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Nanomechanical and Nanotribological Properties of Nanostructured Coatings of Tantalum and Its Compounds on Steel Substrates

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Abstract: The present paper addresses the problem of identification of microstructural, nanomechanical, and tribological properties of thin films of tantalum (Ta) and its compounds deposited on stainless steel substrates by direct current magnetron sputtering. The compositions of the obtained nanostructured films were determined by energy dispersive spectroscopy. Surface morphology was investigated using atomic force microscopy (AFM). The coatings were found to be homogeneous and have low roughness values (<10 nm). The values of microhardness and elastic modulus were obtained by means of nanoindentation. Elastic modulus values for all the coatings remained unchanged with different atomic percentage of tantalum in the films. The values of microhardness of the tantalum films were increased after incorporation of the oxygen and nitrogen atoms into the crystal lattice of the coatings. The coefficient of friction, CoF, was determined by the AFM method in the "sliding" and "plowing" modes. Deposition of the coatings on the substrates led to a decrease of CoF for the coating-substrate system compared to the substrates; thus, the final product utilizing such a coating will presumably have a longer service life. The tantalum nitride films were characterized by the smallest values of CoF and specific volumetric wear.

Keywords: atomic force microscopy; friction coefficient; magnetron sputtering; nanoindentation; nanostructured coatings; tantalum

1. Introduction

The stainless steel (for example, 316L SS), platinum iridium alloys, tantalum, nitinol, cobalt–chrome alloys, titanium and its alloys, and pure iron and magnesium alloys are the basic materials for the production of stents. Stainless steel is the most common material for the production of stents with and without coatings. The stents made of stainless steel demonstrate suitable mechanical properties and excellent corrosion resistance. However, the clinical application of steel is limited by the ferromagnetic nature of the alloy and its low density. Due to these properties, the steel is poorly visible in X-ray and magnetic resonance

imaging [1]. The implants of the stainless steel may cause an allergy to nickel, chromium, and molybdenum, leading to local immune responses and inflammation. Different materials are used as coatings on stainless steel stents that lead to improvements of X-ray visibility and biocompatibility. Titanium and its alloys have excellent biocompatibility, high corrosion resistance, and are intensively used in orthopedics and dentistry. Pure titanium is not suitable for the stent production due to rather low values of the mechanical properties; however, it can be used as a coating for stainless steel stents to improve biocompatibility. Such stents show excellent results in clinical trials [1,2].

Usage of stents that represent a system of the stainless steel substrate with titanium or tantalum coating allows combining the suitable mechanical properties and bioinertness [3–5]. Tantalum is characterized by a good plasticity, high strength, wear resistance, weldability, corrosion resistance, infusibility, biocompatibility, and it is clearly visible in X-rays and magnetic resonance imaging [6,7]. In addition, due to its properties, tantalum is widely used not only in electronics [8,9], protective coatings [10,11], anti-corrosion coatings [12,13], optical coatings [14–17], chemical industry [18], but also in biomedicine [19–24] (orthopedics and dentistry [25–29], endovascular stents, and neurosurgical implants [30]). However, the use of tantalum is difficult due to its high density, manufacturing complexity, and the relatively high cost. For these reasons, a various approaches are currently being proposed to modify the surface properties of metal substrates for the improvement of biological responses by applying coatings based on Ta. The modern processing methods allow obtaining the tantalum coatings with a fine-grained structure and optimal properties (tensile strength up to 600 MPa, and elongation of about 30%) for the stents production [31]. In combination with increased strength, tantalum has a high protective ability that prevents active corrosion processes and the electrochemical destruction of metal surface structures in various environments. For example, β-Ta nanocrystalline coatings on Ti-6Al-4V substrates showed high hardness in combination with good resistance to contact damage [32]. Thus, the corrosion resistance of 316 L stainless steel was significantly improved due to the TaC_xN_{1-x} coatings [33]. These coatings also demonstrated good adhesion characteristics. Thus, depending on the formation conditions, the properties of the coatings change. However, the best conditions for tantalum coatings formation have not yet been determined.

The development of technologies for the formation of functional tantalum nanostructured coatings is currently of high interest for both medical and material science community [34]. The perspective ion–plasma spraying method for creating nanostructured coatings allows to form nanocoatings to change surface properties and obtain biocompatible materials with desired properties. Thus, in [35], it was found that the TaNx coating applied by high-frequency magnetron sputtering at a relatively high bias voltage of 200 V demonstrates good tribological characteristics, hardness, and adhesive strength. The authors of [36] synthesized tantalum nitride films onto silicon using magnetron sputtering (the N_2 content in the gas mixture was changed). As a result, it was revealed which content of N_2 allows obtaining films with the highest hardness, low friction coefficient, and low wear rate. In the present research, a new efficient technology has been developed for the deposition of nanostructured coatings based on tantalum by magnetron sputtering. The optimal modes of metal substrates modification with nanostructured coatings based on Ta were developed in order to create new improved devices for medical applications (cardiovascular surgery, endoscopy, and orthopedics). Remarkably, nanostructured materials have larger surface energy than typical materials enhancing the adhesion of bone cells and producing higher osseointegration [32]. The surface nature of a biomaterial (relief, hydrophobic–hydrophilic properties, chemical composition, etc.) plays an important role in regulating the cellular response of a biological organism to the biomaterial. Since the approach for the deposition of the Ta coatings involves changing the structure and properties of materials at both the micro- and nanoscales, it is advisable to assess changes in the structure and properties at these levels. Such instrumental research methods as atomic force microscopy (AFM) and nanoindentation (NI) allow studying the surface properties of the films of tantalum and its compounds at the nanoscale, as well as to evaluate the nature

of their changes (roughness, friction coefficient) in the biological medium and estimate the possibility of using these nanocoatings as biocompatible materials [37–40].

The aim of the present work was to study the physical, mechanical, and tribological properties of nanostructured tantalum oxynitride coatings on the stainless steel substrates. This complex of characteristics helps to assess the performance characteristics of coatings more accurately than the traditionally used microhardness. Estimation of such a complex is vital for the production of devices for various medical applications.

2. Materials and Methods

The coatings of Ta, Ta_2O_5, TaN, and TaON were deposited on the polished stainless steel (type is 316 L SS) substrates using reactive direct current planar magnetron sputtering. Deposition process was performed on the experimental set-up (KhNU and NSC KIPT NASU, Kharkov, Ukraine) [41,42]. The physical and chemical processes in plasma were investigated during the reactive magnetron deposition of tantalum oxynitride [43]. Prior to the deposition, substrates were cleaned in an ultrasonic bath, then the ion cleaning was performed (Hall type ion source) in argon atmosphere (pressure was 6.65×10^{-2} Pa, ion acceleration voltage—3 kW, ion source current—100 mA) during 5 min. Then, the substrates were placed in a chamber pumped to a residual vacuum of less than 10^{-3} Pa. The ion cleaning was performed (Hall type ion source) in argon atmosphere (pressure was 6.65×10^{-2} Pa, ion acceleration voltage—3 kW, ion source current—100 mA) during 5 min. Then the deposition of the coatings of Ta, Ta_2O_5, TaN, TaON of about 1 μm thickness was conducted. The tantalum target with a diameter of 170 mm was used. The magnetron discharge power was 4–5 kW. The distance between magnetron and samples was about 30 cm. The feature of this system was the additional oxygen activation by discharge plasma source induction. The oxygen was supplied through a plasma source for activation. The deposition parameters of the coatings are summarized in Table 1. These deposition modes were selected after optimization of the spraying technology carried out in [42,43].

Table 1. The parameters of the magnetron sputtering for the coatings of tantalum and its compounds.

Type of Coating	Gas Pressure P [Pa]	Magnetron Voltage U_m [V]	Magnetron Current I_m [A]	Time of Deposition [min]	Gas Mass Flow Rate Q [cm^3/min]
Ta	1×10^{-1} (Ar)	495	6.6	30	-
Ta_2O_5	1.3×10^{-1} (general)	500	6.4	20	25 (O_2)
TaN	1.2×10^{-1} (N_2)	800	3.4	60	95 (N_2)
TaON	1.5×10^{-1} (general)	620	4.0	30	10 (O_2) 45 (N_2)

The morphology of the coatings was evaluated by the AFM Dimension FastScan (Bruker, Santa Barbara, CA, USA) in PeakForce QNM (Quantitative NanoMechanics, Bruker, Santa Barbara, CA, USA) regime with CSG10_SS (Micromasch, Tallinn, Estonia) cantilevers. The study of the microstructure and elemental composition of the samples was carried out on the JSM7001F (JEOL, Tokyo, Japan) scanning electron microscope (SEM) equipped with the X-ray energy dispersive microanalysis probe system INCA ENERGY 350 (Oxford Instruments, Abingdon, Oxfordshire, UK) at x10,000 magnification. The operating voltage and probe current were 20 KV and 5 nA, respectively. The working distance was 10 mm. The microstructure was analyzed in the secondary electron mode (SEI mode).

The phase compositions were studied by X-ray phase analysis (XRD) on a DRON-4-07 (LNPO "Burevestnik", Saint-Petersburg, Russia) unit in copper radiation. To analyze the amorphous and crystal structure formation, coatings were annealed at a temperature of 700 °C for 15 min and one hour in air in a Nabertherm GmbH L5 /13/ B180 furnace.

The method for the investigation of the friction coefficient (CoF) using AFM is based on measuring the twist angle of the silicon cantilever of the probe around its axis under the action of friction between the surface and the tip. It is described in detail in the paper by Chizhik et al. [44]. In the present research, we used NCS 11A silicon cantilevers (Mikromasch, Tallinn, Estonia) with the stiffness 3 N/m to determine the CoF using AFM

NT-206 in a "sliding" mode. During the tests on the five different 20 × 4 μm areas and 256 × 50 points, the probe load was 0.005 μN, and the friction speed was 4.9 μm/s. The radius of curvature of the cantilever was increased to 100 nm by scanning at high loads on the silicon surface in order to prevent these changes during research.

The CoF in a "plowing" mode and the wear of the coatings were studied using a Dimension FastScan AFM in the Contact Mode using a diamond probe on silicon console of D300 type (SCDprobes, Tallinn, Estonia) with an initial tip radius of curvature of 33 nm The stiffness of cantilevers was 13.84 N·m^{-1}. During the tests, the normal load of 1.164 μN (calculated = 0.6 V) per probe was controlled. The process parameters, which were kept constant, were as follows: the scanning area 20 × 4 μm, 100 cycles, 256 × 256 points, friction speed 2.0 μm/s. The movement of the probe on the surface was reciprocating. Thus, the use of silicon and diamond probes with different loads allowed exploring the surface of tantalum coatings by various friction mechanisms (Figure 1). At the "sliding" mode, the action of adhesive forces was influenced on the friction coefficient, and the "plowing" mode characterized the strength properties of the material during friction.

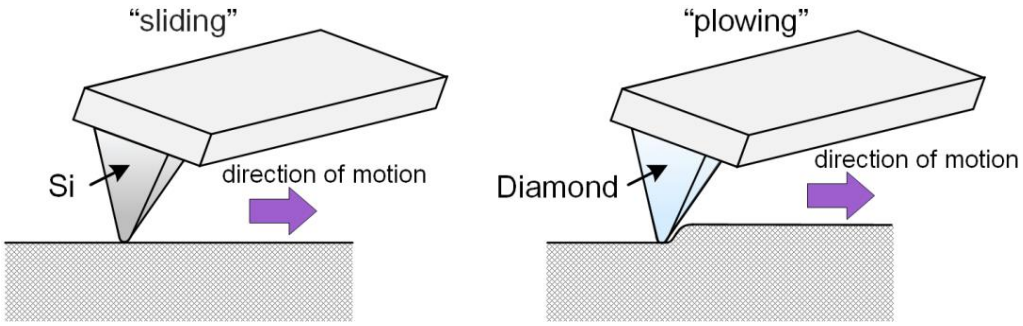

Figure 1. The principle scheme of friction mechanisms: "sliding" and "plowing".

The friction force (F) was recorded separately in the forward and in the reverse scanning. In the processing program, the image of the reverse scanning was subtracted from the obtained image of the forward scanning, and thus the average value of the friction force was determined. The mechanical stresses in the contact zone of the AFM probe with the coating surface (contact pressure) were determined using the AMES (Advanced Mechanical Engineering Solutions) contact stress calculator [45,46], setting the values of the radius of curvature of the probe, the elastic modulus of the coatings, and the probe. The value of the specific volumetric wear k_v was calculated as the ratio of the volume of worn material (V) to the normal load (L) and the indenter path length along the sample (S) and expressed in m^3/N·m:

$$k_v = V/(L \cdot S) \quad (1)$$

The volume of wear V was estimated by the cross-sectional area and the perimeter of the wear track [47].

The thickness of the coatings was determined via AFM scanning of cross sections of coatings–substrate obtained after cooling samples into the fluid nitrogen during 10 min and fracture of cooled samples.

The microhardness (H) and the elastic modulus (E) were measured with using Hysitron 750 Ubi nanoindentation device (Bruker, Minneapolis, MN, USA). The radius of curvature of the diamond Berkovich indenter was 150 nm. For each sample, 9 curves were obtained at the load of 2000 μN. The indentation depth (h) into the coatings was 50–80 nm. The radius of the tip was calibrated by a set of indentations with increasing load into a surface of standard fused silica sample.

3. Results and Discussion

3.1. Elemental Analysis of Coatings

The EDX spectra (Figure 2) confirm the presence of basic characteristic elements in the films, such as tantalum, oxygen, and nitrogen [48]. The amount of tantalum is close to its atomic content in the compounds Ta_2O_5, TaN, and TaON. Except for the main lines of tantalum, the peak at 2.2 KeV corresponds to a secondary line of Ta (Figure 2b–d). Probably, the peak intensity is related to the texture of different Ta-based coatings. Deviations from the stoichiometric composition of coatings can be associated with some method accuracy. Non-uniformity of a scan coating surface and the presence of a small amount of other elements in the spectrum, for example Ar, may affect the error in the results normalizing. Previously carried out research [49] demonstrated the stoichiometric composition of the tested coatings. X-ray photoelectron spectroscopy was carried out using ESCALAB MkII (VG Scientific, East Grinstead, UK) with 1486.6 eV Al Kα radiation. Detailed scans were detected for the C1s, O1s, N1s, and Ta4f regions (Figure A1). An error on the binding energy (BE) values was obtained by standard deviation about 0.2 eV. Data analysis was made with a Shirley-type background subtraction, non-linear least-squares curve fitting with Gaussian-Lorentzian peak shapes. The atomic compositions were calculated using peak areas. The compositional analysis of oxide Ta_2O_5, oxynitride TaON, and nitride TaN coatings by X-ray photoelectron spectroscopy was performed. The photoelectron spectra of Ta4f, O1s, and N1s coatings were observed [49]. The spectrum included the photoelectron lines for Ta (4f7/2) and Ta (4f5/2). The Ta^{+5} signals were detected at binding energies 26.8 eV and 28.7 eV. The O1s high-resolution spectra demonstrated the peak at binding energy position E_b = 530.9 eV, associated with Ta-O chemical bond. The N1s peak was detected at binding energy E_b = 396.2 eV, associated with Ta-N chemical bond. This peak is generally considered to be the evidence for replacement of O atoms by N atoms in Ta_2O_5 crystal lattices [50]. In addition, a slight N1s peak at binding energy E_b = 398.0 eV was corresponded to Ta-N-O chemical bonds [51]. All binding energies of the high resolution spectra were calibrated with the C1s binding energy of 285.0 eV.

XRD spectra of as-deposited and annealed Ta_2O_5 and TaON coatings were analyzed (Figure A2). According to the XRD data, the amorphous nature of the as deposited Ta_2O_5 coatings was confirmed. Changes were detected for the Ta_20_5 coatings after the treatment at 700 °C for 15 min, as confirmed by the XRD pattern peaks which became sharper and more intense (Figure A2). The increase in the crystallinity of the coatings as a function of thermal treatment temperature was detected. After 15 min annealing at a temperature of 700 °C, the peaks typical for the formation of the crystal structure of Ta_2O_5 (001), (110), (111), as well as the peaks typical for Ta (200), were clearly identified. Further heating for 1 h led to an increase in the intensity of main peaks and the appearance of a new one (020) in the angular range of 24–72 degrees (2θ). In the case of TaON, characteristic peaks of oxynitride at angles of 27°, 33°, 36°, 38°, as well as spectra associated with the formation of TaON structure at angles in the range of 61–63 degrees (2θ) were detected after 15 min of annealing. In addition, some characteristic peaks of the nitride structure (110), (111), (220) were revealed. Subsequent annealing for an hour was resulted in the further formation of the oxynitride structure and increase in the characteristic peaks at the angles of 23°, 37°, 47°, and 67°.

3.2. The Thickness of the Coatings and Fracture Microstructure

AFM images of fractures of the investigated coatings of tantalum compounds on steel and their surface profiles are demonstrated on the Figure 3. According to these profiles, the values of the thickness for the coatings were as follows: Ta_2O_5 and TaON—1500 nm, TaN—800 nm, and Ta—500 nm, which is confirmed by the SEM data (Figure A3). In addition, the fracture sites of coatings allow a qualitative assessment of the brittleness of coatings. Thus, the fracture sites of Ta_2O_5 and TaN coatings have in their microstructure significant fragments of a "columnar" texture (arrows in Figure 3a,c), which are typical for more brittle fracture. The microstructure of TaON coatings shows strips with a thickness

of 20–40 nm (arrows in Figure 3b). The layered Ta and fracture sites coatings consist of nanosized grains of 40 nm in diameter (arrows in Figure 3d). In the case of fracture, the grains are arranged in rows under the action of deformation. These structures are typical for the more plastic materials, according to the plasticity values determined by NI: the highest value for Ta (59.2%), the high for TaON (52.3%), the middle for TaN (42.3%), and Ta_2O_5 has the lowest η (27.2%).

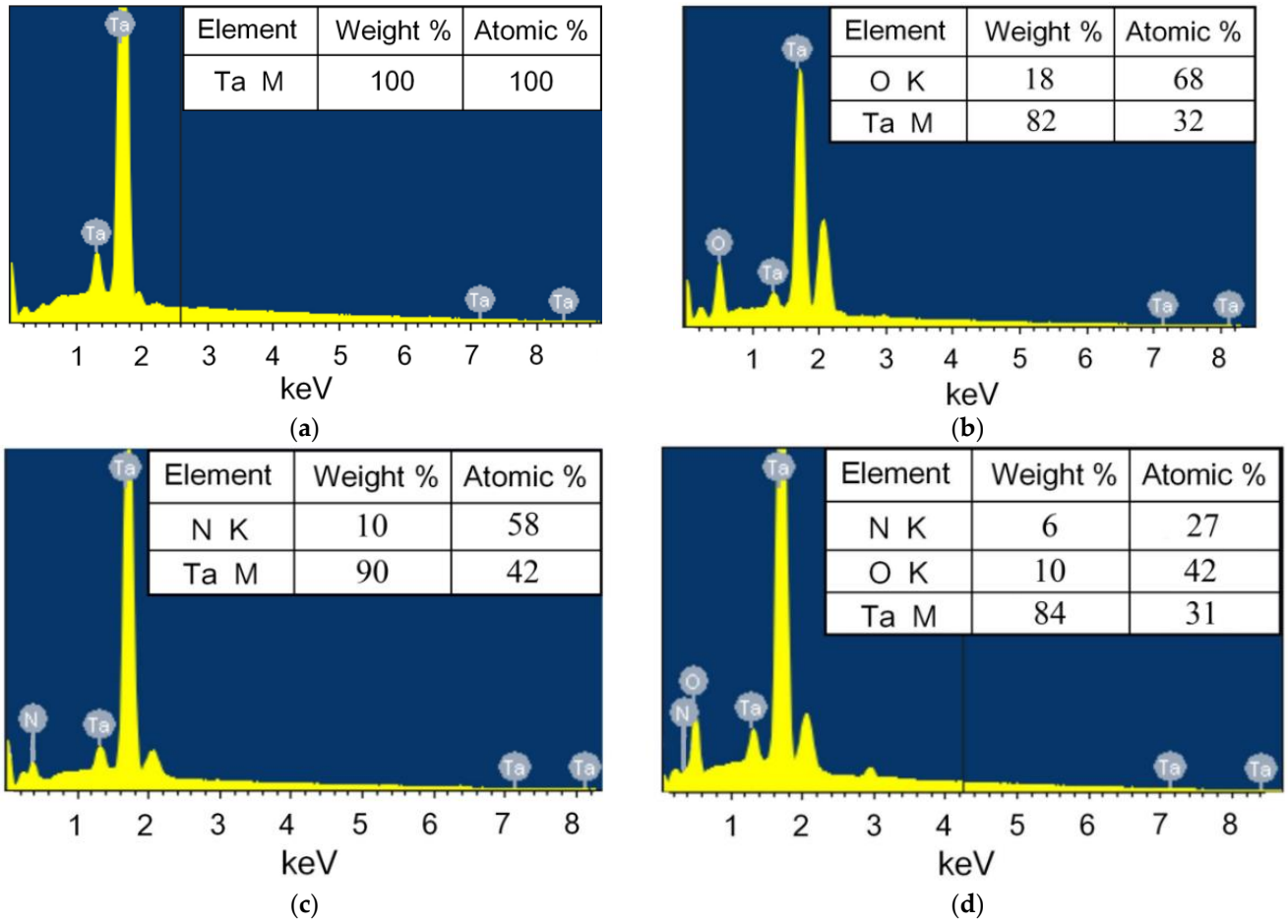

Figure 2. EDX spectra of nanostructured coatings: tantalum (**a**), tantalum oxide (**b**), tantalum nitride (**c**), and tantalum oxynitride (**d**).

3.3. The Surface Microstructure of Coatings

In the process of magnetron sputtering, the mechanism of growth is determined by the balance of the energy of the substrate surface, the deposited material, the energy of the material-substrate interface, and the energy of elastic stresses in the growing film. High-resolution AFM is needed to reveal the surface morphology and roughness of smooth amorphous coatings on polished substrates. According to AFM-images, the polished surface of the stainless steel has a microstructure with irregularities and protruding particles of alloying phases of 20–200 nm in diameter (arrows Figure 4a). The arithmetic mean roughness (R_a) for the steel surface on the area of 4 × 4 μm was 3.8 nm.

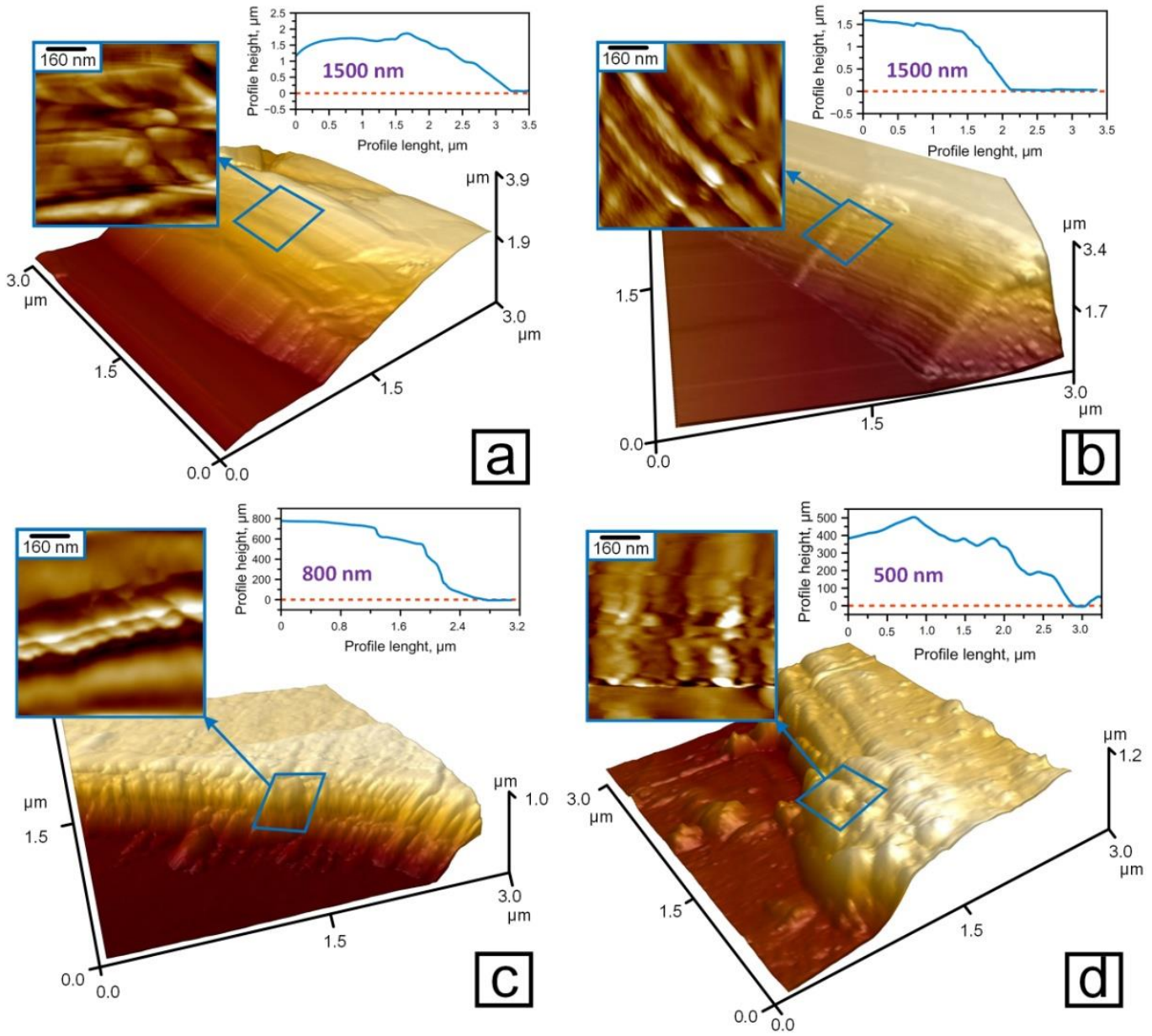

Figure 3. AFM-images of nanostructured coatings fractures: tantalum oxide (**a**), tantalum oxynitride (**b**), tantalum nitride (**c**), and tantalum (**d**).

Surface uniformity was increased after tantalum was deposited on the steel surface. On the area of 1 × 1 μm, Ta coatings have the cellular surface with ribbings that are limitative for the cells (arrows Figure 4b). The ribbings have granular microstructure with the diameter of grains of 20 nm that are shown on the area of 60 × 60 nm scanning field (inset Figure 4b). R_a of Ta coatings on the area 4 × 4 μm was 4.8 nm.

Flat islets with the height of 4–6 nm and the size of 100–500 nm appeared on the Ta_2O_5 coatings in the process of the sputtering (arrows Figure 4c). These flat islets indicate that a growth mechanism of tantalum oxide is different compared to the one of tantalum films. Ta coatings are characterized by polycrystalline growth, while tantalum oxide is characterized by layer-by-layer growth. On the area of 60 × 60 nm (inset Figure 4c), Ta_2O_5 coatings have granular microstructure with the diameter of grains of 5–20 nm. R_a of Ta_2O_5 coatings on the area 4 × 4 μm was 4.2 nm.

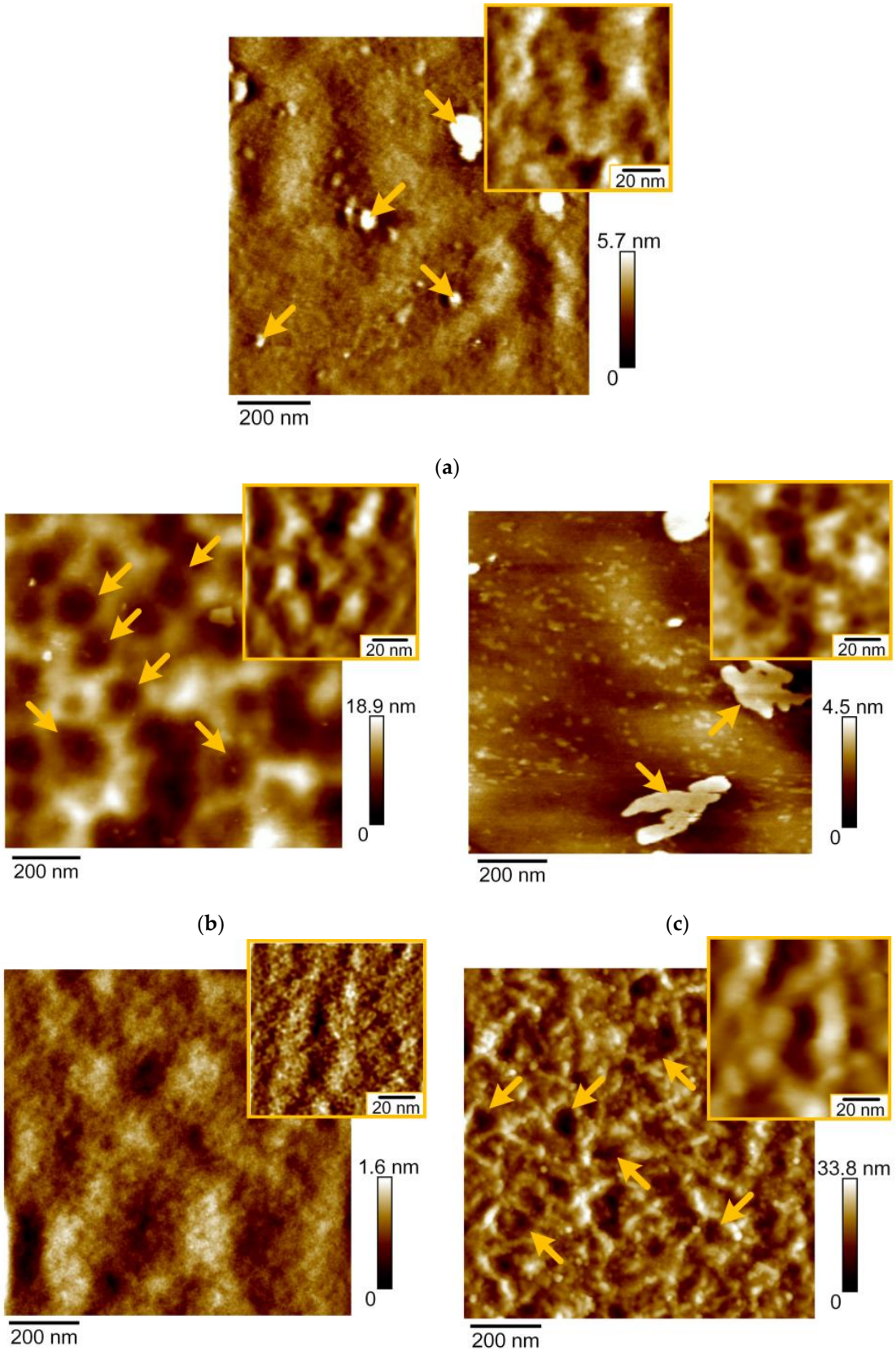

Figure 4. AFM-images of stainless steel (**a**) and the coatings: tantalum (**b**), tantalum oxide (**c**), tantalum oxynitride (**d**), and tantalum nitride (**e**).