of 30 nm (figure B1) is formed on the silicon wafers, $R_q = 2.6$ nm. The surface of the two-layer TaN/Ta$_2$O$_5$ film is also characterized by grains (figure C1), the sizes of which are from 100 to 120 nm, what is reflected in the surface roughness values: $R_q = 3.6$ nm. In addition, there is a non-uniformity of the coating by thickness – difference is from 15 to 20 nm with periodically 2 μm.

![Figure 1. AFM images of the nanostructured coatings surface of tantalum compounds on the silicon, scan area 5x5 μm: Ta$_2$O$_5$ (a), TaN (b) and TaN/Ta$_2$O$_5$ (c).](image)

The stainless steel was used to assess the effect of the substrate on the structure of coatings formed on it. The tantalum oxide film surface on the steel has a granular structure with a grain size of 115–120 nm (figure a2), the value of $R_q$ was 6.6 nm. It should be noted that the tantalum oxide coating replicates the microstructure of the substrates, which is confirmed the presence of scratches inherent on the steel samples. The presence of such defects on the silicon substrates was not established. The
tantalum nitride films on the stainless steel are characterized a dense grain structure and precise boundaries, the formation of which was caused by defects in the initial steel substrate (figure b2). Small grains with a diameter of 30 nm are combined into larger globules. The roughness parameters of the films are not change with an increase in the scanning area (Rq = 9.4 nm), which indicates the uniformity of the deposited coating. The surface of the two-layer TaN/Ta2O5 film (figure C2) is characterized by a granular structure with a small crystallites 85-90 nm in diameter and sticking above the main matrix of grains with a size of 190-250 nm. This microstructure of the two-layer coating is the result of the influence of the TaN layer on the formation of the Ta2O5 structure. The value of Rq was of 7.8 nm.

![AFM images of nanostructured films surface of tantalum compounds on the steel, scan area 3x3 μm: Ta2O5 (a), TaN (b) and TaN/Ta2O5 (c).](image)

Figure 2. AFM images of nanostructured films surface of tantalum compounds on the steel, scan area 3x3 μm: Ta2O5 (a), TaN (b) and TaN/Ta2O5 (c).

An important characteristic of the material surface is wettability, since it has a significant effect on bacteria adhesion. Hydrophobicity can reduce the adhesion force between bacteria and biomaterial surface. The values of Rq, contact angle and surface free energy of the nanostructured films are presented in table 1. It was found that the hydrophilic properties of the tantalum compounds coatings on the steel and silicon substrates are different: coatings on the steel have higher contact angle values, which correlates with high Rq values of these films (the higher the surface roughness, the higher the contact angle). So, the TaN on the steel and two-layer films on the steel and silicon demonstrated the most hydrophobic properties. The contact angles for films were 95.1° in the case of the TaN/Ta2O5 on the steel and 90.0° in the case of TaN/Ta2O5 on the silicon. The surface free energies of the TaN/Ta2O5 films differed insignificantly and amounted to 34.41 mJ/m² and 34.59 mJ/m² on the steel and silicon substrates, respectively.

| Sample                  | Rq, nm | θ°   | γ, mJ/m² | γ′, mJ/m² | γ″, mJ/m² |
|-------------------------|--------|------|----------|-----------|-----------|
| Ta2O5 (AISI 321)        | 6.6    | 92.6 | 36.59    | 35.67     | 0.92      |
| TaN (AISI 321)          | 9.4    | 95.9 | 33.27    | 32.56     | 0.71      |
| TaN/Ta2O5 (AISI 321)    | 7.8    | 95.1 | 34.41    | 33.69     | 0.72      |
| Ta2O5 (Si)              | 1.1    | 84.8 | 41.17    | 38.99     | 2.18      |
| TaN (Si)                | 2.6    | 86.4 | 37.33    | 34.93     | 2.40      |
| TaN/Ta2O5 (Si)          | 3.6    | 90.0 | 34.59    | 32.75     | 1.84      |

Table 1. The values of Rq, contact angle (θ) and surface free energy (γ) of the nanostructured films of tantalum compounds on the steel and silicon substrates.

Based on the NI data (figure 3), it was found that the highest values of E and H are characteristic of the tantalum nitride films regardless of the substrate material. The dependence curves of E and H on
the depth of the TaN film on the steel have a similar form: the studied parameters increase at the indentation depth from 23 nm to 97 nm, then, as a change result of the local mechanical properties of coatings by the film thickness, the values of E and H decrease. In the case of the nitride film on the silicon wafers, the elastic modulus increase from 141 GPa to 155 GPa with an increase of the indentation depth to 43 nm. A subsequent decrease in values of E are observed to a depth of 135 nm then the elastic modulus differs insignificantly (within the experimental error) and averages 144 GPa. The H values of the TaN on the silicon substrates change in direct proportion to the indentation depth: they increase to 18.0 GPa.

The local mechanical properties of the Ta$_2$O$_5$ coatings on the two types of substrates change in the same type with increasing depth: the elastic modulus varies within the experimental error and the microhardness increase linearly. However, the values of E and H for the tantalum oxide films on AISI 321 are higher than on the silicon and amount to 131 GPa and 9.5 GPa, respectively. The mechanical properties of the two-layer TaN-Ta$_2$O$_5$ films and the single-layer Ta$_2$O$_5$ films on AISI 321 and Si substrates do not differ significantly. It is obvious that the bottom layer (TaN) has no significant effect on the elastic modulus and microhardness of the coatings (changes occur within the experimental error). The penetration of the diamond indenter occurs only in the upper layer of the coatings. The E values of TaN-Ta$_2$O$_5$ films increase to 132 GPa and 135 GPa with an increase in depth to 74 nm and 97 nm on the steel and silicon substrates, respectively. A further increase in depth does not lead to changes in the values of the elastic modulus. It should be noted that all investigated films have the
lowest values of E and H at small indentation depth of 23 nm (on the steel) and 21 nm (on the silicon). This can be explained by the fact that the diamond indenter penetrates at low loads into loose near-surface layers of the coating.

4. Conclusions
As a result of the AFM studies, it was found that the coatings are characterized by a granular structure with differing size and spatial distribution of grains on the substrate surface. The TaN films have the best mechanical properties. However, the tantalum nitride does not affect on the values of the elastic modulus and microhardness of the TaN/Ta₂O₅ film as the bottom layer of two-layer coatings. The average values of E and H for the TaN/Ta₂O₅ films were 130 GPa and 8.7 GPa, respectively. It was found by the sessile drop method that TaN film on the steel and two-layer coatings on the steel and silicon substrates are the most hydrophobic. The contact angles were 95.9° (TaN on the steel), 95.1° (TaN/Ta₂O₅ on the steel) and 90.0° (TaN/Ta₂O₅ on the silicon). All investigated coatings are characterized by good mechanical and hydrophobic properties and are promising for the endoprostheses surface modifying.

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