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Titanium nitride coatings synthesized by IPD method with eliminated current oscillations

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This paper presents the effects of elimination of current oscillations within the coaxial plasma accelerator during IPD deposition process on the morphology, phase structure and properties of synthesized TiN coatings. Current observations of waveforms have been made by use of an oscilloscope. As a test material for experiments, titanium nitride TiN coatings synthesized on silicon and high-speed steel substrates were used. The coatings morphology, phase composition and wear resistance properties were determined. The character of current waveforms in the plasma accelerator electric circuit plays a crucial role during the coatings synthesis process. Elimination of the current oscillations leads to obtaining an ultrafine grained structure of titanium nitride coatings and to disappearance of the tendency to structure columnarization. The coatings obtained during processes of a non-oscillating character are distinguished by better wear-resistance properties.

Keywords: *Impulse plasma deposition (IPD) method; nanocrystalline coatings; TiN coatings; wear resistant coatings*

1. Introduction

The Impulse Plasma Deposition method (IPD) has been developed as a practical realization of "unconventional synthesis" concept [1, 2]. The unconventional synthesis bases on thermodynamic parameters of state, different than temperature and pressure, for example energy of electric and/or magnetic field may be a very effective substitute for thermodynamic parameters of state. It is worth mentioning that this development placed the IPD method in the modern trend of plasma surface engineering methods with respect to effective use of high power in pulsed methods, such as Pulsed Magnetron Sputtering (PMS) [3], High Power Impulse Magnetron Sputtering (HiPIMS) [4, 5], Plasma Immersion Ion Implantation (PIII) [6, 7]. The very important advantages of pulsed methods are the increase of internal energy of a thermodynamic system, the achievement of a high degree of plasma ionization during synthesis [8], the improvement of morphology of deposited films [9–11], the possibility of "engineering" the condensate on the surface of a solid phase by hyperthermal plasma species [12, 13].

This paper presents a modification of the plasma source power system used in the IPD method, and consequently the influence of the modification on the synthesis of wear-resistant titanium nitride films. The practical realization of this aim was linked with the specificity of the used plasma source. The IPD method uses a very specific plasma source – a coaxial accelerator – developed by Mather [14] and Filippova [15] – Plasma Focus device. Impulse plasma is generated in the interelectrode space of the accelerator as a result of high voltage and high current discharge ignited by a gas dose injected by an impulse valve [16]. The special feature of the energy source is that the electrodes polarity and current distribution change during each half-period of strongly attenuated current waveform [17]. Experimental and simulation studies concerning the impulse plasma distribution inside coaxial accelerators have shown significant differences between the accelerator work modes: the mode of positive/anodic (first and third

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half periods) polarization and the negative/cathodic (second and fourth half periods) polarization [18, 19]. The convex paraboidal shape of the current sheet observed during anodic polarization of the electrodes is a result of the increased magnetic field intensity with a decreasing radius. During the cathodic polarization, the current sheet was observed as a concave shape, almost perpendicular to the channel walls, which is probably the result of specific distribution of plasma electrons and ions in the interelectrode space in the accelerator. Furthermore, under these conditions, the plasma region is much thicker. The lowered value of discharge energy and diversity of plasma distribution in the consecutive half-periods suggests that the process of film synthesis takes place under extremely dynamic conditions. According to the close relation between the conditions of impulse plasma generation and deposited film morphology [20–25], we have expected that, from the point of view of phase synthesis, the most important period is probably the first half of current waveform. The amplitudes of the next halves are lower so the electric energy introduced into the discharge is relatively smaller than that introduced during the first half. The goal of our work was to make the discharge more energetically monochromatic. We set ourselves the objective to eliminate current oscillations and determine how this modification affects the properties of deposited films.

2. Experiment

The schematic view of two versions of the apparatus used in the experiments is shown in Fig. 1. A practical form of realization of the experiment was to use the bank of six FRED (Fast Recovery Epitaxial Diode) diodes connected in series. The diodes used in the experiment were characterized by a maximum repetitive peak reverse voltage $V_{RRM} = 1200$ V, maximum average forward current $I_{FAVM} = 450$ A and reverse recovery time $t_{rr} = 450$ ns. The fast recovery diodes bank was used to cut off the second and the remaining halves of the period of current waveform.

The coaxial plasma accelerator was built of two titanium electrodes: the electrically

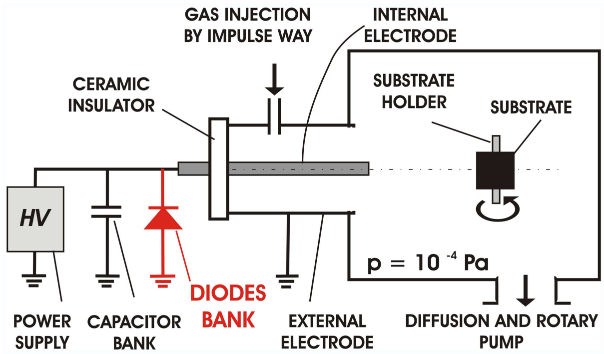

Fig. 1. Schematic diagram of the IPD device equipped with diodes bank.

separated central electrode in the form of a rod, and the grounded outer electrode which has the shape of a hollow cylinder.

The plasma processes were carried out in a nitrogen atmosphere with the total number of plasma impulses equal to 500 (SEM investigations), 5000 (XRD investigations and wear tests). The coatings were deposited on silicon substrates and 10 mm × 10 mm × 5 mm high-speed steel insert cutting edges. The discharge voltage of the capacitor bank of 150 μF was equal to 3 kV and the discharge frequency was equal 1 Hz. During the synthesis process, the impulse valve opening time was about 100 ms. Starting pressure was of the order of 10^{-4} Pa. During the pulse valve work, the pressure was changing dynamically from 10^{-4} Pa to 10^{1} Pa. The gas dose was chosen experimentally to permit the plasma process generation.

The substrates were installed perpendicular to the axis of the accelerator electrode and were not heated from any external heat source before, during or after deposition of the coatings. In the IPD method the substrate was heated just by energy exchange between the pulsed plasma and the surface of the substrate and it reached the level of 2000 K for the short period of time, of a couple of miliseconds during the discharge [26]. The intervals between consecutive discharges were long enough to efficiently cool the substrate by scattering radiation and thermal conductivity and thermal capacity of the substrate material to the level of 400 K [27], with a rate of 10^5 K/s to 10^6 K/s [26].

Additionally, high-speed steel substrates were rotated during the deposition processes which resulted in covering of all the substrate surfaces and edges.

The X-ray diffraction measurements were performed using monochromatic synchrotron radiation (λ = 1.54056 Å) at the W1.1 beamline (equipped with a 6 + 2-circle diffractometer) at DESY-Hasylab. Diffraction patterns were collected in two scanning modes of measurement: a classical 2θ-θ scan and a coplanar 2θ scan in the grazing incidence geometry. During the measurements in the grazing incidence geometry, the ω angle was fixed at 1°. This geometry resulted in a strong diffracted signal with a low background scattering effect originating from the substrate.

The average crystallite size D was estimated from the XRD line broadening using the Debye-Scherrer's formula: $D = (Ax\lambda)/(\cos\theta x\beta)$, where λ is the X-ray wavelength and β is the line broadening at full-width at half-maximum (FWHM) of the Bragg diffraction peak at angle 2θ.

Current-voltage waveform studies were carried out with the use of Agilent 8000 Series Infiniium oscilloscope and with a Rogowski coil as a current probe with sensitivity set to 1kA:1V and voltage probe with sensitivity set to 1:1000.

Cutting inserts made of HS 6-5-2 (SW7M) high-speed steel were used for the investigation of anti-abrasive properties of the TiN coatings deposited by the modified IPD method. Before deposition, the insert edges were polished to R_a = 0.2 μm. The durability studies of the tools have been carried out by turning a 41CrAlMo7 (38HMJ) nitriding steel roller. In each case 4 edges were examined. On the basis of obtained wear curves and in accordance with the Polish Standards PN-ISO 3685:1996, tool life values for TiN coated edges were estimated to the so called mean band width value of the edge corner wear VB_c = 0.3 mm. According to the standards, VB_c plays a role of an indicator of the ultimately acceptable edge corner blunting.

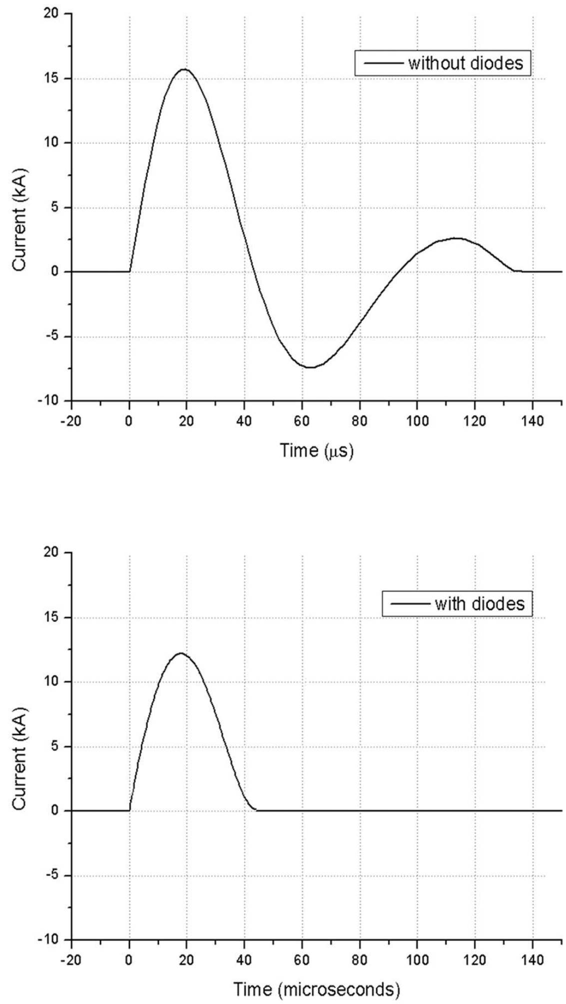

Fig. 2. Current waveforms measured in the plasma accelerator electric circuit equipped with diodes bank (lower graph) and without the diodes bank (upper graph).

3. Results and discussion

The effect of using the diodes bank connected with plasma accelerator electric circuit was measured by oscilloscope probes. Fig. 2 presents the current-voltage waveforms, measured in the electric circuit of the plasma accelerator during the process of coating deposition by the use of the apparatus in oscillating (A) and non-oscillating (B) modes. The current waveform (A) consists of 3 half-periods, about 24 μs long each with amplitudes as follows: 15 kA (positive polarization), 8 kA (negative polarization), and

3 kA (positive polarization). The current waveform is attenuated, because the accelerator electrical circuit is of LCR type. The waveform (B) consists of only one half-period, 24 μs long with the amplitude of 13 kA. As we expected, equipping an electric circuit of plasma accelerator with a diodes bank leads to cutting the rest of the current waveform and thus shortening its length threefold.

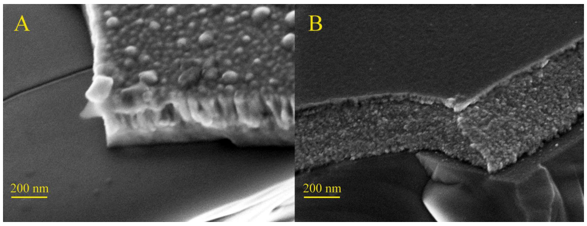

Fig. 3. SEM images presenting structures of TiN coatings deposited by processes with diodes bank connected to accelerator circuit (B) and without it (A).

In Fig. 3 we present the structure morphology of titanium nitride films as a final product of synthesis obtained in both of the process versions described in this work. The films have reached a similar thickness of 500 nm, so the kinetics of the film growth was about 1 nm per single power impulse. The major achievement presented in this paper is obtaining and attempt to explain the presence of the ultra-fine-grained structure with no tendency to columnar growth under the conditions of a non-oscillating type of current flow through the plasma accelerator during discharge (Fig. 3B). The calculated size of crystallites for the deposited films suggests their nanocrystalline structure with crystallites sizes equal to 5.5 nm (standard version) and 4 nm (version equipped with diodes) respectively. However, in the case of a standard process we obtained a very characteristic quasi-columnar structure of the film which is, as literature suggests, typical of a standard IPD process [28]. Hitherto, the literature concerning the structural features developing during the films synthesis under the impulse plasma conditions suggests the existence of strong relations between the conditions of plasma generation, the structural and phase state and properties of the synthesized films [20–25], so we can assume that the current distribution in coaxial accelerator during the discharge also plays an important role in forming the structure of deposited films.

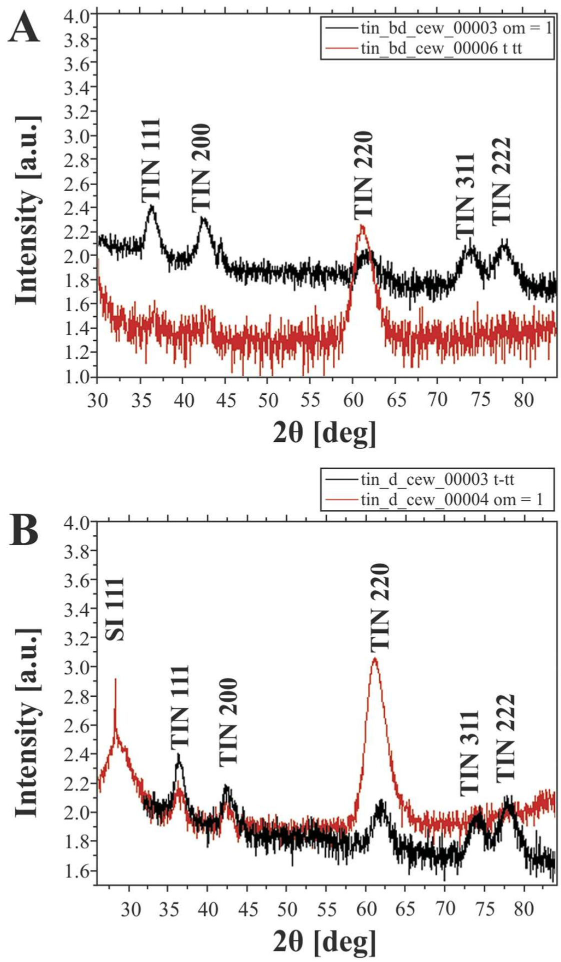

Fig. 4. X-ray diffraction patterns for the films obtained in the standard version of apparatus (A) and in apparatus equipped with diodes bank (B).

The presented results suggest that the dense, well-compacted and nanocrystalline structure presented in Fig. 3B might be achieved in conditions of a more energetic impact of impulse plasma on the film at the stage of its growth, according to the models of film growth known from the literature [29, 30]. The dense and nanocrystalline structure observed is created during a strong bombardment of plasma species. It suggests that the hypothesis of our study is confirmed. In the IPD method, the total energy of plasma is a sum of internal energy of particles and kinetic energy given by Ampere force, accelerating plasma in the form of plasmoid [31], thus the momentum of the plasmoid plays an important role in energy exchange between the impulse plasma and surface of substrate [32]. In case of energetically monochromatized process by eliminating the current oscillations, the spatiotemporal structure of plasma energy is less complex than the standard one because it consists just of the fraction created during the most energetic part of the discharge. An explanation of the presented differences at this stage of studies is speculative since the environment of plasma initiated and spread in the condition of free-oscillating current flow has not been well defined yet, however, we believe that the spatiotemporal structure of the plasma generated in the modified IPD process is more energetically homogenized. We present this study as preliminary and a good starting point for further investigations. The state of plasma generated by non-oscillating current flow should be definitely examined in future. Getting rid of the complexity by eliminating the current oscillations allows us to take more control over the process of synthesis which is a prerequisite for further research on characterizing the physics of plasmo-chemical reactions during IPD synthesis.

Fig. 4 shows the X-ray diffraction patterns registered for the TiN coatings synthesized during the IPD processes corresponding to each version. The results prove that in both cases the coatings show existence of the TiN structure with the preferred ⟨2 2 0⟩ growth direction. The X-ray peaks of TiN are slightly shifted to smaller angles. The calculated average lattice parameter for the films deposited with diodes in electric circuit of accelerator, 4.164 Å, is almost the same as in ASTM standards. The calculated average parameter of TiN films deposited in standard conditions is higher, i.e. 5.091 Å. This might suggest differences in the structure caused by non-stoichiometry of TiN or by stress state of the layers.

Lack of columnar structure is an advantage that was confirmed by wear-resistance examinations of the TiN films. Fig. 5 presents the values of VB_C as a function of turning time. The wear tests were carried out according to the PN-ISO 3685:1996 requirements.

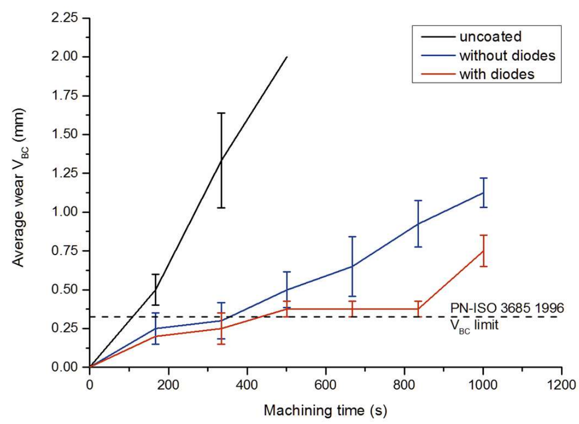

Fig. 5. The indicator of the edge blunting (VB_C) as a function of machining time for three types of inserts.

Our investigation showed that the films deposited during the processes carried out under conditions of a non-oscillating current flow through the accelerator have better anti-wear properties than the films synthesized in a standard electric condition. Usually, the structure of films synthesized under conditions of impulse plasma is characterized by a columnar or conical morphology, whose basic elements of structure are agglomerates of particles as the result of their incomplete coalescence-cluster mechanism during the films growth [33]. The natural nanoporosity of such structures is a disadvantage in terms of adhesion of the coating to the substrate, the hardness and wear resistance. Achieving a dense, compact and ultrafine nanocrystalline structure by shortening the discharge time to one half of the period significantly improved its properties.

4. Conclusions

The literature concerned with the IPD method suggests that the phenomena related to plasma initiation and the distribution mechanism in the coaxial accelerator play the most significant role in the film deposition. We assumed that equipping the accelerator with a diodes bank should lead to taking much more control of discharge and, as a result, much more control of the synthesis process by eliminating the electrodes polarization changes during one discharge. Our experiments showed that the film deposition processes, distinguished by a non-oscillating character allowed us to achieve nanocrystalline, not columnar type structure, with equiaxed, almost unidimensional angular crystallites. It is especially important that such a TiN structure has excellent anti-abrasive properties: by comparison to uncoated tools, 4 fold increase of lifetime; by comparison to TiN coated tool synthesized in standard, current oscillating conditions, 3-fold increase of lifetime.

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