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OES studies of plasmoids distribution during the coating deposition with the use of the Impulse Plasma Deposition method controlled by the gas injection☆

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The article presents the results concerning the OES characterization of plasmoids generated by the Impulse Plasma Deposition method modified by the use of gas injection (Gas Controlled IPD). Both of the electrodes of the coaxial accelerator: the tube (cathode) and the rod (anode—the source of the vapors) are permanently connected with the capacitors charged to the high voltage of few kV value. During the coatings deposition both the electro-eroded vapors of the anode material (Ti) and the working gas (N_2) form the plasmoids which are accelerated by the Ampere force in the coaxial accelerator and ejected to the vacuum chamber in the direction of non-heated substrates forming there the TiN coating. Periodic gas injections which make pressure fluctuations in the accelerator space in the range of critical values and cause the discharge to initiate or vanish accordingly with the chosen frequency. The promising practical effects of the use of gas injection for controlling the plasma processes during the coatings deposition by the GCIPD method was previously proved. On the basis of the present studies one can state that the GCIPD′ plasmoids containing multiple ions both of metallic as well as gas plasmoids constituents are more energetic as compared to the IPD case. Contrary to the IPD during the GCIPD the titanium fraction of the plasmoids structure overtakes the nitrogen one which seems to be important to the coating growth mechanism.

1. Introduction

The origin of the Impulse Plasma Deposition (IPD) method is based on the assumption that non-equilibrium plasma is a favorable environment for a synthesis of phases, in particular those characterized by high barriers of nucleation [1]. In this kind of plasma, the homogenous nucleation on plasma ions is expected and this kind of nucleation is thermodynamically stabilized by ultra-fine particles of the new phase [2]. The clusters, which are present in non-equilibrium plasma and can act as critical nuclei, are components of a particle stream delivering to the surface of a substrate where the coating grows. The clusters' participation during the process of a coating growth makes this mechanism to be a mix of the atomic and cluster type of growth. In the first case, the nucleation at the substrate surface dominates and the further growth of crystallites occurs with morphology dependent by the thermal activation. In the second case, the mechanism of coating growth is determined by kinetics and clusters dispersion reaching the boundary region and the cluster coalescence processes conditioned by thermal activation [1,3].

In search of an efficient method of highly ionized and thermodynamically non-equilibrium plasma generation, attention was turned onto the coaxial accelerator consisting of two concentric electrodes in the form of: a positively biased axial rod as an anode, surrounded by a grounded tube as a cathode. This specific

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construction of the coaxial accelerator causes the forming of magnetic pressure ~ $(\vec{j} \times \vec{H})$, where $\vec{j}$ – interelectrode current, $\vec{H}$ – concentric magnetic field generated by the current flow accelerating the plasma along the accelerator length [4,5]. The source of electric energy in the standard version of an IPD device is a 50–200 · 10^{-4} F capacitor charged to a 1–6 · 10^3 V of voltage [1]. The discharge of the capacitor occurs in the inter-electrode space at a constant 10^1–10^2 Pa pressure and is controlled by a three-electrode spark ignitron. The amplitude of attenuated current waveform in the electric circuit of coaxial accelerator can reach the orders of 10^3–10^5 A during the time of 10^{-4} s range [1]. From a practical point of view, the IPD method is similar to the HiPIMS method–the high power magnetron sputtering with respect to high cathodic current of 10^2 A and the discharge time of 10^{-4} s [12,13]. The electric circuit of plasma source–magnetron in HiPIMS method is practically identical with the electrical circuit used in IPD method. It is worth noting that there is one significant difference between the IPD and HiPIMS methods–the IPD method actively uses the magnetic pressure to attach the plasmoids at a very high drift velocity. The pack of plasma (plasmoid) generated in that way has features of arc discharge and the form of a radial symmetric thin current sheet which is accelerated by magnetic pressure up to velocity at the accelerator outlet of the order of 10^4 m/s [6,7]. The substrate is not intentionally heated from any external heat source, but the dissipation of kinetic energy of the plasmoid at the surface of the substrate raises the temperature of the substrate for a very short period of time up to 2000 K [8]. This thermal peak disperses heat emissions and phonons of the substrate material excitation. This temperature is enough to temporarily heat activation of the substrate surface and the emitted heat is conducted through the material of the substrate resulting from the heat conductivity of solids (rate of temperature decrease – 10^6 K/s [9]). The consecutive plasmoids are generated periodically with a frequency of 10^{-1}–10^0 Hz. The kinetics of growth count in relation to the number of plasmoids, not to the duration of the deposition process like in other methods of plasma surface engineering, which gives the IPD method a digital status as a sum of assumed amount of complete processes of plasma surface engineering. An indicative relative increase of thickness of layers is calculated on about 0.8–1 nm per shot, with a perpendicular fixed substrate holder [10]. The practical advantages of IPD method has been verified in industry to prolong the service life of cutting tools made of SW7M HSS steel coated by titanium nitride coating [11].

Recently we proposed a modification of IPD method relying on the use of the pulsing pressure of working gas to control the process of generating the plasmoids (instead of operation of spark ignitron generating the plasmoids under constant pressure achieved by continuous gas flow) [14]. This pressure changes periodically with specific frequencies applied at the ranges of threshold values: from the 10^{-4}–10^{-3} Pa when the discharge does not initiate, to the 10^{-1} Pa allowing the discharge to initiate and spread in the working gas. In these conditions the spark ignitron has been eliminated from the electric circuit of the plasma accelerator and voltage is applied to electrodes permanently. The process of generation and acceleration of plasmoids is controlled by changeable gas concentration only, resulting from periodical gas injections in the inter-electrode space of accelerator (**G**as **C**ontrolled **I**mpulse **P**lasma **D**eposition, **GCIPD**). The concept and interpretation of the physical effects of this gaseous mode in IPD method application has been widely described in our previous work [14,15]. It can be assumed that the application of the gaseous mode, characterized by a dynamically changeable concentration of working gas molecules in the range of threshold values, contributes to the preservation of the kinetic energy of plasma particles by decreasing the probability of energy dissipation by inelastic collisions with neutral molecules. This assumption corresponds well with the results of our previous research concerning the TiO_2 thin films [16], deposited on glass and silicon unbiased and unheated substrates by pulsed magnetron sputtering method (PMS) [17,18] and modified by applying the gas controlled PMS method – GIMS (Gas Injection Magnetron Sputtering) [19,20]. We were able to deposit the rutile films by GIMS method, while the PMS favors the anatase phase. As is known, the presence of the rutile-crystal structure in titanium oxide films is controlled by heating and/or biasing the substrate [21]. The practical result of "gaseous" modification of IPD method (GCIPD) was the achievement of high durability of cutting tool inserts made of SW7M HSS coated by TiN layers. These layers were deposited by using the coaxial accelerator made of titanium and nitrogen as a working gas periodically injected in doses into the inter-electrode space of accelerator. The durability of coated inserts was 1600% better in relation to the uncoated ones, what should be considered as remarkable for TiN coatings [14].

The aim of the presented study was the spectral characterization of plasmoids generated by coaxial accelerator working in gaseous mode, which can be helpful in the interpretation of dynamic phenomena of plasma interactions with substrate during the growth of TiN coatings deposited by GCIPD method providing this significant growth of cutting tools durability.

2. Experimental part

In our experiments the pulsed plasma was generated by a coaxial accelerator equipped with two cylindrical electrodes made of titanium in the GCIPD apparatus. A schematic view of the apparatus is shown in Fig. 1. The apparatus used in this experiment was equipped with a special gas-injection system [14], contrary to the standard version of the IPD device [1]. In the presented system a pulsed plasma was generated after the injection of the working gas into the inter-electrode region of the coaxial accelerator. Nitrogen was used as a working gas. In our experiment plasma was generated at different technological conditions: – discharge voltage: 3, 4 kV and battery capacity 100 or 200 μF. The main experimental parameters are shown in Table 1. Measurements of optical emission spectra were carried out by means of a Mechelle®900 optical spectrometer that are characterized by the very short exposition time of measurements. During the experiments it operated in the wavelength range from 300 nm to 600 nm at the exposition time (t_{exp}) equals 20 μs – during the time resolved measurements and 100 μs during the measurements of whole spectrum of plasma generated in specific conditions. Exposition was triggered from a current rise measured by 8000 A Series Infinium Oscilloscope from Rogowski coil with sensitivity 1 kA:1 V applied to the electrical circuit of internal electrode. During those experiments the optical

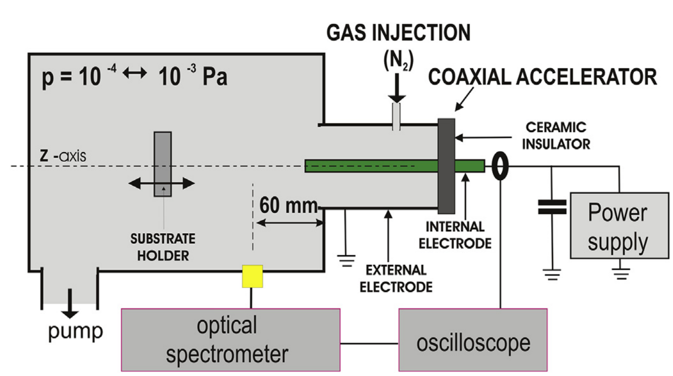

Fig. 1. Schematic view of the IPD apparatus and experiment setup.