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Specific Surface Morphological Properties of end Prostheses-implants Fabricated from Ti6Al4V Titanium Alloy

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ABSTRACT

Titanium alloys approved for clinical use are employed to fabricate various endoprostheses. The article concentrates on endoprostheses based on Ti6Al4V alloy, utilised inmaxillofacial surgery. Survival of anendoprosthesisis characterised bythe direct contact andfunctional connectionwith bothbone tissue (osseointegration),andsoft tissues (fibrointegration). The course of survivallargely depends on the properties of the surface of endoprosthesiscomponents;hence, the surface is treated to form a developedmicroreliefwithvalleys of optimum sizes and form. Sandblasting usingcorundumAl_2O_3 particles has been widely employed for treatment of surfaces.Chemical or electrochemical treatment of the surfaceof endoprosthesis components constitutes another popular process. An anatase-structured titanium dioxide (TiO_2)bioactive coating can further be applied on the surfaces of components to enhance the efficiency of fibro- and osseointegration. Experimental specimens made of Ti6Al4Valloy utilisingsandblasting orchemical or electrochemical treatment of the surface andintended for studyingfibro-andosseointegrationwith the use ofexperimental animals have been examined in the research. The surfaces of these specimens have been analysed by comparison employingscanning electron microscopy and roughness measurements. This has led to a conclusion that chemical and electrochemical etching methods ensuregreater uniformity and homogeneity of surface treatment in various sectionsof both individual specimens, and different specimens from one lot. However,the ultimate conclusion on advantages of a particular type of surface treatment will be drawn during *invitro*studies of specimens, implanted into the bone and soft tissues of test animals, and removedafter withdrawal of animals from the experiments.

KEYWORDS

Titanium Alloy, Endoprosthesis, Surface Treatment, Scanning Electron Microscopy, Stylus Profilometry.

Introduction

MostdentalimplantsproducedworldwidearefabricatedfromTi6Al4Vtitaniumalloy,approvedforclinicaluse,thathasanadequatecompromiseofbiocompatibility, corrosionresistanceandstrength [1].It is commonly supposed that osseointegration is the most acceptable type of interaction between implant and bone tissue, constituting an entire range of physiological responses, directly depending on the morphology of implant surface and its chemical composition [2-4].

Biopassivepropertiesof the surfaces of titanium alloys often impede the healing process after implanting,thus, the survival of implants mainly depends onthe properties of their surface [5-6].Development of various methods for modifying the surface of titanium-based implants is a way to solve this problem. Works [6,7] demonstrated thatbioactivepropertiesof a titanium implantcan be enhanced by applying a layer ofanatase-structured titanium dioxide on the implant surface, whatconverts the implant frombiocompatible into bioactive material. Greaterfibrointegration of titanium- and titanium alloy-based implants is achievedby the use ofwell-developed surfaces with optimally sized valleysfor spatial distribution of cells while in proliferation and for removal of waste products [8, 9]. Sandblasting withcorundum Al_2O_3 particles of sizesfromseveral tens to several hundreds of micrometres has been widely employed for surface treatment [7].Chemical or electrochemical treatment of the surface of titanium implants in various electrolyte-based solutions constitutes another popular process of surface modification.

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Materials and Methods

Polished titanium discs of 5mm diameter, 2mm thick were utilised as initial specimens. The surface of specimens was examined usingJSM-6480LVscanning electron microscope made by the JEOL company (Japan)in the mode of scanningsecondary electrons.

Surface roughness of implants was measured byStylus profilometer Alpha-Step IQ Surfaceprofiler ASIQ from the KLA-Tencor company (USA), that enables measurement of microroughness at up to 0.1nmresolution at both short, and up to 10mm scanning distances. Computer-assisted device control, analysis, and processing of the data acquired make it possible to reduce the influence of specimens' surface non-flatness andcurvature. The specimen surface roughness was determined as a complex of irregularities on the surface profile. To determine numerical values of the surface roughness parameters a "midline system" was employed, which corresponds to ISO recommendations and is accounted for in the Russian Federation GOST[1] [10].The profile surface roughness is evaluated quantitatively using such main parameters as:

Mean roughness (W_a), nm-an arithmetic mean of absolute values of the profile height deviationwithin the studied length$L$; $Wa = \frac{1}{L}\int_0^L |Z(x)|dx$.

Root-mean-square roughness (W_q), nm-a root-mean-square deviation in the profile heightwithin the studied length. This parameter corresponds to the standard deviation in the peak height distribution.

Maximum height of peaks (W_p), nm -the highest value of the peak height measured from the midlinewithin the studied length.

Maximum depth of valleys (W_v), nm - thehighest value of the valley depth measured from the midlinewithin the studied length.

Profile height (W_t), nm– a sum of the maximum peak height and the greatest valley depth, definedwithin the studied length.

Sandblasting Treatment

After sandblasting, the titanium surface becomes rough at a micro-level, and mechanical adhesion forcesserve to enhance the adhesion to biological tissues [11-14].

Sandblasting was performed in a stationary SCC[2]-type chamber. The surface of specimens was treated bycorundum $Al_2O_3$with grain size of several hundreds of microns.

Chemical and Electrochemical Treatments

There are publications, where the processes ofchemical and electrochemical titanium treatment are described, that make it possible to obtain ananoporous surfacewith a large surface area.[15-25].When layers of up to 1.5μm depth are formed, no degradation of mechanical propertiesoccurs. Taking into account the results from these works,the authorswere devisinga technology toreproducibly obtain the developed surface ofTi6Al4Vtitanium alloy specimens throughchemical and electrochemical treatment.

Prior to etching to remove organic impurities from the surface, Ti6Al4V titanium alloy specimens were degreasedthrough soaking in acetoneduring 10 min, then in isopropyl alcohol during 10 min. Chemical etchingwas performedin HF:C_2H_5OH solution in the ratio1:2 during 5minandin H_2SO_4+HF+DMF solution (where DMF – dimethylformamide) in theratio 10:1:9 during 5 minatthe temperature of 20°C.

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[1]the State Standard
[2]stationary cleaning chamber

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Electrochemical etching was carried out in the HF+DMF solution within 60min, in the mode of the constant current densityj of 35, 70, 105 and1495 mA/cm^{2}at thetemperature of 20°C.

Results and Discussion

The image of the original surface oftitanium discs, employed in the experiment, obtained byusing a scanning electron microscope (SEM), is presented in Fig.1.

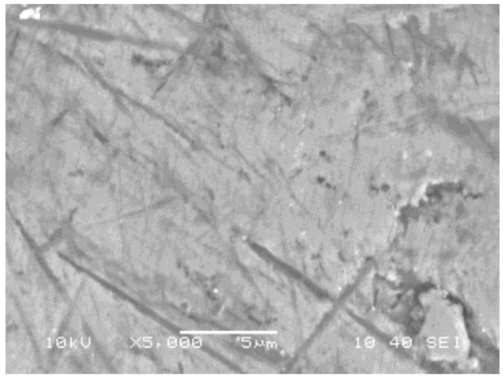

Fig. 1.SEM-image of the original surface oftitanium alloy disks used in the experiment

SEM-imageof the Ti6Al4V specimen surface after sandblasting is presented in Fig.2.

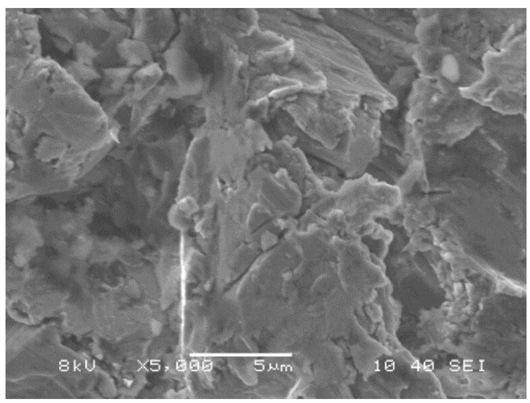

Fig.2.SEM-image of the Ti6Al4V titanium alloy specimen surface after sandblasting

The results of measuring roughness parameters of two specimens Nos.1 and 2after sandblasting are summarized in Table 1.

Table 1. Roughness parameters of Ti6Al4V specimens after sandblasting treatment

Roughness parameters	**Specimen No.1**		**Specimen No.2**	
	Parameter spread [nm]	Parameter spread [%]	Parameter spread [nm]	Parameter spread [%]
Wa	330-471	43	484-537	11
Wq	627-683	9	641-654	2
Wp	2181-2633	21	2030-2290	13
Wv	1668-1980	19	1772-2037	15
Wt	4096-4301	5	3927-4327	10

As judged from roughness parameters of Ti6Al4V specimens aftersandblasting treatment, presentedinTable 1, a significant spread of roughness parameters is seen by three points of each specimen (e.g., WaspreadoverthesurfaceofspecimenNo.1 reaches 43%), what demonstrates a considerable treatment inhomogeneity throughout the surface.The difference in spreadsofroughnessparametersinherenttospecimensNos.1 and 2 inabsolute

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values (nm) andin percentage termsreflects the difference in the quality of surface treatment for specimens from one lot.

SEM-images of Ti6Al4V specimen surface after chemical etching are shown in Fig.3, 4.

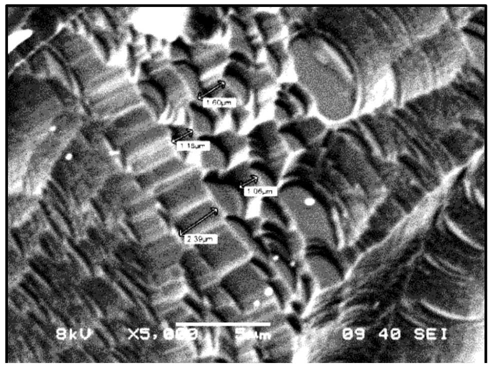

Fig.3.SEM-image of Ti6Al4V titanium alloy specimen surface after chemical etching in HF: C_2H_5OH solution in theratio 1:2 during 5 min

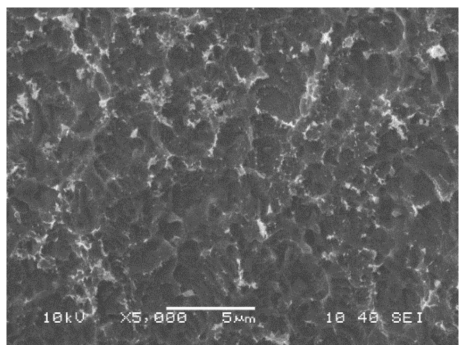

Fig.4.SEM-imageof Ti6Al4V titanium alloy specimen surface after chemical etching in H_2SO_4 + HF + DMF solution in the ratio 10:1:10during 10min

Examination ofSEM-images of Ti6Al4V titanium alloy specimen surface after chemical etching (Fig.3,4) shows thatno porous layer is formed in the course ofchemical etching irrespective of process parameters.Etchingtakes placealong grain boundaries, andthe depth of etching therewith depends on the etching time.

SEM-images of Ti6Al4V titanium alloy specimen surface after electrochemical etching are shown in Fig. 5-7.

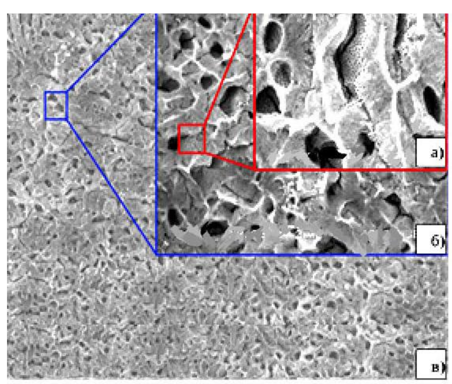

Fig.5. SEM-image of Ti6Al4V titanium alloy specimen surface after electrochemical etching during 60 min, in HF: DMF (1:10) solution, current density 70 mA/cm2.
a)magnification 25000x; b) magnification 8000x, c) magnification 2000x

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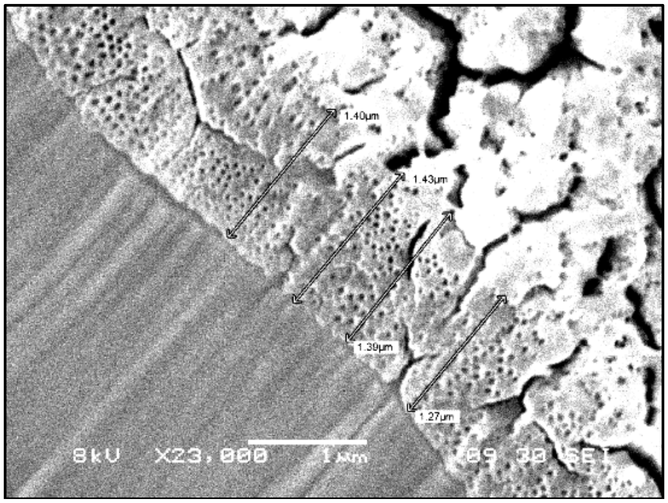

Fig. 6. SEM-image ofspecimen surface after electrochemical etching in HF solution: DMFA (1:10) within 60 min, current density 35 mA/cm^2. Magnification 23000x

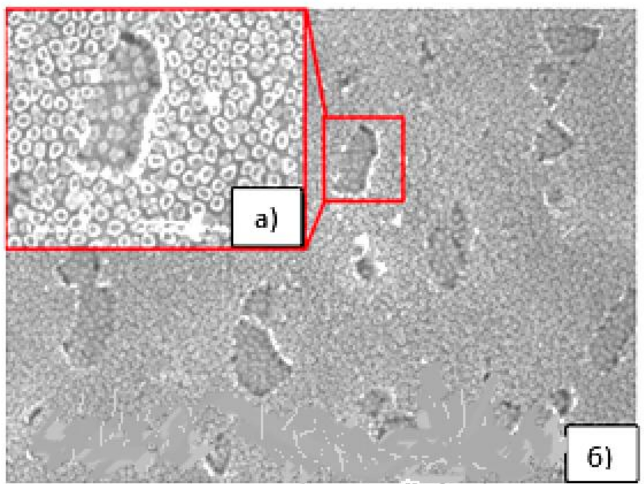

Fig.7. SEM-image of specimen surface afterelectrochemical etching during 60min, in HF solution: DMF (1:10), current density 105 mA/cm2. a) magnification10 000x, b) magnification 40 000x

SEM-images of Ti6Al4V specimen surface after electrochemical etching show that etching occurshomogeneously throughout the entire surface of the specimen. Ti6Al4V is a two-phase alloy with αandβphases. α-phasecontains aluminium, β-phasecontainsvanadium. It has been found that theβ-phase etching rateis higher than that for theα-phase. It is apparent that no pores are formed when etching takes place in the α-phase. Pores are formed only in theβ-phase (Fig.5b). A preliminary estimate has shown thatthe average diameter of pores in the formed porous structure amounts to dcp=0.07 µm. In etching direction throughout the surface of pits, there are pores formed due to the β-phase etching. The cracks resulting from etching are also seen along grain boundaries (Fig.6).

As the current density increases further, a process of specimen surface polishing predominates, when bothβ-phaseand α-phase etching occurs, what causes an extreme thinning of specimens (Fig.7a, 7b).

Roughness parameters of Ti6Al4V specimens after electrochemical treatment are presented inTable 2. Measurements were made by three points on each specimen. Specimen No.1 corresponds toFig.5, specimen No.2 – to Fig. 6.

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Table 2. Roughness parameters of Ti6Al4V specimens after electrochemical treatment

Roughness parameters	**Specimen No.1**		**Specimen No.2**	
	Parameter spread [nm]	Parameter spread [%]	Parameter spread [nm]	Parameter spread [%]
Wa	698-703	0.7	822-845	2.8
Wq	769-781	1.6	937-951	1.5
Wp	1157-1180	2.0	1533-1547	0.9
Wv	1188-1193	0.4	1435-1472	2.6
Wt	2345-2368	1.0	2967-2980	0.4

Angle laps to make a depth-wise analysis of the surface structure profile were formed usinga focused ionic rayinthe StrataFIB 205 (FEI Company, Netherlands) installation.The thickness of porous layer is h=1 μm. Pores are seen to form through the whole depth;the profile analysis provides reasonto statethat poresare cylinder-shaped of uniform diameter (Fig.5).

Fig.8 presentsa SEM-image ofthe Ti6Al4V specimen surface after chemical etchingduring 10minin H_2SO_4+HF+DMF solution in the ratio 10:1:10 and subsequent electrochemical etchingduring 60min, in HF: DMF (1:10) solution at the current density of 35mA/cm^2.

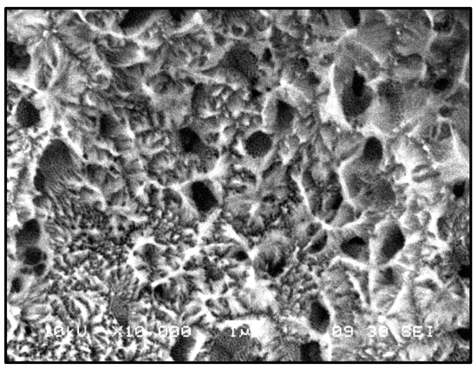

Fig.8. SEM-image oftheTi6Al4V specimen surface after chemical etching and subsequentelectrochemical etching. Magnification10 000x

As viewed in Fig.4-8, a combination ofchemical andelectrochemical etching enables formation ofthe most ramified surface, what beneficially effectsadequatelyrunningfibro- andosseointegration processes.

Conclusion

Different methods for forming a developed titanium surface through sandblasting, chemical and electrochemical etching were examined. A comparative analysis of the obtained results was performed by use of scanning electron microscopy and surface roughness measurements. The employed methods for modifying the surface of titanium alloys make it possible to changeroughness parameters andmorphological characteristics of the surfaceover a wide range and at ahighreproducibility of results. The final conclusion on advantages of a particular type of surface treatment will be drawn while studying*invitro*the specimens, inserted into the bone or soft tissuesof test animals,and removed after withdrawal of animals from the experiments. It makes a particular methodology of structuring the surface appropriate for creating endoprostheses based on titanium alloys.

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