The Influence of Different Parameters of Magnetron Sputtering on the Structure and Chemical Composition of Titanium Alloy Implant Surfaces

DOI: 10.17691/stm2019.11.4.14
Received September 20, 2018

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The aim of the investigation is to study the influence of different parameters of magnetron sputtering on the structure and chemical composition of titanium and titanium alloy surfaces used for endosseous implantation.

Materials and Methods. The study involved the use of the NSC-3500 magnetron sputtering system (NANO-MASTER Inc., USA) providing the possibility to obtain coatings of almost any metals, alloys and semiconductors materials without a shift in the stoichiometric composition. High-purity argon (99.99%) was used as the sputtering gas. A high-purity titanium (99.99%) target was used as the source of the coating material. Polished titanium washers of Grade IV and Grade V (according to ASTM) were used as substrates for growing titanium coatings.

Titanium coatings were grown on the titanium washers at the temperature of 150°C and magnetron sputtering power of 200–300 W. After obtaining the titanium coatings, the samples were heat-treated in vacuum at 450°C for 2 h.

Titanium coating surface morphology was studied using atomic force microscopy on the SOLVER NEXT unit (NT-MDT, Russia).

Results and Discussion. The influence of different technological modes of deposition on the surface morphology and roughness of the obtained titanium coatings was studied. It was found that an increase in the sputtering power (from 200 to 300 W) led to significant structural changes accompanied by the change in the grain size and the resulting surface roughness.

Magnetron treatment of a pure titanium sample with chemically pure titanium allows creating a nanostructured surface bonded to the substrate at the atomic level. The surface morphology varies at the nano-scale depending on the radiation power. Subsequent heat treatment (at 450°C) does not lead to significant changes in morphology, heterogeneity or granularity profile of the sample surface. When the surface of titanium aluminum-vanadium alloy Grade V was coated with chemically pure titanium, the elemental composition of the modified surface corresponded to the composition of titanium Grade IV (there was the complete absence of vanadium and minor aluminum impurities).

Conclusion. Magnetron sputtering of pure titanium onto implants made of titanium and titanium alloys allows obtaining high-quality nanostructured surfaces with unusual physical properties (thickness, porosity, adhesion, etc.).

Key words: endosseous titanium implants; magnetron sputtering; nanostructural morphology.

Introduction

In the last decade, restoration of organs and tissues in the human body by implantation of artificial structures (implants) has taken the lead in such areas of medicine as traumatology, oncology, neurosurgery, maxillofacial surgery, surgical dentistry.

To succeed in restoring certain parts of the skeleton, it is important to achieve osseointegration, i.e., a stable connection between the bone bed and the implant

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surface, formed by bone cells adhering and proliferating in the implant surface or structure. The key technical factors that osseointegration depends on are the quality and structure of the implant material, the shape (design) of the implant and its surface structure. A specific approach to implantation of artificial structures is often required for patients with pre-existing chronic somatic diseases, such as diabetes mellitus, osteoporosis, and radiation therapy consequences. In these cases, the technical characteristics of implants become decisive factors for successful treatment [1].

The high-quality implant surface is the key to optimal osseointegration. Changing the micro- and nanostructure of the surface and providing it with roughness, which is achieved via nano-treatment of the contact element, makes it possible to increase its contact area. In turn, the increase in the implant surface area provides more intensive absorption of plasma proteins on the contact surface after implantation significantly increases the hydrophilic properties of the surface in contact with prosthetic bed biotissues and largely improves the osseointegration of endosseous implants.

Applying nanostructured implants in clinical practice will make implantation possible in patients with comorbidities [2].

Today, the market offers standard dental implants with the nanostructured surface, such as SLActive (Straumann, Switzerland), OsseoSpeed (Astra Tech, Sweden). These implants show a very high level of osseointegration, even in clinical situations among patients with comorbidities (diabetes, osteoporosis, etc.). A disadvantage of these constructions is the fact that these implants are standard and serve to support dental prostheses only. In addition, these implants are quite pricy [3].

Over the past 50 years, considerable experience has been gained in studying bone tissue response to implantable materials, especially in dental implantology. Unlike dental implants with almost all the surface in the bone tissue, the surface of implants for other skeleton parts contacts mostly with soft tissues. However, there are insufficient data on the soft tissue response to the metallic implant surfaces in modern literature.

Today, most endosseous implants are made of chemically pure titanium or its alloys. For this purpose, chemically pure titanium (according to ASTM international standard — Grade IV) and aluminum-vanadium titanium alloy Ti-6Al-4V (according to ASTM international standard — Grade V) are used. On the one hand, aluminum and vanadium improve the strength characteristics of titanium; on the other hand, they worsen the biocompatibility of the implant. However, the cost of implants made of chemically pure titanium is higher than that of the Grade V alloy due to both higher cost of the material and more expensive technology.

In the available literature, there are almost no studies of different implant coatings and their properties in relation to the type of tissue in contact with the implant surface. There are no studies on the differentiation of technologies for applying different coatings to the same implant and tissue response to the resulting surfaces.

Present-day production of endosseous and extramedullary implants is developing to manufacture personalized implants of a particular shape using 3D printing (selective laser sintering). Currently, in Russia and abroad, there has been gained certain experience in manufacturing non-resorbable plastic and metallic implants of individual shape. Experimental and clinical studies have been carried out to study the strength characteristics of these implants and biocompatibility of their materials.

In today's literature, there is evidence on the use of magnetron sputtering for the creation of biocompatible surfaces [4–6]. In Russia, this technology was developed at Tomsk Polytechnic University [7]. The work involved obtaining the calcium-phosphate coatings on implants by RF-magnetron sputtering. With this method, nanostructured films are grown on the implant surface by sputtering the target material in magnetron discharge plasma. The coatings obtained have higher purity compared to the implant surface created by sandblasting treatment and acid etching. Such treatment allows obtaining a surface with preset morphology parameters and regard for cellular response to a foreign body. Researchers have shown that high groove density of the coating reduces cell proliferation; therefore, well-ordered nanopore formation is more effective in this respect. Surface modification in the range of 70–100 nm was found to affect the level of focal adhesion of proteins positively [8]. At present, the problem of creating implant alloy coatings with surface morphology having preset parameters and isolating the substrate materials from the body tissues is understudied in science.

The aim of the investigation is to study the influence of different magnetron sputtering parameters on the structure and chemical composition of titanium and titanium alloy surfaces used for endosseous implantation.

Materials and Methods

The source of coating material was the high-purity titanium (99.99%) target. Magnetron sputtering was performed using the NSC-3500 system (NANO-MASTER Inc., USA). High-purity argon (99.99%) was used as the sputtering gas. Titanium coatings were grown at the residual argon pressure of 0.001 mm Hg. The sputter deposition time was the same for all samples. Prior to the deposition process on titanium washers, the target was sputtered with the shutter closed for 10 min to clean the target from possible contamination. To create titanium coatings, the titanium washers were heated to 150°C. After coating, the samples were heat-treated in vacuum at 450°C for 2 h.

A total of 60 samples (30 for each grade) were examined. All of the samples were divided into 10 groups. Untreated surfaces were studied in the first two

Table 1

Groups of titanium surface samples under study

Deposition modes	Surface samples	
	Grade IV (n=30)	Grade V (n=30)
Used without treatment	6	6
Deposited material: Ti (purity — 99.99%); power — 200 W; treatment time — 120 min; substrate temperature — 150°C	6	6
Deposited material: Ti (purity — 99.99%); power — 300 W; treatment time — 120 min; substrate temperature — 150°C	6	6
Deposited material: Ti (purity — 99.99%); power — 200 W; treatment time — 120 min; substrate temperature — 150°C Preliminary vacuum annealing for 120 min at 450°C	6	6
Deposited material: Ti (purity — 99.99%); power — 300 W; treatment time — 120 min; substrate temperature — 150°C Preliminary vacuum annealing for 120 min at 450°C	6	6

groups, while 8 other groups included surfaces treated under different parameters (Table 1).

Titanium coating surface morphology was studied using atomic force microscopy on the SOLVER NEXT unit (NT-MDT, Russia) and raster electron microscopy (REM) using the scanning electron microscope MIRA 3 LMH (TESCAN, Czech Republic).

The elemental composition of the surface of samples and modified coatings was studied by energy-dispersive spectroscopy using an auxiliary device to AZtecEnergy Standard/X-max 20 microscope (TESCAN, Czech Republic).

Results and Discussion

Examination of Grade IV and Grade V samples with untreated surfaces showed: the surfaces of samples made of both Grade IV and Grade V materials were visually smooth. At 240-fold magnification, the surface relief with concentric circles (traces of processing with the cutting tool) was visible. At 16,000-fold magnification, surface roughness was visible (Figure 1).

The elemental analysis of samples made of Grade IV and Grade V materials prior to sputter deposition confirmed the correspondence of the claimed composition to the actual one. In particular, the following elements were found in Grade V samples: Al — 8.69 at. %, V — 3.04 at. %, Si — 0.10 at. %, O — 0.87 at. %, C — 12.12 at. %, Ti — 75.03 at. %. In Grade IV samples, lower concentrations of impurities were revealed: Al — 0.20 at. %, Si — 0.09 at. %, O — 7.92 at. %, C — 10.11 at. %, Ti — 81.69 at. % (Table 2). Increased oxygen concentrations in Grade IV samples were observed due to a higher degree of their surface oxidation as compared to Grade V samples. The elemental composition of the samples within the same group varied slightly.

The study of samples made of Grade V and Grade IV materials with modifying titanium coatings obtained via magnetron sputtering at a power of 200 W showed: the surfaces of samples made of both Grade IV and Grade V materials were visually smooth. At 240-fold magnification, a uniform fine-grained relief was visible. At 32,000-fold magnification, it was found that the surface of all samples was formed by particles having plate-like morphology. The particles formed agglomerates of several plates; the gaps between the plates were not detected at this magnification. The number of plates in the agglomerate varied from 3 to 10 units. The size of the agglomerates varied from ~150 to 600 nm. The gaps between the agglomerates were 40–50 nm. The agglomerates

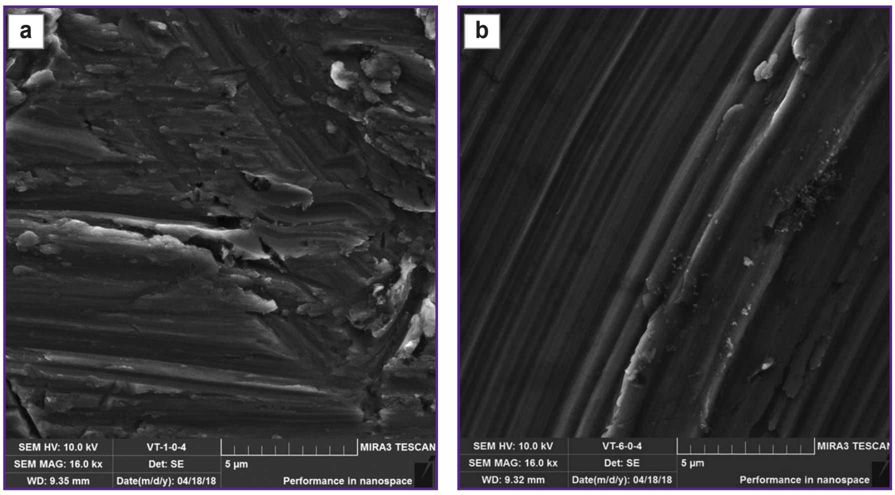

Figure 1. REM micrographs of untreated sample surface of Grade IV titanium (a) and Grade V titanium (b); ×16,000

Table 2

Elemental composition of titanium item surface according to the results of energy-dispersive spectroscopy (M±m)

Chemical elements	Grade IV sample				Grade V sample			
	Untreated surface (n=6)		Treated surface, power — 300 W (n=6)		Untreated surface (n=6)		Treated surface, power — 300 W (n=6)	
	wt. %	at. %	wt. %	at. %	wt. %	at. %	wt. %	at. %
C	2.91±0.06	10.11	3.78±0.10	11.88	3.51±0.07	12.12	4.28±0.05	10.86
O	3.04±0.15	7.92	7.72±0.15	18.22	0.33±0.23	0.87	22.03±0.14	41.99
Al	0.13±0.01	0.20	0.13±0.01	0.19	5.65±0.03	8.69	0.09±0.01	0.10
Si	0.06±0.01	0.09	0.15±0.01	0.20	0.07±0.01	0.10	0.48±0.01	0.52
Ti	93.86±0.16	81.69	87.99±0.17	69.33	86.52±0.21	75.03	73.02±0.13	46.48
V	—	—	—	—	3.73±0.04	3.04	—	—

were located on the sample surface in a random manner. When analyzing the surface structure, we saw no differences in morphology depending on the substrate material, so REM micrographs of the treated surface are given only for titanium Grade V (Figure 2).

When magnetron sputtering power was increased to 300 W, the surface morphology of the grown titanium coatings changed. As shown by the results of studying the samples using the REM technique at 32,000-fold magnification, the coatings were formed by triangular-prism-shaped nanocrystalline particles. The particle size was 100 to 200 nm. The particles were arranged in a random manner, but tightly adjacent to each other, the gaps between them were no more than 15–20 nm (see Figure 2).

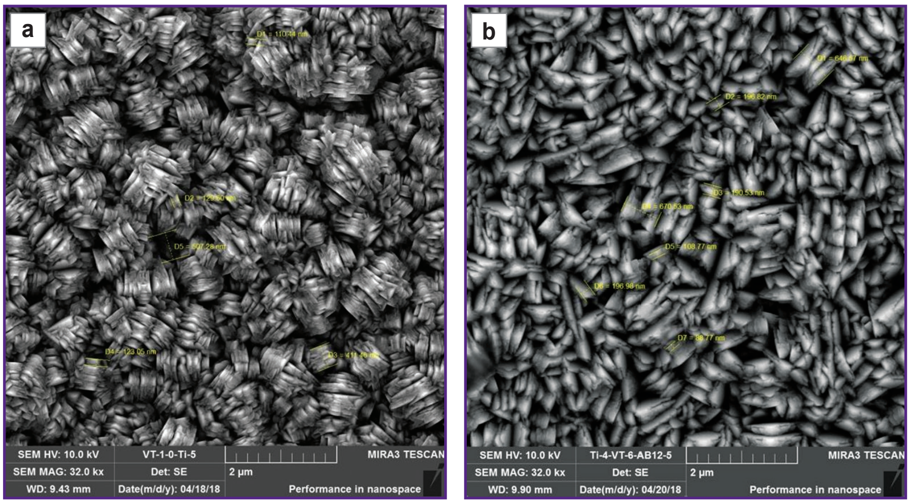

Figure 2. REM micrographs of Grade V titanium sample surface treated at a power of 200 W (a) and 300 W (b); ×32,000

The elemental analysis of coatings grown on item samples made of Grade V and Grade IV evidenced the similarity of their composition including the following elements within the error limit of the analysis method: Al — 0.19 at. %, Si — 0.20 at. %, O — 18.22 at. %, C — 11.88 at. %, Ti — 69.33 at. %. We consider rather high concentrations of oxygen and carbon in the samples to be associated with the developed surface of the grown titanium layers contacting with the atmosphere after extraction of the samples from the magnetron sputtering system reactor.

The results of REM and energy dispersive spectroscopy showed:

magnetron treatment of a pure titanium item with chemically pure titanium makes it possible to create a nanostructured surface adhered to the substrate;

surface morphology at the nanoscale level differs depending on the radiation power applied;

after the magnetron treatment of titanium aluminum-vanadium alloy Grade V surface with chemically pure titanium, the elemental composition of the modified surface corresponds to that of titanium Grade IV (there is a complete absence of vanadium and minor aluminum impurities);

vacuum thermal annealing at temperatures as high as 450°C does not lead to noticeable changes in the coating surface morphology, heterogeneity profile, and granularity, though it significantly affects the oxygen content on the sample surface.

Conclusion

Magnetron sputter deposition of pure titanium thin-film coatings onto the surface of implants made of titanium and its alloys offers the possibility to obtain high-quality nanostructured surfaces with unusual physical properties (thickness, porosity, adhesion, etc.).

Study funding. The study was supported by the Ministry of Health of the Russian Federation, a grant as per the government task of "Development of nanostructured surfaces of endosseous dental implants" for 2018–2020.

Conflict of interests. The authors have no conflict of interests to disclose.

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