THE STUDY OF THE OXIDE COATING EFFECT ON BONE–IMPLANT INTERFACE FORMATION BY MEANS OF ELECTRON MICROSCOPY METHOD WITH ENERGY DISPERSIVE X-RAY ANALYSIS

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The experimental results of the measurement of the tissue constituent elements distribution, as well as impurity elements in the tissues around a Ti-implant with protective TiO_2 oxide coating are presented. Study of morphology, qualitative and quantitative analysis were carried out by means of scanning electron microscopy method with energy dispersive X-ray analysis. The results show weak migration of Ti into the bone tissue near the interface and protective role of the oxide coatings.
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1. INTRODUCTION

Metal orthopedic implants have been applied widely and successfully for various types of bone reconstructions [1]. Titanium and its alloys show excellent biocompatibility, good implant fixation due to the surface oxide, high degree of mechanical strength and corrosion resistance [2]. TiO_2 titanium dioxide is widely used in biomedical application because its high blood compatibility and negative surface charge in physiological solution [3]. Surface treatments such as anodic oxidation, thermal vacuum deposition, chemical vapor deposition, plasma spraying and magnetron sputtering are commonly employed to modify surface properties and enhance interaction between implants and adjacent tissues [4]. The implant material degradation and metal ion dissolution from the metal materials remains the major factor limiting the longevity of total joint replacements [2]. Since interaction between tissues and titanium implants occurred at their interfaces, protective characteristics of titanium should be essential [5,6]. That is, the key factors should involve properties of surface TiO_2 films and their change in biological environment. The protective properties of Ti based materials and oxide coatings play the most important role because of their ability to prevent the detrimental element penetration to surrounding bone tissue on the bone - implant interface [7].

2. MATERIALS AND METHODS

The electrochemical treatment of titanium samples in salt solution of disubstitited sodium sulphate medium at different stabilize voltage values from 10 to 100 V in DC regime was made.

The structural and morphological properties of the interface bone-implant and diffusion of elements into the bone tissue were characterized by the scanning electron microscope REMMA-102, equipped with the multichannel wave-dispersive and energy dispersive X-ray spectrometers manufactured by JSC “SELMI” (Sumy, Ukraine). The X-ray energy dispersive spectrometer, equipped with the semi-conductor Si (Li) detector, had the power resolution 200 eV. The accelerating voltage for an electronic probe was 20 kV, when the current of the probe was 3 nA. The time of the spectrum acquisition in each point was 200 seconds.

To prevent the accumulation of surface electrostatic charge, during electron probe microanalysis, the sample was covered with thin layer of aluminum in the special vacuum equipment.

The Ti holders with investigated coatings were implanted in medial surface of the proximal metaphyse of rabbit cannon bone. The samples were extracted after the implantation into the bone during four months tests duration. The reparative regeneration of the bone tissue and focal reaction of connective tissue under the condition of bone defect reparation by means of Ti implant with oxide coating *in vivo* test was observed.

The content of base elements of substrate material and coating in bone tissue and the weight ratio Ca/P in the bone zone near the interface was measured (see Table).

Quantities of Ti, P, Ca on the interface bone tissue - implant (obtained by using X-ray microanalysis) in areas of analysis (1-4) (see Fig. 1)

	P	Ca	Ti	Ca/P, weight,%	Ca/P, at.,%
1	3,7644	7,6524	0	2,03329	1,572051
2	3,2062	6,8926	0,0242	2,14969	1,662046
3	2,0606	4,2082	0,043	2,042342	1,579049
4	4,3094	9,0894	0,0302	2,109264	1,63079

3. RESULTS AND DISCUSSION

In the present study the qualitative and quantitative analysis of the interface bone-implant and material degradation degree estimation were made. The sample was titanium implant, with protective oxide coating TiO_2, deposited by electrochemical method in salt solution of disubstitited sodium sulphate medium at potential 70V. It was extracted after the implantation into the cannon bone of rabbits in vivo test.

The place of tight contact of the implant with the bone tissue and the horizontal area of bone tissue under Ti-implant were selected for study by scanning electron microscopy. The obtained micrograph of the bone tissue, which formed in cavities and convexities of implant is given below (Fig. 1).

In the Fig. 1 we marked the points of analyses which were studied at magnification x500 and accelerating voltage 20 kV.

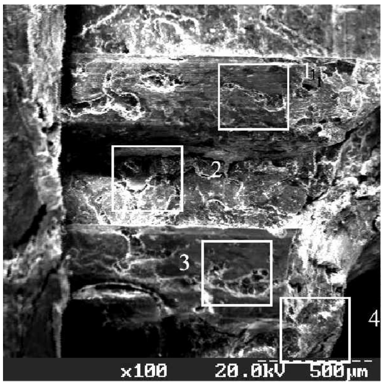

Fig.1. Micrograph of the area of bone tissue which was in tight contact with the Ti implant

Micrographs which show morphology of the bone tissue under the Ti-implant are given in the Fig. 2 (a-d).

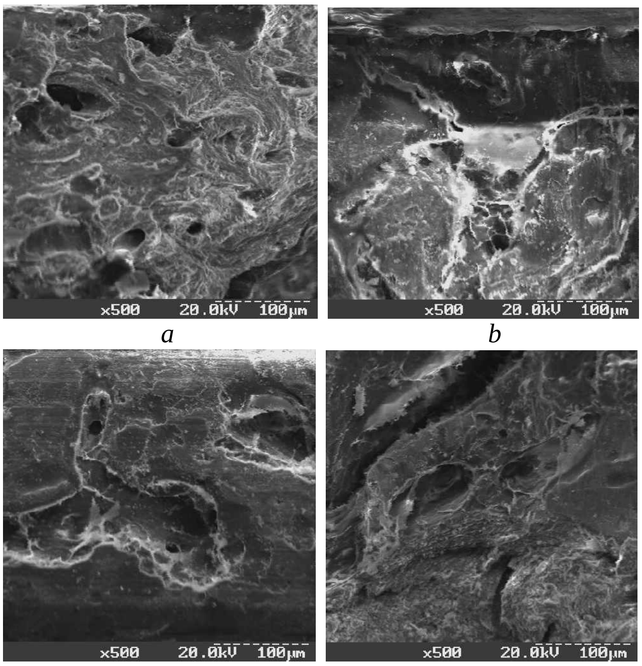

Fig.2. Micrographs of bone tissue horizontal surface which was under Ti-implant obtained at magnification x500: (a, b)1 and 2 points of analyses; (c, d) 3 and 4 points of analyses

The reaction of the living tissue on the introduced implant was estimated by Ca/P ratio in the bone tissue. X-ray microanalysis was carried out using SEM (REMMA-102) with x-ray analyzer.

The results of the qualitative and quantitative analysis are given in the Table above. The concentration of elements was calculated directly from the spectrum.

The obtained results show, that quantity of Ti is rather small, close to the detection limit of device. The weight ratio Ca/P (1,9-2,03) which is typical for HA (hydroxyapatite) observed in the bone zone near the interface region correlate with the ratio for the real bone.

As it is shown at the graph in Fig. 3, first three points were at the surface of implant, where content of Ti was maximal but there was no Ca and P. Then, at the fourth point the quantity of Ti decreases (interface implant-bone tissue), but the quantity of Ca and P increases greatly (which connected with the bone tissue formation). Further, the concentrations of this elements are nearly at the same level.

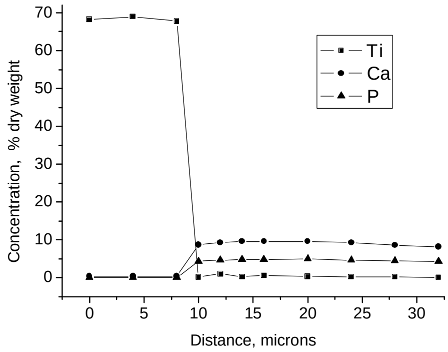

Fig. 3. The Ti, Ca, P concentrations depending on the distance in the zone implant-bone

In the Fig. 4, the Ti concentration at the distances more than 10 μm from the implants are given in the narrower concentration range.

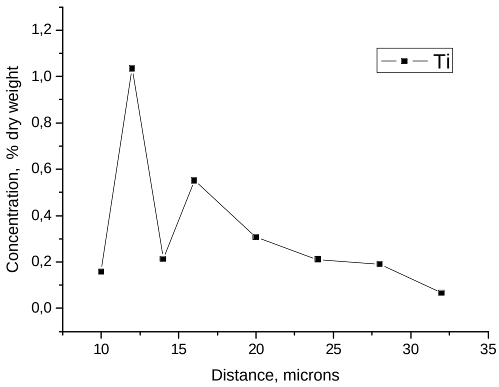

Fig. 4. Dependence Ti concentration (% dry weight) on distance (microns)

At the distance of 10 μm from implant concentration of Ti is low, which is related with the loss of electron beam in the connective tissue. At the points 10, 12, 14 we can see the sudden change of Ti concentration. It could be explained by the presence of connective tissue, in which the distribution of Ti is irregular. At the rest of the points the concentration of Ti gradually decreases with the increase of the distance from the implant.

4. CONCLUSIONS

1. The results show the weak migration of Ti into the bone tissue near the interface. Also, the normal weight ratio Ca/P (1,9-2,03) which is typical for HA (hydroxylapatite) was observed in bone zone near the interface region.
2. These data suggest the major importance of oxide coating deposition for further implant biocompatibility, ingrowth and osteointegration. The oxide coatings form the reliable barrier to the toxicity of metal ion dissolution and keep the normal ratio Ca/P in zone near the bone-implant interface.

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ИССЛЕДОВАНИЕ ВЛИЯНИЯ ОКСИДНОГО ПОКРЫТИЯ НА ФОРМИРОВАНИЕ ИНТЕРФЕЙСА КОСТЬ-ИМПЛАНТ-МЕТОДОМ СКАНИРУЮЩЕЙ ЭЛЕКТРОННОЙ МИКРОСКОПИИ С РЕНТГЕНОСПЕКТРАЛЬНЫМ МИКРОАНАЛИЗАТОРОМ

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Представлены экспериментальные результаты исследования распределения элементов, составляющих костную ткань и примесей элементов в тканях вокруг титанового имплантата с защитным покрытием TiO_2. Изучение морфологии, количественный и качественный анализ проводили с помощью метода сканирующей электронной микроскопии с рентгеновским микроанализом. Результаты показали слабую миграцию титана в костную ткань возле интерфейса и биосовместимость оксидных покрытий.

ДОСЛІДЖЕННЯ ВПЛИВУ ОКСИДНОГО ПОКРИТТЯ НА ФОРМУВАННЯ ІНТЕРФЕЙСУ КІСТЬ-ІМПЛАНТАТ МЕТОДОМ СКАНУЮЧОЇ ЕЛЕКТРОННОЇ МІКРОСКОПІЇ З РЕНТГЕНОСПЕКТРАЛЬНИМ МІКРОАНАЛІЗАТОРОМ

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Представлено експериментальні результати дослідження розподілу елементів, що входять до складу кісткової тканини та слідів елементів у тканинах навколо титанового імплантату з захисним покриттям TiO_2. Дослідження морфології, кількісний та якісний аналіз проводили за допомогою методу скануючої електронної мікроскопії з рентгенівським мікроаналізом. Результати показали слабку міграцію титану в кісткову тканину біля інтерфейсу та біосумісність оксидних покриттів.