Study of the physicochemical properties of the biomedical composite material "Ti-Nb-Ta-Zr with a surface polymer layer"

E O Nasakina1,2, T M Sevostyanova4, A G Alexandrova1, M A Kaplan1, A A Kolmakova1,5, M A Sudarchikova1, K V Sergienko1, O G Kuznetsova1, D A Novikova1, L A Shatova3, A S Baikin1

1Baikov Institute of Metallurgy and Material Sciences, 49 Leninsky Avenue, Moscow, Russia
2All-Russian Research Institute of Phytopatology, Bol’shie Vyazemy, Moscow region, Russian Federation
3Voronezh State Technical University, st. 20-letiya Oktyabrya, 84/4, Voronezh, Russia
4Pirogov Russian National Research Medical University (Pirogov Medical University)
5N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky Pr., Moscow, 119991, Russian Federation

Corresponding author’s e-mail: nacakina@mail.ru

Abstract. A comprehensive study of the physicochemical properties of the created biomedical composite material "Ti-Nb-Ta-Zr with a surface polymer layer" was carried out. The polymer film does not in any way affect the radiopacity of the base material. All materials obtained are radiopaque. X-ray diffraction analysis of polyglycolide lactide (PGLA) samples with molecular weights of 45, 90, 180 kDa showed that the polymers have a completely amorphous structure. On samples with a 40-μm-thick PLA-based coating bare-metal zones are observed, which substantiate anode effects in the potential range of more than 1000 mV.

1. Introduction

Obtaining functional materials is impossible without studying their properties. For the biomedical composite material "Ti-Nb-Ta-Zr with a surface polymer layer", in addition to mechanical parameters and the direct biological response of the body, such performance properties as radiopacity, coating integrity, etc. are important. The basis of this layered composite, represented by a nickel-free alloy, is responsible for the purity characteristic. shape memory, which is a promising replacement for alloys of the NiTi system, surpassing all analogs in biomechanical compatibility (superelasticity, low Young's modulus, delayed response to action), but much inferior in terms of corrosion resistance and biological inertness [1–13]. However, the question arises of shielding X-rays by the surface layer. The polymer component is introduced into the composition of the composite as a carrier of drugs for local therapeutic action; therefore, its structural homogeneity is extremely important.
2. Materials and methods
Composite material from a Ti-Nb-Ta-Zr alloy with a biodegradable surface layer based on biopolymers of various molar mass and concentration was obtained according to the following scheme: chloroform with a volume of 200 ml in a flask with a volume of 500 ml was heated to 80 °C on a magnetic stirrer, 2 g of polylactide or poly (glycolide-lactide) was homogeneously dissolved in chloroform at 80 °C for 1 hour with constant stirring using an electronic overhead stirrer; the resulting homogeneous solution was mixed with the drug in the amount required to obtain 1 (for heparin), 2 (for streptokinase)% solutions, at a solution temperature of 30 °C; The resulting homogeneous solution was dipped at a rate of immersion and extraction of 5 mm/s on a wire made of Ti-Nb-Ta-Zr alloy with a diameter of 280 μm after final processing, washing in alcohol, distilled water, and drying. The obtained samples were dried in a thermostat at 37 °C for 48 hours.

The structure of the obtained samples was investigated on a Tescan VEGA II scanning electron microscope. To study the morphology of particles in a raster mode, the samples were glued to a copper substrate using a conductive carbon glue, and a layer of carbon or gold was sprayed on them (Univex300 sputtering devices - Leybold, Germany; Fine Coat - JEOL, Japan).

The evaluation of the linear attenuation coefficient by the flaw detection method (GOST 20426-82) to determine the radiopacity was carried out by obtaining a contrast image using a transmission X-ray apparatus and matrix detectors.

The study of the integrity of the polymer coating of composite materials was carried out by the method of cyclic voltammetry (CV) in a standard electrochemical cell using an IPC-Pro universal potentiostat. The potential sweep rate was 10 mV/s. Saline 0.9% NaCl at 20 °C served as the electrolyte. Determination of the corrosion parameters (stationary potential, breakdown and repassivation potentials) was carried out according to the methods according to GOST R ISO 10993-15-2009. The working electrodes were studied samples of composite material made of Ti-20Nb-10Ta-5Zr alloy (wire with a diameter of 280 μm) coated with PLGA with different thicknesses (40 and 120 μm), as well as samples of Ti-20Nb-10Ta-5Zr alloy in the form of a wire with a diameter of 280 μm as reference samples. A glass-graphite annular counter electrode was used as an auxiliary one; a saturated silver chloride electrode was used as a reference electrode. The surface of the samples of the Ti-20Nb-10Ta-5Zr alloy was treated with ethyl alcohol and washed with distilled water before the experiments. CV scanning was started with a potential of -1.40 V and was carried out until a current strength of no more than 5 mA / cm2 was reached, based on the recommendations of GOST R ISO 10993-15-2009. Scanning in the opposite direction was carried out up to the value of the repassivation potential. The current density was measured in mA/cm².

To determine the crystallinity of the polymer, the method of X-ray structural analysis was used. X-ray diffraction analysis was carried out on a Rigaku Ultima IV diffractometer. Samples of polyglycolide lactide (PGLA) with molecular weights of 45, 90, 180 kDa were selected for analysis.

3. Results and discussion
It can be noted that the surface structure of the obtained samples as a whole did not differ from the surface structure of model polymer films with an injected drug investigated at the previous stage of the project, which indicates the continuity of the results. The structure is homogeneous, dense, without significant defects, drugs are visible in the form of inclusions and are distributed fairly evenly. The basis of the composite materials - wire made of Ti-Nb-Ta-Zr alloy - is completely coated. The thickness of the obtained surface polymer layer with the introduced drug after single dipping was about 30-40 microns, depending on the type of coating. Examples of images of the surface of composite materials are shown in Figures 1-2. It should be noted that the polymer film does not affect the radiopacity of the base material in any way.

Figure 3a shows a cyclic voltammogram of a composite material made of Ti-20Nb-10Ta-5Zr alloy with a PLGA-based coating 120 μm thick. It can be seen that, in a wide potential range, the electrode currents are close to zero, which may be due to the absence of electrochemical reactions due to the deposition of a thick layer of the PLGA-based coating. With a decrease in the thickness of the coating...
applied to the alloy, anodic effects are observed in the potential range of more than 1000 mV (Figure 3b), corresponding to the breakdown and repassivation potentials of the alloy under study (Figure 3c).

The samples after electrochemical tests were examined on a scanning electron microscope to assess the effect of the process on the polymer coating of the composite material. Figure 4a shows an image of a sample of a composite material made of Ti-20Nb-10Ta-5Zr alloy with a PLGA-based coating 120 µm thick after electrochemical tests. Polymer coating without disturbances, dense, homogeneous, which corresponds to the data of voltammograms. On samples with a thinner coating (composite material made of Ti-20Nb-10Ta-5Zr alloy with a 40-µm-thick PLGA-based coating), we can observe bare-metal zones substantiating anode effects in the potential range of more than 1000 mV (Figure 4b).

Since the lactic acid molecule contains a chiral carbon atom, there are three stereoisomers of the cyclic dimer of lactic acid, or lactide: L-lactide, D-lactide, and meso-lactide. A racemic mixture of L- and D-lactides is designated as D,L-lactide. Polymer D,L-lactide, and meso-lactide (PDLA) are completely amorphous because their chains consist of randomly alternating L-lactide and D-lactide units. Polyglycolide lactide obtained by polymerization of L-lactide or D-lactide is a partially crystalline polymer with a degree of crystallinity up to 60%.

The method of X-ray structural analysis is based on the analysis of the diffraction pattern obtained by scattering of electromagnetic X-ray (λ ∼ 0.1 nm) radiation by scattering centers - electron shells of atoms. The method of X-ray structural analysis makes it possible to unambiguously determine all the details of the crystal structure (coordinates of atoms, bond lengths, bond angles, etc.). Polymers are studied by low angle x-ray. This method is widely used to determine the degree of crystallinity of polymers, which is understood as the ratio of the total scattering of crystallites to the total scattering from amorphous and crystalline regions. For this, the scattering intensity curves for an amorphous reference sample, a crystalline reference sample, and a polymer sample with unknown crystallinity are examined separately.

The application of this method of analysis to the study of the structure of polymers is complicated by the fact that the polymer usually consists of crystalline regions distributed in the mass of an amorphous substance, which leads to obtaining X-ray diffraction patterns of a crystalline substance against a broad blurred background. By analyzing such an x-ray, you can determine the percentage of the crystalline phase. From the diagrams in Figure 5, it was determined that the polymers have a completely amorphous structure.

![Figure 1. SEM image of a composite material made of Ti-Nb-Ta-Zr alloy with a biodegradable surface layer based on PGLA 30/70 (molecular weight: a) 90 kDa, b) 180 kDa with introduced heparin 1%](image-url)
Figure 2. SEM image of a composite material made of Ti-Nb-Ta-Zr alloy with a biodegradable surface layer based on PGLA 30/70 (molecular weight: a) 90 kDa, b) 180 kDa with introduced streptokinase 2%.

Figure 3. Cyclic voltammograms of the test samples in 0.9% NaCl solution at a temperature of 20 °C: a - composite material made of Ti-20Nb-10Ta-5Zr alloy with a coating based on PLGA 120 μm thick, b - composite material made of Ti-20Nb alloy -10Ta-5Zr coated PLGA 40 μm thick, c - alloy Ti-20Nb-10Ta-5Zr.
Figure 4. SEM images of the surface of the studied samples after electrochemical tests: a - composite material made of Ti-20Nb-10Ta-5Zr alloy with a coating based on PLGA with a thickness of 120 μm, b - composite material made of Ti-20Nb-10Ta-5Zr alloy with a coating based on PLGA with a thickness 40 μm.

Figure 5. SEM image of a composite material with tantalum and titanium surface layers.

4. Conclusions
In the course of the research, a comprehensive study of the physicochemical properties of the created biomedical composite material "Ti-Nb-Ta-Zr with a surface polymer layer" was carried out. The polymer film does not in any way affect the radiopacity of the base material. All materials obtained are radiopaque.
X-ray diffraction analysis of polyglycolide lactide (PGLA) samples with molecular weights of 45, 90, 180 kDa showed that the polymers have a completely amorphous structure.

In a wide range of potentials, electrode currents are close to zero when a thick coating layer based on PGLA is deposited, which may be due to the absence of electrochemical reactions. With a decrease in the thickness of the coating applied to the alloy, anode effects are observed in the potential range of more than 1000 mV, corresponding to the breakdown and repassivation potentials of the alloy under study. The polymer coating of the composite material made of Ti-20Nb-10Ta-5Zr alloy with a thickness of 120 μm after electrochemical tests without disturbances, is dense, homogeneous, which corresponds to the data of voltammograms. On samples with a thinner coating (composite material made of a Ti-20Nb-10Ta-5Zr alloy with a 40-μm-thick PLA-based coating), bare-metal zones are observed, which substantiate anode effects in the potential range of more than 1000 mV.

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