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FUNCTIONAL ZrTaN COATINGS FOR ACETABULAR COMPONENT OF HIP JOINT ENDOPROSTHESIS

A.V. Taran[1], P.M. Vorontsov[2], V.B. Makarov[3], O.A. Nikol'chenko[2], Yu.P. Gnidenko[5], S.P. Romaniuk[4], O.I. Tymoshenko[1], I.O. Misiruk[1]

[1]National Science Center "Kharkiv Institute of Physics and Technology", Kharkiv, Ukraine;
[2]Sytenko Institute of Spine and Joint Pathology
National Academy of Medical Sciences of Ukraine, Kharkiv, Ukraine;
[3]Municipal Non-Profit Enterprise "City Clinical Hospital No. 16"
of the Dnipro City Council, Dnipro, Ukraine;
[4]National Centre for Nuclear Research, Otwock, Poland;
[5]V.N. Karazin Kharkiv National University, Kharkiv, Ukraine

E-mail: avtaran@ukr.net

In the present research the structure and phase composition of PVD ZrTaN coatings on acetabular component of hip joint endoprosthesis have been investigated. Raman spectroscopy, scanning electron microscopy (SEM) with microanalysis (EDX), X-ray diffraction analysis were used to study the surface morphology, chemical composition and its distribution. Mechanical properties have been studied with the help of nanoindentation tests. The maximum hardness for nitride coatings ZrTaN was (27.5 ± 2) GPa and the elastic modulus comprised 388 GPa. According to XRD data only cubic zirconium nitride ZrN with a lattice parameter a = 4.589 Å was found. This phase is characterized by a moderate texture with an orientation (111). The grain size of the ZrN nitride is D = 25.9 nm at a level of micro-strains $\varepsilon = 4.3 \cdot 10^{-3}$. The surface is rather smooth with a very low amount of macroparticles from the cathode material. Such results indicated that ZrTaN coatings on titanium hip implants could be very perspective due to high mechanical properties and convenient surface morphology.

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INTRODUCTION

Currently, the common prosthesis materials used are crosslinked polyethylene, titanium alloys, CoCr alloys, stainless steel, zirconium-niobium alloy, tantalum, ceramics, or a composite combination. CoCr alloy remains the preferred metal within these bearing surfaces due to its high hardness and wear resistance (relative to titanium and stainless-steel) [1, 2]. Manufacturers have for several decades made use ceramic coatings in orthopedics and we have seen examples of various hips, knees and other devices coated with Titanium Nitride (TiN). These coatings have been designed to serve as a 'protective layer' between patient tissue and the underlying CoCr, theoretically minimizing the risk of CoCr wear ions being released (and also reducing the risk of wear of the opposing polyethylene component) or protecting patients with metal hypersensitivity [3, 4].

Ceramic coatings offer other theoretical advantages compared with using CoCr alone: greater hardness, low surface roughness, increased wettability and a lower coefficient of friction, helping to improve the lubrication between the metal and polyethylene components [5-8].

Titanium and its alloys are popular metallic implant biomaterials used in THA. Commercially, α + β titanium alloys, such as titanium-6Al-4 V have been the most commonly used alloys for stem and acetabular cementless components of THA, because of its comparatively low density, high mechanical strength, excellent corrosion resistance, and biocompatibility with bone. However, Titanium alloys are not used for manufacturing of femoral head due to their poor wear resistance.

Also available coatings for implants include titanium nitride (TiN), titanium niobium nitride (TiNbN), oxidized zirconium (OxZr) and zirconium nitride (ZrN) based coatings, diamond-like-carbon (DLC), silicon nitride (SiN), chromium nitride (CrN) and tantalum-based coatings (TaN and TaO) [9-13]. The coating materials referred to above that are still at the research stage have been shown to be non-cytotoxic and to reduce wear in a laboratory setting.

In the present research, ZrTaN coatings on titanium hip implants have been deposited and investigated.

1. EXPERIMENTAL SETUP

In order to increase the biological inertness of the acetabular component of the hip joint endoprosthesis made from Ti6Al4V ELI alloy, a ZrTaN coating was applied to its surface.

The coating was deposited using a "Bulat"-type set-up through vacuum-arc discharge plasma condensation. Since the acetabular component has the shape of a bowl, it was positioned in such a way that no part of its surface was in the shadow of another part in the directed plasma flow. The component was fixed on an L-shaped holder, which was partially recessed into one of the holes (Fig. 1). The holder was mounted vertically on a turntable and could rotate around its axis.

To obtain the three-component ZrTaN coating, a $Zr_{80}Ta_{20}$ alloy cathode was used.

The chamber was evacuated to $7\cdot10^{-5}$ Torr. A negative potential of 1200 V at a frequency of 45 kHz was applied to the sample. The vacuum plasma source with a $Zr_{80}Ta_{20}$ cathode was used to clean the sample's surface by ion bombardment. The vacuum arc current was 100 A. After 50…60 s of cleaning, the amplitude of the negative potential was reduced to -50 V, and within 2 min, the ZrTa coating was deposited.

Next, nitrogen was supplied to the chamber, with the N_2 pressure set to $3\cdot10^{-3}$ Torr. The ZrTaN coating was deposited for another 6 minutes. The total coating thickness was 6 μm.

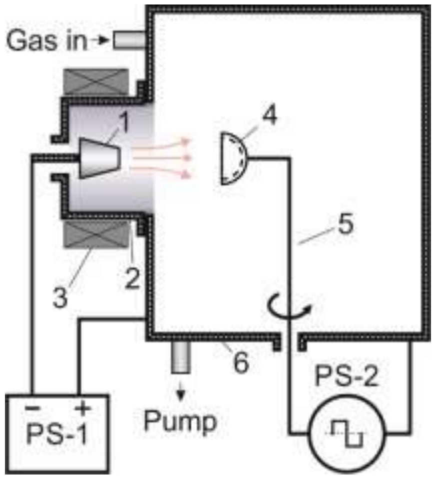

Fig. 1. Experimental Set-up:
1 – cathode; 2 – anode; 3 – coil; 4 – sample;
5 – sample holder; 6 – vacuum chamber;
PS-1 – arc discharge power supply;
PS-2 – pulsed power supply

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.

Specimens were examined by using a confocal Raman microspectrometer, by the WITec alpha 300R model manufactured by Oxford Instruments, UK, which was equipped with a CCD camera. The specimens underwent excitation via a 532 nm Nd:YAG laser emitting 4 mW power. Raman spectra were recorded using a x100 lens within the spectral range of 70 to 3600 cm^{-1}, with an acquisition time of 80 seconds per spectrum, controlled by the Control 5.2 software. The initial data processing phase involved cosmic ray removal (CRR) and baseline correction, employing polynomial functions within the WITec Project FIVE 5.2 PLUS software. Subsequently, the spectra were exported for further analysis in OriginPro 9.9 software to generate the plots.

2. RESULTS AND DISCUSSION

The main view of uncoated and coated titanium hip implants is shown in Fig. 2.

Fig. 2. Titanium hip implants
(top – coated, bottom – uncoated)

According to literature data, the Raman spectra of TaZrN exhibit three primary bands: at approximately 175 and 470 cm^{-1}, corresponding to the longitudinal (LA) and transverse (TA) acoustic vibrations primarily associated with heavy metal ions, and around 620 cm^{-1}, attributed to the optical vibrational modes (LO and TO) of the lighter nitrogen ions. However, the obtained sample does not exhibit these characteristic bands, suggesting a closer attribution to ZrN rather than TaZrN (Fig. 3). Such findings correlate well with XRD data given below (Fig. 4).

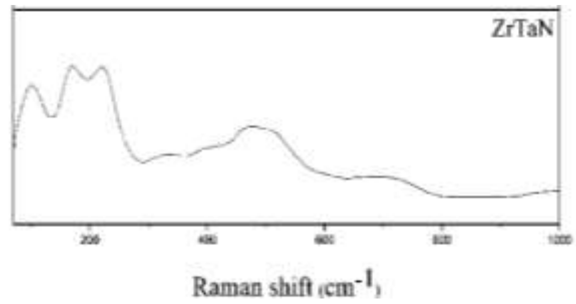

Fig. 3. Raman spectra from ZrTaN coating

According to XRD data (see Fig. 4.) only cubic zirconium nitride ZrN with a lattice parameter a = 4.589 Å was found. This phase is characterized by a moderate texture with an orientation (111). The grain size of the ZrN nitride is D = 25.9 nm at a level of micro-strains $\varepsilon = 4.3 \cdot 10^{-3}$. It is worth noting that the lattice parameters of the phases detected in the coatings (ZrN, Zr-α, Zr-β) differ from the literature values (for ZrN: a = 4.574Å; for Zr-α: a = 3.232Å; c = 5.147Å; for Zr-β: a = 3.545Å). The reason for such deviations may be both the presence of macrostrain in the coatings and the substitution of zirconium by Ta in the elementary cells of the above-mentioned phase.

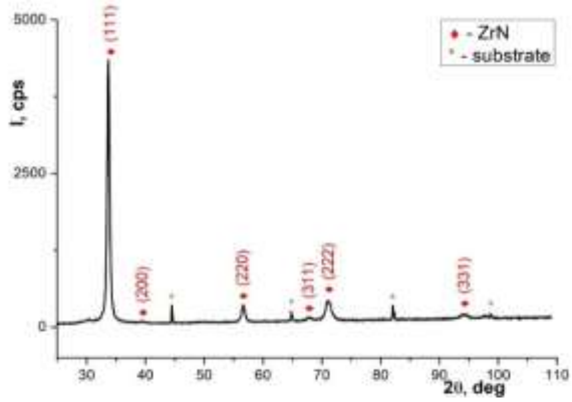

Fig. 4. XRD pattern from ZrTaN coating

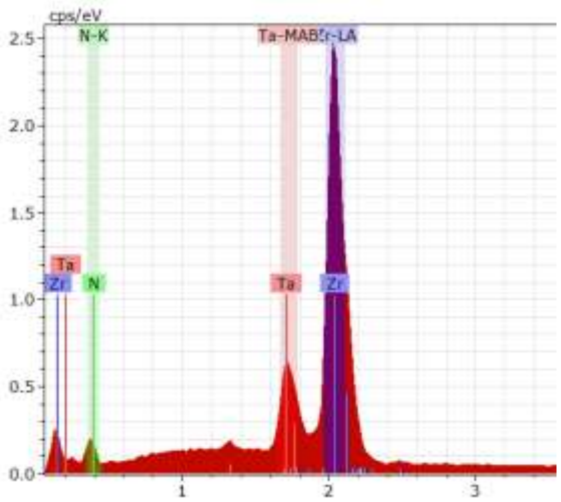

Fig. 5. EDS distribution of chemical elements

SEM images from ZrTaN coatings and EDS spectra are depicted in Figs. 5, 6. The surface is rather smooth with a very low amount of macroparticles from the cathode material.

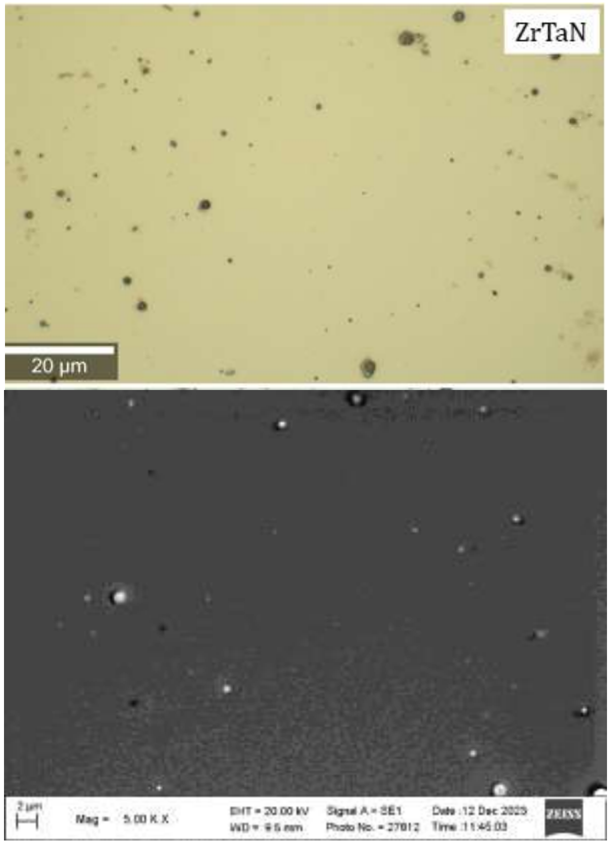

Fig. 6. SEM images from ZrTaN

The hardness and elastic modulus of the deposited coatings are given in Table. The maximum hardness for nitride coatings ZrTaN is (27.5 ± 2) GPa. The elastic modulus was also maximum for the nitride coating, approximately 388 GPa.

Mechanical parameters from ZrTaN coating

Coatings	H, GPa	E, GPa	H/E	H^3/E^2, GPa
ZrTaN	27.5±2	388±10	0.07	0.14

Based on the nanoindentation results, the relative yield strain H/E and the plastic indentation resistance H^3/E^2 were calculated. These ratios H/E and H^3/E^2 are useful indicators of the durability of the coating material under mechanical loading. As can be seen from the calculation results given in Table 1, the values of the coefficients (H/E = 0.07 and H^3/E^2 = 0.14 GPa) correspond to the nitride coating ZrTaN.

CONCLUSIONS

In the present research the structure and phase composition of PVD ZrTaN coatings on titanium hip implants have been investigated. The maximum hardness for nitride coatings ZrTaN was (27.5 ± 2) GPa and the elastic modulus comprised 388 GPa. According to XR data only cubic zirconium nitride ZrN with a lattice parameter a = 4.589 Å was found. This phase is characterized by a moderate texture with an orientation (111). The grain size of the ZrN nitride is D = 25.9 nm at a level of micro-strains $\varepsilon = 4.3 \cdot 10^{-3}$. The surface is rather smooth with a very low amount of macroparticles from the cathode material.

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ФУНКЦІОНАЛЬНІ ПОКРИТТЯ ZrTaN ДЛЯ ВЕРТЛЮЖНОГО КОМПОНЕНТА ЕНДОПРОТЕЗА КУЛЬШОВОГО СУГЛОБА

А.В. Таран, П.М. Воронцов, В.Б. Макаров, О.А. Нікольченко, Ю.П. Гніденко, С.П. Романюк, О.І. Тимошенко, І.О. Місірук

Досліджено структуру та фазовий склад вакуумно-дугових покриттів ZrTaN на титанових імплантатах кульшового суглоба. Для вивчення морфології поверхні, хімічного складу та його розподілу застосовувались: спектроскопія раманівського розсіювання, скануюча електронна мікроскопія (SEM) з мікроаналізом (EDX), рентгеноструктурний аналіз. Механічні властивості досліджено за допомогою тестів наноіндентації. Максимальна твердість для покриттів ZrTaN становила (27,5 ± 2) ГПа, а модуль пружності – 388 ГПа. За даними XRD знайдено кубічний нітрид цирконію ZrN з параметром решітки a = 4,589 Å. Ця фаза характеризується помірною текстурою з орієнтацією (111). Розмір зерен нітриду ZrN D = 25,9 нм при рівні мікродеформацій $\varepsilon = 4{,}3\cdot10^{-3}$. Поверхня покриття досить гладка з дуже малою кількістю макрочастинок матеріалу катода. Такі результати показали, що покриття ZrTaN на титанових імплантатах стегна можуть бути перспективними завдяки високим механічним властивостям та зручній морфології поверхні.