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MICROSTRUCTURE, CHEMICAL COMPOSITION, AND NANOMECHANICAL PROPERTIES OF ARC-PVD ZrTa/$ZrTaO_2$ BILAYER COATINGS

A.V. Taran[1], I.E. Garkusha[1,3], K. Nowakowska-Langier[2], G.N. Tolmachova[1], P.M. Vorontsov[4], O.A. Nikol'chenko[4], Yu.P. Gnidenko[3], S.P. Romaniuk[2], O.I. Tymoshenko[1], I.O. Misiruk[1]

[1]National Science Center "Kharkov Institute of Physics and Technology", Institute of Plasma Physics, Kharkiv, Ukraine;

[2]National Centre for Nuclear Research, Otwock, Poland;

[3]V.N. Karazin Kharkiv National University, Kharkiv, Ukraine;

[4]Sytenko Institute of Spine and Joint Pathology National Academy of Medical Sciences of Ukraine, Kharkiv, Ukraine

E-mail: avtaran@ukr.net

The results of vacuum-arc deposition of thin bilayer ZrTa/$ZrTaO_2$ coatings on the surface of titanium dental implants, AISI-316L stainless steel are presented. The structure, phase and chemical composition of deposited coatings have been investigated by means of scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) and X-ray diffraction analysis XRD. Nanomechanical properties have been investigated by nanoindentation method. The obtained results can be useful for optimization of implant surfaces to prevent corrosion and mechanical failure, thereby improving osseointegration.

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INTRODUCTION

The transition metal nitrides (MeN) have been used as a coating material to improve the mechanical and tribological properties of surfaces used in various fields [1–4]. Additionally, TaN films have been used as diffusion barrier, thin film resistor, biocompatible coatings, corrosion and wear protective films [5, 6]. Different works have demonstrated that tantalum, zirconium, and their nitrides present good biocompatibility [7]. Additionally, TaN and ZrN possess excellent corrosion and wear resistance.

It was found that the addition of another transition metallic element from the same group could improve some specific characteristics; such is the case with the addition of Al to titanium nitride (TiN). TiAlN can have higher hardness and be more resistant to oxidation than TiN at high temperatures [8]. The TaZrN coatings are well described in the literature [9], but there is a lack of data considering TaZrO coatings.

The deposition of a multilayer coatings is another approach to improve the mechanical and tribological properties of the coating. These films have been found to possess superior mechanical and tribological properties as compared with a monolayer coating. Introduction of a number of interfaces parallel to the substrate can prevent cracks or provide barriers to the dislocation motion, increasing the toughness and the hardness of the coating [10].

One of the most common materials used for dental implants is the Titanium-6Al-4/vanadium alloy. But there are important limitations in the use of composite materials such as titanium/vanadium. Contact of the implant surface with blood and colonization by oral bacteria can promote degradation of the implant surfaces, leading to bone loss. Notably, progressive deterioration of implant surfaces frequently leads to failure of the bone-implant interface, which ultimately drives the need for implant replacement. In addition to challenges associated with poor biocompatibility, high amplitude loading forces (which directly act on dental and orthopedic implants) compromise the mechanical properties of implants.

The application of ion-plasma deposition for creating new types of surfaces for implants placed in bone could reduce early implant failure and extend operating lifetimes and implant durability under heavy loads. The central guiding concept is that implant surfaces should be optimized to prevent corrosion and mechanical failure, thereby improving osseointegration.

The aim of the present research is to synthesize bilayer TaZr/TaZrO coatings on titanium dental implants, AISI-316L stainless steel to evaluate the mechanical properties and their structure and phase composition as a first step before implantation and tests on biocompatibility.

1. EXPERIMENTAL SETUP

The synthesis of coatings was carried out using the plasma deposition method in a vacuum arc discharge system of the "Bulat" type. Coatings were applied using alloyed cathode of $Zr_{80}Ta_{20}$ composition. The coatings were deposited on the surfaces of samples made of polished 20x20 mm AISI 316L stainless steel as well as on Ti dental implants.

The samples were cleaned with ethyl alcohol in an ultrasonic bath and placed on a rotary table in a vacuum chamber, as shown in the diagram Fig. 1. The plasma flow was deflected from the horizontal line to the rotary table by the magnetic field of an additional coil at an angle of approximately 45 degrees. This scheme helped

to reduce the number of droplet phase on the surfaces of the samples. The chamber was evacuated to $7 \cdot 10^{-5}$ Torr. Cleaning of the samples surfaces were performed for 30…40 s by ion bombardment in a pulse mode with the application of alternating negative potential to the table with amplitude of 1200 V and a frequency of 45 kHz. Next, both ZrTa and $ZrTaO_2$ coatings were deposited. In the mode of applying a metallic layer the potential was reduced to 50 V, and in the case of oxide deposition, it was floating. Oxide coatings were obtained in an oxygen atmosphere at a pressure of $3 \cdot 10^{-3}$ Torr. The thickness of the coatings was approximately 3.8 μm, and the deposition rate was 30…50 μm per hour at an arc current of 100 A.

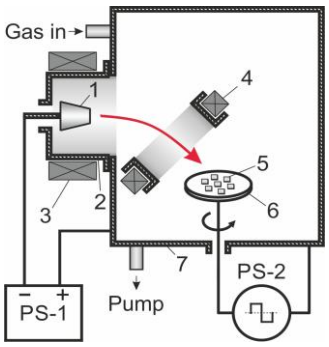

Fig. 1. Experimental Set-up:
1 – cathode; 2 – anode; 3, 4 – coils; 5 – samples; 6 – rotating table; 7 – vacuum chamber; PS-1 – arc discharge power supply; PS-2 – pulsed power supply

Structure and chemical composition of the coatings were investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) by using ZEISS EVO® MA10.

XRD examinations of the samples were carried out using DRON-UM1 X-ray diffractometer under copper Cu-Kα irradiation. The diffracted lines were recorded by a scintillation detector. Qualitative phase analysis of the samples was carried out using the ICDD PDF-2 international database of crystallographic compounds.

The study of the microstructural characteristics (the grain size and the level of microstrain) of the coatings was carried out by the integral width of the peaks using the Williamson-Hall method. The main formula (1) of the method is as following:

$$\beta = \frac{\lambda}{D \cdot \cos(\theta)} + 4 \cdot \varepsilon \cdot \mathrm{tg}(\theta), \qquad (1)$$

where β is the true physical expansion; λ is the wavelength of X-ray irradiation; D – grain size; θ – diffraction angle; ε is the level of microstrain.

The hardness and modulus of elasticity of the coatings were determined by the nanoindentation method using the Nano Indenter-G200 system (Agilent Technologies, USA) equipped with a Berkovich diamond tip. Ten measurements were made on each coated sample. The indentation depth was approximately 300 nm, which is less than 10% of the coating thickness.

2. RESULTS AND DISCUSSION

According to XRD data only three phases were found in the coating (Fig. 2): two zirconium oxides ZrO_2-c (cubic) and ZrO_2-m (monoclinic) and a cubic modification of zirconium Zr-β.

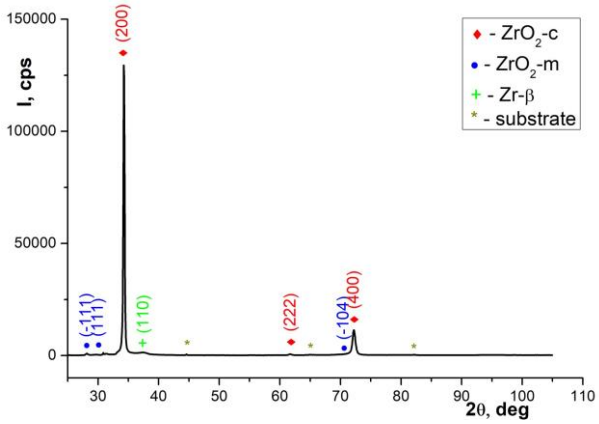

Fig. 2. XRD pattern from ZrTa/$ZrTaO_2$ coating

The results of the phase composition and microstructural characteristics of the coatings are given in Table 1. The intensity distribution of the diffraction peaks of zirconium oxide ZrO_2-c indicates the presence of a strong (200) texture. The lattice parameter of ZrO_2-c oxide is a = 5.228 Å; the grain size is D = 85.1 nm at the level of microstrain $\varepsilon = 2.9 \cdot 10^{-3}$. The lattice parameters of monoclinic ZrO_2-m oxide are: a = 5.169 Å; b = 5.212 Å; c = 5.341 Å; β = 99.23°. The lattice parameter of Zr-β zirconium is a = 3.388 Å. It was not possible to estimate the microstructural characteristics for ZrO_2-m oxide and Zr-β zirconium. However, the blurring of the Zr-β zirconium diffraction peak is very significant. That indicates that zirconium is in a nanostructured state close to X-ray amorphous.

Table 1

Microstructural characteristics of the coatings

Coatings	Phases	Lattice parameter	Grain size	Microstrain
ZrTa / $ZrTaO_2$	ZrO_2-c	5.228	85.1	$2.9 \cdot 10^{-3}$
	ZrO_2-m	a = 5.169; b = 5.212; c = 5.341; β = 99.23°	–	–
	Zr-β	3.388	–	–

It should be noted that the lattice parameters of the phases detected in the coatings differ from the literature values. The reason for such deviations can be both the presence of macrostrain in the coatings and the replacement of zirconium atoms in the sublattice of Zr by Ta elements, so the TaO phases could not be identified.

Fig. 3. Image of ZrTa/$ZrTaO_2$ coatings on Ti dental implants

Fig. 3 shows the image of ZrTa/$ZrTaO_2$ coatings on dental implants before being implanted.

The typical SEM surface morphology and EDS chemical composition of the as-deposited films are depicted in Fig. 4. It is demonstrated that the as-deposited films have some surface defects, microdroplets, particles and craters, which are mainly caused by liquid droplets emitted from the surface of the ZrTa alloyed target during coating deposition process. Cross-section SEM image of bilayer ZrTa/$ZrTaO_2$ coating reveals columnar growth (see Fig. 4,a).

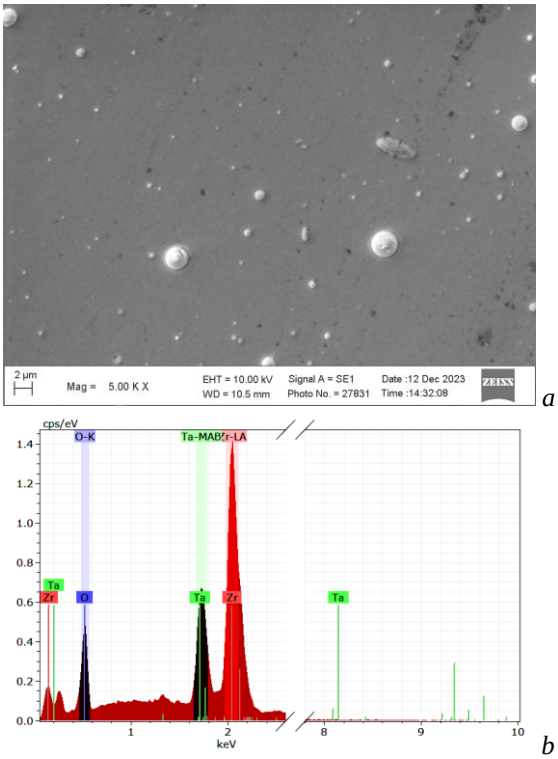

Fig. 4. SEM image (a) of ZrTa/$ZrTaO_2$ coating and EDS spectrum (b)

In Fig. 5 the EDS mapping, EDS spectrum of the chemical composition and distribution of chemical elements are presented.

The coating consisted of two layers: the first of metallic TaZr film with a thickness of ~1.5 µm that was deposited to improve the adhesion of the coating to the metallic substrate and prevent dislocations migration, and the second of $TaZrO_2$.

The hardness and modulus of elasticity of the deposited coatings are shown in Table 2. The hardness of the oxide ZrTa/ZrTaO is (16.1 ± 1) GPa. The measured nanohardness for ZrTa/ ZrTaN (*H*) at 5 and 10 mN was (18.9 ± 1.485) GPa and (19.7 ± 1.810) GPa, respectively (the penetration depth at 10 mN was less than 15% of the thickness of the layer); this value is within the range (11 to 31 GPa) reported in the literature [9]. The modulus of elasticity turned out to be 226 GPa (ZrTaO).

Based on the results of nanoindentation, the relative yield strain H/E and resistance to plastic indentation H^3/E^2 were calculated. These H/E and H^3/E^2 ratios are useful indicators of the durability of the coating material under mechanical stress conditions.

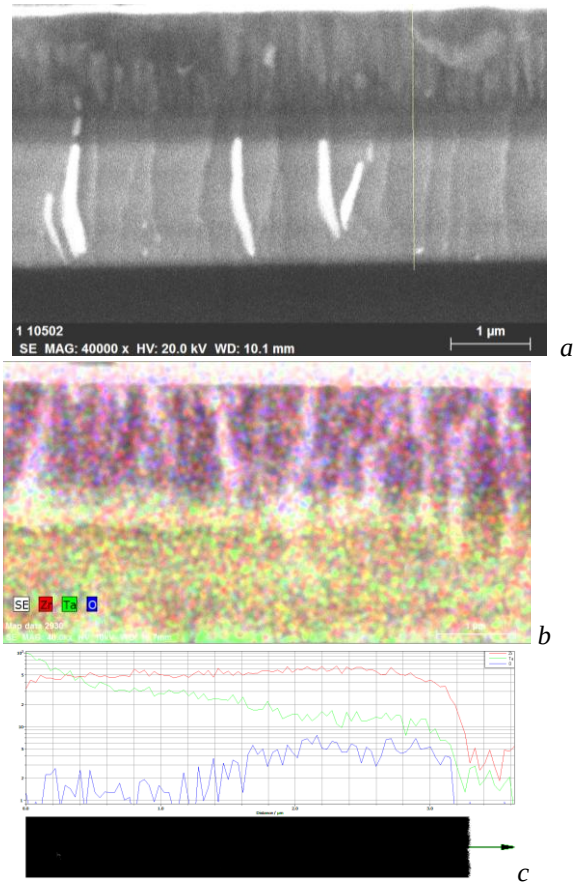

Fig. 5. Cross-section SEM image (a) of ZrTa/$ZrTaO_2$ coating, EDS mapping (b), distribution of elements (c)

Table 2

Physical-mechanical characteristics

Coating	H, GPa	E, GPa	H/E	H^3/E^2, GPa
ZrTa/ZrTaO	16.1±1	226±10	0.07	0.08

As can be seen from the results of the calculations given in Table 2, the values are H/E=0.07 and H^3/E^2=0.08 GPa. The maximum load is determined from the load-displacement curves for a fixed indentation depth, Fig. 6. The penetration depth of the indenter was estimated for the loaded and unloaded state.

The index of plasticity of coatings is defined as the ratio of the depth in the unloaded state to the maximum penetration depth of the indenter. For coatings containing tantalum $ZrTaO_2$, plasticity is high and is about 50%.

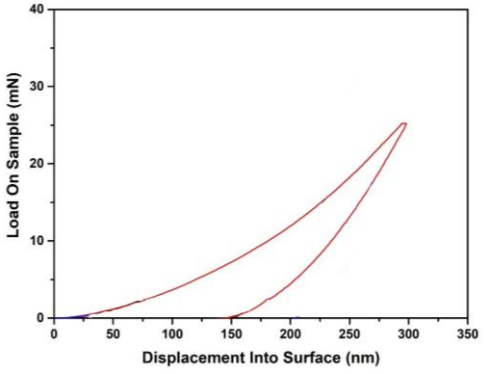

Fig. 6. Load/unload diagram

CONCLUSIONS

Bilayer TaZr/TaZrN coatings were deposited on Ti dental implants and AISI-316 L stainless substrates by means of vacuum-arc deposition of TaZr alloyed target. The nanohardness of the bilayer ZrTa/ZrTaO comprised (16.1 ± 1) GPa and Young's module 226 GPa. A value of near 0.07 in the relation H/E could indicate a high resistance to plastic deformation and is associated with good wear resistance. According to XRD data only three phases were found in the coating: two zirconium oxides ZrO_2-c (cubic) and ZrO_2-m (monoclinic) and a cubic modification of zirconium Zr-β. We suppose that TaO phases were not detected due to the presence of stress in the coatings, or replacement of zirconium with (Ta) in the lattice cell. The obtained results can be useful for optimization of implant surfaces to prevent corrosion and mechanical failure, thereby improving osseointegration.

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МІКРОСТРУКТУРА, ХІМІЧНИЙ СКЛАД ТА НАНОМЕХАНІЧНІ ВЛАСТИВОСТІ ДВОШАРОВИХ ВАКУУМНО-ДУГОВИХ ПОКРИТТІВ $ZrTa/ZrTaO_2$

А.В. Таран, І.Є. Гаркуша, K. Nowakowska-Langier, Г.М. Толмачова, П.М. Воронцов, О.А. Нікольченко, Ю.П. Гніденко, С.П. Романюк, О.І. Тимошенко, І.О. Місірук

Наведено результати вакуумно-дугового осадження тонких двошарових покриттів $ZrTa/ZrTaO_2$ на поверхню титанових дентальних імплантатів, зразків з нержавіючої сталі AISI-316L. Структуру, фазовий та хімічний склад нанесених покриттів досліджено методами скануючої електронної мікроскопії (СЕМ) з енергодисперсійною спектроскопією (ЕДС) та рентгеноструктурним аналізом (РСА). Методом наноіндентування досліджено наномеханічні властивості осаджених покриттів. Отримані результати можуть бути корисними для оптимізації поверхонь імплантатів для запобігання корозії та механічного пошкодження, тим самим покращуючи остеоінтеграцію.