THE BIOMEDICAL APPLICATION AND CORROSION PROPERTIES OF IMPLANTED MATERIALS WITH PROTECTIVE COATINGS

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For purposes of orthopedic and trauma surgery operations various stems, spokes, screws, pins made of pure metal and alloys are widely applied. As a result of metal materials using the problems of the patient organism protection from deleterious effects of metallogenic and electrochemical reactions, metal toxicosis – complications, connected with metal ion effect on organism, arise. The present study is devoted to realization of the comparative analysis of corrosion properties of modern implanted materials and coatings in simulated body fluid and their long-term behaviour in animate organism.

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1. INTRODUCTION

Annually in the world needs for operations, concerned with traumas of a spine, hip, femoral and knee joints, ligaments and sinews, and also maxillofacial defects will increase. The number of the patients requiring for replacement worn out or defective ligaments, joints, skeleton and support-motor system elements by implants constantly grows [1,2,3,4]. The problem of characteristics advancing of existed prosthesis is very actual, because in the case of damage of artificial limbs there is a great necessity for repeated operations (their probability in Europe makes to 10 %, depending on a type of a used artificial prosthesis [5]).

The special problems arise at application of pure metal materials and alloys widely used in modern medical practice as stems, spokes, screws, pins. As a result of their application the various medical complications are observed: allergic reactions, metallogenic and electrochemical reactions, metal toxicosis. Thus the important role play not only local reaction immediately in a direct contact zone of prosthesis[6], but also common organism reaction on a used material. The coating deposition allows to improve the performances of implants and to prolong term of their effective application in the patient organism [2,7].

2. EXPERIMENTAL TECHNIQUE

The aim of present study was the investigation of corrosion resistance properties of implanted materials with functional coatings in the artificial isotonic physiological solution. The coatings were deposited by means of Arc PVD Methods [8,9]. The main process parameters were as follows: the cathode material –Ti, Zr; substrate materials - stainless steel (Fe –60%, Ni – 18%, Cr – 12%, Ti – 10%) with coatings – Ti; Zr; TiN; ZrN and NiTi (Ti – 48,5%, Ni- 48,5%, and impurities Fe, Mo) with coatings Ti; Z; reactive atmosphere –N_2, deposition pressure - $8\cdot10^{-2}$Pa, arc current – 100A, substrate bias – 150V, deposition temperature T=593°K, the thickness of deposited coatings was 7-10 μm depending on coating type.

3. CORROSION TESTS

The corrosion resistance tests were made by electrochemical test methods. The electrolyte was artificial physiological solution – 0,9% NaCl isotonic solution (pH=6,0) at room temperature. The test duration was 6h up to equilibrium potential stabilization . Corrosion behaviour was appreciated by measuring the changes of corrosion current depending on corrosion potential (anodic curve) for various types of coatings (Fig.1).

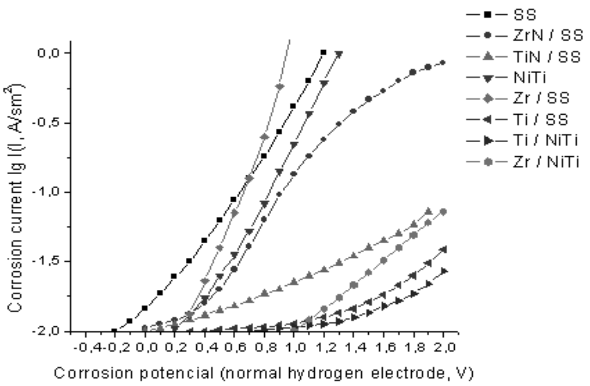


Fig.1. Corrosion current depending on corrosion potential for various types of coating (Ti, Zr, TiN, ZrN) on the stainless steel (SS) samples and Ti, Zr on the titanium nickelide (NiTi) in 0,9% NaCl isotonic solution (pH=6,0)

4. BIOLOGICAL ASPECTS

At the same time, the cylindrical shape implants (length - 2,6mm and diameter -1,3mm) of various composition were inculcated in distal part of rat femoral bone (white rat, male, Vister line).The test duration was 4 months. The analysis of biochemical components of blood serum, local and common metabolic organism reaction (glycoproteins, chondroitinsulphates, common proteins level, contents of creatinine and others) on various material implantation was carried out.

5. EMISSION SPECTROSCOPY ANALYSIS

The content of microelements (ME) in the bone, liver and kidneys tissue was measured by means of emission spectroscopy and X-ray radiometric analysis methods.

Elemental probe analysis was carried out by means of coal electrode in DC arc. The test duration was 60 s, current strength 18-20 A. Spectrum fixation was carried out by means of optical devices and analyzed by computer program for elements concentration depending on spectrum lines intensity.

At the same time some probe part was analyzed by means of X- ray radiometric analysis method. The comparison of results allow to detect small amount of Cd in animate liver and presents of Mo, Ba in bone tissue.

The contents of base elements of substrate materials and coatings (Fe, Ti, Ni, Zr) and some impurities in bone, liver tissue were shown (Fig.2)

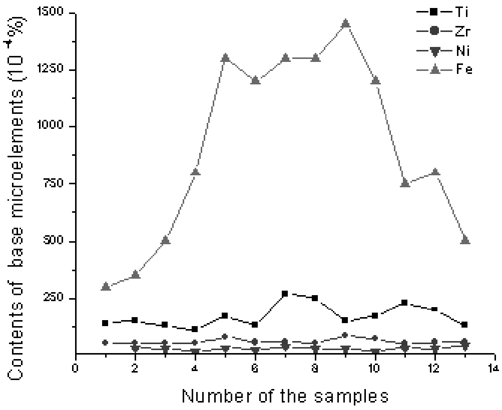


Fig.2. Contents of base microelements in the liver for various types of coatings (the samples number: 1-4– Ti / SS, 5,6 – Zr / SS, 7,8 – TiN / SS, 9,10- ZrN /SS, 11,12 –Ti / NiTi, 13,14 Zr / NiTi)

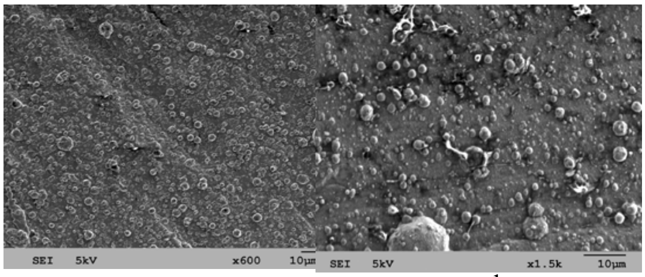
6. SURFACE MORPHOLOGY

The surface morphology was observed by means of JSM-840 scanning microscope.

The research of character of surface modification for samples with: a) pre-deposited coatings Zr/SS, Ti/SS, ZrN/SS, TiN/SS, Ti/NiTi, Zr/NiTi; b) the same coatings after 4 months in animate organism; c) the same coatings after corrosion test was carried out (Fig.3)

7. RESULTS AND DISCUSSION

The analysis of the obtained results shows, that most active corrosion behaviour in isotonic 0,9 % NaCl solution demonstrates SS, NiTi, Zr/SS according to corrosion curves. The intermediate position is taken by coatings ZrN/SS and TiN/SS. The coatings of Zr/NiTi, Ti/NiTi, Ti/SS behave the most inertially in simulated body fluid solution (Fig.1). And though the base materials SS, NiTi are active enough, they can demonstrate the different behaviour with various types of coatings.



a b

Fig. 3. The surface structure of the samples with coatings Ti / SS: a)pre-deposited, b) 4 months after implantation

At the biological tests the distinction of metabolites level (level of common proteins, sum of proteins fractions of blood serum, glycoproteins, chondroitinsulphates and so on) depending on implant type and coating composition was observed. The best results (minimum metabolic organism reaction) and the minimum figures were recorded in a case of coatings Ti/SS, TiN/SS, Ti/NiTi . The maximum figures demonstrated the samples Zr/SS, ZrN/SS.

Based on the data of the emission spectroscopic analysis and results of the X-ray radiometric analysis of a bone, kidneys and liver animal tissue it is possible to note the specialities of base microelements migration from a sample and coating to a tissue of animate organism. The Fe level is the highest in groups, where the basic sample was stainless steel. The coatings Ti/ SS and ZrN/SS were the best prevention from Fe penetration in a tissues of interior organs. The coatings Zr/SS and TiN/ SS worse all prevent from element penetration. Ni and Zr feeblly migrate in organism tissues for various type of coatings. The greatest migration Ti was observed in case of TiN/SS and Ti/NiTi coatings, and to a lesser degree for a coatings Ti/ SS.(Fig.2)

The similar dependencies were observed in the case of not base microelements, such as Cr, Mn, Si- maximum figures in a case of Zr / SS, TiN/ SS , and minimum in a case of ZrN / SS, Ti/ SS, Ti/ NiTi coatings.

Thus samples from stainless steel with a coating Zr/SS demonstrate more aggressively behaviour , then samples ZrN/SS and TiN/SS which possess intermediate character and the most reliable organism protection demonstrate Ti/SS, Ti/NiTi, Zr/NiTi coatings, according to the data obtained from the analysis of corrosion curves (Fig.1).

CONCLUSIONS

The corrosion resistance characteristics of implanted materials play the most important role because of their ability to prevent from the detrimental element penetra-tion to both surrounded bone tissue and patient internal organs.

The results were shown the existence of some correlation between corrosion resistance of various metal and coating materials and their behavior in organism. The corrosion properties of the system metal – coating depend strongly on electrochemical properties of both components (SS - Ti/SS, NiTi – Zr, Ti/NiTi).

It is possible to assume, that the microelements which are included in a composition of implants and coatings, migrate to neighboring tissues (bone, for example) and further with a blood current penetrate to a tissue of interior organs performing function of toxin neutralization.

The using of corrosion resistance tests allow to make some preliminary prognosis and estimation of degree of common metabolic organism reaction on implantation.

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БИОМЕДИЦИНСКОЕ ПРИМЕНЕНИЕ И КОРРОЗИОННЫЕ СВОЙСТВА ИМПЛАНТАЦИОННЫХ МАТЕРИАЛОВ С ЗАЩИТНЫМИ ПОКРЫТИЯМИ

А.В. Зыкова, В.В. Лукъянченко, В.И. Сафонов

В настоящее время различные изделия из металлов и сплавов широко применяются в современной ортопедии и травматологии. В результате использования металлических материалов возникает проблема защиты организма от электрохимических реакций, токсикозов и других осложнений, связанных с негативным воздействием металлических ионов на организм пациента. В работе проведен сравнительный анализ коррозионных характеристик современных имплантационных материалов и покрытий в физиологическом растворе и их последующего поведения в живом организме.

БІОМЕДИЧНЕ ЗАСТОСУВАННЯ ТА КОРОЗІЙНІ ВЛАСТИВОСТІ ІМПЛАНТАЦІЙНИХ МАТЕРІАЛІВ З ЗАХИСНИМИ ПОКРИТТЯМИ

Г.В. Зикова, В.В. Лук'янченко, В.Й. Сафонов

В даний час різні вироби з металів і сплавів широко застосовуються в сучасній ортопедії і травматології. У результаті використання металевих матеріалів виникає проблема захисту організму від електрохімічних реакцій, токсикозів і інших ускладнень, зв'язаних з негативним впливом металевих іонів на організм пацієнта. У роботі проведений порівняльний аналіз корозійних характеристик сучасних імплантаційних матеріалів і покрить у фізіологічному розчині і їхньому наступному поводженні в живому організмі.