Effect of the pulse bias voltage parameters on the properties and composition of ZrN coatings deposited by vacuum arc method

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Abstract. In the work it is revealed that it is possible to control the structure, the phase and elemental composition of ZrN coatings by the change of the parameters of bias voltage (pulse repetition frequency, amplitude, pulse duty factor, etc.). It is established that optimum parameters of pulse bias voltage for the formation of ion-plasma ZrN coatings with a high hardness and wear resistance are \( U_b = -150 \) V, \( \gamma = 85\% \), \( f = 50 \) kHz. At these parameters the synthesized coating based on ZrN consists of ZrN crystallites with a cubic crystal lattice, which has \([111]\) texture. The coating has the high hardness (30.5 GPa) and high wear resistance (\(1.1 \times 10^{-6} \) mm\(^3\)/N\(\cdot\)m\(^{-1}\)).

1. Introduction
Nitride ion-plasma coatings are actively used to increase the service life and improvement of exploitation characteristics of various tool, details and products [1,2]. The coatings based on ZrN have the high hardness, corrosion resistance, wear resistance and can be applied as protective coatings [3,4]. However, the appearance of new technological capabilities of the coating deposition equipment leads to further optimization of the deposition processes for the purpose of further improvement of the properties for this type coatings [5,6]. In the present work the use of the power supply of pulse bias voltage developed in Institute if high current electronics SB RAS (Russia, Tomsk) for the modes optimization of vacuum arc deposition of wear-resistant ZrN coatings is suggested [7].

The main feature of a pulsed mode of potential supply is the multiple increase of an ion current on the substrate on the pulse rising edge. It is shown by the authors of [8] that an ion current on a substrate increases by 1.5-3 times at \(-300\) V upon transition from stationary to a pulsed mode depending on pulse repetition rate. It should be noted that the value of ion current doesn’t reach the saturation at increase of amplitude bias voltage in pulse mode as that is in the case of the stationary mode, and grows in the proportion to amplitude of pulses and their pulse repetition rate. The rise rate of ion current value at increase of pulses amplitude rises at increase of pulse repetition rate [9]. The increase of an ion current is followed by corresponding change of plasma parameters: temperature of electrons and ionization degree of working gas [9].

The following possibilities appear by means of pulse potential supply application:
• preliminary cleaning of substrate surfaces from oxide inclusions and adsorbed gases without breakdowns, and, therefore, without introduction of defects on the surface of the treated substrates;
• dielectric substrates and films can be supplied with bias voltage during coating deposition.

It is explained by compensation of a positive charge on the specimen surface (dielectric or dielectric inclusion) by the flow of electrons during the pause between pulses (about 5 μs) [10]. The frequency of pulse repetition ≥1 kHz are necessary for the effective compensation [10].

Key parameters of the mode of ion-plasma coating deposition are the composition and pressure of gas mixture, ion current density on the substrate, bias voltage parameters, process duration, etc. They directly influence on the coating growth rate and energy delivered to a substrate during its formation. The energy of the ions delivered on the substrate can be changed by the variation of bias voltage parameters. It in turn leads to the change of the composition, properties and structures of the formed coating. Thus the positive effect of the use of negative pulse bias voltage at synthesis of coatings is the wide range of parameters control. In the range it is possible to obtain the condensates with various structural and phase state and, therefore, with various physical and mechanical characteristics.

Present work is directed to the identification of the dependences of the properties, composition and structure of coatings on the parameters of pulse bias voltage parameters: amplitudes, pulse duty factor, frequency of pulse repetition; and on optimization of the modes of ZrN coatings deposition by vacuum arc plasma-assisted method.

2. Material and research techniques

For the coating synthesis the QUINTA vacuum ion-plasma setup was used. The generation of gas-metal plasma for formation of coatings based on ZrN was carried out at collaboration of several plasma sources of different type: PINK-P source of gas plasma based on non-self-sustained arc discharge with thermionic and hollow cathodes of an extended design and arc evaporator (DI-80) with the zirconium cathode (diameter of 80 mm). The method of magnetic separation of metal plasma flow from droplet fraction in a curvilinear plasma-guide was used. Zirconium alloy (E110, Russian grade) was as material of the cathode (Zr-1 wt.% Nb). Argon-nitrogen mixture with the ratio of 1:1 was used as working gas. The operating pressure of the mixture was equal to 0.2 Pa. The current of the arc discharge for the arc evaporator with the zirconium cathode was constant in all experiments and was equal to 150 A.

One of the advantages of the deposition equipment is the use of the combined power supply of pulsed and stationary negative bias voltage. Its key parameters in the pulsed mode are the amplitude of negative bias voltage $U_b = (0-1000)$ V, the pulse duty factor $\gamma = (10-90)\%$, the frequency of pulse repetition $f = (10-50)$ kHz.

The amplitude of negative bias voltage, pulse duty factor, frequency of pulse repetition were as the varied parameters in the present work. They were varied in the following ranges: $U_b = -(50-150)$ V, $\gamma = (25-85)\%$, $f = (10-50)$ kHz respectively.

A set of specimens with coatings with 3-5 μm thickness on substrates from hard WC-8% Co alloy were obtained. After coating deposition, the specimens were investigated by the methods of modern materials science. The coating thickness and deposition rate were measured by the calotest method (Calotest CAT-S-0000). The parameters of the surface roughness were measured on the optical MNP-1 profilometer. The surface morphology, structure and elemental composition of coatings were investigated by the method of scanning electron microscopy (Philips SEM 515 microscope, EDAX ECON IV microanalyzer). The phase state and structure were analyzed by the results obtained by the method of the X-ray diffraction analysis (Shimadzu XRD 6000 diffractometer). Microhardness was measured on the microhardness PMT-3 tester at normal load of 500 mN. Manohardness, Young’s modulus and elastic recovery degree were investigated by the results of a nanoindentation at normal load of 30 mN (ultramicrotester Shimadzu DUH-211). Tribological researches were carried out with the use of Pin on Disc and Oscillating TRIBOtester and the contact profilometer (TRIBOtechnic, France).
3. **Results and discussion**

At the variation of amplitude of negative bias voltage in the range of 50-150 V during formation of ZrN coatings the obvious change of elemental coating composition is not observed (Table 1). It can be explained by the low value of ion current density, which is equal to 3.5 mA/cm².

### Table 1. The elemental composition of ZrN coatings deposited at different pulse bias voltage values by vacuum arc plasma-assisted method ($U_b$ — bias voltage; $C_{Zr}$ — zirconium concentration; $C_N$ — nitrogen concentration)

| $U_b$, V | $C_{Zr}$, wt.% | $C_N$, wt.% | $C_{Zr}$, at.% | $C_N$, at.% |
|----------|----------------|-------------|----------------|-------------|
| –50      | 78.46          | 21.54       | 35.87          | 64.13       |
| –100     | 78.50          | 21.50       | 36.02          | 63.92       |
| –150     | 78.60          | 21.40       | 36.06          | 63.94       |

At the change of amplitude of negative bias voltage, the change of roughness parameters, nanohardness, Young's modulus and elastic recovery degree (Table 2) is practically not observed for ZrN coatings. The best tribological characteristics belong to the coating deposited at $U_b = –150$ V. That has following characteristics: friction coefficient $\mu = 0.355$, wear factor $V = 1.05 \cdot 10^{-6}$ mm³N⁻¹m⁻¹.

### Table 2. The properties ZrN coatings deposited at different pulse bias voltage values by vacuum arc plasma-assisted method ($R_a$ — arithmetical mean roughness and roughness height measured on ten values respectively, $HV$ — hardness, $E$ — Young’s modulus, $W$ — elastic recovery degree, $\mu_{av}$ — average friction coefficient, $V$ — wear factor)

| $U_b$, V | $R_a$, µm | $R_z$, µm | $HV_{0.03}$, GPa | $E$, GPa | $W$ | $\mu_{av}$ | $V$, $10^{-5}$ mm³N⁻¹m⁻¹ |
|----------|------------|------------|------------------|----------|-----|-----------|--------------------------|
| –50      | 0.0293     | 0.321      | 30.6             | 356.9    | 0.36| 0.442     | 3.142                    |
| –100     | 0.0297     | 0.307      | 30.8             | 363.0    | 0.36| 0.365     | 3.032                    |
| –150     | 0.0350     | 0.291      | 30.5             | 385.3    | 0.34| 0.355     | 0.105                    |

The results of the X-ray diffraction analysis for ZrN coating (figure 1) with the best properties in the chosen range of bias voltage values showed that the coating consists of ZrN crystallites with a cubic crystal lattice (Table 3). The crystal lattice parameter is $a = 0.4600$ nm, the size of coherent-scattering region (CSR) is 50 nm, the value of crystal lattice deformation is $0.78 \cdot 10^{-3}$. The crystallites of zirconium nitride have preferred orientation along [111] direction. Due to the low intensity reflexes its interpretation is not possible; they indicate by squares in the figure 1. It is suggested that they belong to Zr-Nb system phases.

It should be noted that the decrease of amplitude of negative bias voltage from 150 to 50 V led to the disorientation of ZrN crystallites with a cubic crystal lattice and appearance of the new phases such as Zr$_{0.3}$Nb$_{0.3}$N with a cubic crystal lattice, Zr$_{0.7}$Nb$_{0.3}$ with a hexagonal crystal lattice, Zr with a hexagonal crystal lattice with the general volume fraction of 8% (figure 1a, b, Table 3) in the ZrN coatings.

The increase of frequency of pulse repetition from 10 to 50 kHz led to insignificant increase of nitrogen concentration in ZrN coating volume, to increase of the nanohardness from 28.2 to 30.5 GPa (Table 4), and to decrease of friction coefficient and wear factor (Table 5). The coating deposited at frequency of pulse repetition of 50 kHz has the best characteristics. The decrease of that from 50 to 10 kHz did not lead to significant changes of the phase composition and structure of the coatings (figure 1c, Table 3).
Figure 1. X-ray diffraction pattern for ZrN coatings deposited on a WC-8% Co hard-alloy substrate in plasma of arc discharges at the following parameters: 

- $U_b = -50 \text{ V}, \gamma = 85\%, f = 50 \text{ kHz}$; 
- $U_b = -150 \text{ V}, \gamma = 85\%, f = 50 \text{ kHz}$; 
- $U_b = -150 \text{ V}, \gamma = 85\%, f = 10 \text{ kHz}$; 
- $U_b = -150 \text{ V}, \gamma = 25\%, f = 50 \text{ kHz}$.

Table 3. The results of the X-ray diffraction analysis of ZrN coatings deposited by vacuum arc plasma-assisted method with plasma separation from macroparticles at the different modes of bias voltage.

| Parameters $U_b, \gamma, f$ | Phases, type of crystal lattice | Phase content, wt.% | Crystal lattice parameters, Å | Size of CSR, nm | Elastic deformation value $\Delta d/d, \times 10^{-3}$ |
|----------------------------|--------------------------------|---------------------|------------------------------|----------------|-----------------------------------------------|
| $\text{-50 V, 85\%; 50 kHz}$ | WC, hexagonal                  | 9                   | $a = 2.9095$                 | 40             | 1.8                                           |
|                             | ZrN, cubic                     | 83                  | $a = 4.5931$                 | 18             | 9.8                                           |
|                             | $\text{Zr}_0.5\text{Nb}_0.5\text{N}$, cubic | 6       | $a = 4.5190$                 | 32             | 0.8                                           |
| $\text{-150 V, 85\%; 50 kHz}$ | $\text{Zr}_0.7\text{Nb}_0.3$, hexagonal | 1       | $a = 5.0150$                 | 20             | 1.7                                           |
|                             | Zr, hexagonal                  | 1                   | $a = 3.2258$                 | 28             | 5.9                                           |
|                             | WC, hexagonal                  | 10                  | $a = 2.905$                  | 60             | 7.3                                           |
Table 4. The elemental composition of ZrN coatings deposited at different frequency of pulse repetition by vacuum arc plasma-assisted method

| f, kHz | C_{Zr}, wt.% | C_{N}, wt.% | C_{Zr}, at.% | C_{N}, at.% |
|--------|--------------|--------------|--------------|--------------|
| 10     | 79.76        | 20.24        | 37.69        | 62.31        |
| 25     | 79.50        | 20.50        | 37.32        | 62.68        |
| 50     | 78.60        | 21.40        | 36.06        | 63.94        |

Table 5. The properties ZrN coatings deposited at different frequency of pulse repetition by vacuum arc plasma-assisted method

| f, kHz | HV_{0.03}, GPa | E, GPa | W | R_{a}, μm | R_{z}, μm | μ_{av} | \( V \times 10^{-5} \) mm^3N^{-1}m^{-1} |
|--------|----------------|--------|---|-----------|-----------|--------|--------------------------------|
| 10     | 28.2           | 295.7  | 0.38 | 0.0302    | 0.269     | 0.521  | 47.12                              |
| 25     | 29.3           | 413.9  | 0.32 | 0.0427    | 0.366     | 0.487  | 45.99                              |
| 50     | 30.5           | 385.3  | 0.34 | 0.0350    | 0.291     | 0.355  | 0.105                              |

The increase of pulse duty factor from 25 to 85% during vacuum arc deposition led to the increase of nitrogen concentration of ZrN coating from 59.2 to 63.9 at.% (Table 6) and to considerable reduction (by 10 times) of wear factor (Table 7). The other characteristics did not change or slightly changed (Table 7). The decrease of pulse duty factor from 85 to 25% did not lead to significant changes in the phase composition and structure of the coatings (figure 1d, Table 3).

Table 6. The elemental composition of ZrN coatings deposited at different pulse duty factor by vacuum arc plasma-assisted method

| γ, %  | C_{Zr}, wt.% | C_{N}, wt.% | C_{Zr}, at.% | C_{N}, at.% |
|-------|--------------|--------------|--------------|--------------|
| 25    | 81.79        | 18.21        | 40.82        | 59.18        |
| 50    | 80.55        | 19.45        | 39.01        | 60.99        |
| 85    | 78.60        | 21.40        | 36.06        | 63.94        |

Table 7. The properties ZrN coatings deposited at different pulse duty factor by vacuum arc plasma-assisted method

| γ, %  | HV_{0.03}, GPa | E, GPa | W | R_{a}, μm | R_{z}, μm | μ_{av} | \( V \times 10^{-5} \) mm^3N^{-1}m^{-1} |
|-------|----------------|--------|---|-----------|-----------|--------|--------------------------------|
| 25    | 30.1           | 289.6  | 0.40 | 0.0358    | 0.343     | 0.481  | 6.56                               |
| 50    | 28.6           | 304.5  | 0.38 | 0.0366    | 0.341     | 0.674  | 1.07                               |
| 85    | 30.5           | 385.3  | 0.34 | 0.0316    | 0.277     | 0.355  | 0.105                              |

It is shown that the change of pulse bias voltage parameters (frequency of pulse repetition, amplitude, pulse duty factor, etc.) it is possible to change the structure, phase and elemental
composition of ZrN coatings. It is revealed that optimum parameters of bias voltage for formation of wear-resistant coatings based on ZrN with a high hardness are followings: $U_b = -150 \, \text{V}$, $\gamma = 85\%$, $f = 50 \, \text{kHz}$. At such parameters the ZrN coating is formed from ZrN crystallites with a cubic crystal lattice and it has texture [111]. The coating has the high hardness (30.5 GPa) and high wear resistance of $V = 1.1 \cdot 10^{-6} \, \text{mm}^3\text{N}^{-1}\text{m}^{-1}$.

4. Conclusion
The possibility of synthesis of single-layer ZrN coatings with a high hardness and wear resistance by a vacuum arc method with magnetic filtration of metal plasma flow from macroparticles in the mode with plasma assistance is shown. It is shown that the change of the pulse bias voltage parameters (frequency of pulse repetition, amplitude, pulse duty factor, etc.) leads to change the structure, the phase and elemental composition of ZrN coatings. The optimization of the deposition modes allowed to reach the following noteworthy characteristics of ZrN coatings: low roughness ($R_a = 0.03 \, \mu\text{m}$), high nanohardness ($HV_{0.03}$ up to 30.5 GPa), rather low friction coefficient ($\mu$ to 0.36), high wear resistance ($V$ to $1.1 \cdot 10^{-6} \, \text{mm}^3\text{N}^{-1}\text{m}^{-1}$), good elastic recovery degree ($W$ up to 0.34), rather low Young's modulus ($E$ to 385 GPa). ZrN coating synthesized in the optimum deposition modes consists of ZrN crystallites with a cubic crystal lattice and it has [111] texture. For obtainment of wear-resistant ZrN coatings it is recommended to use the following parameters of pulse bias voltage: amplitude of negative bias voltage $U_b = -150 \, \text{V}$, pulse duty factor $\gamma = 85\%$, the frequency of pulse repetition $f = 50 \, \text{kHz}$.

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