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Correlation between spatial distribution of the components of reactive plasma flow and the stoichiometry and defectiveness of deposited coatings

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ABSTRACT

Purpose: The subject of the presented research was reactive plasma generated by circular vacuum-arc sources used for deposition of thin hard coatings.
Design/methodology/approach: Experimental investigations on spatial distribution of ionized and excited plasma components were performed with the use of the optical emission spectroscopy. Quantitative analysis of microdroplets distribution was carried out using measuring optical microscope supplied with the numerical image analysis system.
Findings: Based on the obtained radial distributions of volatile and condensed components the general picture of plasma flow emitted by a single circular arc source was reconstructed. Radial distributions of analysed emitting elements and analysed fractions of microdroplets showed layered structures that depended on the discharge conditions.
Research limitations/implications: The spectral method used for the reconstruction of concentration distributions of ionised and excited plasma components generated by a single circular arc source could not be used for reconstruction of such distributions in the vacuum chamber of the industrial device.
Originality/value: The carried out investigations showed that the differences in spatial distributions of plasma active elements determine the uniformity of crystallization conditions in vacuum-arc deposition processes performed in large-scale multi-source industrial devices.
Keywords: Thin & Thick Coatings; Arc evaporation; Titanium nitride and carbonitride; Colorimetry

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1. Introduction

Plasma flow generated by a single vacuum arc source includes ions, atoms and macroparticles of the cathode material emitted from a few microns in diameter cathode spots, chaotically moving on the cathode surface. Due to intense power concentration within cathode spots, and resulting high temperature and pressure of the cathode material, the emission of arc plasma from the cathode occurs explosively in the form of numerous separated flows of particles, which then join into a total flow of interelectrode plasma [1, 2]. In consequence of explosive plasma expansion three mechanisms of ions acceleration occur [3]: by collisions with faster electrons, under the effect of the near-cathode potential hump, and under the effect of the ion pressure gradient. Such way of the plasma flow formation by a single vacuum arc source determines its space structure inside the deposition chamber, thus the space distributions of crystallization conditions.

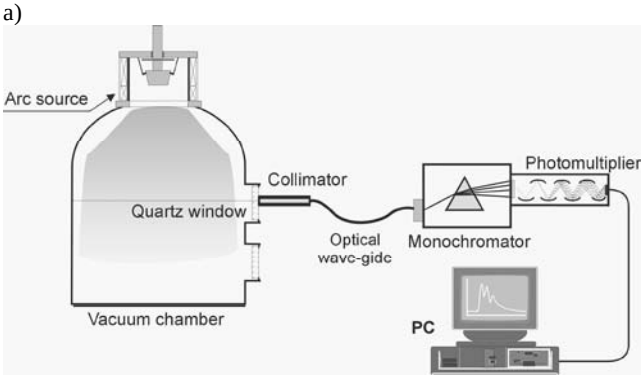
The deposition chamber of a multi-source arc vacuum device is filled with plasma, composition and parameters of which are determined by the parameters of the flows emitted by individual arc sources. The problem of the instability of chemical composition of coatings deposited by the vacuum-arc method in large-size devices concerns first of all those processes, in which mixtures of reactive gases are used as process atmospheres [4-7]. In such atmospheres, as a result of the heterogeneity of the gas mixture composition within the deposition chamber and the heterogeneity of electron concentration due to discrete arrangement of arc sources, the contribution of different elementary processes to excitation, dissociation and ionisation of gaseous atmosphere components varies in different regions of the deposition zone.

The aim of the research presented in the paper was reconstruction of the spatial distribution of components of vacuum-arc generated plasma both within the flow emitted by a single circular arc source as well as within the deposition chamber of a multi-source large-size industrial device.

2. Experiments

Investigations of radial distribution of optical emission of selected plasma components and radial distribution of cathode material microdroplets were performed with the use of circular arc source of the CDS device manufactured by the Institute for Sustainable Technologies - National Research Institute in Radom. Experiments were carried out in the coaxial arrangement consisting of the investigated arc source installed on the top of vertically situated cylindrical vacuum chamber 510 mm in diameter and 670 mm high (Fig. 1a). The arc source was equipped with a cone-shaped cathode, a high-voltage arc ignition system and a double-coil electromagnetic system of the cathode spot localization. One coil was aimed at maintaining the discharge on the cathode frontal surface 79 mm in diameter, the second one formed the plasma flow. Radial distributions of plasma flow components were reconstructed in the horizontal cross-section of the vacuum chamber located 370 mm from the cathode surface. Integrated emission intensities of Ti^0, Ti^{1+}, Ti^{2+}, N_2 and N_2^+ (TiI 335.464 nm, TiII 368.520 nm, TiIII 298.475 nm N_2 357.69 nm, N_2^+ 427.81 nm) were recorded in seven measurement zones fixed in the observation cross-section of the vacuum chamber (Fig. 1b). The first zone (N = 1) was located in the vicinity of the deposition chamber wall, the last zone (N = 7) overlapped the chamber diameter. Then in result of Abel inversion, performed by the Meacker's calculation method [8], radial distributions of recorded intensities, and thus radial distributions of volatile components were determined.

a)



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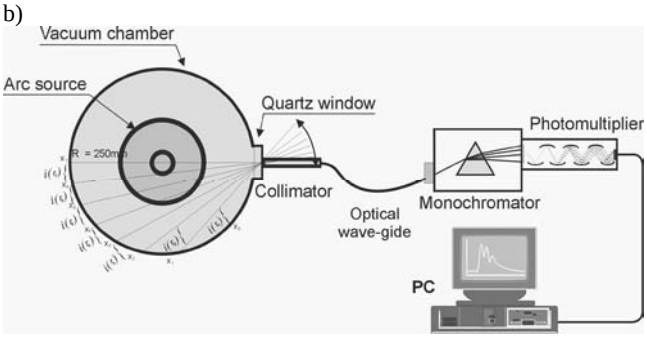

Fig. 1. Schematic of the experimental stand for plasma emission investigations: a) side view; b) top view

In order to reconstruct radial distribution of condensed components of reactive plasma flow, microdroplets of the cathode material were deposited on polished substrates with the dimensions 12×8×5 mm made of Armco iron. The samples were located in the same measurement zones of the vacuum chamber cross-section as used for integrated emission intensities registration. Radial distribution of the microdroplets was reconstructed for four dimensional fractions: 0-1.4 μm, 1.4-2.5 μm, 2.5-5.0 μm and over 5 μm. In order to avoid creation of chemical compound coating on the substrate surface deposition processes were performed in inert argon atmosphere. Quantitative analysis of microdroplets distribution was carried out by using measuring optical microscope Nikon MM-40/L3FA supplied with the numerical image analysis system MultiScan v.8.08 developed by Computer Scanning Systems. Conditions of the experimental investigations of radial distribution of Ti–N_2 plasma components and radial distribution of Ti cathode microdroplets are shown in Table 1.

Table 1.
Conditions of the experimental investigations of radial distribution of Ti–N_2 plasma components and radial distribution of Ti cathode microdroplets

Monochromator	Focal distance 250 mm; Holographic grating 1800 lines/mm; Photomultiplier Hamamatsu R928
Atmosphere/Pressure	Ar / 4.0×10^{-4}mbar; Ar / 1.2×10^{-2}mbar; N_2 / 1.2×10^{-2}mbar
Arc source cathode	Ti
Arc current	80 A
Substrate polarization voltage	$U_{BIAS} = 0$
Microdroplets deposition time	10 min

Investigations of spatial distribution of crystallization conditions in real production deposition processes were carried out in the vacuum chamber of the large-scale multi-source vacuum-arc device MZ-383 manufactured by Metaplas Ionon, Bergisch Gladbach. For the assessment of the crystallization conditions homogeneity within the deposition zone a numerical method of analysis of the characteristic points of deposited material reflectance curves was applied [9]. The substrates were located in three immovable vertical planes turned relative to each other by 120° (Fig. 2). Investigated Ti(C,N) coatings were deposited at four different compositions of the gas atmosphere N_2+C_2H_2 (Table 2). Reflectance curves of coatings deposited in different regions of the deposition zone were recorded with the use of the spectrophotometer Color-Eye 7000A manufactured by Gretag Macbeth, supplied with quality control software Optiview. The interpretation of the reflectance curve shapes was carried out in relation to TiN, *i.e.* the reference material with well defined colorimetric characteristics [10-12].

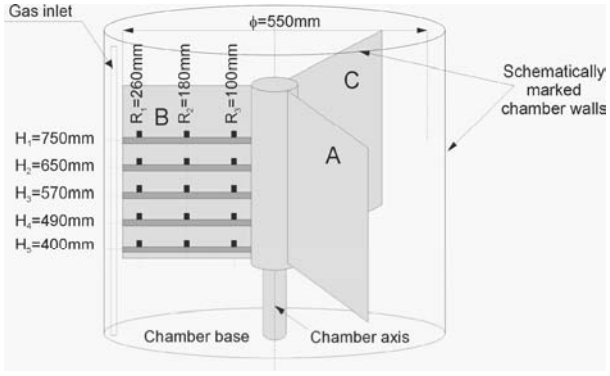

Fig. 2. Arrangement of the substrates within the deposition zone of the MZ 383 device: A, B, C – substrate location planes; H – substrate distance from the chamber base; R – substrate distance from the chamber axis

Table 2.
Parameters of Ti(C_x,N_{1-x}) coatings deposition for assessment of chemical composition homogeneity within deposition zone of MZ 383 device

Coating symbol	Atmosphere composition	Pressure	BIAS voltage	Arc current
TiN	100% N_2	1,2 Pa	– 150 V	60 A
Ti(C,N)17	83% N_2 + 17% C_2H_2	0,8 Pa		
Ti(C,N)25	75% N_2 + 25% C_2H_2	0,8 Pa		
Ti(C,N)30	70% N_2 + 30% C_2H_2	0,8 Pa		

3. Results and discussion

3.1. Radial distribution of selected emitters in plasma flow generated by a single circular arc source

Plasma spectra recorded in the central measurement zone (N = 4) in argon ($p_{Ar} = 4.0\times10^{-4}$ mbar) and nitrogen ($p_{N2} = 1.2\times10^{-2}$ mbar) atmospheres as well as reconstructed radial distributions of TiI 335.464 nm, TiII 368.520 nm, TiIII 298.475 nm N_2 357.69 nm and N_2^+ 427.81 nm emission intensities are shown in Fig. 3. Radial distributions of titanium emission lines TiI, TiII, TiIII and nitrogen bands N_2, N_2^+ were smoothed by using 5-order polynomials in order to decrease their sensitivity to fluctuations of experimentally recorded integrated intensities. Reconstructed distributions of emission intensities illustrate concentration distributions of titanium excited and ionized atoms Ti^0, Ti^{1+}, Ti^{2+} as well as excited and ionized nitrogen molecules N_2, N_2^+, which are transported by plasma flow generated by a single, axially symmetrical arc source in the experimental conditions shown in Table 2.

In the arc evaporation processes carried out in argon atmosphere at low pressure ($p_{Ar} = 4.0\times10^{-4}$ mbar), *i.e.* in the conditions of weak influence of gas atmosphere on evaporated atoms flow, radial distributions of all investigated titanium lines have in the analyzed cross-section of the vacuum chamber a ring-shaped form with two-layer internal structure (Fig. 3b). For both excited atoms (Ti^0) and ions (Ti^{1+}, Ti^{2+}) two maxima of concentration occur in the same measurement zones: N = 1 and N = 5, *i.e.* at the distances of 21.4 cm and 7.1 cm from the chamber axis. Such distribution indicates that two preferential zones of excited atoms and ions generation occur at the cathode surface (this hypothesis was confirmed by the authors during investigations of cathode spots location carried out with the use of a fast video camera [13]). In the near-axis zone of the vacuum chamber (up to 3.6 cm from the axis) no titanium atoms or ions were detected. Similar form of Ti^0, Ti^{1+} and Ti^{2+} radial distribution confirms dominating role of electrons in the

excitation and ionization processes of titanium atoms evaporated from the cathode surface.

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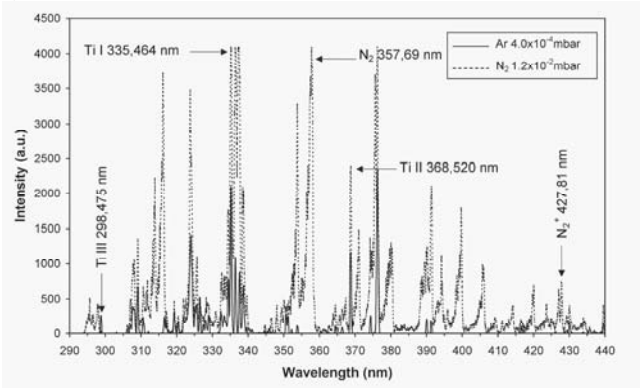

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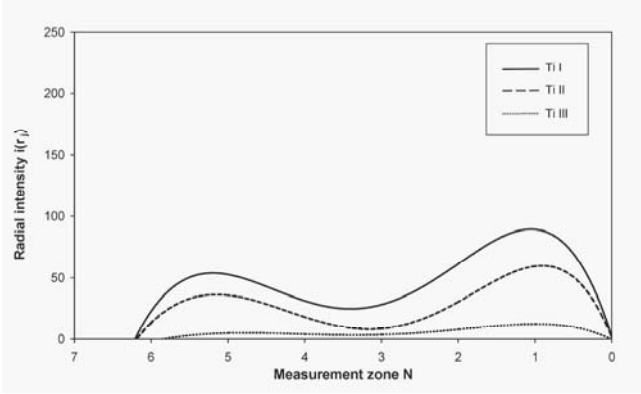

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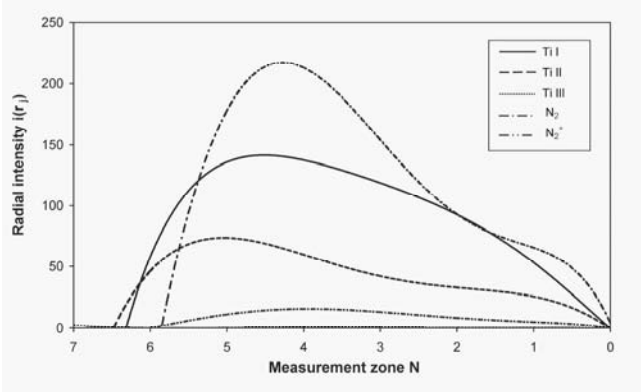


Fig. 3. Distribution of TiI, TiII, TiIII, N_2 and N_2^+ emission: a) spectra recorded in the zone N = 4 for $p_{Ar} = 4.0\times10^{-4}$ mbar and $p_{N2} = 1.2\times10^{-2}$ mbar; b) radial distributions for $p_{Ar} = 4.0\times10^{-4}$ mbar; c) radial distributions for $p_{N2} = 1.2\times10^{-2}$ mbar

Distinct forms of plasma elements radial distribution were obtained for the arc evaporation process performed at higher pressure of reactive nitrogen atmosphere of $p_{N2} = 1.2\times10^{-2}$ mbar (Fig. 3c). In such conditions, typical for deposition processes, an intensive emission of TI, TiII, N_2 and weak emission of N_2^+ was detected, while emission lines of double-charged titanium ions TiIII faded out. Localization of all detected emitters (Ti^0, Ti^{1+}, N_2 and N_2^+) in the same region of the vacuum chamber cross-section ($0 < N < 6$) points to intensive collisions between titanium ions and nitrogen molecules according to the scheme: $Ti^{n+} + N_2 \rightarrow Ti^{(n-1)+} + N_2^+$. Also changes of analyzed intensity values caused by changed evaporation conditions, which can be observed by comparison of radial intensity distributions reconstructed for low pressure argon atmosphere and high pressure nitrogen atmosphere (Fig. 3b and 3c), correspond to the scheme given by I. I. Demidenko *et al.* [14] for the mean-pressure arc discharge in nitrogen. According to this scheme, after exceeding the threshold pressure of $p_{th} = 10^{-1}$ Pa double-charged titanium ions Ti^{2+} practically decay and the concentration of nitrogen molecular ions N_2^+ is also low, while high concentrations of single-charged titanium ions Ti^{1+} and excited titanium atoms Ti^0 are observed.

3.2. Radial distribution of the cathode material microdroplets in plasma flow generated by a single circular arc source

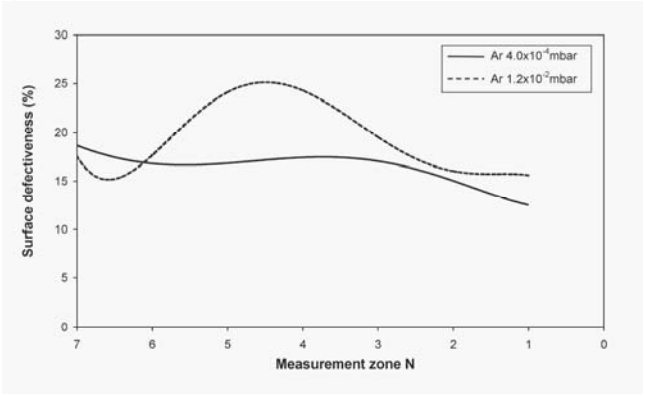
The change in microdroplets radial distribution caused by argon pressure increase is illustrated in Fig. 4 by the surface defectiveness ratio determined by the MultiScan image analysis system as a ratio of the image area covered by microdroplets to the total image area. The majority of the microdroplets population was included in two the finest fractions. The population of the fraction 0 – 1.4 μm amounted to 91000 particles/mm^2 at $p_{Ar} = 4.0\times10^{-4}$ mbar and 160000 particles/mm^2 at $p_{Ar} = 1.2\times10^{-2}$ mbar. The surface densities of particles within the fraction 1.4 – 2.5 μm deposited at the same argon pressures were 17000 particles/mm^2 and 23000 particles/mm^2 respectively. Fractions 2.5 – 5.0 μm and over 5 μm are definitely less numerous (maximum 6800 particles/mm^2 at $p_{Ar} = 1.2\times10^{-2}$ mbar within the fraction 2.5 – 5.0 μm). Therefore the radial distribution of the surface defectiveness ratio was influenced mostly by two the most numerous microdroplet fractions.

At low argon pressure radial distribution of microdroplets surface density, thus distribution of surface defectiveness ratio, is smooth with slight increase towards the zone N = 7, *i.e.* towards the axis of the deposition chamber (Fig. 4a). Increase of the argon pressure from 4.0×10^{-4} mbar to 1.2×10^{-2} mbar leads to significant change in distribution of surface defectiveness ratio. Distinct maximum caused by microdroplets concentration appears in the central measurement zones ($3 \le N \le 5$).

Clear correlation can be noticed for both argon pressures between radial distributions of TiII emission, which illustrate radial distribution of Ti^+ ions concentration, and radial distribution of the surface defectiveness ratio, which illustrate radial distribution of the total density of condensed components in the plasma flow (Fig. 4a and 4b). In the regions of maximum densities of the condensed phase minimum concentrations of titanium ions can be observed and vice versa. This effect is especially clear for higher argon pressure of 1.2×10^{-2} mbar. It

seems that high density of fine-dispersed condensed phase of the cathode material favours deactivation of ionized and excited particles, thus hampers elementary collision processes with charge and energy transfer, which determine plasma structure.

a)



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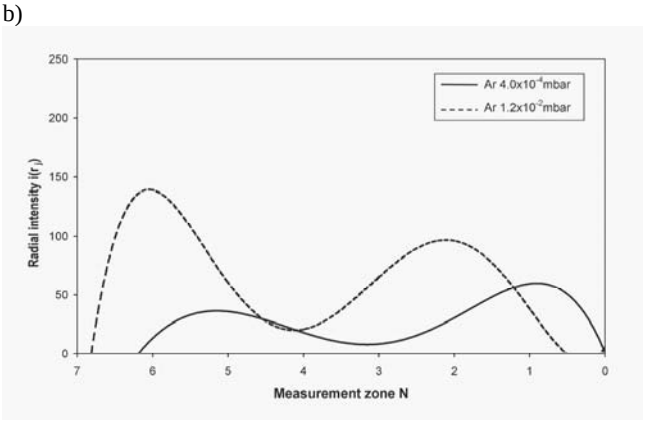
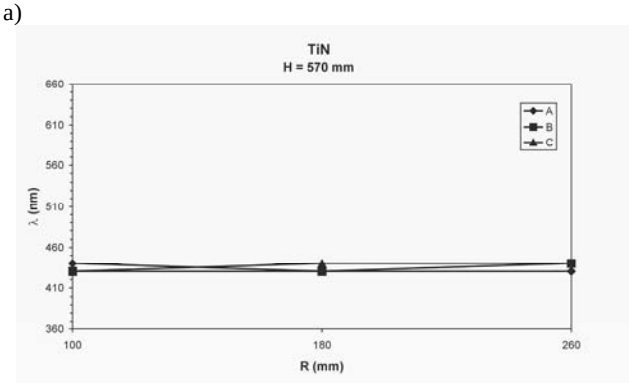


Fig. 4. Radial distributions of plasma flow components in argon atmosphere at $p_{Ar} = 4.0\times10^{-4}$ mbar and $p_{Ar} = 1.2\times10^{-2}$ mbar: a) surface defectiveness ratio; b) TiII emission

3.3. Spatial distribution of crystallization conditions within deposition chamber of a large-scale multi-source vacuum-arc device

Investigations of the homogeneity of deposited coatings composition were performed with the use of A. J. Perry's method consisting in determination of the location of reflectance curve minimum on the wavelength scale [10-12]. For TiN coatings location of the reflectance curve minimum is practically constant (430 – 440 nm), irrespective of the substrate position within the deposition zone (Fig. 5a). This indicates high homogeneity of deposited material stoichiometry, thus high homogeneity of the crystallization conditions within investigated chamber zone.

a)



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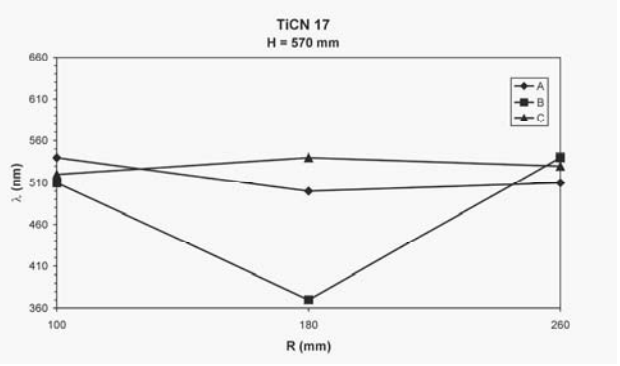

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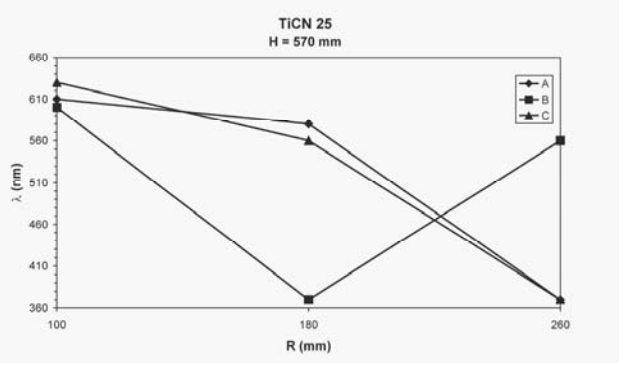

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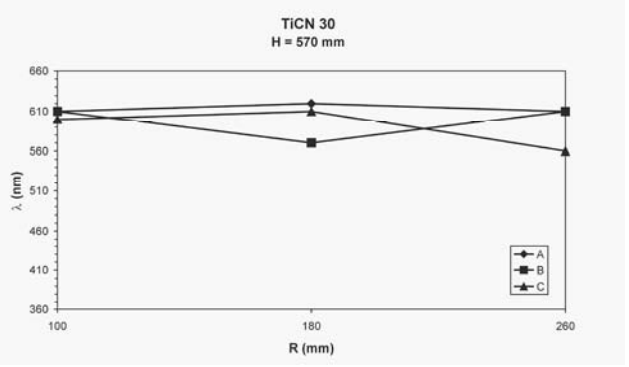

Fig. 5. Distribution of $Ti(C_x,N_{1-x})$ coatings stoichiometry within deposition zone of the MZ 383 device at H = 570 mm: a) TiN; b) TiCN17; c) TiCN25; d) TiCN30

As the content of acetylene in the process atmosphere increases (Table. 2) locations of reflectance curve minima of $Ti(C_xN_{1-x})$ coatings move towards longer wavelengths (Figs 5b – 5d).

It is connected with decreasing density of free electrons, in consequence of their location in growing number of covalent bonds, resulting in the drop of plasma frequency of deposited material. The homogeneity of deposition conditions is much lower in mixed N_2+C_2H_2 atmosphere in comparison to pure nitrogen atmosphere. The most probable reason of this heterogeneity is non-uniform spatial distribution of plasma active elements (ions, excited atoms and molecules) resulting from different intensity of hydrocarbon molecules dissociation within deposition zone and from non-uniform electron density distribution caused by discrete arrangement of arc sources. This effect is especially clearly visible in the plane B, which was located in the vicinity of one of the arc sources and the inlet of gas atmosphere (Fig. 2). The highest non-uniformity of the crystallization conditions was observed for the atmosphere composed of 75%N_2 and 25%C_2H_2 (Fig. 5c).

The influence of acetylene content in N_2+C_2H_2 atmosphere on the crystallization conditions in vacuum-arc deposition of $Ti(C_xN_{1-x})$ coatings is similar to determined earlier by one of the authors [15] influence of hydrogen content in N_2+H_2 atmosphere on the nitriding ability in plasma nitriding processes. In both cases specific properties of the process atmosphere were revealed for the content of 25% of hydrocarbon (or hydrogen) in the mixture with nitrogen. It seems most probable that the characteristics of mixed atmospheres composed of nitrogen and hydrogen-containing gas are determined by hydrogen influence on the collision processes of dissociation, excitation and ionization of active species (*e.g.* nitrogen, carbon).

4. Conclusions

(1) The flow of titanium excited atoms (Ti^0) and ions (Ti^{1+}, Ti^{2+}) generated in the discharge operating in high vacuum on the cathode of a single circular arc source, supplied with double-coil electromagnetic system of the discharge localization, has a layered structure with two concentration maxima located outside the axis of the "arc source – vacuum chamber" system. Such distribution indicates that two preferential zones of excited atoms and ions generation occur at the cathode surface.

(2) In the regions of maximum densities of the cathode material microdroplets minimum concentrations of titanium ions were observed. It indicates that high density of condensed phase favours deactivation of ionized and excited particles.

(3) Spatial distribution of plasma active elements and hydrogen influence on collisions between heavy particles (V-V, V-T) as well as between heavy particles and electrons (e-V) determine the crystallization conditions in vacuum-arc deposition processes performed in large-scale multi-source devices in mixed atmospheres composed of nitrogen and hydrogen-containing gas.

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