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Nanostructured composite materials on the base of titanium and zirconium with modified surface layers for medicine and engineering

K e y w o r d s

Titanium, zirconium, modified surface layers.

S u m m a r y

This paper presents the results of the investigations of mechanical and tribological properties of ultrafine-grained and nanostructured titanium and zirconium under microplasma and ion beam treatments. It indicates that the nitrogen ion beam treatment of titanium and zirconium at low temperatures essentially increases the wear resistance by 35–50 times and reduces the friction coefficient by 40%. The biocomposite (nanostructured titanium - calcium phosphate coating) demonstrates a high friction coefficient (0.4–1.0) in tribological interaction with an ultrahigh molecular polyethylene imitated of subcutaneous tissue and bone tissue that allows to eliminate the microdisplacements of an implant against bone tissue under friction and to increase its fixation. A considerable improvement of tribological characteristics of the nanostructured titanium and zirconium with the modified surface layers give the advantages for these materials in medicine and engineering.

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1. Introduction

The surface modifications of materials by ion beam and microplasma (also known as plasma electrolytic oxidation (PEO) and micro-arc oxidation (MAO)) methods are advanced perspectives for the enhancement of tribological and anticorrosive characteristics. Moreover, the use of severe plastic deformation methods ensures the formation of the bulk ultrafine-grained and nanostructured states that allows the improvement of the mechanical and tribological properties. Thus, the bulk structure and surface modification methods open new perspectives to the development of novel composite materials with modified surface layers for medical and engineering applications.

Over the years, the scientific groups from Institute of Strength Physics and Materials Science SB RAS, Physical&Technical Institute of NASB, Joined Institute of Mechanical Engineering of NASB take part in the development and investigation of ultrafine-grained and nanostructured titanium and zirconium with modified surface layers.

The paper presents the results of the systematic investigations of structure and phase states, mechanical and tribological properties of ultrafine-grained and nanostructured titanium and zirconium under microplasma and ion beam treatments.

2. Experimental details

Technically pure titanium (VT1-0 and VT1-00 in Russia or Grade 1 and Grade 2 abroad) and iodide zirconium were chosen to prepare the investigation subjects. Two methods of severe plastic deformation were used to obtain titanium and zirconium billets in ultra-fine-grained and nanostructure states. These methods are equal-channel angular pressing [1] and uniaxial abc-pressing in a press-mould with the rolling in groove rollers [2]. Then the samples were cut from the billets to modify the surface layer with ion-beam and microplasma methods.

Ion beam processing was performed on the vacuum installation equipped with a gas ion source of self-contained electron drift [3]. The nitrogen ion energy was equal to 3 keV and the ion current density was equal to 2 mA/cm^2. The titanium sample temperature during ion-beam nitration varied in the range of 620 – 820 K.

In order to form calcium-phosphate coatings on the titanium surface, the technological technique Micro-Arc-3.0 was developed [4]. The aqueous solution of phosphoric acid with hydroxyapatite and calcium carbonate powders was used as the electrolyte. Tribological tests were carried out by using an automated tribometer [5]. The speed of titanium specimen movement was kept near 0.1 m/s. The tribological testing was carried out with the initial pressure of 1 MPa.

3. Experimental results

3.1. Ion-beam modification

The research results show that a fragmented structure is formed in titanium and zirconium during severe plastic deformation in the range of e = 0.8 – 1.44. This structure contains a high density of dislocation tangles (Fig. 1). The increase in deformation up to e = 2.1 leads to the formation of ultradispersed subgrains transformed from extended band fragments. The subsequent increase in deformation up to e = 2.49 leads to the formation of ultrafine-grained structure with the grain size of 0.2 – 0.3 μm [6]. The microhardness of deformed titanium increases by 55–60%, that of zirconium, by 90-100%.

The nitrogen ion-beam treatment of titanium and zirconium at the temperatures of 770–820 K results in the formation of a modified surface layer with the thickness of ≈5 μm containing nitrogen solid solution in hexagonal lattice α-Ti and α-Zr. Thus, the microhardness of the surface layer increases up to 3500–3700 MPa [7].

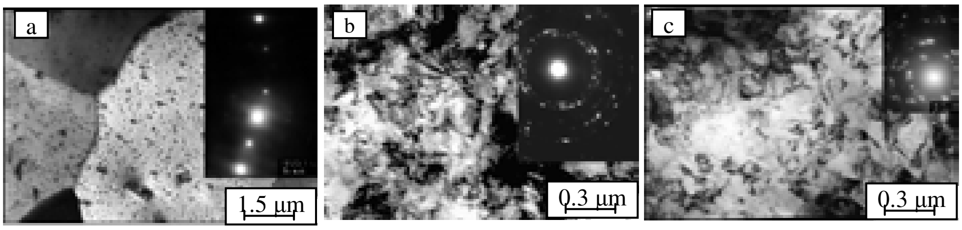

Fig. 1. TEM bright field images and corresponding selected area diffraction of titanium microstructure: a) the initial state; b) after severe plastic deformation of e = 1.44; c) after severe plastic deformation, e = 2.1

Fig. 2a shows the dependence of mass wear on the friction path of the titanium in the initial state (Curve 1), after the equal-channel angular pressing (e = 2.1) (Curve 2) and after a nitrogen ion implantation at the temperature of 820 K (Curve 3). Fig. 2b shows the dependence of the friction coefficient of titanium specimens on the friction path. The mentioned data have shown that the curves of mass wear in the initial state and after the severe plastic deformation almost coincide. The intensity of titanium wear for these conditions of pre-treatment is 0.11–0.12 mg/m. The values of the friction coefficient of titanium samples in the initial state and after severe plastic deformation also keep the same level of 0.45–0.5.

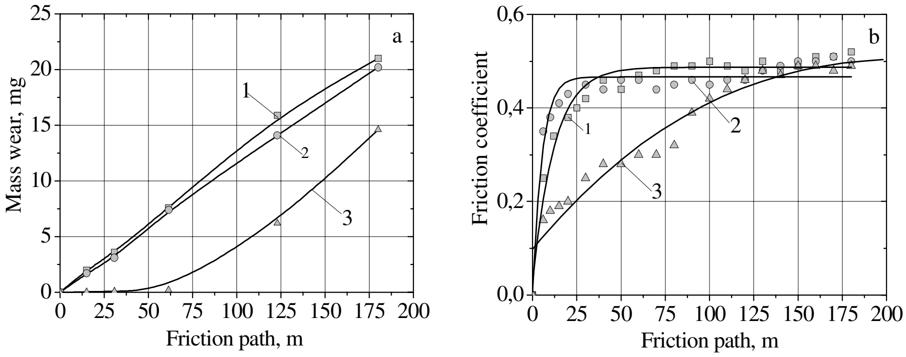

Fig. 2. The dependencies of mass wear (a) and friction coefficient (b) on the friction path for titanium specimens subjected to treatments under various conditions (dry friction, $P_a = 1$ MPa). 1) the initial state; 2) the same + the severe plastic deformation, e = 2.1; 3) the same + the severe plastic deformation, e = 2,1,+ the nitrogen ion implantation at 820 K

Nitrogen ion implantation has a considerable influence on the tribological properties of its surface layers. In particular, the titanium samples with a nitrogen ion-modified surface have a low wear rate of 0.003 mg/m at the initial stage of the tests. This stage is also characterised by the reduced friction coefficient level of 0.2–0.3. Subsequently, with the increase in the friction path and the wear of nitrogen-modified layer, the wear rate and the friction coefficient increase up to the value level corresponding to the initial unimplanted state of material.

Similar regularities of the dependence of the friction coefficient and mass wear on the friction path have been discovered during the testing of the iodide zirconium samples (Fig. 3). In particular, at the initial state, the wear rate is 0.23–0.25 mg/m, the friction coefficient is 0.4–0.5. A severe plastic deformation does not have an effect on a wear rate or a friction coefficient as in the case of titanium. The subsequent nitrogen ion-beam treatment leads to a significant decrease in a wear rate of 25–30 times down to ~0.009 mg/m and a friction coefficient down to 0.2–0.3.

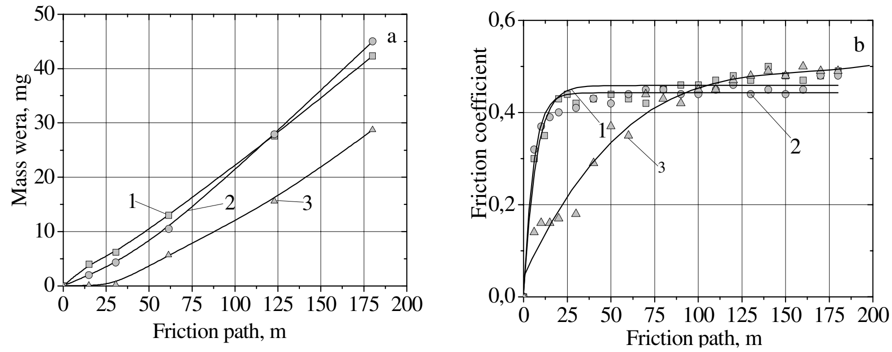

Fig. 3. The dependencies of mass wear (a) and friction coefficient (b) on the friction path of zirconium samples subjected to treatments under various conditions (dry friction, $P_a = 1$ MPa). 1) initial state; 2) the same + the severe plastic deformation, e = 2.1; 3) the same + the severe plastic deformation, e = 2.1 + the nitrogen ion implantation at 820 K

Thus, the nitrogen ion-beam treatment of the VT1-00 titanium and zirconium increases considerably (25-30 times) the wear resistance of its surface layer and reduces the friction coefficient in tribocontact by 40%.

3.2. Microplasma electrolytic oxidation

In order to form bioactive surface layers enhancing the properties of metallic substrate (titanium in nanostractured state), depositing the calcium-phosphate coatings in the plasma of microarc discharges was suggested. The influence of electrophysical parameters of micro-plasma process (voltage and current values, pulse period and frequency, deposition time) and electrolyte compositions on physical, chemical, mechanical, and biological properties of coatings have been investigated. It was shown that the electrolyte based on an aqueous solution of orthophosphoric acid, hydroxyapatite, and calcium carbonate allows the production of porous calcium-phosphate coatings with high biocompatability. The coating structure is formed by layers, and it consists of thick oxide sublayer and upper porous layer, the basic components of which are spherolytes (Fig.4). Directly after depositing, the coating is in an X-ray amorphous state. Its interaction with a biological environment is characterised by a high speed of dissolution that indicates its bioactivity [8–9].

The optimal characteristics of the coatings connecting the high osseointegration and adhesion to substrate have been found. They are the following: Roughness is 2–6 μm, porosity is 20–35%, adhesion strength to the nanostructured titanium surface is up to 35 MPa, atomic Ca/P ratio is 0.7. The high adhesion strength of coatings was achieved by preliminary preparation of a titanium surface by corundum particles sandblasting and subsequent chemical etching in acid solutions of hydrochloric and sulphuric acids heated to boiling temperature.

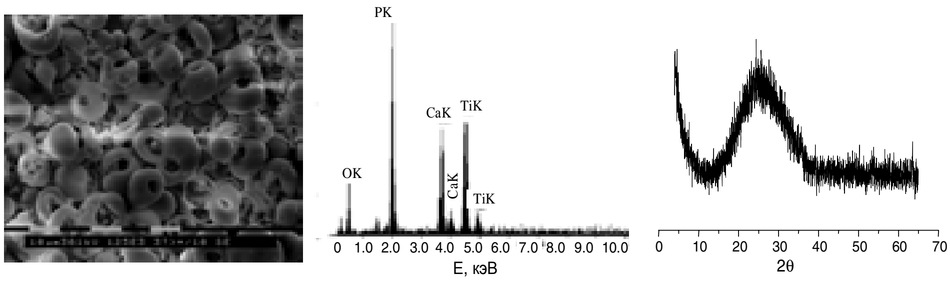

Fig. 4. Microplasma calcium-phosphate coating produced in an electrolyte on the basis of orthophosphoric acid, hydroxyapatite and calcium carbonate: a) SEM image, b) energy-dispersion X-ray spectrum, c) X-ray diffraction pattern

During the introduction of biocomposites in a living organism on the boundary "implant-bone," there is a probability of microdisplacements that can lead to the friction processes [10]. The behaviour of the biocomposite based on nanostructured titanium and calcium phosphate coating under the of dry friction condition and in biological fluid (0.9% sodium chloride solution) has been studied. The ultrahigh-molecular polyethylene samples were used as a counterface, since they are the most suitable to the strength properties of a bone (ultimate strength is 35-50 MPa). Moreover, the bone tissue samples were also used.

Tribological tests of the nanostructured titanium without a coating against ultrahigh-molecular polyethylene and bone tissue have shown a high wear resistance both under the dry friction condition and in 0.9% sodium chloride solution. Wear was not registered during the tests and a small friction coefficient of $\mu = 0.09 - 0.15$ was observed (Fig. 5).

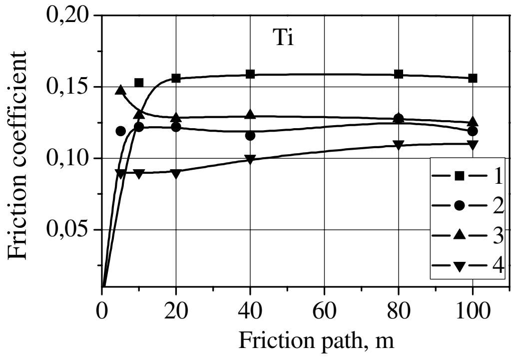

Fig. 5. The dependence of the friction coefficient on the friction path for the nanostructured titanium samples produced by abc-pressing: 1) dry friction, counterface – ultrahigh-molecular polyethylene; 2) friction in 0.9% sodium chloride solution, counterface – ultrahigh-molecular polyethylene; 3) dry friction, counterface – bone tissue; 4) - friction in 0.9% sodium chloride solution, counterface – bone tissue

At the same time, the tribotesting of calcium-phosphate coatings against ultrahigh-molecular polyethylene under the dry friction conditions have shown an invariably high friction coefficient within the range of 0.35–0.4 during all tests. However, the wear rate of the coating was small, and it is equal to 0.001 mg/m (Fig. 6). The longevity of the calcium-phosphate coatings in the 0.9% sodium chloride solution was less in comparison with the tribological tests without a lubricant. The wear rate was 0.002 mg/m, and the friction coefficient was up to 0.4-0.5. It is connected to the simultaneous dissolution of a coating in the solution. When using bone tissue as a counterface, the friction coefficient was up to 0.8-0.9 (Fig. 6).

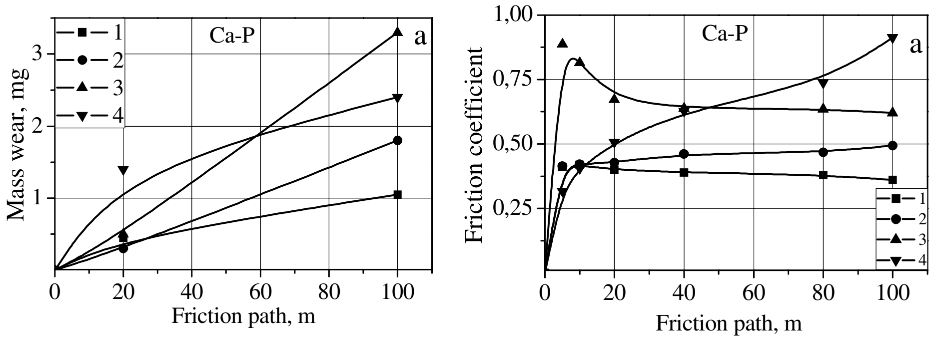

Fig. 6. The dependence of a mass wear (a) and a friction coefficient (b) on the friction path for the nanostructured titanium samples with a calcium-phosphate coating: 1 – dry friction, counterface – ultrahigh-molecular polyethylene; 2 – friction in physiologic solution, counterface – ultrahigh-molecular polyethylene; 3 - dry friction, counterface – ultrahigh-molecular polyethylene – bone tissue; 4 - friction in 0.9% sodium chloride solution, counterface – bone tissue

Thus, a calcium phosphate coating stimulates an osseointegration, and, as the tribological tests have shown, an infallible fixation of an implant due to a high friction coefficient.

Conclusion

The formation of ultrafine-grained and nanostructured states under severe plastic deformation of titanium and zirconium does not have a considerable influence on their wear resistance and friction coefficient under dry friction conditions. The nitrogen ion-beam treatment of the tested materials provides an increase in the wear resistance of their surface layers (25-30 times) as well as a decrease in the friction coefficient of the tribological interaction by ~40%. The microplasma electrolytic oxidation of the titanium in the orthophosphoric acid, hydroxyapatite and calcium carbonate solution allows the production of porous calcium-phosphate coatings with high physical-mechanical and tribological properties. A high friction coefficient of 0.4-1.0 during the frictional interaction with a ultrahigh-molecular polyethylene and a bone tissue allows one to avoid the displacements during the friction of the implant against a bone tissue, thus intensifying its fixation. A considerable increase in the tribological properties of nanostructured titanium and zirconium with the modified surface layers makes these materials quite promising in medicine as well as in engineering.

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