Mechanical properties of tantalum-based ceramic coatings for biomedical applications

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Abstract. The properties were studied of Ta, Ta2O5 and Ta/Ta2O5 coatings deposited by reactive magnetron sputtering on stainless steel (AISI 316) substrates. The compositional, structural and morphological parameters of the coatings were investigated by means of X-ray photoemission spectroscopy (XPS), energy dispersive X-ray (EDX) spectroscopy, and scanning electron microscopy (SEM). The roughness parameters, adhesion strength, hardness, elastic modulus, and \( H/E \) ratio were evaluated by standard techniques. The hardness parameters of the Ta2O5 and Ta/Ta2O5 coatings increased in comparison with pure Ta films, while the relatively low Young's modulus was related to high elastic recovery and high resistance to cracking. The tantalum-based coatings possessed good biomechanical parameters for advanced implant and stent applications.

1. Introduction
Tantalum is one of the most attractive materials for biomedical applications [1,2]. However, the clinically-used Ta-based metallic implants and stents have limitations due to their poor biomechanical properties. To solve the problem, different Ta-based coatings have been deposited on the surface of metals and alloys to improve the quality of modern medical products. Tantalum (Ta) [3, 4], tantalum nitride (TaN) [5-8], and tantalum oxide (Ta2O5) coatings [9-11] have demonstrated high electrochemical and dielectric properties, and excellent biocompatibility. Coating with Ta is among the most practical ways of improving the long-term stability of biomedical implants made of stainless steel (AISI 316L) [12], Co–Cr [5], Ti-6Al-4V [13] and NiTi [14] by enhancing their \textit{in vitro} bioactivity and biocompatibility, which would widen their applications as orthopedic and dental implants. The results of tests on implanting Ta in both soft and hard rat tissues showed the good osteogenesis of this metal [15]. TaC and TaN possess a relatively high hardness due to the covalent bond.
nature of their bond [16], and a superior corrosion resistance [17]. Moreover, the biomedical properties of TaN coatings have also been investigated. The blood compatibility of TaN films was shown to be better than that of Ta [18] for applications in artificial heart valves.

The novel stent types have demonstrated low rates of platelet aggregation and better endothelialization, especially in the case of patients with high-risk of in-stent restenosis. The positive effect results in lower rates of myocardial infarction and stent thrombosis [19, 20]. The clinically used metallic stents have limitations because of their low mechanical and bio-inertness properties. As proved in a clinical trial [21], surface treatment of artificial vessels and deposition of coatings reduce the likelihood of thrombosis, control the blood coagulability, and diminish platelet’s adhesion compared with metal stents.

Deposition of Ta, TaN, and the Ta/TaN bilayer system as protective coatings has been studied in view of biomedical applications [22]. It was found that the Ta phase improves the corrosion and biomechanical properties of the bilayer system in comparison with the monolayer TaN film. The mechanical properties of functional coatings are strongly correlated with the coatings’ properties, such as microstructure, phase and chemical composition, and surface parameters. The hardness (H), the Young's modulus (E), and the H/E ratio of the samples provide an elastic-strain-to-failure value correlated to the wear resistance. The aim of the present work was exploring the effect of the compositional, structural and surface properties of the tantalum-based films on the biomechanical characteristics of Ta₂O₅ and Ta/Ta₂O₅ coatings.

2. Materials and methods
The substrates were made of stainless steel SS (AISI 316) discs with a diameter of 32 mm and a thickness of 3 mm. Before deposition, the samples were cleaned by standard methods in an ultrasonic bath. The tantalum target had a diameter of 170 mm. The deposition of Ta, Ta₂O₅, and Ta/Ta₂O₅ coatings was performed by ion-source-assisted magnetron sputtering in a high-vacuum system with a base pressure of about 10⁻⁷ Pa. Oxygen for the reactive deposition was delivered through the ICP plasma source at q = 30 – 60 sqcm; the magnetron voltage was U_m = 700 V, with a magnetron current of about 1_m = 5.7 A. The ion source was also used to clean the samples’ surface before deposition.

The coatings’ thickness was measured by a JSM-5500 LV (JEOL) SEM (figure 1). The composition of the coatings was analyzed by EDX spectroscopy (Oxford Link ISIS 300). X-ray photoelectron spectroscopy was carried out using ESCALAB MkII (VG Scientific) electron spectrometer with an AlKα X-ray source (excitation energy hν = 1486.6 eV). The surface roughness parameters were measured by a Hommel-Etamic T8000 profilometer, while the hardness and Young's modulus were measured using the Fischerscope HM 2000 nanohardness testing instrument (with a diamond Berkovich tip). The adhesive properties were measured using a REVETEST® (CSM) scratch tester and a Rockwell indenter.

3. Results and discussion
Fundamentally, the deposited films’ functions should be strongly affected by their microstructure, surface roughness, and chemical composition. We evaluated the thickness and roughness values (Rₐ, Rₛ) of the Ta, Ta₂O₅, and Ta/Ta₂O₅ coatings (table 1). In the cases of Ta₂O₅ and Ta/Ta₂O₅ coatings, an increase in the films’ thickness and the formation of a bilayer resulted in a decrease in the roughness

| Material/Coating | Thickness (μm) | Roughness Rₛ (μm) | Roughness Rₐ (μm) |
|------------------|---------------|------------------|------------------|
| SS / Ta          | 0.72          | 0.018            | 0.280            |
| SS / Ta₂O₅       | 0.98          | 0.011            | 0.083            |
| SS / Ta/Ta₂O₅    | 1.0           | 0.008            | 0.055            |
parameters. The cross-section and surface structure of the Ta, Ta₂O₅ and Ta/Ta₂O₅ coatings, as studied by SEM, are shown in figure 1. The coatings’ surfaces have smooth relief with uniform cross-section structure. The EDX spectra and the elemental compositions of the coatings are presented in figure 2.

![Figure 1. SEM micrographs of coatings: a) Ta, b) Ta₂O₅ and c) Ta/Ta₂O₅.](image1)

![Figure 2. EDX spectra of a) Ta, b) Ta₂O₅ and c) Ta/Ta₂O₅ coatings.](image2)

The XPS data on the coatings’ surface composition (figure 3) showed various Ta oxidation states. The spectrum includes the photoelectron lines for Ta (4f7/2) and Ta (4f5/2). The Ta⁵⁺ signals attributed to the stoichiometric oxide were detected at binding energies of 26.8 eV and 28.7 eV (figure 3a). Also, Ta⁰ (Ta in its metallic form) was observed for the Ta/Ta₂O₅ bilayer coatings. The doublet peaks (figure 3b) located at binding energies of 22 eV and 26.3 eV correspond to Ta⁰ (metallic Ta); and Ta⁵⁺ (Ta₂O₅), respectively. The O(1s) spectrum is presented in figure 3c. The peak around 530.9 eV can be assigned to the formation of Ta oxide [23, 24].
An effect arising from the formation of a very thin Ta$_2$O$_5$ film on the surface was discussed in [25]. Ta is a transition metal with a strong affinity to oxygen. Oxygen could be incorporated during the deposition process, thus forming an oxide layer covering the metallic Ta. The presence of oxygen and the possible contamination in the transition layers of the samples with Ta coating may lead to a lower adhesive strength and a higher brittleness of the coatings. In some studies, a poor adherence of the Ta thin film deposited on the AISI 316 steel was reported and attributed to the large mismatch between the steel and Ta lattices. The adhesive strength to the substrate was very poor and delamination was observed as a result of the very high residual stresses. The bilayer deposition has changed the Ta films’ adhesion parameters [22, 25].

The coatings’ mechanical behavior is strongly correlated with their properties, such as microstructures, phase and chemical composition, surface parameters. The mechanical behavior is characterized by the ratio $H/E$ [26, 27], which is proportional to the fracture toughness of the film and to the resistance of the material to plastic deformation. It means that the films with enhanced resistance to cracking and plastic deformation should have lower values of the effective Young’s modulus. Materials with a high plastic resistance ratio $H/E^2$ have exhibited a higher yield strength [26]. Moreover, the formation of coatings improves the mechanical properties of the coated materials. The elastic modulus of bilayer coatings is reduced in comparison with monolayer coatings. The hardness parameters of Ta$_2$O$_5$ and of bilayer Ta/Ta$_2$O$_5$ coatings increase in comparison with those of Ta films. The mechanical advantages of multilayer formations in comparison with monolayer Ta-based coatings for long lifetime’s component applications have been reported earlier [22].

The values of the adhesion strength, hardness ($H$), Young’s modulus ($E$), $H/E$ and $H/E^2$ of the coatings deposited on the stainless steel samples (AISI 316) substrates are summarized in table 2. The Ta-based coatings demonstrated a relatively high hardness and a low Young’s modulus, corresponding to a high elastic recovery and a high resistance to cracking. We further calculated the $H/E$ ratio, which is related to the wear resistance. The coatings exhibited an elastic-strain-to-failure ratio from 0.05 to 0.08

| Material/Coating | Mechanical parameters (averaged results of 10 tests) |
|------------------|-----------------------------------------------------|
|                  | Hardness, $H_v$ | Young Modulus ($E$) | $H/E$ | $H/E^2$ | Adhesion ($N$) |
| SS / Ta          | 681.2          | 127.3              | 0.05  | 0.02    | 14.6           |
| SS / Ta$_2$O$_5$ | 846.4          | 108.1              | 0.07  | 0.05    | 24.8           |
| SS / Ta/Ta$_2$O$_5$ | 861.5          | 109.0              | 0.08  | 0.06    | 15.9           |
and a plastic resistance ratio from 0.02 to 0.05, higher than the respective values for metals (0.01) and other modern implant materials [28]. The best hardness parameters were found for the bilayer Ta/Ta$_2$O$_5$ coatings, while the highest adhesive strength was exhibited by the Ta$_2$O$_5$ monolayer.

The above results demonstrate that Ta$_2$O$_5$ and Ta/Ta$_2$O$_5$ coatings formed by reactive magnetron sputtering deposition on stainless steel (AISI 316) substrates possess structural and mechanical properties differing from those of pure Ta films. Thus, the hardness parameters of Ta$_2$O$_5$ and Ta/Ta$_2$O$_5$ coatings increase in comparison with pure Ta films, while the highest adhesive strength was shown by the Ta$_2$O$_5$ coatings. The insufficient adhesion parameters of Ta films due to possible contamination in the transition layer were improved by forming oxide and bilayer coatings.

4. Conclusions
The microstructure, surface roughness, and chemical composition were determined of Ta, Ta$_2$O$_5$, and bilayer Ta/Ta$_2$O$_5$ coatings deposited by magnetron sputtering. Increasing the films thickness and forming of a bilayer resulted in a decrease in the roughness of Ta$_2$O$_5$ and Ta/Ta$_2$O$_5$. The coated surfaces had smooth relief with uniform cross-sectional structure. The elemental compositions of Ta, Ta$_2$O$_5$, and bilayer Ta/Ta$_2$O$_5$ coatings were also investigated. The XPS spectra obtained revealed the presence of Ta$^{5+}$ (stoichiometric oxide) and Ta$^6$ (metallic form) in the Ta/Ta$_2$O$_5$ bilayer coatings. The hardness parameters of the Ta$_2$O$_5$ and bilayer Ta/Ta$_2$O$_5$ coatings were higher than those of Ta films. The bilayer Ta/Ta$_2$O$_5$ coatings demonstrated a relatively high hardness and a low Young's modulus corresponding to a relatively high elastic recovery and a high resistance to cracking. The coatings exhibited an H/E ratio in the 0.05 – 0.08 range and a plastic resistance ratio ranging from 0.02 to 0.05, higher than for metals and other modern implant materials. The best hardness parameters were found for bilayer Ta/Ta$_2$O$_5$ coatings, while the highest adhesive strength was observed in the case of monolayer Ta$_2$O$_5$. The tantalum-based coatings are promising candidates as materials for advanced implant and stent applications.

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