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Bioinert coatings of Ti-Ta-N for medical implants obtained by electric explosion spraying and subsequent electron-ion-plasma modification

Denis A Romanov^{1,2,*} , Kirill V Sosonin², Sergei Yu Pronin², Stanislav V Moskovskii², Victor E Gromov² , Vladimir A Bataev³, Yuriy F Ivanov⁴ and Alexander P Semin²

¹ College of Mechanical and Electrical Engineering, Wenzhou University Institute of Laser and Optoelectronic Intelligent Manufacturing, Wenzhou, 325024, People's Republic of China

² Department of Natural Science Disciplines of Professor V. Finkel, Siberian State Industrial University, 42, Kirov St., Novokuznetsk, 654007, Russia

³ Department of Materials Science in Engineering, Novosibirsk State Technical University, Novosibirsk 630073, Russia

⁴ Institute of High Current Electronics of Siberian Branch of the Russian Academy of Sciences, Tomsk 634055, Russia

* Author to whom any correspondence should be addressed.

E-mail: romanov_da@physics.sibsui.ru, k.sosnin@mail.ru, psu17psu@gmail.com, psk-svm@yandex.ru and gromov@physics.sibsui.ru

Keywords: bioinert coating, structure, mechanical properties, proliferative activity of fibroblasts, antimicrobial activity, tantalum, titanium

Abstract

The purpose of the research was to form a Ti-Ta-N- system bioinert coating on Ti6Al4V alloy surface as well as to study its structure and properties. The main contribution of the research is in the following. Electro-explosion spraying of tantalum coating on VT6 titanium alloy surface was pioneered in the research. After that the processing of the coating by low-energy high-current electron beam and subsequent nitriding was carried out in a single technological cycle. It has been established that a nanocrystalline coating based on tantalum, nitrogen and titanium was formed as a result of the technological operations. The phase composition of the coatings has been detected. The variations in crystal lattice parameters being formed in coating of phases and coherent scattering regions of these phases depending on power density of electron beam have been determined. Structural characteristics of the coatings at nano- and microlevel have been detected. Tests of coatings for nanohardness, the Young modulus, wear resistance and friction factor have been carried out. By all technical characteristics Ti-Ta-N-system coating exceeds titanium of VT6 grade. The cause of the increase in mechanical characteristics of the Ti-Ta-N-system coating is their nanostructural state and strengthening phases. Tests for proliferation activity of fibroblasts and antimicrobial activity have shown better results in comparison with VT6 titanium alloy as well. It is due to escape of vanadium ions from VT6 alloy into nutrient cell medium and their destructive effect on cell cultures. Variations in proliferation and antimicrobial activity develop due to amplification of cell proliferation. A complex of the obtained characteristics makes it possible to recommend Ti-Ta-N-system coating for its application as a bioinert coating on different implants in future.

1. Introduction

The development and manufacture of medical products are among the most intensively developing directions of scientific and technical activity in the world [1]. These include the development of new materials [2], technologies of designing [3], manufacturing [4] and quality control [5], the improvement of production base, the training of technical and medical personnel [6]. In XXI century the medical science and technology are among the main driving forces of modern technical civilization [7] gradually going hand in hand with cosmonautics and information technologies intensively developing during last thirty years. According to the

British government predictions the most demanded specialists until 2030 will be bioengineers developing new medical products [8] and medical workers using highly technological methods of treatment [9] which should inevitably decrease an evidently excessive role of pharmacology in modern health service.

The volume of medical products in world market increased the most intensively from 2006 to 2012. Volume of sales of medical products amounted to: in the USA—\$100 bn.; in Japan—\$ 29 bn.; in Germany—\$ 19.5 bn.; in Russia—\$ 6.4 bn. in 2010 [10]. In Russia only 18% of market demand for medical products is covered by domestic manufacture. The largest manufacturers of titanium implants are Germany, USA, China [11].

The main materials used for manufacture of implants are metal alloys (titanium [12], cobalt [13], stainless steel [14]), polymers [15] and ceramics [16]. In spite of intensive growth of application of ceramic materials and polymers in implanted products the metallic products retain their leading role (about 60% of all implants). Share of products from titanium alloys may be estimated approximately as 28%.

Metallic materials used for manufacture of implants should possess corrosion resistance [17], biological inertness [18], high complex of physical and mechanical properties [19] and relatively low cost. By the first two parameters the titanium alloys are far ahead of their competitors - stainless steels and cobalt alloys. In this case, it should be kept in mind that stainless steels are alloyed by a large quantity of nickel and chromium that form disordered solid solutions in basic metal and may easily go out from implant as toxic ions [20]. The same is referred to Co-Cr-Mo- system alloys. In titanium alloys vanadium is of some hazard. However, in main medical alloy of Ti_6Al_4V a content of toxic vanadium amounts to no more than 4% by mass [21], while in stainless steels and in Co-Cr-Mo alloy the mass concentration of toxic nickel and chromium (in total) exceeds 30% [22]. By absolute values of strength the Ti_6Al_4V alloy is as good as cobalt alloys and is superior to stainless steels. By specific strength a titanium alloy is superior to competitors by 2.0–2.5 times. Besides, it should be noted that elastic modulus in titanium alloys is 2—fold lower than that in steel and cobalt alloys [23]. For medical application (implants for osteosynthesis, endoprostheses of bone structures, joints, etc) it is a great advantage because it provides a higher mechanical compatibility of implant with dense bone structures of human organism whose plastic modulus amounts to 5.20 GPa.

Nowadays Ti_6Al_4V alloy surface is protected by different bioinert coatings [24]. Their application enables one to obtain a better adaptability of implants in human organism. A method of electric explosion spraying of coatings of different systems has recently been developed including bioinert ones [25]. Electron beam processing [26] makes it possible to improve a surface quality of electroexplosive coatings and to nanostructurize them.

Classification of traditional methods of spraying of coatings includes electric-arc spraying, flame spraying, plasma spraying. The methods develop intensively during last hundred years. They are widely used in aircraft, electric-power, oil, gas, chemical and paper-converting branches of industry for recovery of dimensions, protection against wear and corrosion of all types (including a high-temperature one) and other purposes. The equipment for their realization is constantly improving, and technology is studied well and described.

In recent years the new pulsed and pulse-periodic methods of spraying using supersonic, gas and plasma jets have appeared. Among these are detonation-gas spraying, pulse-plasma spraying, cold gas dynamic spraying and electric explosion spraying. The coatings obtained by these methods are distinguished by high density, good adhesion and cohesion strength, low porosity with pores disconnected between themselves, low content of oxides being formed in spraying of metal coatings, low losses of alloying elements with chemical composition, highly dispersed and homogeneous microstructure, low residual stresses, high microhardness, possibility to obtain coatings of larger thickness, smooth surface.

Discharge-pulsed technologies are widely used for material processing with shock waves application of thin films and coatings on them. The effect of plasma jets being obtained at electric explosion of conductors is used for surface alloying. Its main idea consists in melting the surface layers and saturation of them by products of explosion followed by self-hardening by heat removal deep into metal and into environment. But application of electric explosion spraying enables one to produce porous-free coatings of 50 MPa and more.

In comparison with thermal techniques the method of electric explosion spraying has a number of advantages:

1. A coating is applied in vacuum at any temperature values.
2. In application of coatings the product being covered is subjected to negligible heat effect (surface temperature is in pre-melting state) that excludes the initiation of internal stresses in products and their deformation as well as oxidation of coating materials and component.
3. Technology of application of coatings is ecologically safe (dangerous gases and radiations are absent, there are no chemically aggressive wastes requiring a special neutralization).
4. Under the action of high-speed flow a cleaning of surface from technical contaminations, oil, paints and activation of crystal lattice of product's material takes place.

Table 1. Chemical content of tantalum foil. Content of impurities and gases, mass %.

Nb	Fe	Ti	Si	W	W and Mo in total	C	O	H	N	Na	Mg	Al	Ca	Cr	Mn	Co	Ni	Cu	Zn	Sn	Ta
0.478	0.01	0.03	0.01	0.01	0.025	0.02	0.02	0.001	0.01	0.001	0.003	0.003	0.003	0.003	0.003	0.003	0.001	0.005	0.001	0.001	99.35

Table 2. Modes of processing of electric explosive tantalum coatings by low-energy high-current electron beam (LHEB) and subsequent nitriding.

Mode of complex processing	Parameters of low energy high-current electron beam			Parameters of nitriding
	Surface density of energy (E_s), J cm ⁻²	Pulse duration (t), μ s	Number of pulses (N)	
1	20	150	3	Time (τ), 5 h; temperature (T), 520 °C
2	30			
3	40			
4	20			
5	30			Time (τ) 3 h, temperature (T), 600 °C
6	40			

5. Flow of particles being sprayed is narrow-directed and it has a small cross-section. In contrast to traditional gas-thermal methods of spraying it enables one to apply the coatings on local (with sharp boundaries) portions of products' surface.
6. It is possible to apply multi-component coatings with alternating content of components in its thickness.
7. It is possible to apply different types of coatings by means of one setup.
8. It is possible to use equipment not only in stationary but in field conditions.

The only disadvantage of electric explosion spraying is a possibility of application of coatings only on the surface of metal and ceramic materials.

The purpose of the research was to form a Ti-Ta-N- system bioinert coating on Ti₆Al₄V alloy surface as well as to study its structure and properties. The following tasks were set and solved to achieve the purpose in view.

1. To work out the technique of formation of Ti-Ta-N-system bioinert coatings. The procedure includes electric explosion spraying of tantalum coatings, their subsequent nitriding and irradiation with high-intensity pulsed electron beam in definite modes.
2. To find regularities of variation in structural and morphological properties, phase and elemental composition of Ti-Ta-N-system coating depending on mode parameters.
3. To investigate the effect of coating formed on nanohardness, Young modulus, wear-resistance, friction coefficient, proliferation of fibroblasts and antimicrobial activity *in vitro*.

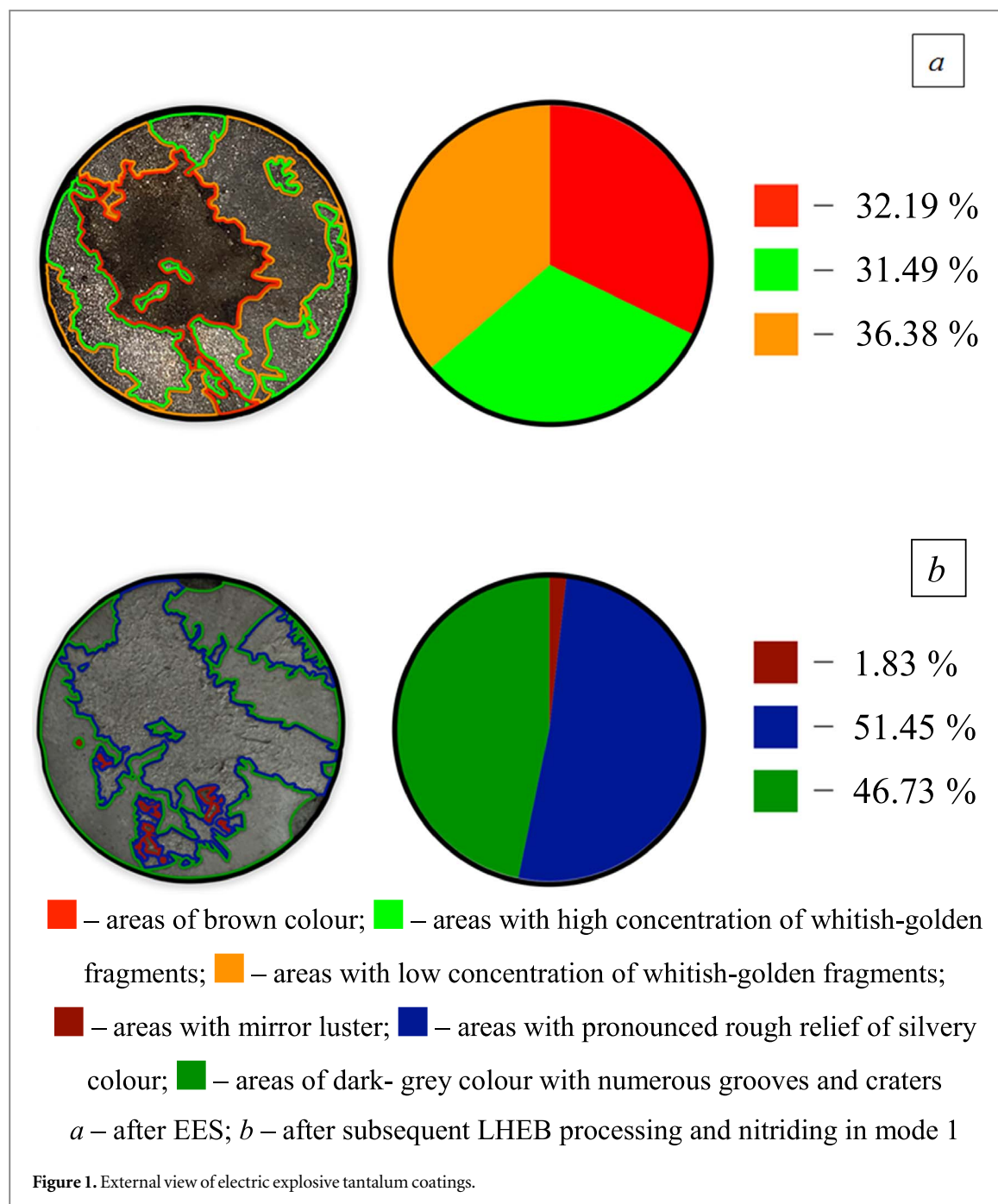
2. Materials and methods

The formation of Ti-Ta-N- system coatings was carried out in two stages. At the first stage the electric explosion spraying (EES) of tantalum coating was performed. At the second stage the electron-ion-plasma modification was carried out. Prior to EES the samples were cleaned by ultrasound in ethanol and dried in the air. For preparation of samples with titanium coatings to electron-ion-plasma modification the same technique of surface cleaning was used.

EES of coatings was performed on updated electric explosion setup EVU60/10 M [27]. The coatings were applied to a base surface (round surface) of cylindrical titanium samples (Ti₆-Al₄V) of 3.14 cm² in area (diameter of cylindrical sample was 2 cm, height-0.5 cm). EES was done using tantalum foil of 400 mg in mass. Chemical composition of tantalum foil is shown in table 1. The absorber power density at EES amounted to 1.5 GW m⁻², titanium nozzle diameter – 20 mm, distance of sample from nozzle cut – 20 mm.

Electron beam modification of electric explosive coatings followed by nitriding was carried out on setup KOMPLEX. The modes of low-power high-current electron beam (LHEB) and subsequent nitriding are listed in table 2.

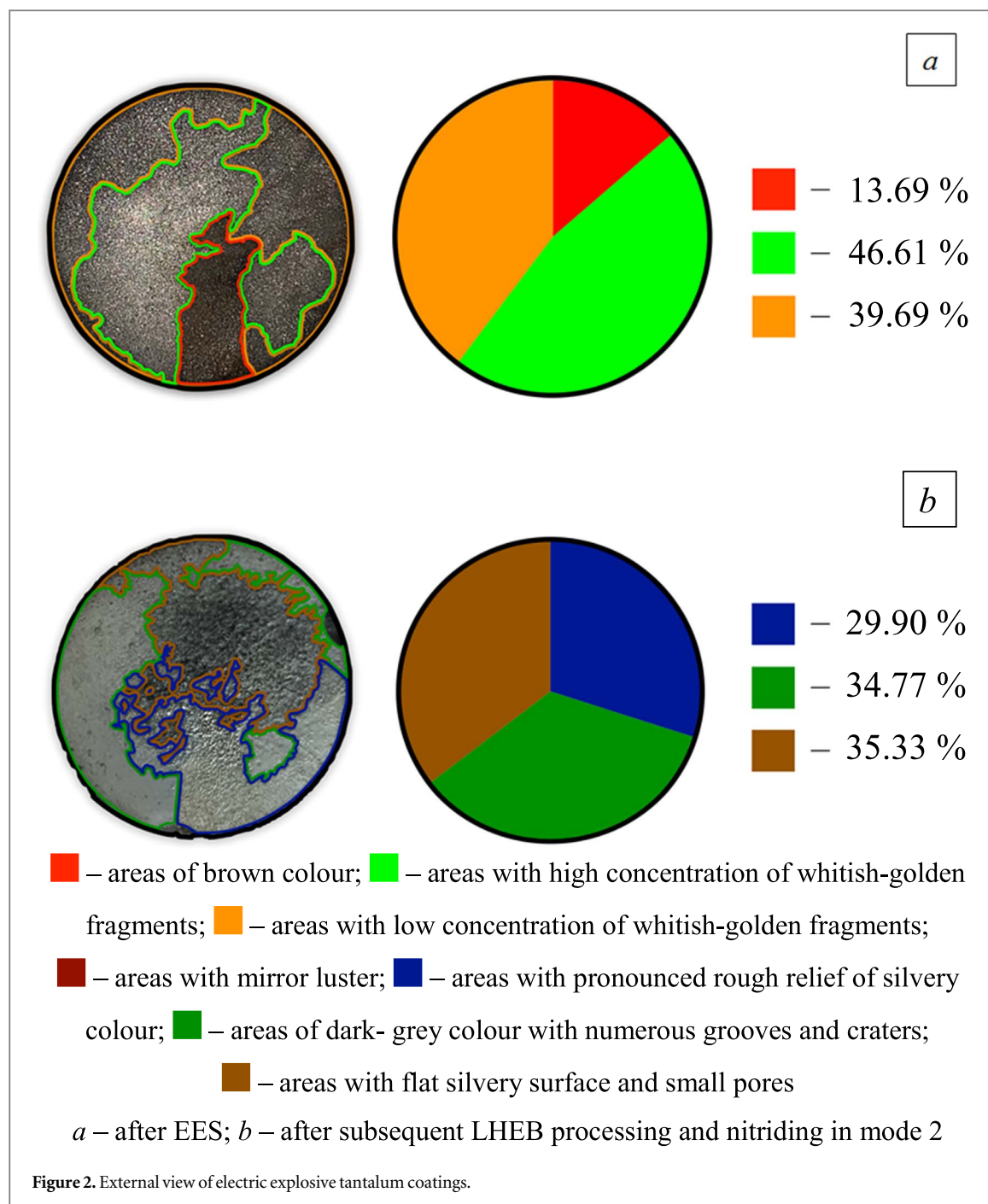
Preparation of straight microsections before metallographic examination included a cutting of samples at a right angle to coating surface. For it a diamond disc was used. The surface of metallographic sections was treated by abrasive papers for intermediate grinding and polishing. The last abrasive paper for grinding was Micro-Mesh 8000 Grit paper. Then samples's surface was polished by cerium oxide to 0.1 μ m. Finishing treatment of microsections consisted in polishing with diamond suspension to values of 0.05 μ m. Etching of microsections



was performed by solution based on hydrofluoric and nitric acids and distilled water taken in equal relation in volume fractions. Etching time was 15 min.

The obtained coatings were examined by the methods of scanning electron microscopy (electron microscope Carl Zeiss EVO50 XVP with attachment for X-ray spectral energy dispersion analysis EDS X-Act), transmission electron microscopy (TEM) (electron microscope FEI Tecnai 20 G2 TWIN) and X-ray structural analysis (X-ray diffractometer ARLX TRA). Foils for TEM were prepared using electric chemical system Solartron Analytical 12558WB. Tribological parameters (friction factor and wear resistance) of coatings were examined using geometry Pin-On-Disk on tribometer CSEM (Switzerland) at temperature 23 °C and relative humidity of 50% r.H in atmosphere of air. A ball made of silicon monocarbide with the Young modulus of 380 GPa was used as a counterbody. Track diameter amounted to 2 mm, rotational velocity—25 mm s⁻¹, load—12 N, distance to the stop—100 m. Volume of surface layer wear was determined after profilometry of the track formed using a laser profilometer MicroMeasure 3D Station (Stil, France). Nanohardness and Young modulus were measured using a system Agilent U9820A Nano Indenter G200.

Proliferation activity of cells lines was determined by the method of direct calculation of cells quantity after their contact with the samples with applied coatings using optical microscope. Investigations were carried out on cell culture of fibroblasts of hypodermic connective tissue of mouse (L929).

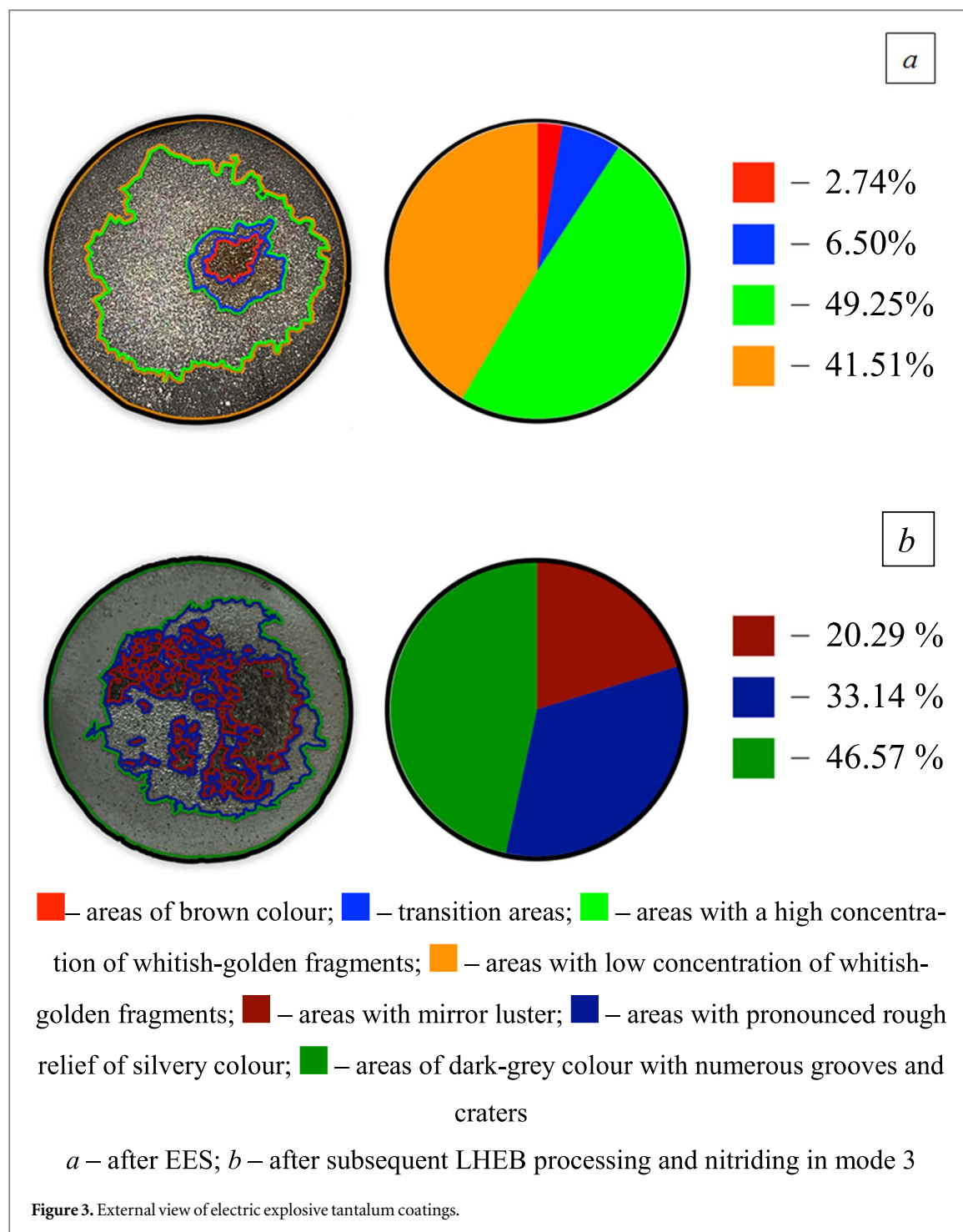


Antimicrobial activity of samples was tested by the method of viable bacteria calculation. In this method *in vitro* a dynamics of bacteria elimination in sample was measured by calculation of residual bacteria in comparison with titanium substrate without the coating. Cell culture of *Staphylococcus aureus* microorganisms was used.

3. Results and Discussion.

3.1. Quality control of coatings' surface

Quality control of titanium samples' surface subjected to electric explosion spraying of tantalum coating (figures 1(a)–6(a)) showed that a coating having inhomogeneous colour formed on their surface. The appearance of surface after EES in colour may conditionally be divided into four main areas: regions of bark-brown nonmetallic colour being supposedly a deposition remained after electric explosion. They surround transition zones, central parts with whitish metallic tint and edge parts of dark-metallic colour. Aside from the enumerated parts of surface the transition zones may be present in some samples. Over the entire surface of the

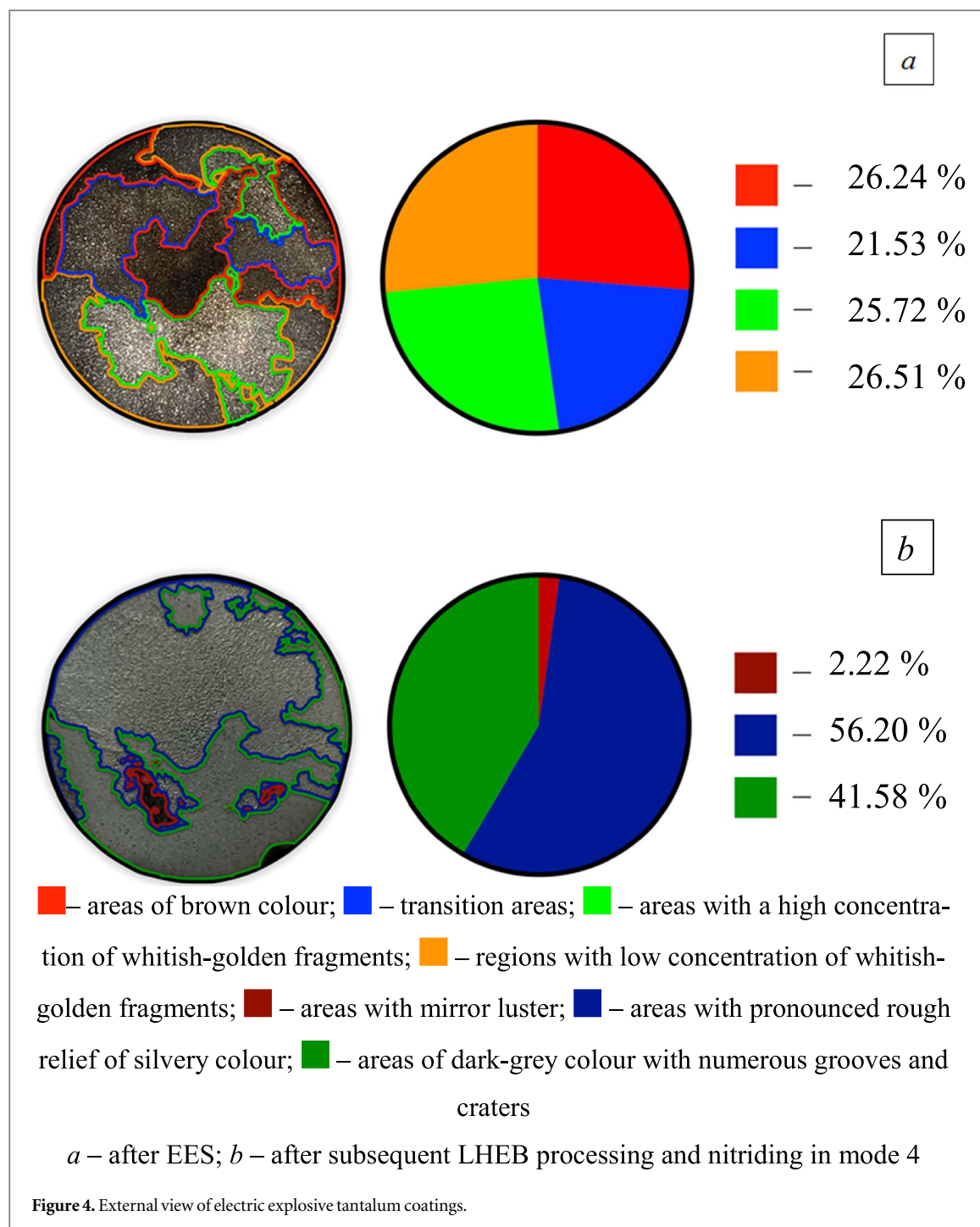


processed samples the inclusions of small sizes of golden tint are observed. Their concentration decreases from center to edges. Maximum size of individual fragment is less than 1% of sample surface area.

After LHEB processing and nitriding (figures 1(b)–6(b)) the coating surface colour changes into silvery in all modes, and relief transforms: new regions with different profiles of roughness appear.

The large dark-brown spot of inhomogeneous colour with jagged boundaries occupying 32.19% is designated by red lines in the figure (figure 1(a)). Regions with a large concentration of whitish-golden fragments designated by green lines are located irregularly along sample surface. Their total area is equal to 31.43%. Among zones presented in the sample under study the largest one is the region with a small concentration of whitish-golden fragments wherein grey tints dominate, its area is 36.38%.

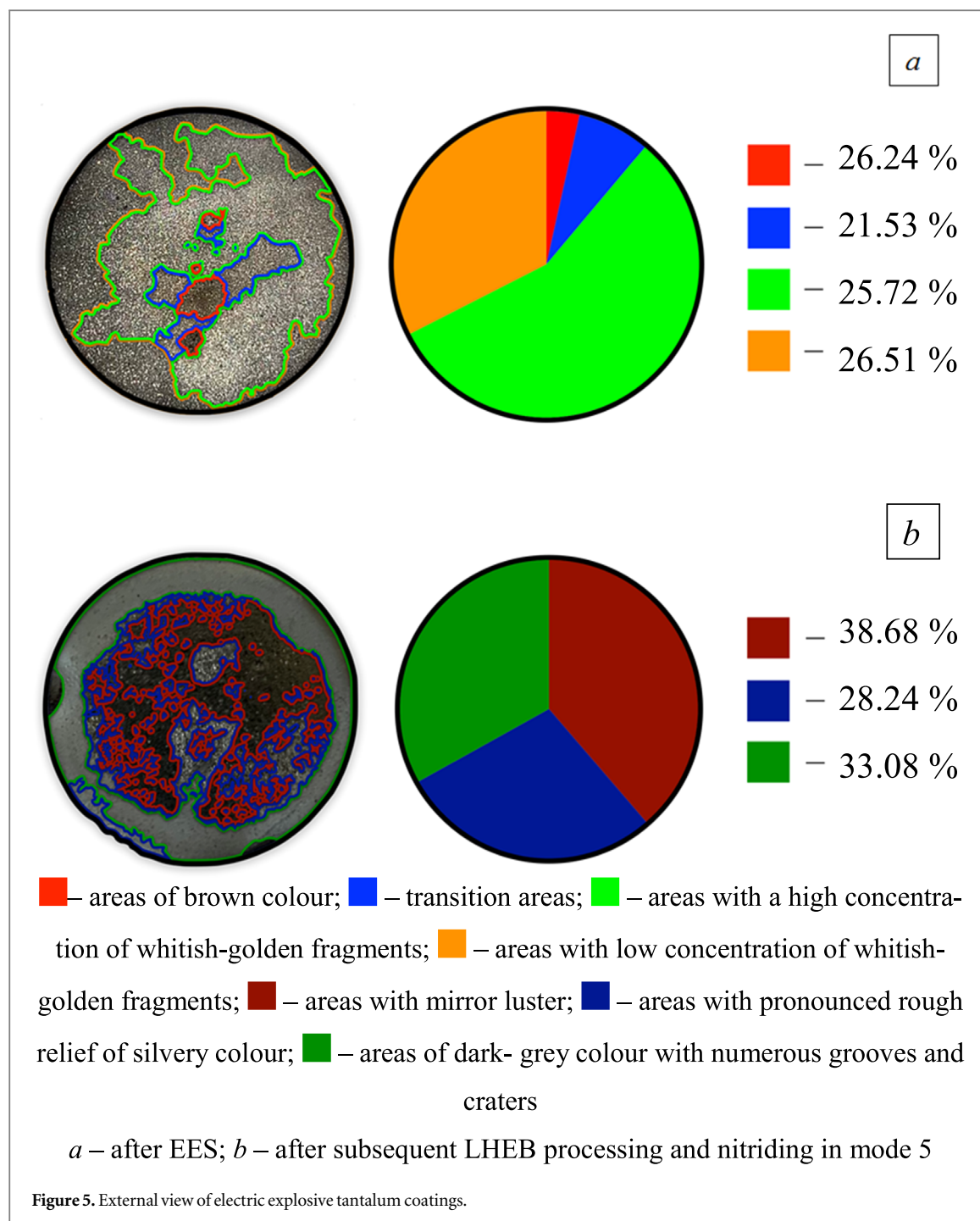
After LHEB processing at energy density of 20 J cm^{-2} and nitriding during 5 h at 520°C (mode 1) the sample surface transforms (figure 1(b)). The regions with a mirror surface designated in the figure by dark-red boundaries and occupying 1.83% of total area of the coating become the smallest ones. The remaining surface of



the sample consists of two large zones of silvery tint the largest of which designated by dark-blue boundaries in the figure has a pronounced relief and is the largest with total area being equal to 51.45%. The second of the regions under study designated by dark-green boundaries in the figure possesses a plane surface on which many small black points being pores are located. Its area is 46.73% of sample surface.

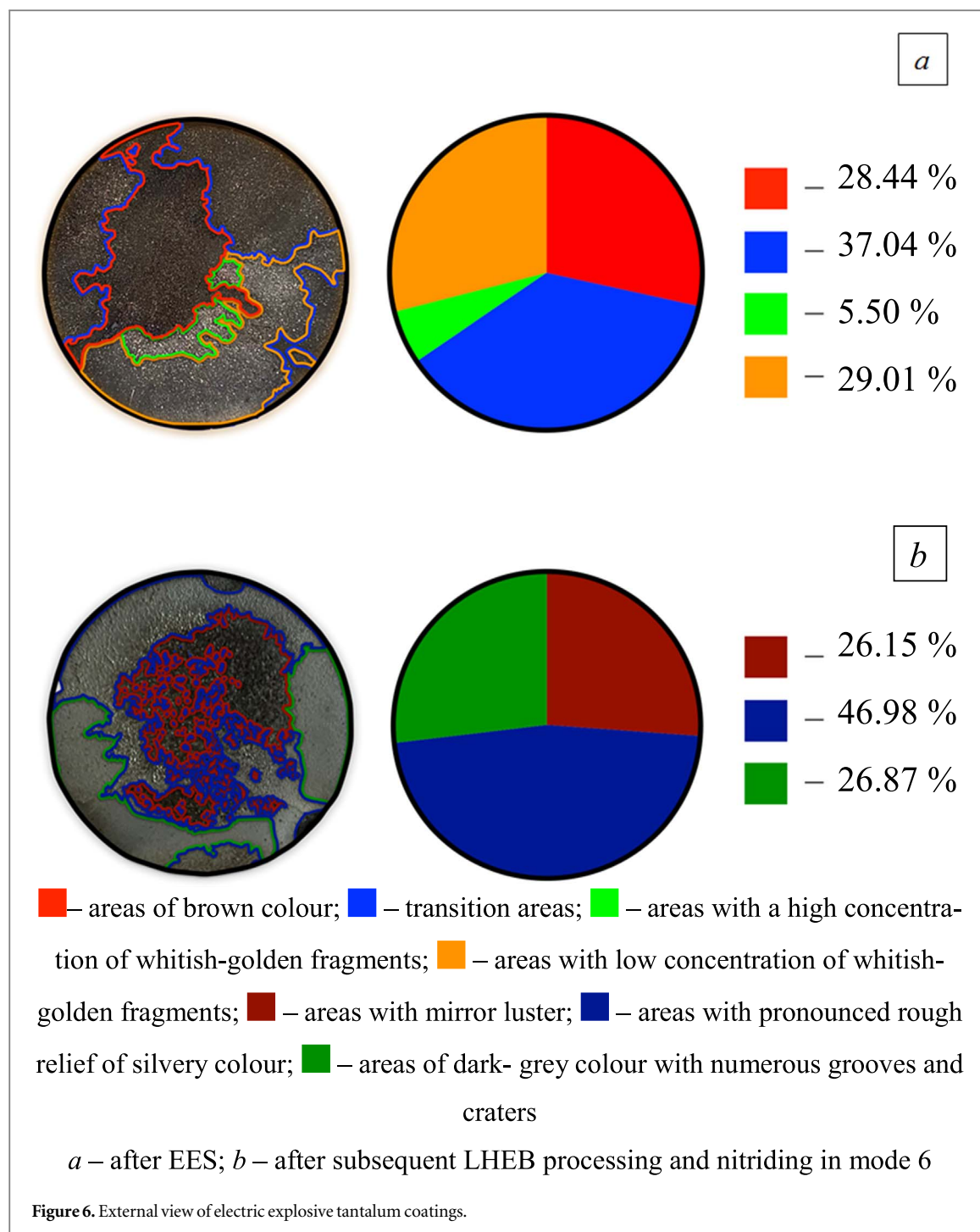
The smallest zone designated by red lines is presented by a spot of dark-brown tint extending from center to edge of the sample, its area is equal to 13.69% of sample surface (figure 2(a)). From two sides to the region under consideration two areas of whitish-golden tint separated by green boundaries adjoin. Their total area is the largest and equals to 46.61%. The main factor determining the colour of the zones under study is a presence of a large number of whitish-golden fragments. The external part of sample surface wherein dark-grey metallic tints predominate is designated by orange boundaries. Concentration of whitish-golden inclusions in it is far less. Its area is 39.69% of surface area of the coating.

After LHEB processing at energy density of 30 J cm^{-2} and nitriding during 5 h at 520°C (mode 2) the largest part of coating surface being equal to 35.33% is occupied by the area extending from sample center to its edge, it is designated by brown boundaries in the figure (figure 2(b)). Its surface covered by numerous deep grooves has a



dark-grey tint. From one of the sides a zone of light-silvery tint with pronounced relief is adjacent to it, the size of elements in the relief decreases from large asperities to small roughness near boundary. In figure 2, b the zone under examination occupies the smallest area of 29.9% and is designated by dark-blue boundaries. The flat silvery surface with sparse pores limited by dark-green lines in figure 2, b occupies the remaining part of sample being equal to 39.38%.

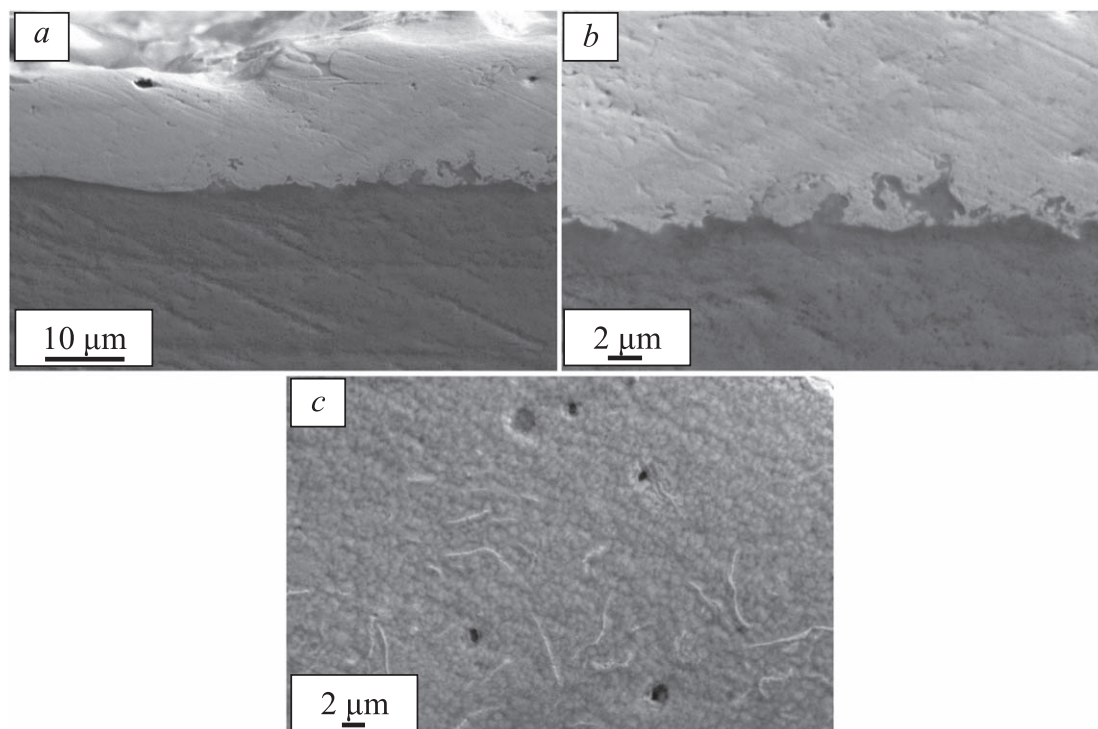
The area designated by red colour is presented by a spot of dark-brown colour lying in central part of the sample and occupying 2.74% of its surface area (figure 3(a)). The region under examination is displaced relative to geometrical center of the sample. It is surrounded by the area designated by light-green boundaries and having whitish-golden tint. The colour is due to large concentration of small whitish-golden fragments. The area of the region is 49.25%. The zone of dark-brown colour is separated from the area with a large concentration of whitish-golden inclusions by a transition region designated by blue boundaries. The region has a light-brown tint. The region under examination occupies 6.5% of sample surface. In addition, the transition area and the zone of dark-brown colour also consist of the similar small fragments but of light and dark- brown tints. In the peripheral part of the sample the area with a far smaller concentration of whitish-golden fragments having



dark-grey metallic tint similar to the colour of substrate material colour is located. The area is limited by lines of orange colour. It occupies 41.51% of surface.

After LHEB processing at energy density of 40 J cm^{-2} and nitriding during 5 h at 520°C (mode 3) a zone consisting of a large number of regions with a rough mirror surface is formed in central part of the sample, their total area is the smallest and is equal to 20.29% of sample surface (figure 3(b)) In figure 3, b these are designated by dark-red boundaries. Around and inside of them there are numerous asperities of silvery tint forming a relief of the zone designated in figure by dark-blue lines, the zone area is 33.14%. The area limited by dark-green lines having a silvery surface on which small pores are scattered randomly occupies the remaining part of the coating.

The smallest in the sample under study is the transition area consisting of two regions occupying 21.53% of coating surface and having light-brown colour with whitish-golden inclusions designated by dark-blue boundaries in figure 4(a). The largest area consists of 3 large and 2 small regions designated by orange boundaries inside of which the concentration of whitish-golden fragments is small and different tints of grey colour are prevailing. Their total area is 26.51%. Three spots having inhomogeneous dark- brown tint are shown in



a – cross-section of coating and substrate; *b* – boundary of coating with substrate; *c* – characteristic structural components

Figure 7. Structure of cross-section of surface layer of bioinert tantalum coating modified by nitrogen ions and electron beam.

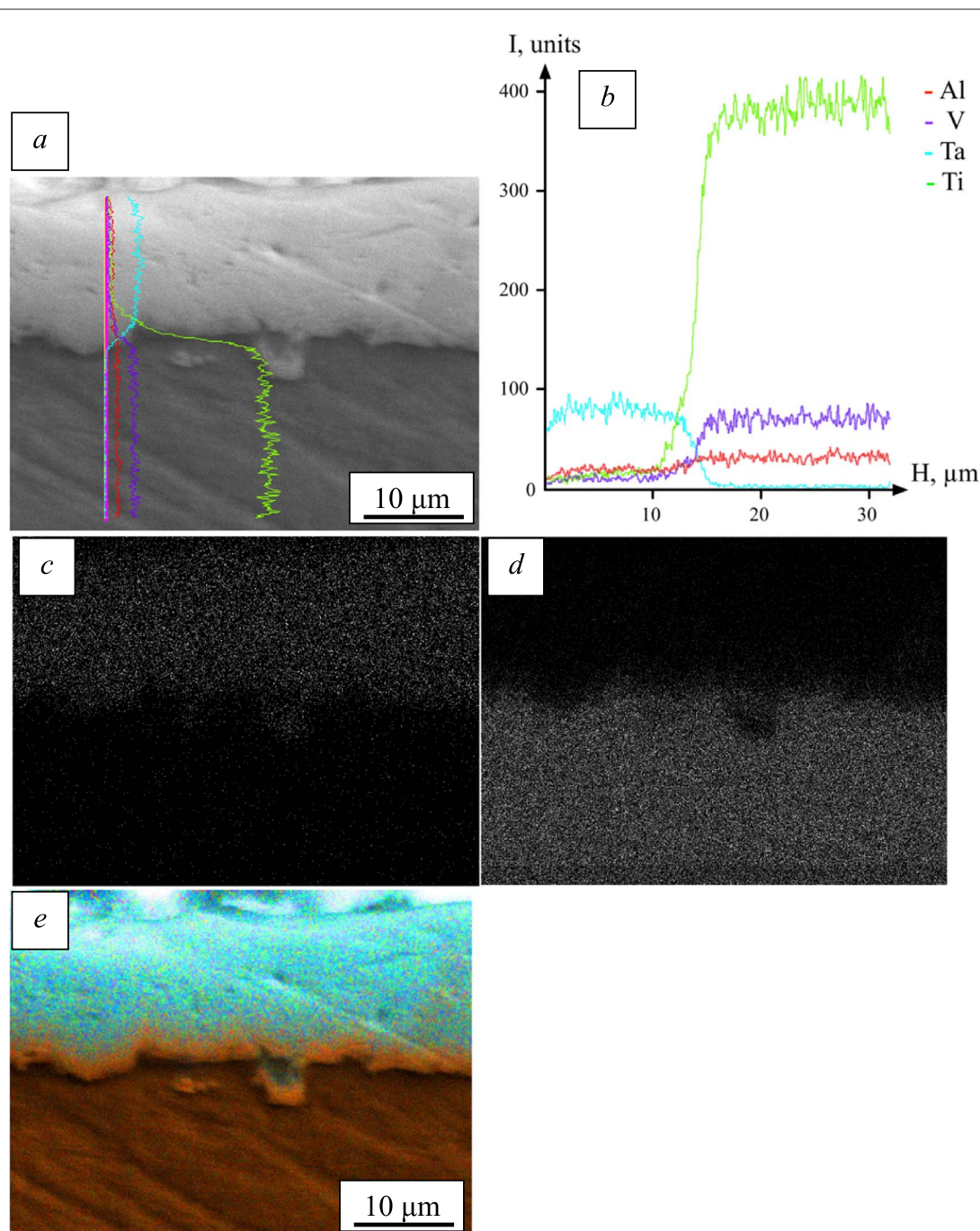
Table 3. Data of X-ray phase analysis of sample without bioinert coatings.

Sample	Detected phases	Phase content, mass %	CSR, nm	Parameter of lattice, Å	
				a	c
Check sample (before deposition of coatings)	Ti (P6 MMM)	67.18	28.51	4.6081	2.8382
	Ti _{0.85} Al _{0.15}	32.82	not detected	2.9697	4.7046

figure 4(a) by red boundaries. Their total area is 26.24% of processed sample surface. The regions of whitish-golden tint with a large concentration of fragments of the colour occupy the remaining part of the sample being equal to 25.72% of the coating.

After LHEB processing at energy density of 20 J cm^{-2} and nitriding during 3 h at 600°C (mode 4) the small regions appear with a flat mirror surface designated by dark-red boundaries in figure 4(b). Their total area is 2.2% and is the smallest among the presented areas. The largest area designated by dark-blue boundaries in figure 4(b) occupies 56.2%. Its surface of silvery tint is spotted with many small asperities concentrated to a greater extent in a central part of the sample and near the regions with mirror surface. The region also possessing a silvery tint and designated in figure by dark-green boundaries occupies the remaining part of sample being equal to 46.57%, small pores are randomly scattered over its area.

Four small spots of dark - brown colour and total area of 3.48% form the smallest zone designated by red boundary in figure 5(a). A transition area of a lighter tint limited by dark-blue lines (figure 5(a)) is adjacent to this zone. Its area is 7.64%. Small fragments of different brown tints being present in large concentrations determine the relief of the regions under examination. Area designated in figure 5 a by green boundaries and having a whitish-golden tint due to a large concentration of small whitish-golden fragments occupies the largest area of 56.37% of sample surface. A region limited by orange lines and occupying 32.51% of sample surface is in a peripheral region of the sample. A concentration of small whitish-golden fragments in the region under examination is far less, because of this its surface obtains a dark-grey metallic tint.



a – position of line for analysis (straight line of pink colour), *b* – dependence of elemental composition on depth of coating, *c* – image of figure (a) in characteristic radiation Ta(La1), *d* – image of figure (a) in characteristic radiation Ti (Ka1), *e* – superimposed image of coating structure with characteristic radiation of titanium (orange colour) and tantalum (blue colour)

Figure 8. Examination results of bioinert tantalum coating modified by nitrogen ions and electron beam obtained by method of micro-X-ray spectral analysis.

After LHEB processing at energy density of 30 J cm^{-2} and nitriding during 3 h at 600°C (mode 5) the numerous regions with a rough mirror surface whose total area is 38.68% (figure 5(b)) occupy the largest part of sample. These are designated by dark-red boundaries in figure 5(b). Numerous silver asperities inside and along circumference of mirror regions form a silvery zone with a pronounced relief whose area is the smallest and is equal to 28.24%. A peripheral part of the sample with area of 33.08% is occupied by the region designated by dark-green boundaries in figure 5(b). The surface of peripheral part contains numerous small pores and has a silvery tint.

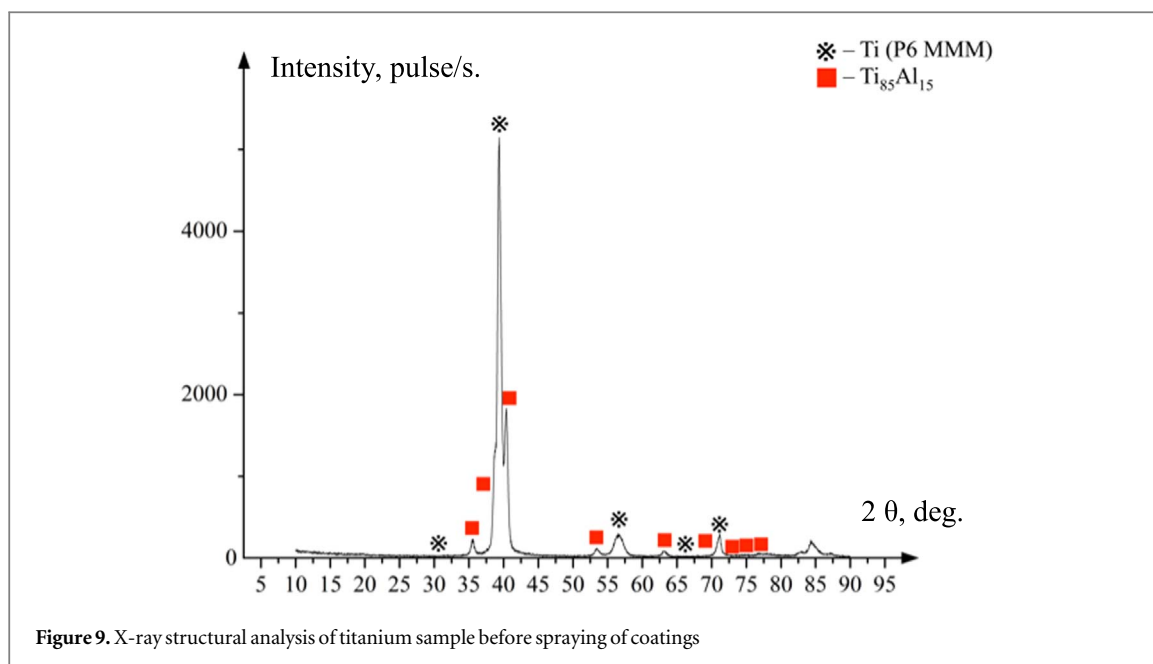
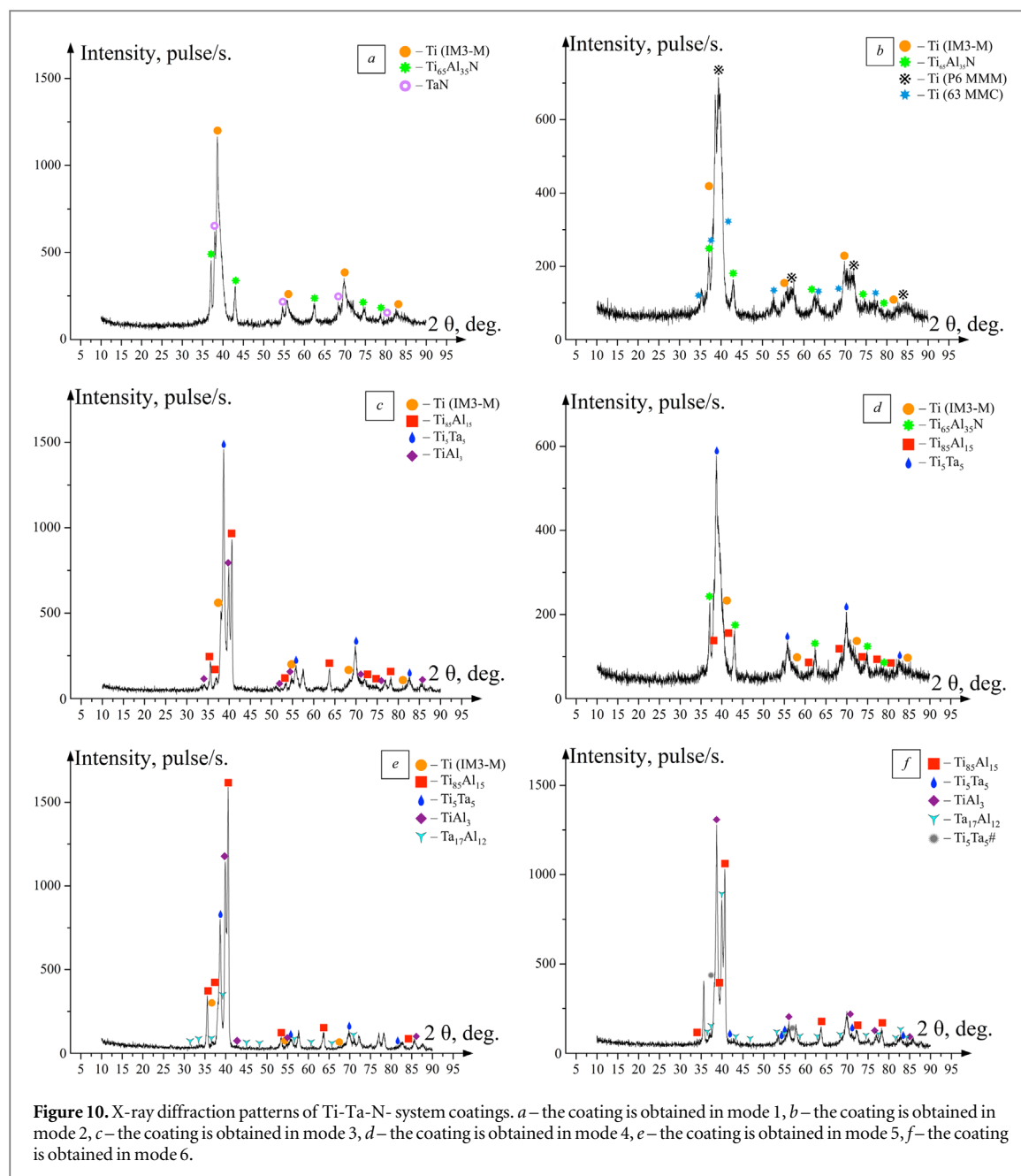


Table 4. Data of X-ray phase analysis of samples with Ti-Ta-N- system coatings.

Sample	Detected phases	Content of phases, mass %	CSR, nm	Lattice parameter, Å	
				a	c
1	Ti (IM3-M)	76.43	10.09	3.3082	
	Ti ₆₅ Al ₃₅ N	18.46		4.2450	
	TaN	5.11	41.46	3.3843	
2	Ti (IM3-M)	9.11	47.5	3.3002	
	Ti ₆₅ Al ₃₅ N	8.44		4.2098	
	Ti (P6 MMM)	52.1	48.84	4.5615	2.8442
3	Ti (63 MMC)	30.35	10.32	2.9526	4.7610
	Ti (IM3-M)	44.78	11.73	3.3161	
	Ti ₈₅ Al ₁₅	17.72	20.5	2.9348	4.6541
4	Ti ₅ Ta ₅	7.76		3.3038	
	TiAl ₃	29.74	28.76	3.7727	8.6156
	Ti ₆₅ Al ₃₅ N	26.95		4.2279	
5	Ti ₈₅ Al ₁₅	28.32	11.29	2.9799	4.7379
	Ti (IM3-M)	28.32	20.72	3.2389	
	Ti ₅ Ta ₅	16.41	14.59	3.3053	
6	Ti ₈₅ Al ₁₅	19.17	42.23	2.9343	4.7132
	Ti (IM3-M)	30.67	62.97	3.638	
	Ti ₅ Ta ₅	25.69		3.3142	
7	TiAl ₃	2.92	16.72	3.7977	8.4983
	Ta ₁₇ Al ₁₂	21.55		9.8984	
	Ta ₁₇ Al ₁₂	19.07	17.39	9.98	
8	Ti ₅ Ta ₅	12.51		3.2683	
	Ti ₈₅ Al ₁₅	10.65	16.72	2.9049	4.5660
	Ti ₅ Ta ₅	9.38	8.57	3.2544	
9	TiAl ₃	48.39		3.7460	8.4940

A large dark-brown spot of inhomogeneous colour wherein whitish-golden inclusions are noticeable and occupying 28.44% is designated by red lines in figure 6(a). A transition area of grey-brown tints, wherein the regions with inclusions of whitish-golden fragments designated by dark- blue boundaries are observed, is adjacent to it from two sides. Its area is 26.68%. The area designated in figure by green lines due to a large concentration of whitish-golden fragments is the smallest one, the prevailing colour of the area under study becomes the fragments' colour. Its area is 5.5% of sample surface. The largest zone designated in figure by orange



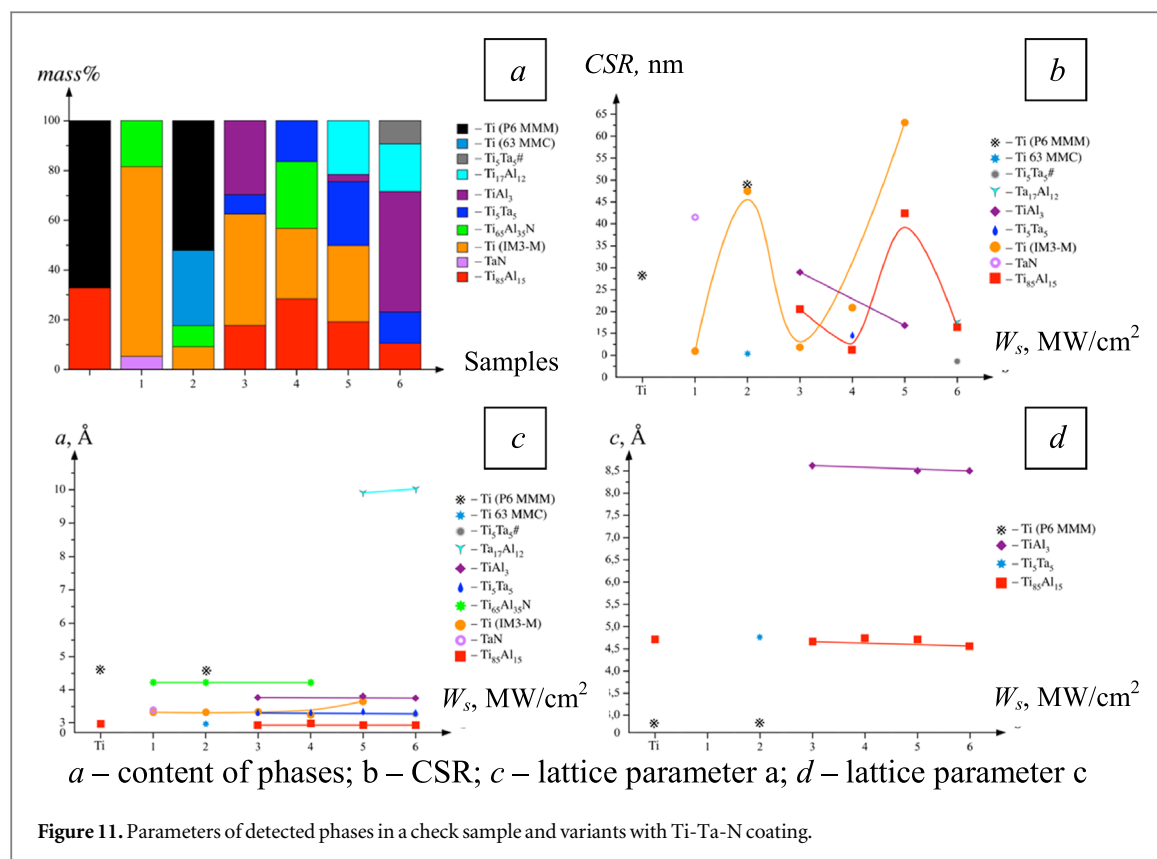
boundaries occupies the remaining area being equal to 29.01%. The tints of grey colour similar to that of a substrate are predominant in it due to a small concentration of whitish-golden inclusions.

After LHEB processing at energy density of 40 J cm^{-2} and nitriding during 3 h at 600°C (mode 6) numerous large and small regions with a rough mirror surface designated in figure by dark-red boundaries form a zone with the smallest area being equal to 26.15% of sample (figure 6(b)). A zone of silvery tint with a pronounced relief, presented by numerous asperities and designated in figure by dark-blue lines, occupies the largest part of the sample. Its area is 46.98%. The remaining part of sample 26.87% is occupied by a region with a flat surface of a silvery tint on which small pores are randomly scattered. In figure 6(b) it is designated by dark-green boundaries.

The analyses carried out allowed us to establish the variety of structural components of surface relief. It creates conditions for better osteointegration of titanium implants with Ti-Ta-N-system coatings into human organism.

3.2. Study of the coatings by the method of scanning electron microscopy

Studies by the method of scanning electron microscopy showed that in electric explosion spraying of titanium implants by electric explosion of tantalum foil at absorbed power density of 1.5 GW/m^2 a formation of tantalum



coating occurs. The indicated mode at which the absorbed power density is 1.5 GW/m^2 is established empirically and is optimal because at the intensity lower than 1.5 GW/m^2 no relief formation occurs between the coating and titanium substrate in consequence of which a flaking of the coating is possible, and when the intensity of effect is higher than 1.5 GW/m^2 a formation of developed surface relief of coating being sprayed takes place. At mass value of Ta foil less than 400 mg the coating distributes unevenly on Ti implant surface. At mass value of Ta foil of more than 400 mg the coating based on tantalum on surfaces of titanium implants has a large quantity of defects. A boundary of electric explosion coating with a substrate is not even that enables one to increase adhesion of the coating with a substrate.

Figure 7(a) shows a cross-sectional structure of surface layer of bioinert tantalum coating modified by nitrogen ions. Figure 7(b) shows a cross-sectional structure of surface layer of bioinert tantalum coating modified by nitrogen ions and titanium substrate. Figure 7(c) shows the structure of bioinert tantalum coating modified by nitrogen ions. Thickness of the coating amounts to 15–20 μm (figure 7(a), figure 8(a)).

At nitriding time of less than 3 h at temperature below 500°C the surface layer of electric explosion tantalum coatings saturates weakly by nitrogen ions that fails to provide antibacterial effect to the coatings being formed. At nitriding time of less than 5 h and temperature above 600°C the solid solutions based on nitrogen and tantalum nitrides form in surface layer of electric explosive tantalum coatings that increases hardness and wear resistance of the coatings but makes them unfit for operation in human organism. In this case a bone tissue wears.

A pulse-periodical electron-beam processing of surface layer results in the formation of a more disperse and homogeneous structure in it. The indicated mode is optimal because at surface energy density of less than 20 J cm^{-2} , pulse duration of shorter than 150 μs , pulse number of less than 3 pulses the formation of homogeneous structure in coating fails to occur. At surface energy density of more than 40 J cm^{-2} , pulse duration of longer than 150 μs , pulse number of more than 3 pulses the formation of surface relief occurs.

The examination results of bioinert tantalum coating modified by nitrogen ions and electron beam obtained by the method of micro-X-ray spectral analysis (figure 8) enable one to state that the coating is formed by titanium and tantalum. Nitrogen is not detected by the method.

3.3. Study of the coatings by the method of X-ray phase analysis

By means of X-ray phase analysis (XRA) two phases were detected in the initial titanium sample (figure 9, table 3) without creation of bioinert coatings on its surface. The first phase is Ti (P₆MMM) a mass fraction of which is

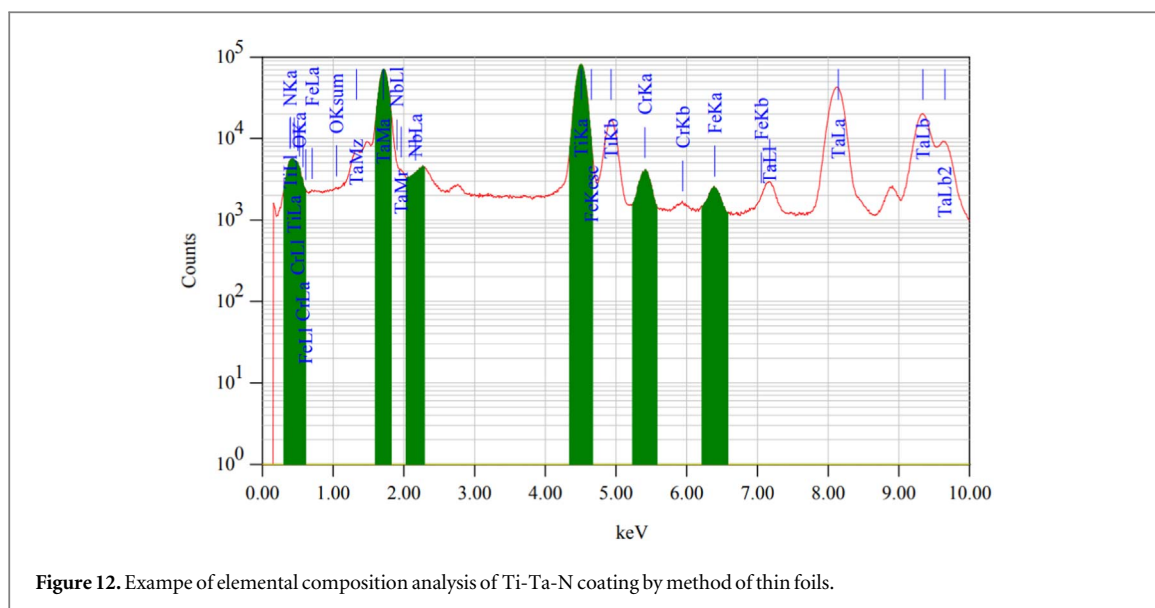


Figure 12. Exampe of elemental composition analysis of Ti-Ta-N coating by method of thin foils.

Table 5. Results of layer-by-layer analysis of sample elemental composition.

Element, wt. %	Distance from sample surface, μm			
	3	10	25 (interface)	45 (substrate)
N	4.69	0.5	2.31	6.06
O	1.18	0.76	0.23	0.0
Ti	42.69	47.66	59.72	89.61
Cr	1.36	1.83	1.79	1.91
Fe	0.76	1.03	1.0	1.25
Ta	49.32	48.22	34.96	1.17

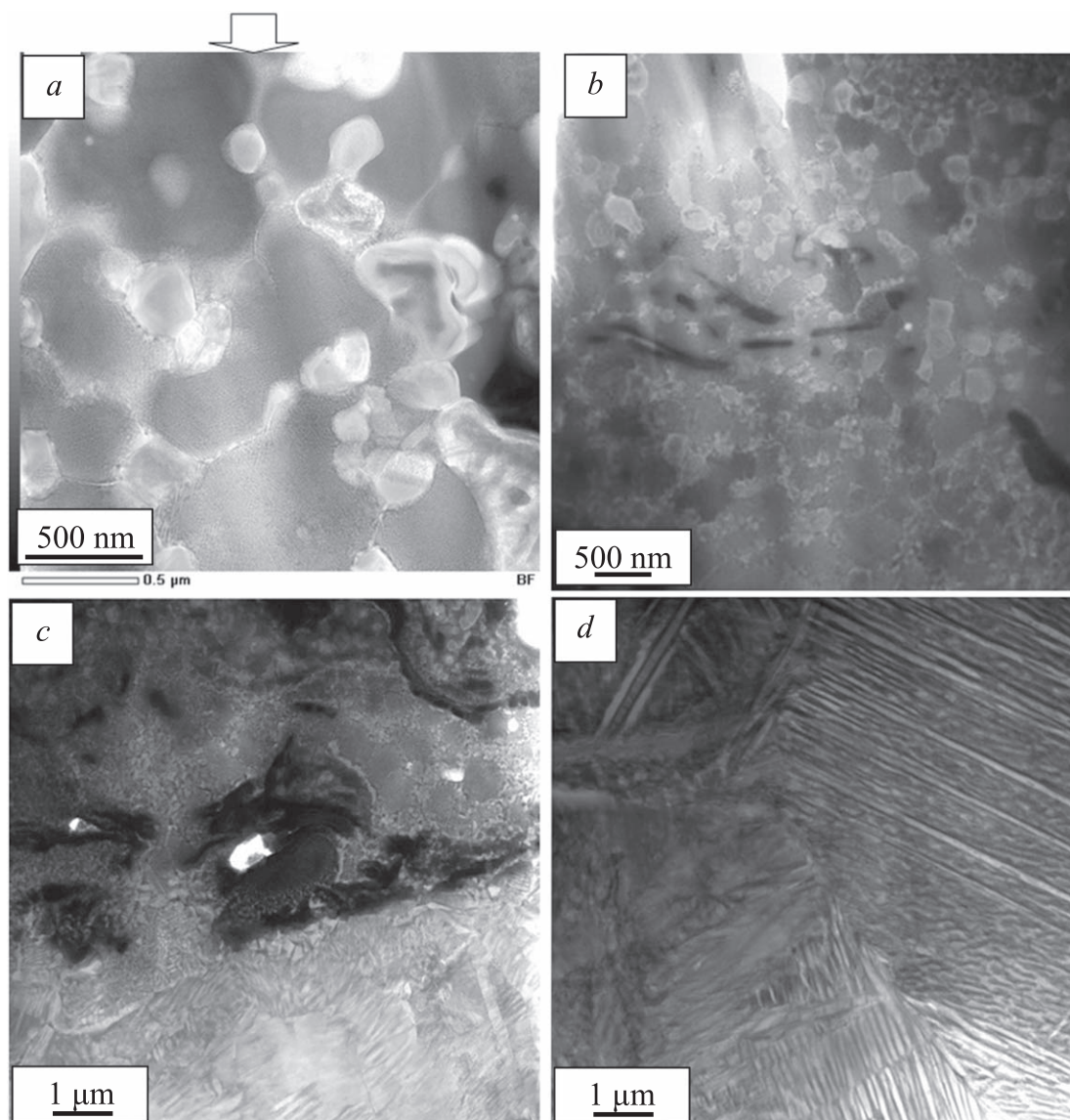
67.18%. The parameters a and c of crystal lattice of the phase under study are equal to 4.6081 Å and 2.8382 Å, respectively, and coherent scattering region (CSR)—28.51 nm (table 3). The second phase is $\text{Ti}_{85}\text{Al}_{15}$, with mass content of 32.82%, the parameter a of crystal lattice is 2.9697 Å, the parameter c —4.7046 Å (table 3).

The data of XRA of the coatings under study are summarized in table 4, and X-ray diffraction patterns are presented in Figure 10.

Three phases were detected in the coating obtained in the processing model № 1. Phase Ti (IM3-M) (figure 11(a)) has the largest mass fraction of 76.43%. The value is maximum for the phase under study among all samples in which it is presented. CSR value of the phase is 10.09 nm (figure 11(b)) that is the smallest among all samples wherein phase Ti (IM3-M) is present. The parameter a of its crystal lattice is 3.3082 Å (figure 11(c)). The phase $\text{Ti}_{65}\text{Al}_{35}\text{N}$ with the value of 18.46% (figure 11(a)) is at the second place in content. The parameter a of crystal lattice has a minimum value of 4.245 Å (figure 11(c), table 4) among all samples where in it is presented. The phase TaN is presented in minimum quantity with mass fraction of 5.11% (figure 11(a)). Its CSR is 41.46 nm (figure 11(b)) and the parameter a crystal lattice is 3.3843 Å (figure 11(c)). In other samples the phase is not found.

In the coating obtained in the mode of processing № 2 four phases were revealed by means of XRA among which the phase Ti (P_6MMM) possesses the largest mass fraction being equal to 52.1% (figure 11(a), table 4). Its CSR value is 48.84 nm (figure 11(b)). The parameters a and c of crystal lattice are 4.5615 Å (figure 11(c)) and 2.8442 Å (figure 11(d)), respectively. The phase is observed only here and in the sample without a coating. The Ti (IM3-M) phase content decreases to its minimum of 9.11%. In this case CSR increases to 47.7 nm and the crystal lattice parameter a decreases to 3.3002 Å. The $\text{Ti}_{65}\text{Al}_{35}\text{N}$ phase has the smallest mass fraction of 8.44% in the sample under study. In comparison with the previous sample its crystal lattice parameter a increases to the maximum value of 4.2098 Å. The phase Ti (63MMC) is observed only in this sample. Its content is 30.35% CSR is 10.32 nm, and crystal lattice parameters a and c —2.9526 Å and 4.761 Å, respectively.

In the coating obtained in the mode of processing № 3 (figure 11, table 4) four phases were detected among which TiAl_3 with mass fraction of 29.74% appeared for the first time. The CSR of the phase is 28.74 nm. The

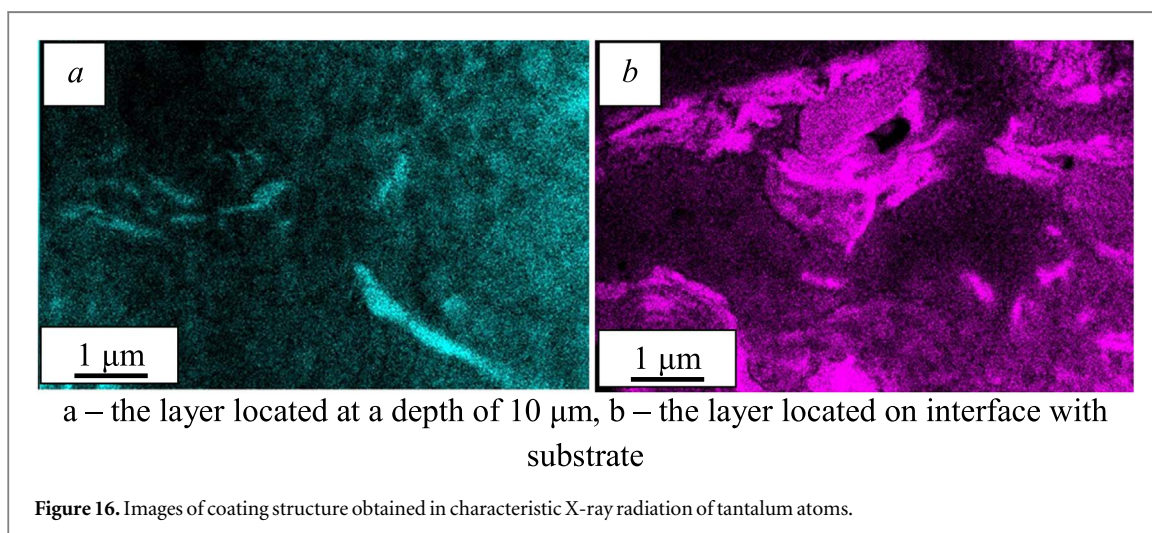
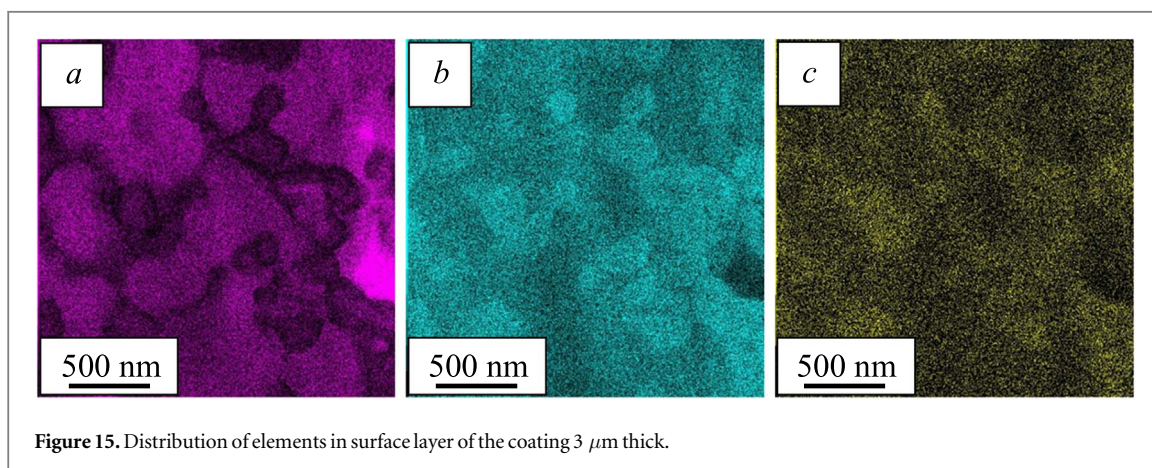
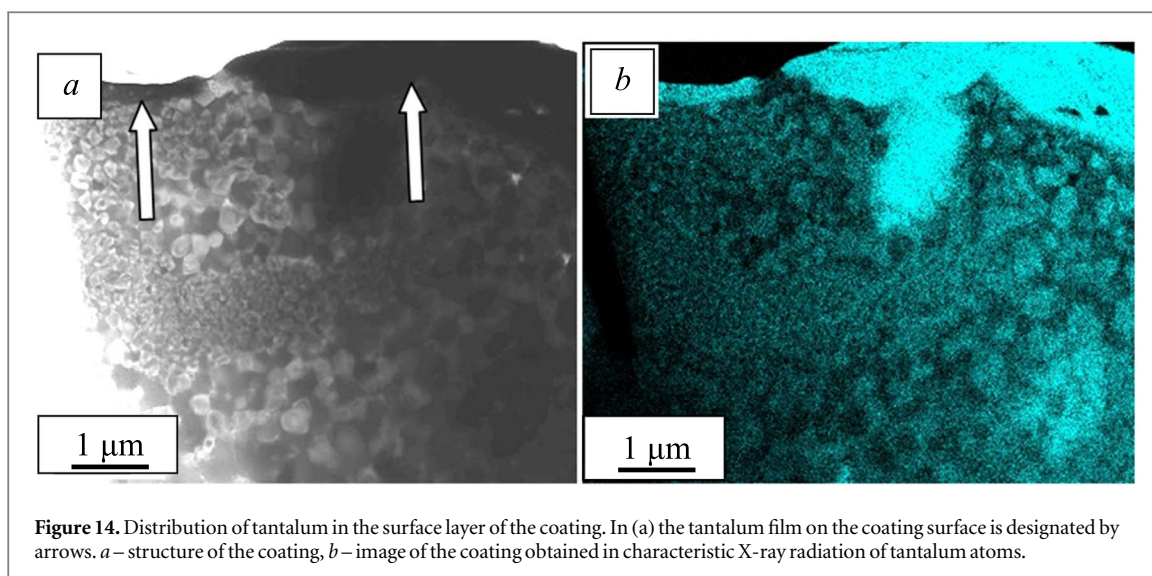


a – the surface layer (surface of sample is designated by the arrow), *b* – the layer at a depth of 10 μm , *c* – the layer at a depth of 25 μm ,
d – the layer at a depth of 45 μm

Figure 13. Structure of Ti-Ta-N system coating (*a*), (*b*), transition layer “coating/substrate” (*c*) and substrate (*d*)

crystal lattice parameter a is 3.7727 Å at the same time the parameter c is equal to 8.6156 Å. The value of parameter c is the maximum among all samples wherein the phase described above is observed. The Ti (IM₃-M) phase demonstrates the largest mass fraction being equal to 44.78%. In comparison with the previous sample the CSR size decreases to 11.73. The value of crystal lattice parameter a increases to 3.316 Å. The mass fraction of 7.76% of the Ti₅Ta₅ phase is the smallest. Its crystal lattice parameter a is 3.3038 Å. The result is the smallest among all samples wherein the phase described above is observed. The minimum mass fraction of 17.72% is demonstrated by the Ti₈₅Al₁₅ phase. Its CSR size is equal to 20.5 nm and the crystal lattice parameters a and c have the values of 2.9348 Å and 4.6541 Å, respectively.

In the coating obtained in the mode of processing № 4 (figure 11, table 4) four phases were found among which Ti₈₅Al₁₅ and Ti (IM₃-M) possess the largest mass fractions whose values are the same and amount to 28.32%. In this case the CSR of the Ti (IM₃-M) phase increases to 20.72 nm and the crystal lattice parameter a decreases to the minimum value of 3.2389 Å. At the same time the CSR of the Ti₈₅Al₁₅ phase reaches its minimum value of 11.29 nm and the crystal lattice parameters a and c , on the contrary, increase to their maximums of 2.9799 Å and 4.7379 Å, respectively. The Ti₆₅Al₃₅N phase content increased to its maximum of



26.95%, the crystal lattice parameter a increases to 4.2279 Å. The Ti_5Ta_5 phase is presented least of all in the sample under study. Its mass fraction is 16.41%. Its CSR is 14.59 nm. The crystal lattice parameter is equal to 3.3053 Å.

In the coating obtained in the mode of processing № 5 (figure 11, table 4) five phases were detected among which the $\text{Ta}_{17}\text{Al}_{12}$ phase with mass fraction of 21.55% was found for the first time. The crystal lattice parameter a of the phase is 9.8984 Å. The Ti_5Ta_5 phase content increased to its maximum of 25.69%. The crystal lattice

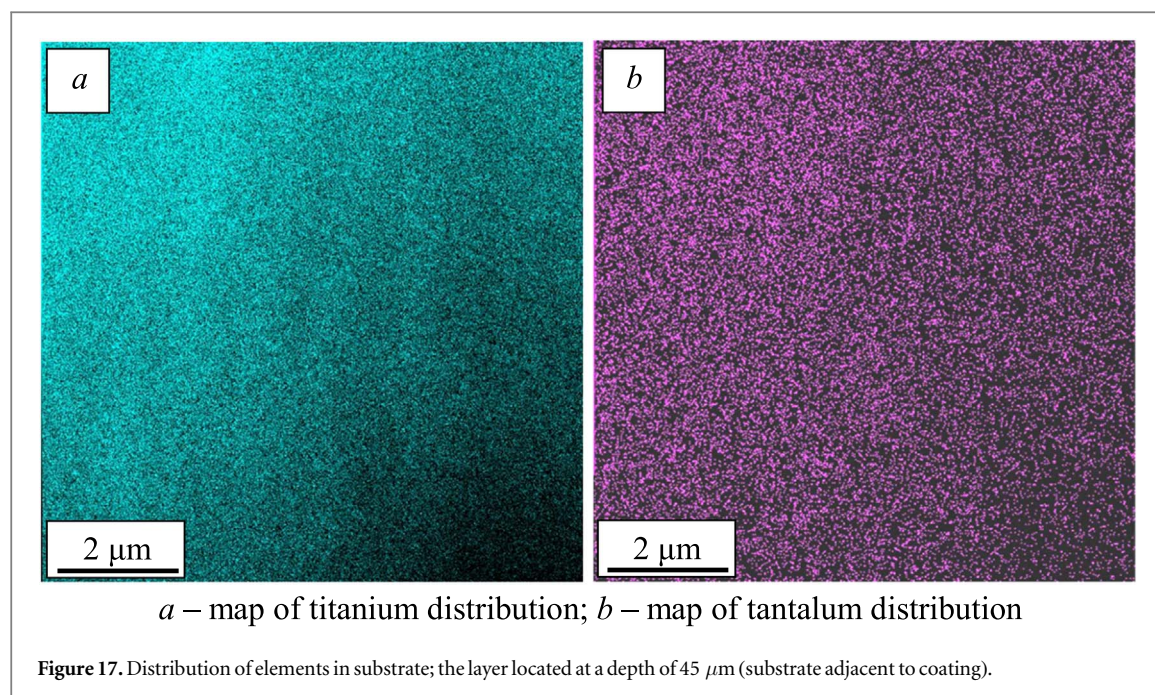


Table 6. Results of tests for wear resistance and friction factor.

Sample	Friction coefficient	Wear rate, $\text{mm}^3/\text{N}\cdot\text{m}$
VT6 without coating	0.495	9.2
Coating Ti-Ta-N	0.3	2.6

parameter a of the phase increased to 3.3142 Å. The Ti (IM3-M) phase possesses the largest mass fraction of 30.67%. In the sample under study the CSR and the crystal lattice parameter a of the phase increases to their maximum values of 62.97 and 3.638 Å. The mass fraction of the TiAl_3 phase, on the contrary, reaches its maximum of 2.92%. Moreover, the phase is the smallest in the sample under study. The CSR of the phase decreases to 16.72 nm in comparison with the previous sample. The crystal lattice parameter a decreases to its minimum value of 3.7977 Å, the parameter c increases by contrast to 8.4983 Å.

In the coating obtained in the mode of processing № 6 (figure 11, table 4) five phases were revealed among which TiAl_3 possesses the largest mass fraction being equal to 48.39%. The value is also the maximum one for the phase under study among all samples wherein it is presented. The crystal lattice parameter a and c also reach its maximums of 2.904 Å and 4.566 Å, respectively. The Ti_5Ta_5 phase content decreases to 12.51%, its crystal lattice parameter a decreases to its minimum value of 3.2683 Å. The mass fraction of the $\text{Ta}_{17}\text{Al}_{12}$ phase decreases to its minimum of 19.07%. In this case, the CSR of the phase is 17.39 nm. The crystal lattice parameter a increases to 9.98 Å. The mass fraction also reaches its minimum of 10.65%. Its CSR size decreases to 16.72 nm. The parameters a and c decrease to minimum values of 2.9049 Å and 4.566 Å, respectively. The Ti_5Ta_5 phase demonstrates the smallest value of 9.38% found nowhere except the sample under study. The CSR of the phase is 8.57 nm, the crystal lattice parameter a is 3.2544 Å.

Thus, in the coatings under study the presence of the following phases: $\text{Ti}_{17}\text{Al}_{12}$, Ti (IM3-M), Ti (P_6MMM), Ti_5Ta_5 , $\text{Ti}_{65}\text{Al}_{35}\text{N}$, $\text{Ti}_{85}\text{Al}_{15}$, TiAl_3 was established by the method of X-ray phase analysis. The dependences of crystal lattice parameters and coherent scattering regions of the phases on power density of electron beam were obtained. The variation in the crystal lattice parameter of the material relative to the tabular value means a distortion of crystal lattice. It will undoubtedly result in the increase in hardness and the Young modulus of the material and its effect on the biological properties in future is not understandable. The decrease in the value of coherent scattering region should lead to the increase in hardness and the Young modulus but insignificantly.

3.4. Study of coatings by the method of transmission electron microscopy

The elemental composition of the coating was also studied by the methods of micro-X-ray spectral analysis in STEM investigation of thin foils in transmission electron microscope JEM 2100 F. The example of realization of the method used is shown in figure 12. The results of layer-by-layer analysis of elemental composition of the sample are listed in table 5.

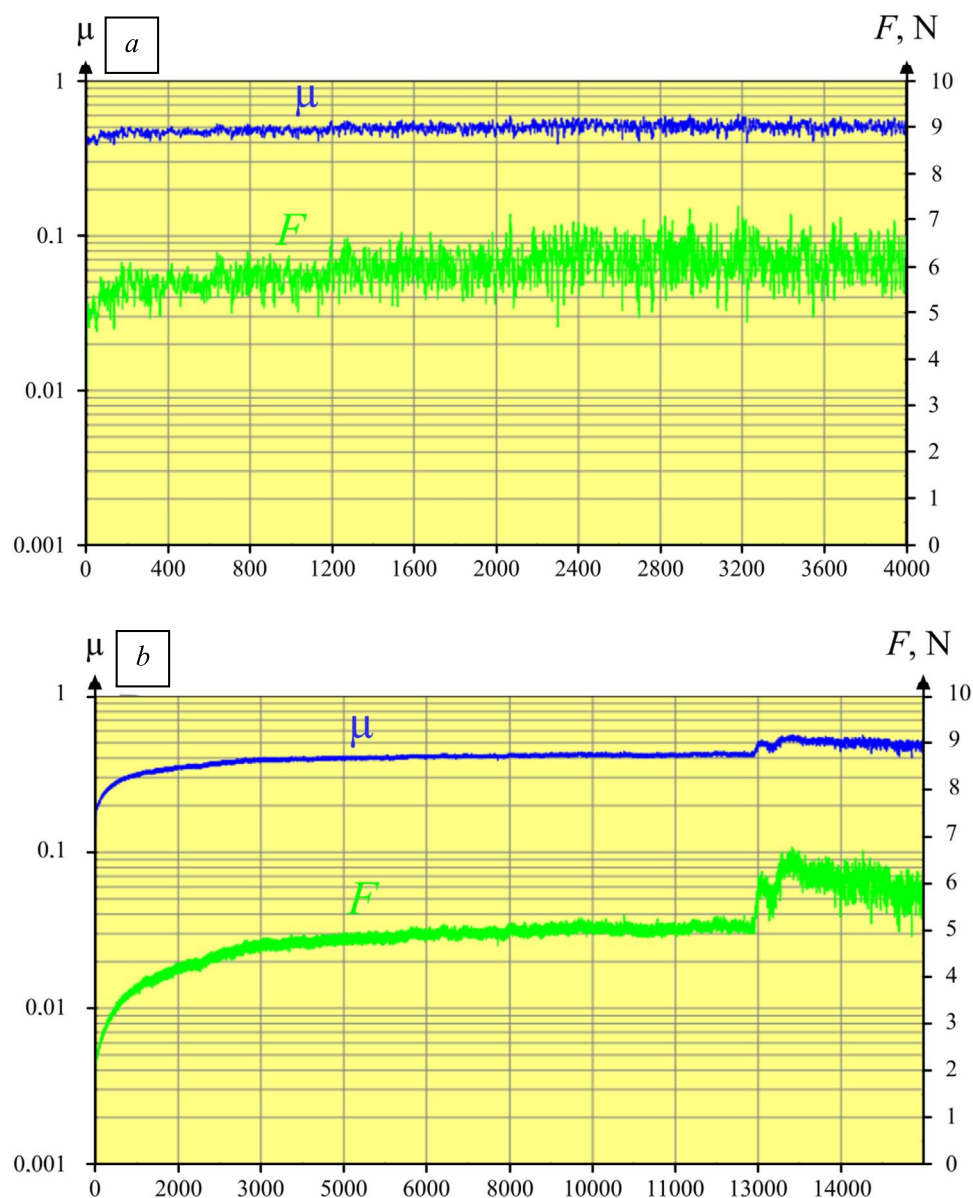


Figure 18. Dependences of friction coefficient and friction force on test time. *a* – VT6 alloy without coating, *b* – Ti-Ta-N-system coating.

When analyzing the results presented in table 5 it may be noted that firstly, oxygen atoms, whose concentration decreases with a greater distance from the surface of the coating, are present in the coating. Secondly, the concentration of nitrogen and titanium atoms increase with a greater distance from the coating surface, and the concentration of tantalum atoms decreases. Thirdly, the impurity atoms of chromium and iron are present in the coating. Fourthly, the tantalum atoms in a small number are detected at a depth of $45\mu\text{m}$ corresponding to the substrate as judged from the structure (figure 13). At the fifth place, the concentration of chromium and iron atoms increases with the distance from the coating surface, it is indicative of the fact that the elements are impurity atoms of the substrate.

The results of coating structure investigation and the substrate layer adjacent to the coating are shown in figure 13. When analyzing the results presented in figure 13 it may be noted that the coating is polycrystalline and is formed by crystallites of two dimensional classes (figures 13(a), (b)): firstly, by crystallites of $300\text{--}550\text{ nm}$ in sizes and secondly, by crystallites of $150\text{--}400\text{ nm}$ in sizes (figure 13(a), crystallites of light contrast). The crystallites of the first dimensional class are separated by the interlayers having a nanocrystalline structure with sizes of $20\text{--}30\text{ nm}$ (figure 13(a)). The coating in the contact zone with the substrate has a coarse structure, the crystallite's size reaches $2.5\mu\text{m}$ (figure 13(c)). The substrate in contact zone with the coating has a lamellar structure (figures 13(c), (d)).

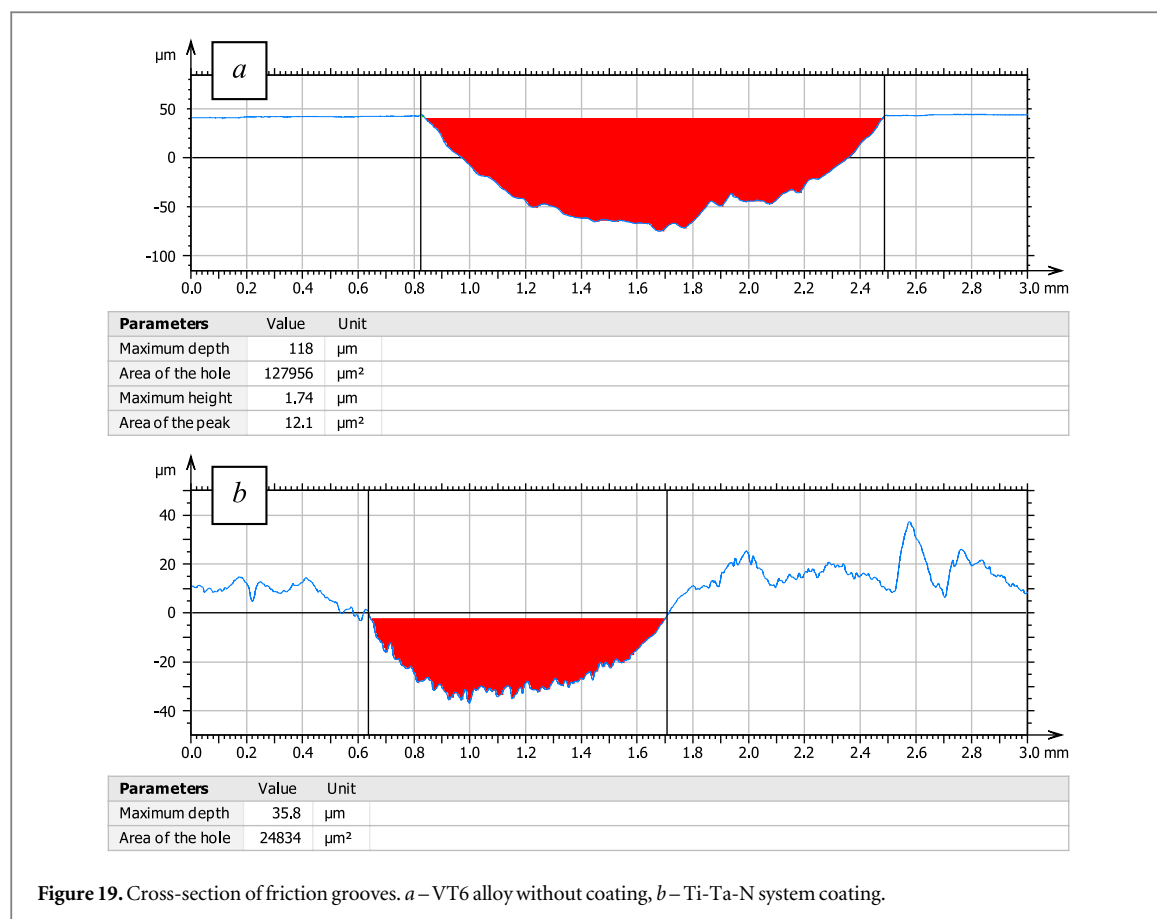


Figure 19. Cross-section of friction grooves. *a* – VT6 alloy without coating, *b* – Ti-Ta-N system coating.

The studies performed by the methods of micro-X-ray spectral analysis (method of mapping) permit one to carry out the analysis of elemental distribution in the structure of the coating. The results presented in figure 14 show that 0.5–1.0 μm thick tantalum film is present on the surface of the coating.

It was shown in figure 13(a) that two types of grains were present in the surface layer. The results of micro-X-ray spectral analysis show that the crystallites of the first class (300–550 nm) are enriched by tantalum atoms (figure 15(a)). The grains of the second dimensional class - by titanium atoms (figure 15(b)). The analysis of results presented in figure 15(c) indicates that nitrogen is inhomogeneously distributed in the coating. The inhomogeneous distribution of tantalum atoms is observed in the volume of the coating (figure 16) as well.

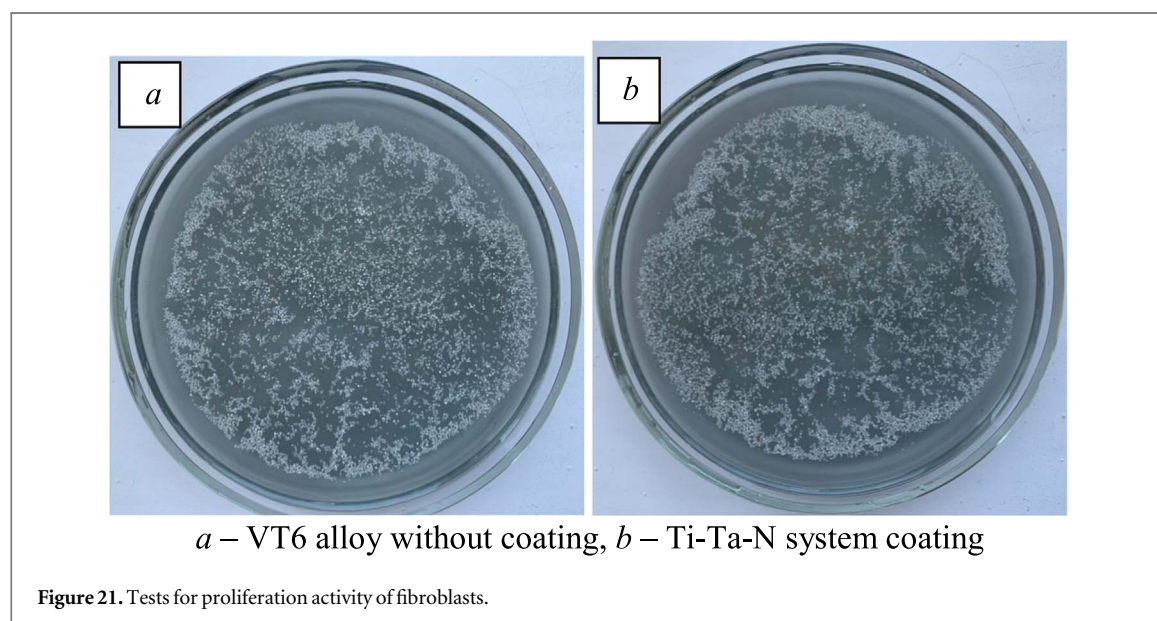
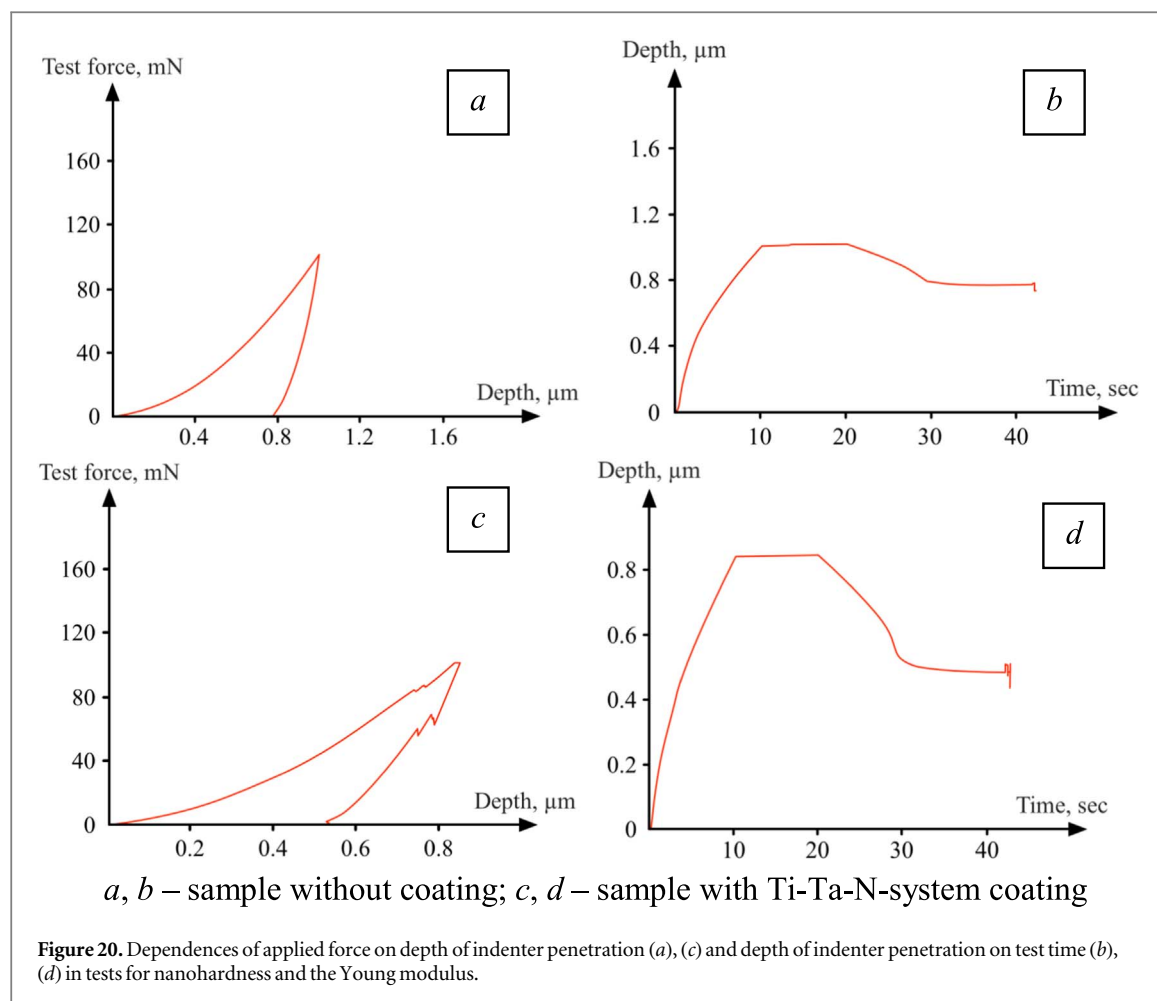
It was shown in figure 13(d) that the structure of substrate layer adjacent to the coating has a lamellar structure. By the methods of micro-X-ray spectral analysis it is established that the plates are enriched by tantalum atoms and are located in grains formed by titanium atoms (figure 17).

Thus the coating formed has a sub-micro-nanocrystalline structure. The chemical elements forming the coating are inhomogeneously distributed in the layer, the crystallites enriched by tantalum and titanium are present. The tantalum film was detected on the coating surface.

3.5. Analysis of physical-mechanical and tribological properties of the coatings

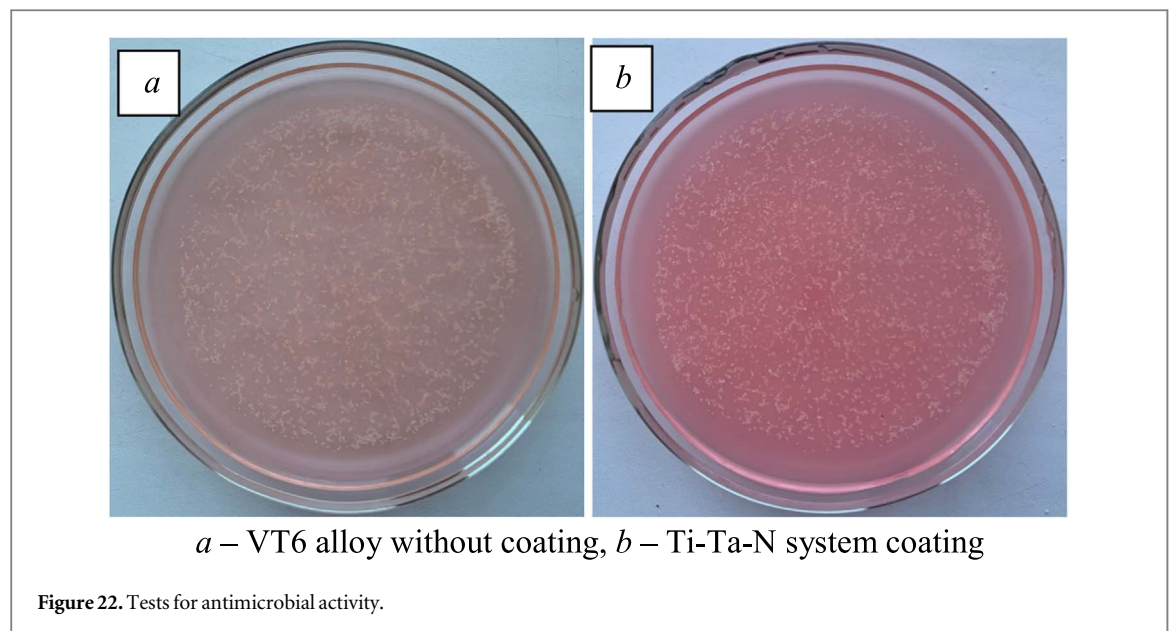
Tests for wear resistance showed that after formation of Ti-Ta-N-system coating the increase by 3.5 times in wear resistance of the modified layer took place, in this case, the friction factor decreased by 1.65 time (table 6). Dependences of friction factor and friction force on test time of VT6 alloy without the coating and with the coating of Ti-Ta-N system as well as cross-sections of friction grooves are shown in figures 18 and 19.

The recent nanoindentation technique which enables one to measure nanohardness and Young modulus at a depth of indentation much less than 1 μm has widely been used to investigate the properties of materials in nanoscale. That is the reason that the technique to determinate nanohardness as a perspective method to investigate the material hardness was chosen. Dependences of applied force on depth of indenter penetration on testing time in tests for nanohardness of samples without the coating and with Ti-Ta-N-system coating are presented in figure 20. The average nanohardness of Ti-Ta-N coating amounted to 876.396 HV. Without the coating the nanohardness amounted to 498.7 HV. The created coating possesses an increased nanohardness by the factor of 1.7. The average value of the Young modulus of Ti-Ta-N coating amounted to $1.27 \cdot 10^5 \text{ N mm}^{-2}$.



Without the coating the Young modulus amounted to $1.15 \cdot 10^5 \text{ N mm}^{-2}$. The created coating possesses the increased Young modulus by 10%.

The coating obtained in the research belong to the class of viscoelastic materials. Intensive relaxation processes occur in such materials at room temperature. The presence viscoelastic component of deformation results in overstating the contact stiffness and, consequently, elastic modulus of a sample. In our opinion, the nanohardness value of Ti-Ta-N-system coatings turned out to be understating, because of partial recovery of indentations after full removal of load. The phenomenon is caused by presence of considerable relaxation



component of deformation in electroexplosive coatings. Analysis of figure 20 showed that unloading curve is typical for the material with pronounced plasticity because a very small part of indentation is recovered during unloading.

3.6. Tests for proliferation activity of fibroblasts and antimicrobial activity

Proliferation activity of fibroblasts was determined by the method of direct calculation of cells' amount after their content with the sample with the applied coatings by means of optical microscope according to recommendations [28]. Investigations were performed on cell culture of fibroblasts of mouse hypodermic tissue [L929]. It was detected as a result of the studies carried out that the percent of survived cells on the surface of bioinert tantalum coatings modified by nitrogen ions is 100% that is indicative of the high proliferation activity of fibroblasts. In this case, on the sample without the coating (VT6 titanium alloy) the percentage of survived cells amounted to 91% (figure 21). It is due to escape of vanadium ions from VT6 alloy to cell culture medium and their destructive effect on cell cultures.

Antimicrobial activity of samples was tested by the method of calculation of viable bacteria. In this method *in vitro* the dynamics of bacteria destruction in the sample was measured by calculating the remaining bacteria in comparison to titanium substrate without the coating. The cell culture of staphylococcus aureus microorganisms was used. Citotoxic effect of the sample with bioinert tantalum coatings modified by nitrogen ions was determined by MTT-test on cell culture of fibroblasts of mouse hypodermic tissue [L929]. The sample with tantalum coatings modified by nitrogen ions are not toxic (figure 22) that is supported by citotoxicity tests. In this case, the amount of survived cells after contact with the sample with tantalum coatings modified by nitrogen ions is higher by 3% than in the sample without the coating (VT6 titanium alloy).

The optimal mode of electric explosion spraying and subsequent electron-ion -plasma modification of the Ti-Ta-N-system coating has been detected (from the point of view of structural-phase states and results of tests for nanohardness, Young modulus, friction factor, for proliferation activity of fibroblasts and antimicrobial activity). The optimal mode should be considered the following: an electric explosion of tantalum foil 400 mg in mass, the formation of pulsed multiphase plasma jet from explosion products, the melting of titanium implant surface by the jet at absorbed power density of 1.5 GW m^{-2} , the deposition of explosion products on the surface, the formation of bioinert tantalum coating on the surface, the nitriding during 3 h at 500°C and the subsequent pulsed-periodical electron beam processing of the coating surface at absorbed energy density of 30 J cm^{-2} , pulse duration of $150 \mu\text{m}$ and pulse number of 3.

Implanted materials should meet the definite requirements including the absence of pathological changes in tissues of organism and violation of vital activity of organs and tissues during the whole period of their functioning. Implanted materials should have no toxic, carcinogenic and allergic effect on human tissue and organs. Biocompatible materials should be used for obtaining the implants. The results of proliferative activity of cell lines (figure 21) and antimicrobial activity (figure 22) correlate with analogous tests of calcium phosphate coating [29–31].

Volume and quality of surgical operation have effect on the process of bone wound healing. Capacity for regeneration of bone is determined by absence of considerable structures (osteons and trabecules). Character of bone regeneration will be determined by shape and material of which the implant is made, surface state of intraosseous part as well as presence of close contact between a bone and implant surface. After implantation the density of bone connection with implant surface is realized at the expense of formation of collagen fibres and physico-chemical bond as a result of reaction between mineralized matrix of bone and oxide film layer of titanium implant surface or its hydroxyapatite coating. Subsequent clinical studies of coatings obtained in the research are planned for the future.

4. Conclusions

Key research findings.

1. Ti-Ta-N bioinert coatings for medical implants have been obtained.
2. Ti-Ta-N coatings possess a complex of high mechanical characteristics.
3. Ti-Ta-N coatings have reasonable proliferative and antimicrobial activity.
4. Ti-Ta-N bioinert coatings belong to the class of nanomaterials.
5. Ti-Ta-N bioinert coatings may be competitive to modern implants.

Visual examination of the samples subjected to electric explosion spraying of tantalum coating has shown that the coating having inhomogeneous colour forms on their surface. After the processing of the coating by low-energy high-current electron beam and its nitriding the colour of coating surface varies to silvery and the relief transforms: areas with various profiles of roughness appear. The diversity of structural components of surface relief creates conditions for a better osteointegration of titanium implants with the Ti-Ta-N-system coatings in human organism. The investigations by the method of scanning electron microscopy has shown that after electric explosion spraying the 15–20 μm thick tantalum coating is formed. The processing of surface layer by low-energy high-current electron beam and nitriding results in the formation of a more disperse and homogeneous structure in it. The elemental composition of the coating is presented by tantalum, titanium, aluminium and vanadium. By means of X-ray phase analysis the presence of the following phases: $\text{Ta}_{17}\text{Al}_{12}$, Ti (IM3-M), Ti (P_6MMM), Ti_5Ta_5 , $\text{Ti}_{65}\text{Al}_{35}\text{N}$, $\text{Ti}_{85}\text{Al}_{15}$, TiAl_3 has been established. Dependences of crystal lattice parameters and coherent scattering regions of the phases on power density of electron beam have been obtained. The coating is polycrystalline and is formed by crystallites of two dimensional classes: the crystallites of 300–550 nm in size enriched by tantalum atoms and those 150–400 nm in size enriched by tantalum atoms. The crystallites of the first dimensional class are separated by interlayers of 20–30 nm in size having a nanocrystalline structure. The coating in the zone of contact with the substrate has a coarser structure, the crystallites' size reaches 2.5 μm . The substrate has a lamellar structure in contact layer with the coating. The plates are enriched by tantalum atoms and locate in the grains formed by titanium atoms. The tantalum film 0.5–1.0 μm in thickness is present on coating surface. After the formation of the Ti-Ta-N system coating the increase in wear resistance by 3.5 times takes place, in this case the friction factor decreases by 1.65 time in comparison to VT6 titanium alloy. The average nanohardness of Ti-Ta-N coating amounted to 876.4 HV. Without the coating the nanohardness amounted to 498.7 HV. The average value of the Young modulus of Ti-Ta-N coating amounted to $1.27 \cdot 10^5 \text{ N mm}^{-2}$. The Young modulus without the coating amounted to $1.15 \cdot 10^5 \text{ N mm}^{-2}$. The created coating possesses the increased (by 10%) Young modulus. The tests for proliferation activity of fibroblasts showed that percentage of survived cells on the surface of the Ti-Ta-N-system coating amounts to 100%. It is indicative of the high proliferation activity of fibroblasts. The percentage of survived cells amounted to 91% on the sample without the coating (VT6 titanium alloy). As a result of tests for antimicrobial activity it was established that the amount of survived cells after the contact with the sample with tantalum coatings modified by nitrogen ions is higher by 3% than in the sample without the coating (VT6 titanium alloy). The optimal mode should be considered the following: the electric explosion of tantalum foil 400 mg in mass, the formation of pulsed multiphase plasma jet from explosion products, the melting of titanium implant surface by the jet at absorbed power density of 1.5 GW m^{-2} , the deposition of bioinert tantalum coating on the surface, the nitriding during 3 h at 500 °C and the subsequent pulsed-periodical electron-beam processing of the coating surface at absorbed energy density of 30 J cm^{-2} , pulse duration of 150 μs and pulse number of 3.

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ORCID iDs

Denis A Romanov  <https://orcid.org/0000-0002-6880-2849>

Victor E Gromov  <https://orcid.org/0000-0002-5147-5343>

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