The study of titanium oxynitride coatings solubility deposited by reactive magnetron sputtering

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Abstract. To improve hemocompatibility of cardiovascular stents the coatings based on titanium oxides and oxynitrides were used. In the present work the morphology, surface properties (wettability and surface energy), and in vitro solubility of the ternary system Ti-N-O coating were investigated. Experimentally, low dissolution rate of the coating in saline NaCl (0,9%) was confirmed. Instrumental methods of quantitative analysis (XRF, AES) revealed that the Ti-N-O coating is chemical-resistant and does not change the qualitative and quantitative composition of body fluids.

1. Introduction

Surface biocompatibility is a significant problem of medical implants used in cardiovascular surgery. About 10% of patients suffer the re-narrowing of blood vessel at the stent site. Hemocompatible coatings are formed on the implant surfaces to prevent the aversive response of human organism [1]. Titanium oxides and oxynitride coatings have attracted interest due to their excellent biocompatibility, high chemical stability, corrosion resistance, and nontoxicity [2]. Complex (Ti-N-O) films are promising coatings for coronary and vascular stents because of ability to prevent thrombus formation and fibrinogen adhesion to the implant surface [3].

It is well known fact [4] that this coating type protects the metal base of the implant from the corrosive effects of body fluids (blood, lymph, interstitial fluid).

The aim of this work was to investigate the solubility of titanium oxynitride coatings in NaCl saline (0.9%).

2. Experimental part

Titanium oxynitride coatings were deposited by reactive magnetron sputtering using midrange magnetron sputtering installation "UVN-200MI" (TPU, Tomsk). As the substrate for one-side coatings the NaCl crystal plate with dimensions of 10×10 mm and a thickness of 1 mm was used. Sputtering parameters [1]: the cathode material is Ti, the working chamber pressure is 0.1 Pa, power is 1 kW, current is 3 A, working gas leakage rate is 5 ml/min, distance between the substrate and the magnetron is 100 mm. The ratio of the partial gases pressure O_2 and N_2 in the magnetron chamber was equal unit. The substrate temperature during deposition was 120° C, the deposition time was one hour.

Coating morphology was obtained by scanning electron microscope (SEM) Quanta 400 FEG, FEI.

The experimental samples were dissolved in NaCl saline (0.9%, pH = 7) during 30 days. Condition of NaCl solution volume depends on the area of the specimen and were determined according to ISO

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10993-12 recommendation [5]. The solvent acidity changed to pH=6 with the maximum exposure time.

Further, the samples were removed, and the solution was filtered through a "blue tape" filter and analyzed to detect elements of the coatings. The sample with the same coating not immersed in NaCl solution was served for the control. For these purposes, we used the X-ray fluorescence (XRF) analysis based on the X-rays interaction with the examined substance and the atomic-emission spectroscopy (AES). The AES is based on determining the elemental composition of substance using optical line spectra of atoms and ions irradiation of the sample excited by the light sources. The spectra obtained with XRF spectrometer Thermo Electron QUANT'X (EDXRF, USA) are shown on figures 1, 2.

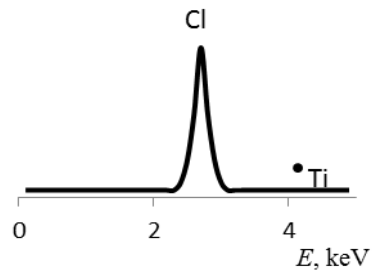

Figure 1. XRF spectrum of the solvent

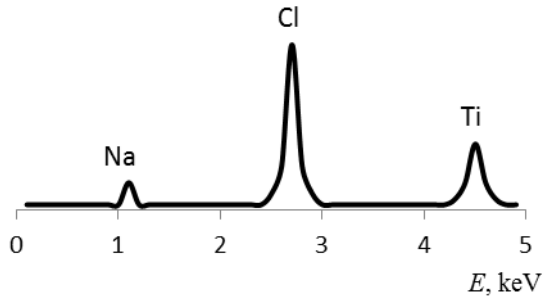

Figure 2. XRF spectrum of the Ti-N-O coating

AES analysis was carried out using an atomic emission spectrometer ICAP 6300 Duo (USA). As the standard reference solutions the state standard MES-1 and MES-2 samples were used. Obtained results are shown in table 1.

Table 1. The results of AES analysis of the samples after 30 days

No of measurement	The elements concentration in the test solution, mg/L	
	Na	**Ti**
1	119600	0.0005
2	120500	0.0006
average value	120000	0.0005

Surface properties such as wettabillity and surface free energy were studied for determination of Ti-N-O coating solubility.

The contact angles of the coating were measured by the OCA 15 (Plus DataPhysics Instruments GmbH) with sessile drop method, where liquid drop is set on a surface and the contact angle is measured from the drop shape [6]. The wetting angle from the interfacial surface tensions was calculated by Young's equation (figure 3). It describes the interactions between the cohesion and adhesion forces referred as surface energy [7].

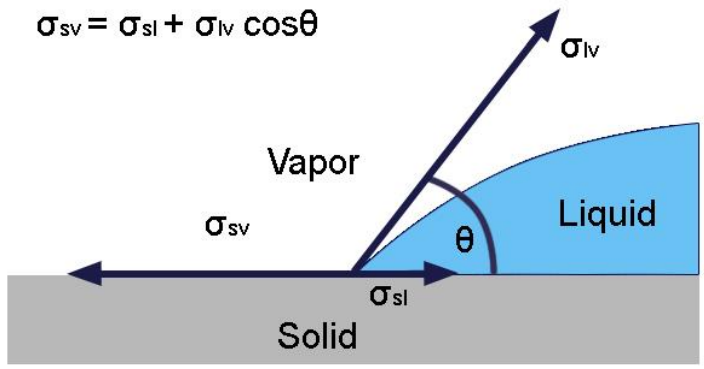

Figure 3. Schematic representation of the Young's equation (θ is the contact angle, σ_{lv} is the surface tension of the liquid, σ_{sl} is the solid/liquid interfacial tension, and σ_{sv} is the surface free energy of the solid, [mN/m = mJ/m^2])

The Owens, Wendt, Rabel and Kaelble method (the OWRK) was used for calculating the surface free energy using several liquids such as deionized water (θ_w), glycerol (θ_g), and diiodomethane (θ_d). The OWRK method calculates the surface free energy and its polar (σ^P) and dispersion (σ^D) parts using the equations 1-3 [8]:

$$\sigma_{sv} = \sigma_{sv}^D + \sigma_{sv}^P \tag{1}$$

$$\sigma_{lv} = \sigma_{lv}^D + \sigma_{lv}^P \tag{2}$$

$$\sigma_{sl} = \sigma_{sv} + \sigma_{lv} - 2\left(\sqrt{\sigma_{sv}^D\,\sigma_{lv}^D} + \sqrt{\sigma_{sv}^P\,\sigma_{lv}^P}\right) \tag{3}$$

The linear regression method is used to obtain the surface energy of solid, which is described by equation 4:

$$\frac{1+cos\theta}{2}\,\frac{\sigma_{lv}}{\sigma_{lv}^D} = \sqrt{\sigma_{sv}^P}\sqrt{\frac{\sigma_{lv}^P}{\sigma_{lv}^D}} + \sqrt{\sigma_{sv}^D} \tag{4}$$

These interactions along the boundary of both phases are important for solving wetting and adhesion.

3. Results and discussion

3.1. Surface morphology of Ti-N-O coating

SEM images show that the coating has fine-grained surface morphology (figure 4*a*). Figure 2*b* demonstrates the homogeneous compact coating structure consisting of spherical elements (grains). Grains size is in the range of (6–75) nm [9].

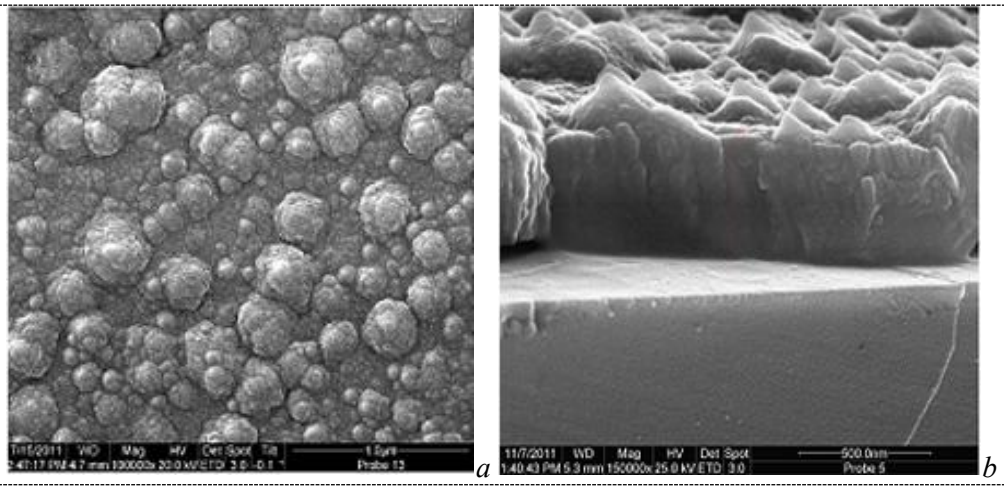

Figure 4. SEM images of Ti-N-O coating: (*a*) surface morphology and (*b*) cross-section [9]

3.2. Interpretation of the XRF spectra

Identification of elements from XRF spectra is based on the conformity of the spectral lines energy of element characteristic radiation and their relative intensities with tabulated values. The energy maximum of the signal was determined. The position the maximum is 2.8 keV that corresponds to Cl element: from NaCl solution (see in figure 1) and the crystal NaCl (see in figure 2). The maximum corresponding to Ti element with energy of 4.5 keV was not detected on the spectrogram (figure 1). While, on the XRF spectrum of the Ti-N-O coating the characteristic radiation titanium line is sufficiently intense (see on figure 2). The N and O elements cannot be detected using XRF spectrometer.

3.3. Interpretation of the AES spectrum

AES analysis allows determining not only qualitatively but also quantitatively elemental composition of the sample solution. It is obvious that with decreasing of an element concentration in a series of samples with the same composition, the spectral lines intensity in the corresponding spectra will decrease provided invariance excitation parameters and recording of spectra [10]. Since the spectral lines corresponding to an element have different intensities, the weaker lines will disappear in the spectrum faster than more intensive lines. As a result by the absence in the spectra of the certain lines and presence more intense of the element line we may estimate its concentration in the sample.

Using AES experimental data we identified the ions presence of Na and Ti elements in solution. AES results as well as XRF indicate expected high concentration of Na in the solution, and trace amounts of Ti confirm good chemical resistance of titanium oxynitride coating.

3.4. Measurements of wettability and surface energy

The wetting angle measurements (table 2) show that Ti-N-O coating is hydrophobic because the water contact angle is over 90 degree (θ_w), and the surface free energy is low [7]. Currently, most implant surfaces used in clinical application are hydrophobic, according to studies [6]. Hydrophobic surfaces are prone to entrap of air bubbles due to hydrocarbon contamination that can prevent the protein adsorption and cell receptor adhesion [6].

Table 2. Data of contact angle and surface energy measurements of Ti-N-O coating

Coating	θ_w (deg.)	θ_g (deg.)	θ_d (deg.)	σ (mN/m)
Ti-O-N	116±0.2	108±0.4	70±0.2	20±0.8

Conclusions

A low degree of dissolution of the titanium oxynitride coating in saline NaCl (0,9%) was confirmed experimentally. By means of modern spectroscopic methods of analysis (XRF, AES) it is proved corrosion-resistant properties of the Ti-N-O coating and does not change the qualitative and quantitative composition of the saline. The results obtained using two methods of analysis are in good agreement. Low solubility and hydrophobicity of Ti-N-O coating deposited on the implant surface can prevent the metallic surface corrosion and also stop the foreign ions yield from steel stents surface.

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