Investigation of the phase structure and surface morphology of the titanium nano-structured coatings for dental implants deposited by the method of magnetron sputtering

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Abstract. In this work we develop a technology for deposition of titanium nano-structured coatings on titanium plain washers by magnetron sputtering and investigate the influence of technological conditions on the structural parameters of the deposited titanium coatings. Magnetron sputtering of pure 99.99% titanium coatings on titanium washers VT1.0 and VT6.0, has been developed. It is shown that by this method it is possible to form coatings of pure titanium with a nano-relief surface. Titanium coatings under varying deposition parameters were characterized by Scanning Electron Microscopy and Atom Force Microscopy. It is shown that titanium coatings deposited by magnetron sputtering technique have a nano-granular structure. The maximum surface irregularities vary within ± 150 nm, and the grain sizes vary from 50 nm to 450 nm. The obtained result is of great interest for further investigation of the influence of titanium coatings morphology and its nano-dimensional characteristics on the biochemical mechanisms responsible for the process of bone remodeling around the implant.

It is established that titanium coatings allow not only to form on the implants a nano-relief surface, but also drastically reduce on this surface the concentration of toxic elements that are initially present in the implant material VT6.0.

1 Introduction

As the main material of the implant, titanium is used as materials most suitable due to their physical and biomedical parameters for biocompatible implants. Medico-biological indicators of osseointegration directly depend on the relief of the surface of the implant and

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its chemical composition. Further development of the implant surface morphology should be based on a clear understanding how the parameters of the micro- and nanostructure of the implant surface can influence the osseointegration processes. Two main characteristics of the implant surface that are responsible for osseointegration processes can be distinguished: the first is the hydrophilicity of the surface and the second is the surface roughness.

Hydrophilicity of the surface: The hydrophilic surface due to the increased affinity for water molecules provided intermolecular interaction forces promotes more effective interaction of the implant surface with biological fluids, cellular elements, which is especially important in the early stages of osseointegration [1, 2]. The hydrophilicity of the surface depends on many facts, for example, on the micro- and nano-structural characteristics of the surface, on the properties and sizes of the fluid molecules in contact with it, on the chemical composition of water, etc. Taking into account all these factors and assessing the role of each they are very important for modification of the implant surface.

Surface roughness: The surface roughness of implants can be conditionally divided into macro-, micro- and nano-roughness. Macroscopic roughness is characterized by the size of irregularities in the range from millimeter to micrometer. A number of studies have revealed that the macroscopic roughness of the implant surface contributes to their long-term mechanical stability [3,4]. Macroscopic granularity of the implant surface on one hand promotes a "cohesion" between the newly formed bone tissue and the surface of the implant itself, on the other hand, a large surface granularity is undesirable, because it creates favorable conditions for adhesion of microorganisms around the implant.

The microscopic level of roughness is characterized by the size of irregularities from 1 to 10 microns. It is generally accepted that roughness with a size of 1-2 micron irregularities is the most optimal for osseointegration [5-7]. However, the clinical data do not look as promising. Esposito et al. did not notice a statistically significant difference in the clinic when using implants with a different type of surface [8].

Successful osseointegration is performed by remodeling the bone around the implant [9]. The process of bone tissue remodeling is accompanied by the process of resorption of the old bone matrix and its replacement with a new bone tissue. The process of bone resorption occurs with the osteoclasts, and the process of formation of new bone tissue with the participation of osteoblasts (cells with a diameter of 15-20 microns).

The main mineral component of the matrix is the hydroxyapatite, the crystals of which are deposited along the collagen fibers. The collagen molecule is a left-wound spiral with a length of 300 nm and thickness of 1.5 nm. Obviously, the formation of a new bone tissue requires a balanced activity of osteoclasts and osteoblasts [10-12].

The rough surface of the implant contributes to the formation of fibrous tissues, which consists of collagen and elastic fibers, activation of osteoblasts and to improve ostiointegration [13, 14]. Despite the already recognized fact that the micro-rough surface contributes to the improvement of osseointegration processes, the influence of the relief features of surfaces and its micro- and nano-dimensional characteristics on biochemical mechanisms responsible for bone tissue remodeling around the implant is still not fully understood.

The various methods used to modify the surface of implants, unfortunately, are unsuitable for forming of nano-dimensional surface. However, implants with nano-relief topology that can have a profound effect on ostiointegration processes and will help to better understand the process of bone tissue remodeling. For benefit of this assumption is evidenced the ability of increased interaction of the nano-relief surface with such nano-dimensional biological substances as fibrous tissue, calloglene, components of damaged cells and blood, which ultimately affects the intensity of differentiation and proliferation of osteogenic cells [15].

The purpose of our work are: a) develop a technology for deposition of titanium nano-structured coatings on titanium implants by magnetron sputtering, b) investigate the influence of technological conditions on the morphology of the surface and the structural parameters of the deposited titanium coatings, c) preclinical evaluation of the effect of titanium coatings with various nano-dimensional relief on their biocompatibility and ostiointegration by means to study the level of proliferation and viability of fibroblasts on cell cultures.

2 Materials and methods

2.1 Formation of titanium coatings with nano-scale topography

For the deposition of titanium coatings for dental implants, we for the first time suggest and used the DC magnetron sputtering method. In the capacity of working gas was used pure argon 99.999%. Titanium coatings were deposited simultaneously on glass substrates and polished titanium plain washers of BT 1.0 and BT 6.0 with a diameter of 4 mm.

The surface morphology of titanium coatings were carried out by AFM using the NT-MDT "SOLVER NEXT" installation. The SEM images of titanium coatings and its elemental composition was investigated by using the MARA3 TESCAN unit.

2.2 Results of the investigations of titanium coatings surface morphology

The results of studies have showed that the surface morphology of the titanium coatings does not depend on the type of substrate (titanium washers or glass) and is determined only by the parameters of the process, namely, the substrate temperature, the distance between the substrate and the target, the working pressure of argon and the power of the magnetron. Particularly, the results of these studies showed that the dimensional characteristics of the nano-relief surface and its morphology strongly depend on the magnetron power. Figure 1a, 1b are presented SEM images of the surface morphology of titanium coating obtained at different powers of the magnetron.

Fig. 1. SEM images of titanium coating deposited on BT 6.0 titanium plain washers at deferent power of magnetron (W), a) W = 200Wt, b) W = 300Wt.

In the Figure 2 for comparison is presented the SEM image of the implant surface of IRIS Liko-M. The porous surface of the implant was formed by chemical etching.

Fig. 2. SEM image of surface of “IRIS” Liko-M implant, diameter 4.0 mm, magnification x2000.

This surface, as an example of the surface of most implants used in practical stomatology, has a rough surface at the level of micro-irregularities. Thus, as show the results of SEM images, the method of magnetron sputtering, unlike other methods of the implant surface modifying, allows to obtain nano-relief surfaces with different morphologies.

Figures 3 and 4 show 2D and 3D images of surface morphology, grain size distribution and surface profile of the same samples (Fig.1) obtained by atomic force microscopy (AFM).

Fig. 3. Results of AFM measurements of titanium coatings obtained at a magnetron sputtering power $W = 200\text{W}$; a) and b) 2D and 3D images of surface morphology respectively, c) surface profile, d) grain size distribution.

Fig. 4. Results of AFM measurements of titanium coatings obtained at a magnetron sputtering power $W = 300\text{W}$; a) and b) 2D and 3D images of surface morphology respectively, c) surface profile, d) grain size distribution.

As can be seen from Figures 3 and 4, the maximum surface irregularities lie within $\pm 150\text{ nm}$, and the grain sizes vary from 50 nm to 450 nm . The results of our studies have shown that changing the parameters of magnetron sputtering can control the dimensional characteristics of the nano-relief of titanium coatings.

Table 1 shows the results of the elemental composition measurements in titanium washers VT6.0 without a titanium coating and after coating with a layer of pure titanium by magnetron sputtering. As can be seen from Table 1, the concentration of elements, such as vanadium, aluminum, iron and carbon, which are toxic to osseointegration, decreased considerably.

Table 1. Atomic and weight concentration of elements on the surface of a titanium washer VT6.0.
a) Without titanium coating, b) After application of the titanium coating

Element	Weight %	Sigma weight %	Atom. %	Element	Weight %	Sigma weight %	Atom. %
C	4.43	0.07	14.62	C	3.38	0.06	10.71
O	1.78	0.22	4.40	O	7.83	0.15	18.61
Al	5.40	0.03	7.94	Al	0.13	0.01	0.19
Si	0.08	0.01	0.11	Si	0.18	0.01	0.24
Ti	84.40	0.21	69.89	Ti	88.36	0.16	70.17
V	3.73	0.04	2.90	V	0	0	0
Fe	0.19	0.02	0.14	Fe	0.12	0.02	0.08
SUM	100.00		100.00	SUM	100.00		100.0

3 Conclusion

The technology of magnetron sputtering of very pure 99.99% titanium coatings on titanium washers VT1.0 and VT6.0, which are used for the manufacture of dental implants, has been developed. It is shown that with the help of this method it is possible to form coatings of pure titanium with a nano-structural surface relief. Based on SEM and AFM measurements of the surface morphology and this surface profile of relief, it is shown that titanium coatings have a nano-granular structure. The maximum surface irregularities lie within ± 150 nm, and the grain sizes vary from 50 nm to 450 nm.

It is shown that changing the sputtering conditions it is possible to deposit titanium coatings with different surface morphology.

It is established that titanium coatings allow not only to form a nano-relief surface with the required roughness, but also drastically reduce on this surface the concentration of such toxic elements as vanadium, aluminum, iron and carbon that are initially present in the material of the implant VT6.0.

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