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Multilayer CrN/TiN coatings deposited at low temperatures by unbalanced magnetron sputtering for implant applications

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A multilayer CrN/TiN coating was developed and deposited onto high speed steel (HSS) specimens by unbalanced magnetron sputtering in a closed-field magnetron configuration at a temperature lower than 200 ºC from Cr (99.99 %) and Ti (99.99%) targets. Multilayers were deposited at different nitrogen partial pressure, a target current ratio ranged from 0.7 to 1 and a bias voltage of -60 V, -70 V and – 80 V. The study of mechanical properties indicated that the highest hardness value of 31 GPa and elastic modulus of 378 GPa were achieved at a bias voltage of -80 V and a target current ratio I_{Cr}/I_{Ti} = 0.7. The performed scratch tests exhibited good adhesion of the coating to the substrate as no cracks and delamination in the scratch track were observed. The coating thickness varied between 1.2 µm and 1.7 µm. The wear rate of the film was estimated to be 4.8 $x10^{-6}m^3N^{-1}m^{-1}$. X-ray photoelectron spectroscopy (XPS) was used to determine binding energies between Cr, Ti and N elements in the coatings. The surface roughness was evaluated to be 16.2 nm by Atomic force microscopy (AFM). The coating surface was characterized by Scanning Electron Microscopy (SEM). Energy-dispersive X-ray spectroscopy (EDX) analysis defined the elemental composition in the multilayer coating layer to be 46.73 at.% chromium, 43.67 at.% nitrogen, 9.61 at.% titanium.

Keywords: Physical Vapour Deposition (PVD), unbalanced magnetron sputtering, low-temperature deposition, CrN/TiN layers, surface morphology, composition

INTRODUCTION

Due to rapid changes in the age structure of the world's population, an increasing number of people need their failed tissues to be replaced by artificial implantable devices. Because of the decreased age that patients are considered for the operation, and a population which is living longer, the need for long lasting implants is becoming a larger concern. The current average life span of 15 years for hip implants is not sufficient in a population that may require 30–40 years of service [1-3].

Over the previous decade there has been a significant impact of metallic implant materials such as stainless steels and titanium (Ti), widely used for surgical prostheses as joint replacements, mechanical heart valves and dental implants [4]. The important disadvantage of the metals is their tendency to corrode in physiological conditions. Although conventional materials technology has resulted in clear improvements in implant performance and longevity, rejection or implant failures still happen [5]. For this reason, metals and alloys were found unsuitable for implantation as being too reactive in the human body. To solve the problem it is necessary to deposit wear and corrosion resistant coatings.

The most commonly used coatings for biomedical applications are TiN and CrN. These films are well known for their high hardness and wear and corrosion resistance [6, 7], which are not enough for many modern applications. The increase in average life expectancy, as well as rapid advances in modern surgery require new generations coatings with enhanced mechanical, tribological and corrosion properties.

Advances in titanium and chromium manufacturing technologies are expected to play an important role in the development of the next generation wear and corrosion resistant coatings [8, 9]. A multilayer CrN/TiN coating for deposition on implants was elaborated based on the advantages of the alternately deposited single layers. As a sizable part of biomedical materials such as stainless steel, plastics, glass and polymers are unstable at high temperatures; low-temperature technology for achievement of a

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layered structure on the base of the closed-field unbalanced magnetron sputtering was developed.

This study presents the results of mechanical, tribological, morphological and compositional properties of the multilayers CrN/TiN coatings deposited at low-temperatures by unbalanced magnetron sputtering for biomedical applications.

EXPERIMENTAL DETAILS

The multilayer CrN/TiN coatings were deposited onto hardened high-speed steel (HSS) substrates with diameter of 12 mm by unbalanced magnetron sputtering in UDP 850-4 equipment (Teer Coatings Ltd.) from one titanium (99,99 %) and one chromium (99,99%) rectangular targets in a closed-field configuration. Prior to coating deposition, the substrates were ultrasonically cleaned in an alkaline solution at 60 °C for 10 minutes to remove the surface contaminations and subsequently rinsed in de-ionized water. After that, they were dried in a furnace at 100 °C before being loaded into the deposition chamber. Immediately before the deposition, the substrate surface was etched by Ar+ plasma for 15 min at a pulsed substrate bias of −500 V with a frequency of 250 kHz and low magnetron power in order to improve the coating adhesion.

Prior to the deposition, the vacuum chamber was evacuated to a base pressure of 1×10^{-3} Pa. After the evacuation, Ar or Ar + N_2 mixture was introduced into the chamber. The Ar flow was controlled by a mass flow controller, while the reactive N_2 gas flow was controlled by an Optical Emission Monochromator (OEM). The distance between the substrates and the targets was 150 mm. In the deposition process, the substrates were rotated biaxial at a speed of 2 rpm in order to obtain homogenous film thickness and composition.

The deposition of the multilayer coating started with an adhesion Cr layer, followed by a gradient CrN layer, in which the nitrogen was gradually increased up to values corresponded to stoichiometric CrN. After that alternate periods of CrN and TiN sublayers were formed. The structure of the multilayer coating is shown in Fig.1.

Two sets of experiments were carried out at different technological parameters. The first set of coatings was made to assess the influence of the nitrogen partial pressure on the mechanical properties of the obtained coatings. For this purpose 12 samples were investigated at different deposition temperatures and a bias voltage of – 70 V. The second series of coatings was generated to evaluate the effect of the bias voltage and target current ratio I_{Cr}/I_{Ti} on the coatings hardness. That`s why the 3 specimens were deposited at a bias voltage of - 60 V, - 70 V and - 80 V, target current ratio from 0.7 to 1 at a temperature of 130 ^{o}C. The choice of this deposition temperature was made on the base of literary research for the thermal resistance of the materials. The Ar flow rate was kept a constant (25 sccm) in the all of the experiments. The values of target current ratio were chosen to be between 0.7 and 1 because of the use of different technological regimes and change of targets currents.

Measurements of the coating thickness were performed by a Calotest, which is a suitable method for obtaining quick information about layer configuration, abrasion resistance and thickness. A stainless steel ball with a diameter of 30 mm was used with diamond slurry with particles of 0.25 μm in a diameter. The coating was abraded until the substrate was reached by the ball. The thickness was determined from the crater imaged using an optical microscope with high magnification. The mechanical and tribological properties of the deposited coatings were investigated using Compact Platform CPX (MHT/NHT) CSM Instruments equipment. Nanoindentation was performed by a triangular diamond Berkovich pyramid in the loading interval of 10 - 200 mN. The adhesion of the coating was evaluated by a micro-scratch technique, using a Rockwell diamond indenter with a radius of 200 μm. During the test, the normal load was progressively increased in a linear mode from 1 N to 30 N over the scratch length of 1 mm at a constant scratch speed of 0.5 N/min. Wear tests were accomplished at a load of 5 N in linear mode at scratch length of 3 mm at a constant scratching velocity of 0.2 mm/min.

The Atomic force microscopy (AFM) studies were carried out by NanoScope VAFM (Bruker Inc.) in air in tapping mode. Silicon cantilevers with reflective aluminium coating with a thickness of 30 nm, Tap 300Al-G (Budget Sensors, Innovative solutions Ltd, Bulgaria) were used. All images, taken at a resolution of 512×512 pixels in JPEG format were processed by means of Nanoscope software. Images from three independent locations of the samples were taken for reproducibility purposes. The arithmetic average roughness (Ra) and root mean square roughness (Rq) were determined from the analysis applied to an image; the statistical values were calculated according to the relative heights of each pixel in the image.

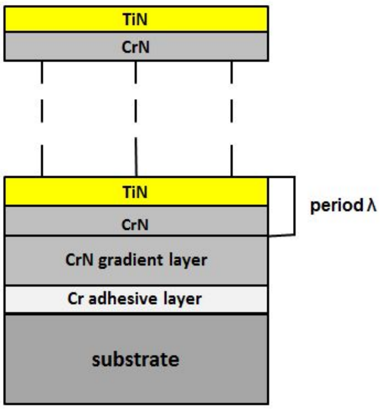


Fig.1. A principal scheme of the multilayer CrN/TiN coating

The XPS spectra were acquired on a Kratos AXIS Supra photoelectron spectrometer using a monochromatic Al K source with energy of 1486.6 eV. The base pressure in the analysis chamber was 5 x 10^{-8} Pa. The binding energies were corrected relative to the C1s peak at 285.0 eV. The concentration of the elements was derived on the basis of the core level peak areas, corrected by the corresponding relative sensitivity factor values.

Surface observations, morphology and elemental analysis are performed on JEOL JSM 6390 scanning electron microscope, equipped with INCA Oxford EDS energy dispersive detector. Surface images are obtained in secondary electrons (morphology contrast) and back-scattered electrons (density contrast) as well. The elemental analyzer is capable to detect all elements from carbon to uranium.

RESULTS AND DISCUSSION

Coating thickness

The thickness measurements were performed for all 12 coatings deposited at different technological parameters. However, the multilayer CrN/TiN coating obtained at a temperature of 130 °C, a bias voltage of – 80 V, target current ratio 0.7 and a nitrogen partial pressure 8x10^{-2} Pa demonstrated better combination of mechanical properties- high coating hardness (32 GPa) and excellent adhesion to the substrate material than the other coatings properties. For this multilayer, the thickness was estimated to be 1.7 µm and an image of the multilayer CrN/TiN coating surface after performing the calotest is indicated in Fig.2.

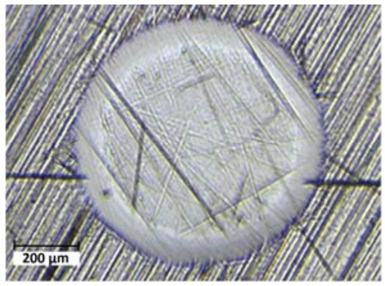


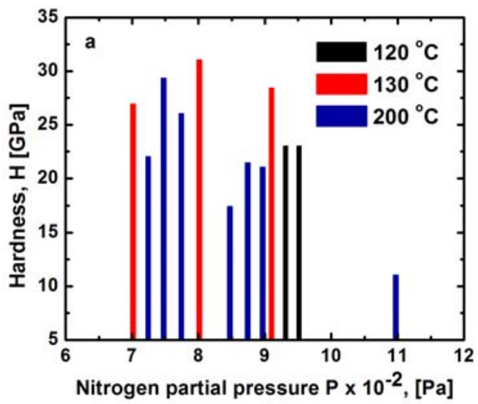
Fig.2. A segment of the optical microscopy image of the multilayer CrN/TiN coating, obtained by ball cratering test

The calculated total thickness for all deposited coatings was in the range of 1.2 –1.7 µm. The thickness of the multilayers depends mainly on the speed of rotation and the applied target currents during the process.

Mechanical properties

The mechanical properties were studied using the Depth Sensing Indentation technique. The nanohardness and elastic modulus were estimated by an Oliver & Pharr method from the load-displacement curve using 10 % of the coating thickness as the indentation depth [10].

The influence of the technological parameters on the mechanical properties of the deposited film was investigated. Dependence of the hardness and elastic modulus of multilayer CrN/TiN coatings on the nitrogen partial pressure is presented in Fig.3. The multilayer CrN/TiN coating hardness varied between 11 GPa and 32 GPa. As it is seen from Fig.3a, maximum hardness value (32 GPa) was achieved at a partial pressure of 8 x10^{-2} Pa and a substrate temperature of 130 ^{o}C which was created by cathode's power only. The further increase of the nitrogen partial pressure to 11x10^{-2} Pa at a temperature of 200 ^{o}C leads to strong decrease of the hardness (11 GPa) probably due to diversion of the stoichiometry in the thin films. A big nitrogen amount introduced in the vacuum chamber to a definite value contributes for the nitride composition formation and the mechanical properties are enhanced. At a relatively high nitrogen flow and high pressure in the chamber stoichiometric structure is not obtained. The latter is due to the poisoned surface of the Ti target with the lower applied current.



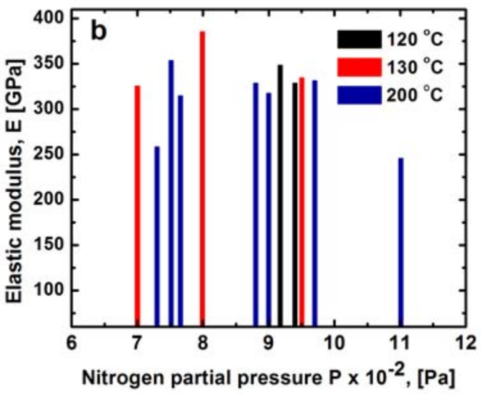


Fig.3. Dependence of the nanohardness (a) and elastic modulus (b) of the CrN/TiN coatings on the N_2 partial pressure at different temperatures

Thus, an increase of the Cr amount in the composition causes decrease of the coating hardness. The low deposition temperature (130 ^{o}C) cannot promote the surface kinetics, which results in low density of the films. Increase of the deposition temperature accelerates the particle migration on the surface supporting the dense structure formation and enhancement of the coating hardness, respectively. Despite, the coating deposited at 200 ^{o}C possesses almost the same hardness as the one obtained at lower temperature (130 ^{o}C). This result is due to the thermal instability of the substrate at temperatures of 200 ^{o}C and higher ones. The elastic modulus was found to be relatively insensitive to changes in nitrogen partial pressure at all temperatures (Fig.3b). The elastic modulus is an interesting material property, which depends on the material structure of the deposited coating. The lowest value of the elastic modulus (265 GPa) was estimated at 200 ^{o}C and 11 x10^{-2} Pa nitrogen partial pressure.

The substrate bias and target current play an important role determining the mechanical properties of the coatings. The use of ion bombardment allows deposition of adherent coatings at low substrate temperatures. The influence of the substrate bias and targets current ratio on multilayer CrN/TiN coating hardness is depicted in Fig.4.

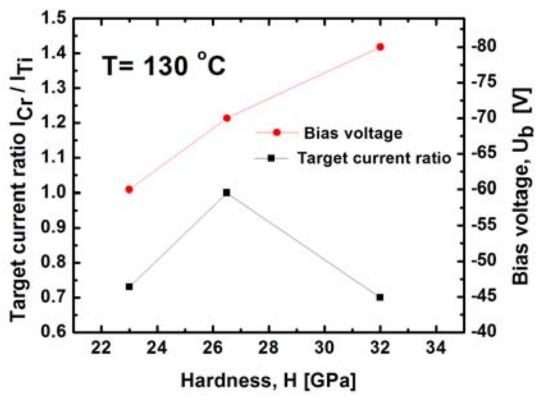


Fig.4. Influence of target current ratio I_{Cr}/I_{Ti} and bias voltage on the nanohardness of the multilayer CrN/TiN coatings

Maximum hardness of 32 GPa was achieved in a film deposited at a bias voltage of - 80 V and target current ratio 0.7. As the bias voltage was diminished to – 60 V, the multilayer hardness decreased to 23 GPa. The most probably reason for lower values of the hardness is the presence of strong tensions and defects in the layer. Moreover, low bias voltage leads to porous structure and not enough dense layer. In general, the hardness increases with the substrate bias up to 100 V, and then decrease significantly at higher bias values (e.g. ≥ 200 V), presumably because of ion beam intermixing effects at the interfaces and interface roughening [11].

The variation of hardness and elastic modulus with indentation depth of the investigated multilayer CrN/TiN coating is given in Fig.5. The highest value 32 GPa of the multilayer hardness is achieved at an indentation depth of 140 nm and a load of 10 mN. The high strength of the multilayer thin film is a result from many interfaces which block dislocation movement [12]. The hardness decreases slowly at indentation depth larger than ~200 nm, which was attributed to the substrate effect. It is expected that substrate effect becomes more important with increase of the indentation depth. It was experimentally proved that the hardness decreases with increasing indentation depth based on the presence of strain gradients in the deformation zone around the indent [13]. With an indentation depth increase to ~ 900 nm, an elastic modulus value slightly decreases. The lower value of the elastic modulus was measured to be 270 GPa.

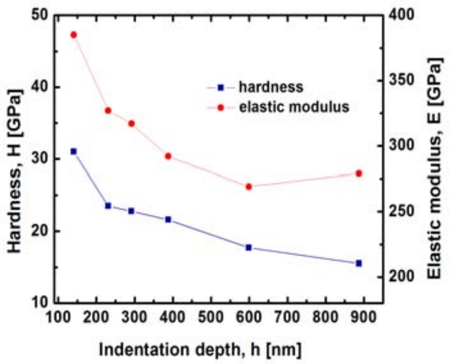


Fig.5. Dependences of the multilayer CrN/TiN coating nanohardness and elastic modulus on the indentation depth

The multilayer adhesion and friction coefficient were studied using a micro-scratch test technique. The results revealed that multilayer thin films possess good adhesion to the substrate (Fig.6). No cracks, track edge chipping and delamination were observed in the scratch track at a load friction force (Ft) from 1 N to 30 N.

The estimated friction coefficient of the coatings was in the range 0.09-0.15.

Surface morphology

The surface morphology of the multilayer CrN/TiN coating was examined by Atomic force microscopy (AFM) and Scanning electron microscopy (SEM). The AFM measurements showed low surface roughness. The 2D and 3D AFM images of the multilayer thin film are shown in Fig.7. They exhibit a smooth surface without hills and vales. The grown film repeats the surface morphology of the substrate.

The measurement revealed an average surface roughness Ra = 16.2 nm on an area of 9.51 μm^2 of the multilayer CrN/TiN coating with the highest nanohardness. The low surface roughness is associated with relatively small grain sizes, typical for the used bias voltages during deposition [14].

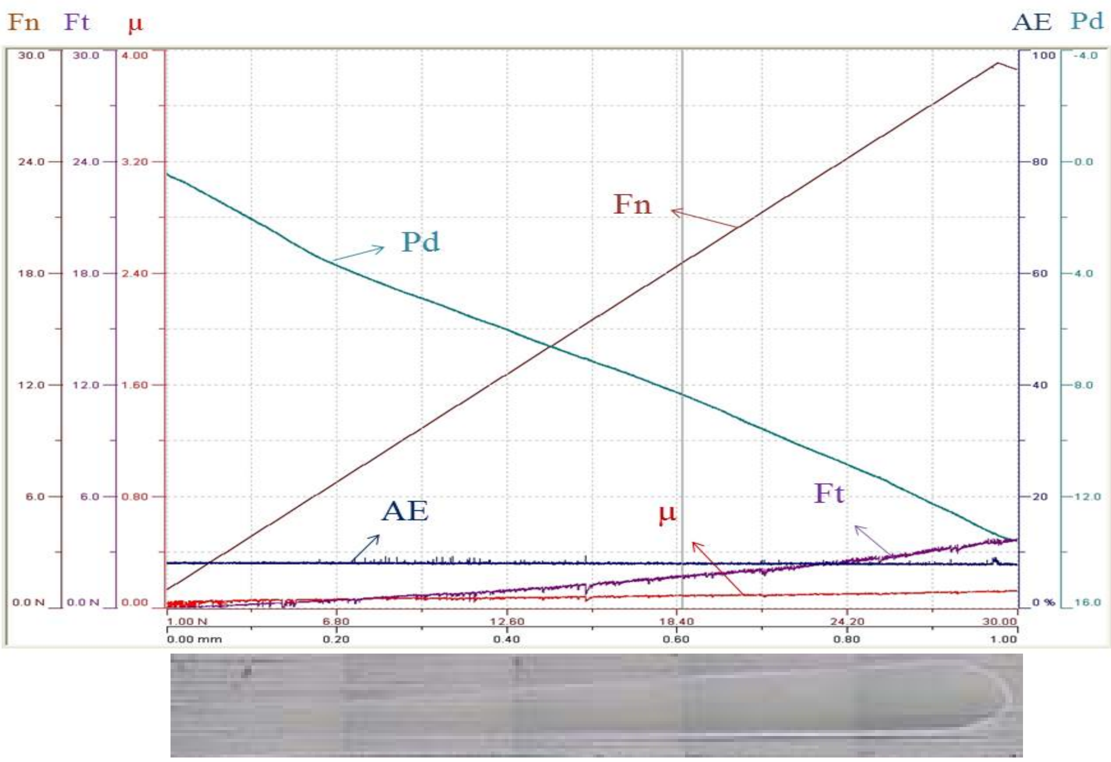


Fig.6. Optical image of the scratch track in the CrN/TiN coating and scratch test results of the normal force (Fn), penetration depth (Pd), acoustic emission (AE), friction force (Ft) and coefficient of friction (μ)

The observed by AFM surface morphology is confirmed by the SEM images. Fig.8. shows the SEM micrograph of the multilayer CrN/TiN coating surface deposited at the same technological parameters as one investigated by AFM measurement.

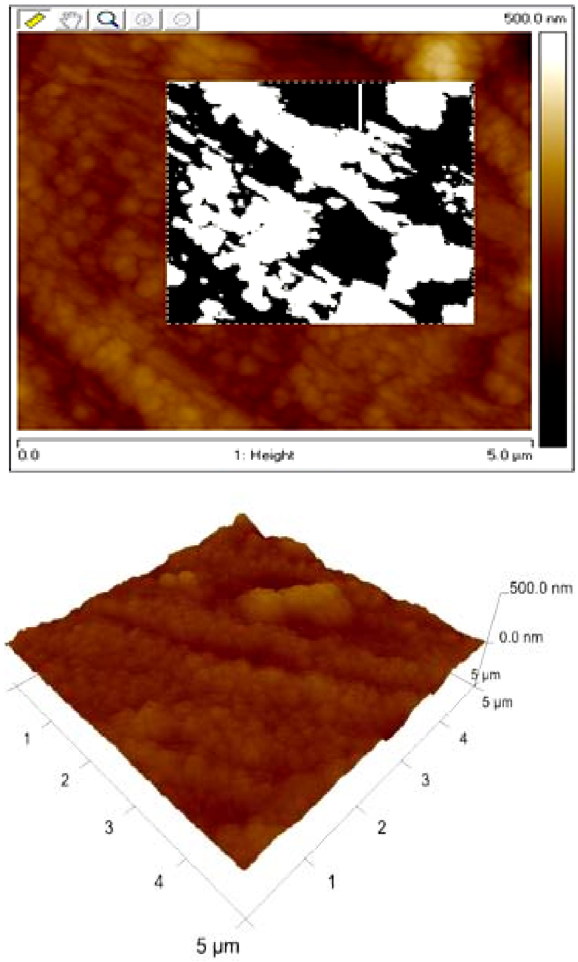


Fig.7. Two-dimensional and three- dimensional AFM images of the CrN/TiN multilayer surface

The results depicted that the coating has dense packed texture, built mainly by grains with an average size of 150- 200 nm. The grains of a higher size 500 nm – 700 nm are very rare. The elemental composition of the multilayer coatings was defined by an Energy-dispersive X-ray spectroscopy (EDX) analysis.

The results indicated that concentrations of chromium, nitrogen, titanium are 46.73 at.%, 43.67 at.% and 9.61 at.%, respectively, supposing formation of CrN and TiN compounds. The CrN part is dominated because of the Cr-based adhesion and transition layers.

XPS analysis

The chemical state and composition of the outermost layers of the Cr/CrN/CrN-TiN coating were obtained by XPS. From the intensity of the core level Cr2p, N1s, O1s and Ti2p peaks, an element composition was estimated using the atomic sensitivity factors (ASF). It was assumed that carbon belong to a contamination layer and was not taken into account. The element concentrations in atomic [%] are: Ti -10.6, O - 24.9, N- 37.4 and Cr - 27.1. The surface overlayer contains significant oxygen amount. Probably, the air exposure of the coating induced the formation of a thin surface layer, whose composition is a mixture of Cr and Ti oxynitrides and oxides. High-resolution Cr 2p, Ti 2p, N 1s and O1s spectra are shown in Fig.9.

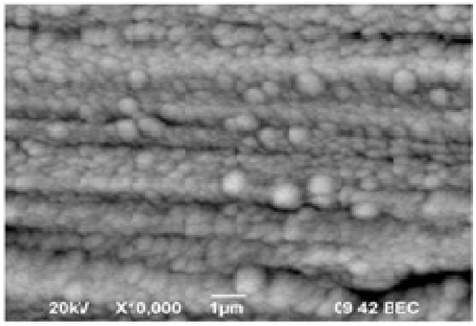


Fig.8. Typical SEM surface image of the multilayer CrN/TiN coating

The spectra are deconvoluted and peaks are assigned to different chemical states according to reference data. The Cr 2p3/2 peak on Fig.9a is centred at 574.5 eV and possesses an asymmetric shape. Three main components corresponding to different chemical chromium species could be resolved in the spectrum. The first peak at 574.5 eV was assigned to CrN and the second peak at 576.2 eV to Cr_2N, in accordance with literature findings [15,16]. The contribution of the component assigned to Cr_2N peak could coincide with a contribution from Cr_2O_3 and CrO_2 (usually between 576.1 and 576.6 eV[17]. The third component in the Cr 2p3/2 peak is centred at 578.1 eV and it may be related to Cr (VI) species observed in this binding energy range (578.1 - 579.8 eV) or to many body interactions [18].

The deconvolution of the Ti2p peaks gives four features (Fig.9b). These features were assigned to Ti species in different chemical environment. The position of the first component at 455.2 eV and the presence of characteristic shakeup satellite at 456.3 eV confirm the formation of TiN [19]. The peaks at 457.5 eV and 459.1 eV can be associated with Ti–N–O and Ti–O bonds, respectively [20]. These findings also reveal the formation of an overlayer on the coating containing Ti oxynitride and oxide. The N1s spectrum in Fig.9c. shows a wide peak at 396.7 eV, which can be decomposed into five components. These peaks are assigned to different chemical states formed on the surface of the coating. The first component at 395.7 eV represents nitrogen in nitride bond N-Ti [21], while the next two peaks at 396.7 and 397.5 eV could be assigned to nitrogen in CrN and Cr_2N, correspondingly [22]. The formation of a surface overlayer due to exposure of the coating to air is also reflected in two contributions at 398.6 eV and399.7 eV, which are ascribed to different chromium and titanium oxynitrides [23, 24].

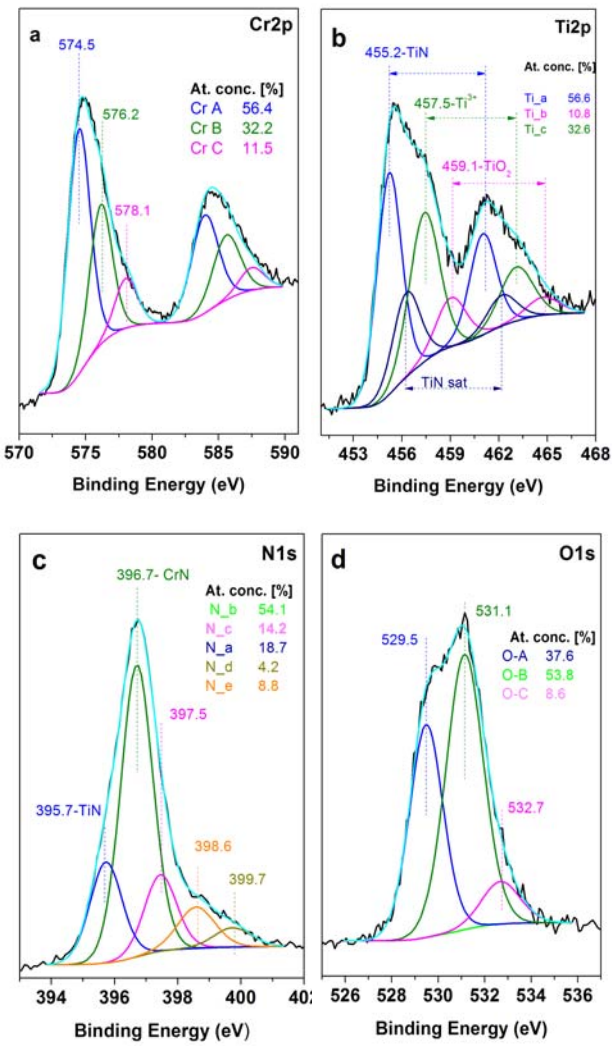


Fig.9. XPS spectra of CrN/TiN multilayer coating (a) Cr2p, (b)- Ti 2p, (c)- N 1s and (d) O 1s

The analysis of the oxygen O1s peak in Fig.9d. presents information about the nature of the oxygen species participating in the surface layer of the coating. The deconvolution of the oxygen O 1s peak gives three components. The peak at 529.5 eV could be attributed to CrO_2 in accordance with [17]. The most intensive peak at 531.1 eV contains probably a mixture of contributions from different chromium and titanium oxynitrides and oxides.

Tribological behaviour

Wear rate and friction coefficient are of vital significance for the durability of surgical implants, especially for hard tissue replacements like hip and knee joints consisting of mating components. The tribological measurements of the multilayer CrN/TiN coating were performed based on multi pass scratch test (Fig.10). The number of multi passes through the scratch was 10. The multi pass scratch test gave information about the wear resistance at high applied force on a short distance.

The wear and wear rates were investigated for three multilayer structures with the best mechanical parameters. In the scratch wear test, the measurement device registered the friction force, indenter penetration depth and acoustic emission along the scratch track. The observed picks in the acoustic emission (AE) are due to the reciprocal movement of the indenter during the multi pass scratch. The average penetration depth as determined from the plotted curve was found to be 110 nm. The average width of the worn track was determined to be 64 μm. Thus, during the scratch wear test a material volume of $1.06x10^{-5}mm^3$ was worn at a force of 5 N applied on a length of 30 mm.

After wear resistance test of the films, no delamination, cracks and critical loads were observed inside and outside the track.

The amount of worn volume (V) is calculated by equation (1) from the cross section area of the worn track and the passed length [25]:

$$V = S \times l \qquad (1)$$

where:

S- cross section area of the worn track, mm^2;

l- passed length, mm

The wear rate of the coatings is estimated by equation (2) [26]:

$$K = \frac{V}{F_n \times L} \qquad (2)$$

where:

K- wear rate, m^3/Nm;

V- worn volume, m^3;
Fn- applied normal load, N;
L- sliding distance, m.

Based on these calculations, the average value of the wear rate of the multilayer CrN/TiN coatings was calculated to be 4.8 $x10^{-6}$ m^3/Nm.

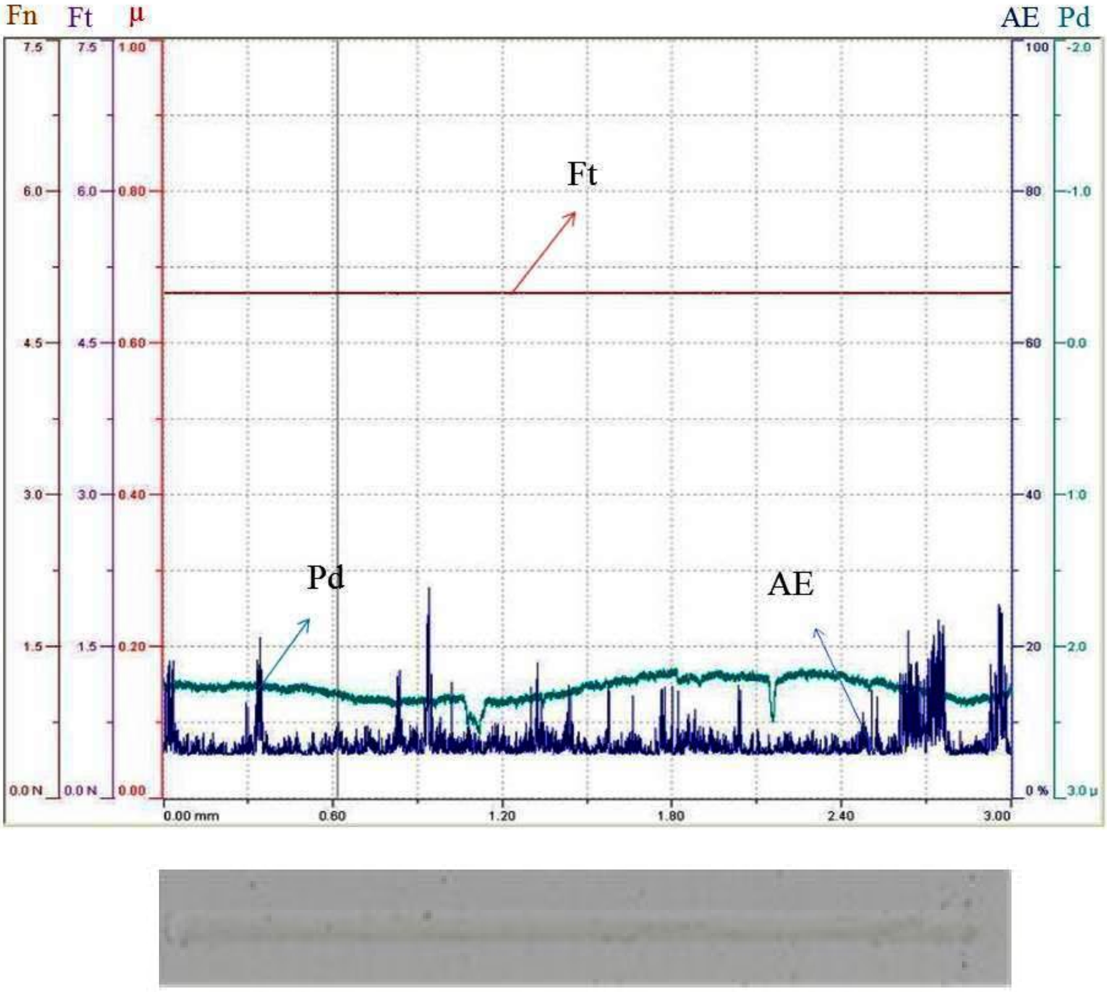


Fig.10. Multi pass scratch test results of the acoustic emission (AE), friction force (Ft) and penetration depth (Pd) and an optical micrograph of the scratch track in the CrN/TiN coating

CONCLUSIONS

Low-temperature technology for deposition of multilayer CrN/TiN films was developed on the base of optimized technologies of CrN and TiN monolayers. Twelve specimens were deposited at different technological conditions. The influence of the bias voltage, target current ratio and nitrogen partial pressure on the coatings properties was evaluated. The mechanical properties of multilayers were studied at temperatures of 120°C, 130 °C and 200 °C. The coating deposited at a bias voltage of – 80 V, at a temperature of 130 °C, 8 $x10^{-2}$ Pa partial pressure of nitrogen and target current ratio 0.7 possessed the best combination of mechanical properties - the highest hardness 32 GPa, low friction coefficient 0.1 and excellent adhesion to the substrate. The enhanced properties of the the developed CrN/TiN coating prove the advantages of the multilayer structure to the single layers. The presence of many interfaces in the coating structure causes crack deflection, dissipation of the defects and crack energy, which results in good tribological properties. AFM and SEM measurements demonstrated a low roughness of the multilayer film surface which is an essential requirement for the implants because it influences directly on the friction. Besides,the low friction coefficient prolong the lifetime of the implants and reduce the pain of the patients. XPS measurements showed that the multilayer CrN/TiN coating consists of CrN and TiN compounds. EDX analysis revealed that the amount of Cr is predominated due to Cr-based adhesion and transition layers.

The presented results in this work evidence that the developed multilayer CrN/TiN coating is suitable for implant applications.

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