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Modification of implant material surface properties by means of oxide nano-structured coatings deposition

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ABSTRACT

The deposition of functional coatings on the metal surface of artificial joints is an effective way of enhancing joint tribological characteristics. It is well-known that nanostructured oxide coatings have specific properties advantageous for future implant applications. In the present study, we measured the high hardness parameters, the adhesion strength and the low friction coefficient of the oxide magnetron sputtered coatings. The corrosion test results show that the oxide coating deposition had improved the corrosion resistance by a factor of ten for both stainless steel and titanium alloy substrates. Moreover, the hydrophilic nature of coated surfaces in comparison with the metal ones was investigated in the tensiometric tests. The surfaces with nanostructured oxide coatings demonstrated improved biocompatibility for in vitro and in vivo tests, attributed to the high dielectric constants and the high values of the surface free energy parameters.

1. Introduction

The total and module replacement of hip-femoral, shoulder, knee and elbow joints is one of the most successful and effective surgery operations in modern medicine practice [1–7]. Recently the main directions of the joints' tribological parameters improvement are the advancing of existed joint sliding couple characteristics (metal–metal, metal–ceramic, ceramic–ceramic) and search for alternative materials (metal, ceramic, coatings) [8–10]. The ceramic materials allow us to improve the joints' wettability characteristics and fluid friction conditions [11]. They possess high hardness, wear resistance and biocompatibility in comparison with metal elements, but there is a risk of brittle failure of ceramic heads [12,13]. Other negative results of application of metal and ceramic materials are an accumulation of a toxic wear debris in surrounding implant tissues and further dissemination of wear particles to the internal organs: liver, spleen and kidneys [14–17]. Corrosion is one of the major processes that causes problems when metals and alloys are used as implants in the body [18–20]. Nanostructured oxide coatings exhibit unique properties [21–23]: high inductivity, density, bio- and chemical inertness, which are very important for future implant and tissue engineering applications [24,25]. The deposition of functional coatings on metal substrates (stainless steel, titanium and zirconium alloys) combines the biocompatibility of ceramic materials with fracture toughness and failure strength of metals for the next generation of joint tribology.

The effect of the coatings composition, electrochemical properties, surface energy and topography on cell functions should be thoroughly studied using in vitro and in vivo tests. The aim of the present study was the investigation of the influence on material and surface properties of the magnetron sputtered oxide films on the further biological response.

2. Materials and methods

The substrates were popular load-bearing materials such as the stainless steel SS (AISI 321) and titanium alloy Ti (Ti_6Al_4V) samples. The substrates were cleaned in ultrasonic bath with standard technology. The oxide magnetron sputtering deposition was performed in a high vacuum pumping system with the base pressure about 10^{-3} Pa. The details of the magnetron and ion source in the sputtering chamber can be found in Ref. [26]. The magnetron

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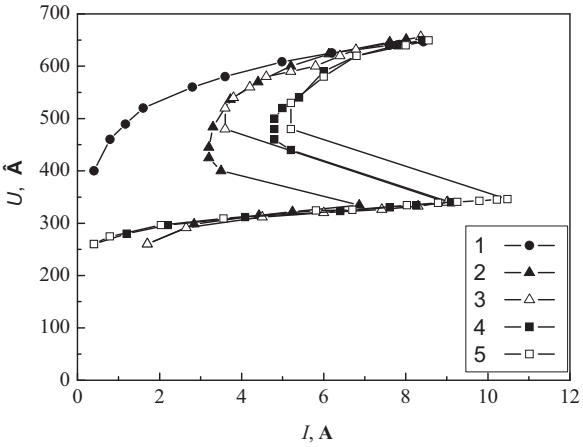

Fig. 1. Current–voltage characteristics of the magnetron discharge in argon with oxygen: Ar pressure was 6×10^{-2} Pa, oxygen flow 1 – $q = 0$ sccm (standard cubic centimeter/minute), 2, 3 – $q = 17$ sccm, 4, 5 – $q = 26$ sccm for aluminum target material.

discharge power was 1–4 kW, the power of activated oxygen source was up to 1 kW, with the coating deposition rate being 8 μm/h. An ion source was used for cleaning the samples' surface before deposition.

Fig. 1 presents the current–voltage characteristic of the magnetron with target of aluminum in a mixture of argon with oxygen at various reactive gas mass flow rates.

At excessive oxygen flow conditions, the process shifts to the so-called target-poisoning mode. Thus, we conducted the sputtering process in regimes far from the target-poisoning mode, in view of the oxide coatings deposition with a highly stoichiometric composition. In addition, such deposition conditions allow one to avoid micro-arcs and micro-drops formation that would worsen the corrosion-resistance properties. The optimum conditions were realized for the upper part (>450 V) of current–voltage curves of magnetron discharge in argon with oxygen.

The structure of Al_2O_3 magnetron sputtered films was investigated by means of X-ray diffraction (XRD). X-ray diffraction profiles of Al_2O_3 were observed using diffraction device "DRON-3" with filtered Cu-Ku radiation. X-ray photoelectron spectroscopy was carried out using ESCALAB MkII (VG Scientific) electron spectrometer using AlKalpha X-ray source (excitation energy $h\nu = 1486.6$ eV). The instrumental resolution measured as the full width at half maximum (FWHM) of the $Ag_3d_{5/2}$, photoelectron peak is 1 eV. The coating's thickness, hardness and elastic moduli were evaluated by standard methods with the use of the Revetest (CSM Instruments).

The adhesion parameters and the friction coefficients were measured using the Rockwell indenter with a tip radius of 200 μm, within the load range of 0–200 N.

The surface roughness was estimated by profilometer Hommel T-2000. The contact angles were measured by means of the tensiometric method. Prior to contact angle measurements, samples were ultrasonically cleaned in acetone and deionised water and dried. The surface free energy (SFE), polar and dispersion components were determined by means of the Wu method [27].

The corrosion tests were made by potentiodynamic method (Potentiostat, PARSTAT 2263, AMETEK, USA). The corrosion examinations of anodic polarization were conducted in the potential range −1.0 V to +2.0 V with scanning rate 1 mv/s in the simulated body fluid solution (SBF, NaCl – 8.035, $NaHCO_3$ – 0.355, KCl – 0.225, $K_2HPO_4{\cdot}3H_2O$ – 0.231, $MgCl_2{\cdot}6H_2O$ – 0.311, $CaCl_2$ – 0.292, Na_2SO_4 – 0.072) at pH = 7.4 and temperature 37 °C. The surface morphology was investigated by means of scanning electron microscopy SEM and atomic force microscopy AFM (Quesant Instrument Corporation, USA).

Cytotoxicity and cytocompatibility were evaluated using in vitro tests. In the process of cell cultivation (fibroblasts) with coated and uncoated samples, the cell cytology, morphology and vital capacity were determined after 24 h, 3 days, and 5 days cultivation. Rat hypodermic cellular tissue was extracted to obtain an initial fibroblast culture. The suspension of extracted cells was centrifuged at 750 orb/min during 15 min. Sowing cell area was 3×10^5 cell/ml density of cultural medium. The fibroblast cultivation at 3 ml of Dulbecco modified Eagle's medium (DMEM, Sigma), supplemented with 10% fetal calf serum (FCS), 80 mg/ml penicillin, and 100 mg/ml streptomycin was made by the method of monolayer culture under thermostat conditions (temperature 37 °C in 5% CO_2 atmosphere during 5 days). The cells that adhered on the samples were cleaned by buffer solution (pH 7.2) and double distilled water and fixed at 2.5% glutaraldehyde on 0.1 M buffer solution during 2 h and 1% OsO_4 solution during 1 h. Then the samples were dehydrated using a graded series of alcohol exposures. Other samples with adhered cells were trypsinized with 0.01% trypsin/0.5 mM EDTA. The experiments were independently repeated in triplicate.

In vivo experiments were performed on Wistar nonlinear rats (male, mass 400–500 g) population. The sterilized samples were implanted in close contact with the femur bone. The animals were divided into some test groups of 10 rats each: control group, group with uncoated titanium implants and group with Al_2O_3 coated implants.

All groups of rats were anesthetized and sacrificed after a period of 5 months according to the ethical protocols. Histological and morphological tests were carried out. For the morphology research the part of the rat femoral bone with a fragment of acetabulum of the hip-femoral joint were prepared according to the standard protocols, in order to evaluate the presence of fibrous capsule and the next inflammatory processes. Histological sections with a thickness 6–10 μm were prepared with the microtome "Reichert", and were studied by optical microscopy (Micros-50) methods. After the test finished (5 months), the congruence of the interface between the femoral head and the acetabulum of the hip-femoral joint was observed by radiographic data.

3. Results and discussion

The structure of the Al_2O_3 thin films was investigated by means of the XRD method. X-ray diffraction profiles of as-deposited Al_2O_3 coatings demonstrated an amorphous nature, since no peaks were observed. The compositional analysis of the deposited oxide coatings by means of the XPS method was made (Fig. 2).

The high-resolution photoelectron spectra of Al2p, O1s, C1s were observed. The chemical composition was found to be close to stoichiometric composition. The Al2p peak with binding energy position $E = 75$ eV, corresponding to the Al_2O_3 composition was observed. The O1s high-resolution spectra demonstrated the peak at binding energy position $E = 531$ eV, associated with the Al—O chemical bond. The presence of the carbon peak at binding energy position $E = 285.0$ eV is probably due to adventitious carbon contamination.

The surface structure, morphology and topography of the deposited oxide coatings was estimated by the AFM and the SEM methods (Fig. 3)

The coating thickness was 2.1 μm for the stainless steel and 1.8 μm in the case of titanium alloy substrates. Hardness and elastic moduli evaluated by standard methods are presented in Table 1.

The roughness parameters R_a/R_z of the uncoated and oxide coated stainless steel substrates were 0.007/0.040 μm and 037/0.240 μm, correspondingly. In the case of titanium