Antibacterial properties of Ta-based ceramic coatings deposited by magnetron sputtering

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Abstract. Combatting the bacterial infections is an important aspect of any postoperative therapy. Bacterial adhesion to the surface of a biomaterial depends on its properties, such as surface roughness, topography and wettability. The present study analyzes the composition and surface parameters of nanostructured Ta, Ta₂O₅, TaON coatings and the correlation with their antibacterial properties. The elemental distribution, phase and chemical composition of the coatings were explored by X-ray phase analysis and energy dispersive X-ray spectroscopy. The surface morphology and topography were observed by atomic force microscopy and electron scanning microscopy. The coated surfaces’ advancing contact angles were evaluated by tensiometric measurements. The results of the bacterial viability tests demonstrated the strong bactericidal activity of Ta-based coatings deposited by magnetron sputtering.

1. Introduction
One of the main problems in applying implants in traumatology, orthopedics and cardiovascular surgery is the risk of bacterial infections. Reducing the bacterial infections is an important aspect of the postoperative therapy. The factors influencing the adhesion of bacterial to biomaterial’s surface are complex and dependent on the properties of both the surface and the bacteria [1]. One way of solving this problem is developing new biomaterials with antibacterial components, such as copper or silver doping [2-4]. Another approach is to use photocatalytic materials with the ability to generate highly reactive hydroxyl radical, oxygen and nitrogen species that act on various bacterial strains. This method has been successful in killing Escherichia coli (E. coli) cells and some other types of bacteria [5-7].

The development has also been attempted of hybrid antibacterial materials by combining photocatalysis with the hydrophobicity and bactericidal activity of some metals. Thus, combining oxides and Ag particles (e.g., Ag-InTaO) with visible light irradiation led to an improved antimicrobial effect against Escherichia coli [8].
Modifying the surface of implants via the formation of ceramic coatings is a promising way of improving the antimicrobial properties of medical devices. The biocompatibility, antibacterial properties, and cytocompatibility characteristics have been reported of tantalum-based coatings. Tantalum has been proposed as an alternative to other commonly used metallic materials for orthopedic implant applications [9]. Tantalum-based thin films have exhibited antimicrobial potential against several microorganisms, such as Staphylococcus aureus and Staphylococcus epidermidis [10].

The higher photocatalytic activity of TaO₃Nₓ was explained by the higher separation efficiency of electrons and holes in TaO₃Nₓ [11, 12]. The enhanced oxynitride content was associated with the favorable antibacterial properties of Ta films as related to Salmonella.

The antimicrobial properties of modern biomaterials depend on their composition and surface properties, namely, roughness, topography, and wettability [13]. The surface free energy of a given material depends on the chemical composition of the surface and directly affects the bacterial adhesion.

The aim of the present study was to study the effect of the composition and surface properties of metal Ta, oxide Ta₂O₃ and oxynitride TaON films on the functional characteristics of ceramic coatings and on their bactericidal activity in in vitro tests.

2. Materials and methods

Stainless steel samples (AISI 316) were used as substrates. The magnetron sputtering deposition of Ta, Ta₂O₃ and TaON coatings was performed in a high-vacuum pumping system with a base pressure of about 10⁻⁴ Pa. The tantalum target had a diameter of 170 mm. The magnetron discharge power was 4 – 5 kW; the RF power of the ICP source for oxygen activation was up to 1 kW. The main parameters of deposition process were the following: Ar pressure \( p_{\text{Ar}} = 2.3 \times 10^{-4} \) Pa, oxygen mass flow rate \( q = 35 \) sccm, nitrogen mass flow rate \( q = 27 \) sccm, air mass flow rate \( q = 25 \) sccm, magnetron voltage \( U_m = 500 – 520 \) V, magnetron current \( I_m = 7.0 – 7.6 \) A, total pressure \( p = 2.8 – 3.0 \times 10^{-1} \) Pa, coating deposition rate 6 – 8 μm/hour. A Radical type ion source was applied for cleaning the surface of samples before deposition [14].

The coatings thickness and adhesion properties were evaluated by standard methods. The coatings thickness values measured were 0.89 μm (Ta), 1.12 μm (Ta₂O₃), 0.91 μm (TaON). The surface morphology and topography were observed by using a JSM-7100F electron scanning microscope (SEM, JEOL, Japan) and an NT-206 atomic force microscope (AFM, Mikromasch, Belarussian Republic). The surface roughness parameters (arithmetical mean \( R_a \) and root mean square \( R_q \)) were measured by using CSC 38 girder cantilevers (Mikromasch, Estonia). The elemental distribution and chemical composition of the coatings were analyzed by energy dispersive X-ray (EDX) spectroscopy (Oxford Link ISIS 300). The phase compositions were studied by X-ray phase analysis (XRD) on a DRON-4-07 with copper radiation. X-ray photoelectron spectroscopy was carried out using an ESCALAB MkII apparatus (VG Scientific, UK). The advancing contact angles of the coated surfaces were evaluated by tensiometric measurements using DSA 100 E (Kruss, Germany). Three test liquids were used: water, glycerol and diiodomethane. The surface free energy (SFE) was calculated following the Owens, Wendt, Rabel and Kaeble’s method [15].

The Gram-negative Escherichia coli ATCC 11229 microbial strain was selected for testing. Microorganisms of E. coli were diluted with sterile saline to a cell density of 10⁸ CFU/ml (colony-forming units per milliliter) and 0.1 ml of the bacterial cells suspension was applied to the surface of sterile and fat-free plates in Petri dishes. The Ta-based coated and negative control (stainless steel) plates were held for 24 hours at room temperature. To determine the number of surviving cells, 10 ml were washed from plates with sterile saline. The suspension was seeded on tryptone soy agar and incubated at 37 ± 1 °C for 18-24 hours. The ratio was calculated of the number of surviving microorganisms on the coated samples to the number of surviving microorganisms on the negative control (stainless steel) and the statistical correlation of the antibacterial activity tests results was determined.
3. Results and discussion
The X-ray diffraction profiles and XPS spectra of nanostructured Ta-based films were analyzed. As was previously reported, the as-deposited Ta-oxide coatings initially appeared to have an amorphous structure [14, 16]. After a 15-min annealing at a temperature of 700 °C, the peaks were detected characteristic for the formation of the Ta$_2$O$_5$ crystal structure (001), (110), (111), (002), (200) in the angular range of 24-72 degrees (2θ). Further heating of the Ta for one hour led to an increase in the peaks intensity. In the case of TaON (figure 1), characteristic peaks of oxynitride at the angles of 27°, 33°, 36°, 38°, as well as spectra associated with the formation of TaON structure at angles in the range 61-63 degrees (2θ) were detected after 15 minutes of annealing. In addition, some characteristic peaks of the nitride structure (110), (111), (220) were revealed. The subsequent annealing for one hour resulted in the further formation of the oxynitride structure and an increase in the characteristic peaks at the angles of 23°, 37°, 47°, and 67°.

![Figure 1](image1.png)

**Figure 1.** X-ray diffraction profiles of TaON coatings: a) as deposited, b) annealed at temperature 700 °C during 15 min and c) 1 hour

XPS compositional analysis was conducted of the oxide Ta$_2$O$_5$ and oxynitride TaON coatings. The photoelectron spectra were observed of Ta4f, O1s, N1s coatings. The spectra included the photoelectron lines for Ta (4f7/2) and Ta (4f5/2). The Ta$^{5+}$ signals were detected at the binding energies of 26.8 eV and 28.7 eV. The O1s high-resolution spectra exhibited a peak at the binding energy position $E = 530.9$ eV associated with the Ta-O chemical bond. The N1s peak was detected at the binding energy $E = 396.2$ eV associated with the Ta-N chemical bond. This peak is generally considered to be the evidence for replacement of O atoms by N atoms in the Ta$_2$O$_5$ crystal lattice [17]. In addition, a weak N1s peak at $E = 398.0$ eV was assigned to Ta-N-O chemical bonds [18].

Figure 2 shows SEM and 3D AFM images of the Ta, Ta$_2$O$_5$ and TaON coatings deposited by magnetron sputtering. The coatings surface was smooth without delamination. The EDX spectra revealed the presence of the main characteristic elements, namely, tantalum (Ta), oxygen (O), and nitrogen (N).
The surface properties, such as topography and wettability, affect significantly the bacterial adhesion. The hydrophobicity can reduce the adhesion force between bacteria and biomaterial surface. Smooth surfaces do not favor bacterial adhesion. This is explained by the fact that a rough surface has a greater area with more favorable sites for bacterial colonization [19]. On the other hand, micron-sized features may favor bacterial adhesion, whereas nano-sized features may create surface conditions difficult for attachment of the bacterial cells [20].

Figure 3 presents the surface parameters of the Ta, Ta$_2$O$_5$, TaON coatings, namely, surface roughness and surface free energy. The deposition of Ta$_2$O$_5$ and TaON coatings leads to a smoothing of the surface roughness parameters and increases the surface hydrophobicity.

The roughness parameters assume minimal values in the cases of Ta$_2$O$_5$ and Ta films. The advanced contact angles shift to a higher hydrophobicity for the TaON (94.1°) and Ta$_2$O$_5$ (89.0°) coatings. The existence of a relationship between bacterial adhesion and surface free energy is well known; thus, surface free energy values between 23 mN/m and 30 mN/m have been related to the lowest bacterial adhesion. Moreover, a minimum *Escherichia coli* adhesion has been reported for the surface free energy range between 21 mN/m and 29 mN/m. In the present study, all Ta-based coatings demonstrates SFE parameters in the range 29.1 – 31.9 mN/m. The results are in a good agreement with reported values for bacterial adhesion reduction [12].
Table 1 presents the ratio of the number of surviving microorganisms *E. coli* ATCC 11229 on the coated samples to the number of surviving cells on the negative control (stainless steel).

**Table 1.** Number of surviving bacterial cells *E. coli* ATCC 11229 on the Ta, Ta$_2$O$_5$, TaON coated samples and the negative control (stainless steel) after 24-hour incubation.

| Materials     | Surviving bacterial cells, CFU/ml | Surviving bacterial cells % |
|---------------|-----------------------------------|-----------------------------|
| SS (AISI 316) | 1.1×10$^3$                        | -                           |
| Ta            | 4.0×10$^2$                        | 36.4                        |
| Ta$_2$O$_5$   | 3.0×10$^2$                        | 27.3                        |
| TaON          | 1.2×10$^2$                        | 10.9                        |

As seen, that hydrophobic TaON and smooth Ta$_2$O$_5$ coatings demonstrate the best antimicrobial properties in comparison with the Ta coated and stainless steel substrates.

**4. Conclusion**

The results presented demonstrate that the deposition of Ta-based coatings leads to a smoothing of the surface roughness parameters and shifts the surface properties to more hydrophobic values in comparison with stainless steel samples (AISI 316). Further, the bacterial viability tests demonstrate the strong bactericidal activity of Ta-based coatings deposited by magnetron sputtering. Activating the surface antimicrobial properties of medical products is very challenging for many biomedical applications and has a significant potential for reducing the risk of postoperative infections.

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