XPS study of native oxide films formed onto TiNi-based alloy modified by ion-beam treatments

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Implementation of novel titanium alloys in the medical industry is manifested by social needs to heal (or replace) damaged tissues, treat diseases of the musculoskeletal system. Biochemical laboratory (*in-vivo, in vitro*) tests of the developed medical devices in simulated physiological conditions are required in order to assess their biocompatibility. To date, the corrosion characteristics of TiNi shape memory alloys are widely described [1, 2]. It is shown that the mechanisms of corrosion destruction of these alloys are associated with selective corrosion and anodic oxidation of nickel being toxic for human body. So far, the issue of corrosion performance remains complex and can not be solved without understanding the structure of the protective oxide layer [3, 4]. Surface modification of the TiNi alloys by ion beams is a promising method aiming to form the nanocomposite oxide films with enhanced dielectric properties. The physical reasons responsible for the corrosion resistance of the ion-modified alloys are still unclear. The purpose of this work is to reveal the mechanisms of anodic oxidation of metals (Ti, Ni, Cu, Zr) and determine their chemical state in the oxide layer of the developed Ti-Ni-Cu-Zr alloy modified by ion beams.

The Ti-Ni-Cu-Zr alloy was prepared in a vacuum arc furnace by six-fold remelting of pure components. The nominal chemical composition of the alloy was $Ti_{35}Ni_{35}Cu_{15}Zr_{15}$ (at. %). Test samples were mechanically grinded (using SiC abrasive) and electrolytically polished in acid mixture (CH_3COOH + $HClO_4$). Then, the samples were modified by niobium ions using Mevva-5.Ru setup: an irradiation dose was $5 \cdot 10^{16}$ cm^{-2}, an accelerating voltage was 30 kV and a residual vacuum was $5 \cdot 10^{-4}$ Pa. The corrosion rate was estimated in artificial saliva and 0.9 wt. % NaCl using the Tafel extrapolation method in a three-electrode electrochemical cell consisting of a working electrode, an Ag/AgCl reference electrode and a counter graphite electrode. Studies of the chemical state of the elements {Ti, Ni, Cu, Zr, O} were carried out by X-ray photoelectron spectroscopy by means of K-Alpha Nexsa spectrometer (Thermo Scientific, USA) using a monochromatic X-ray source Al Kα (λ = 1486.6 eV).

It has been found that after ion implantation the Ti-Ni-Cu-Zr alloy exhibits a significant decrease in the corrosion rate (by ~7 times) in comparison with the reference unirradiated alloy. The high-resolution XPS spectra of the ion-modified alloy possess O1s peak consisting of two lines belonging to the oxidized form (O^{2-}) and hydroxyl group (OH^-). The chemical state of titanium, according to the fitting of the Ti $2p_{3/2}$ line, corresponds to TiO_2 oxide. The Nb 3d energy band is complex and corresponds to Nb^{5+} in the Nb_2O_5 oxide phase. It is suggested that the low rate of anodic oxidation of the alloy treated by ion beams is associated with depletion of the outer layer in nickel and formation of Nb_2O_5 dielectric oxide phases onto the surface of the alloy.

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