QUINTA equipment for ion-plasma modification of materials and products surface and vacuum arc plasma-assisted deposition of coatings

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Abstract. The paper presents the detailed description of QUINTA experimental equipment for ion-plasma modification of materials and products surface and vacuum arc plasma-assisted deposition of coatings, which was developed at the laboratory of plasma emission electronics of the Institute of High Current Electronics SB RAS. It is in the list of unique electrophysical setups of the Russian Federation (UNICUUM). In the paper there is the example of the use of QUINTA setup, it is the vacuum arc plasma-assisted deposition of wear-resistant ZrN-based coatings. The mechanical characteristics of the coatings, the elemental and phase composition are presented.

1. Introduction
One of the most promising directions in the field of the creation of new functional materials with unique properties, which successfully develops and finds the application in various directions of industry, is development and formation of relatively thin (~ 1–10 μm) ion-plasma coatings with multiphase nanocrystalline structure, which have gradient, monolayered design [1–3]. The relevance of the direction is due to the need to significantly improve the mechanical and tribological properties of the parts, tools and various products, and therefore to significantly increase their service life by a relatively simple, efficient and inexpensive method.

One of the attractive solutions of that is to create wear-resistant ion-plasma coatings on the surface of materials and products by vacuum arc plasma-assisted method [4–5].

This paper presents a detailed description of the original vacuum ion-plasma equipment developed in the Institute of High Current Electronics of SB RAS (IHCE SB RAS, Tomsk, Russia) and used primarily for synthesis of protective coatings on the metal and composite products, as well as for modification of the working surface layer of materials and products in order to give them the unique physical and mechanical, tribological properties.

As a successful example of the use of deposition equipment, the results of experiments on the synthesis of the protective coatings of the Zr-N system and detailed research of their properties, elemental composition, phase state and structure are presented.

2. Experimental equipment
The experiments on the coatings deposition were carried out on QUINTA vacuum ion-plasma setup developed in IHCE SB RAS. The setup is designed for complex research in the field of generation of volume low-temperature gas, metal and metal-gas plasma of low pressure discharges, as well as in the
field of technological applications of such plasma in order to improve functional properties of materials and products surface layer. The general view of the setup is shown in figure 1.

![Figure 1. The view of QUINTA ion-plasma setup.](image)

The QUINTA setup is equipped with PINK-P-0.4M gas plasma source of extended design with aperture of 80×400 mm² [6–8], DP400 extended electric arc evaporator with working square of a cathode of 80×400 mm² [8, 9], three electric arc evaporators with cathodes with a diameter of 100 or 80 mm, and plasma flow separator from droplets fraction with rotation of plasma flow by an angle of 120° [10]. Thus, five plasma sources with different construction are installed in the setup, which can operate in various combinations, including a parallel mode. Therefore, the setup is named QUINTA. The setup scheme is shown in figure 2.

![Figure 2. The scheme of the QUINTA ion-plasma setup: 1 – vacuum chamber; 2 – the magnetic filter; 3 – DI80 arc evaporator; 4 – PINK-P-0.4M gas-plasma source; 5 – an extended DP400 arc evaporator; 6 – a manipulator with planetary rotation of details; 7, 8 – a DI100 arc evaporators.](image)
The vacuum chamber was made in the form of a vertical cylinder with a door on the lateral side. The height of the chamber is 750 mm, and its diameter – 650 mm. The chamber is made of stainless steel. On the bottom part of the chamber the system of planetary rotation of the treated details which allows to use the details of 500 mm high, diameter up to 550 mm and weigh up to 100 kg is equipped. On the upper and sidewalls of the chamber there are three arc evaporators. One of them is equipped with the magnetic filter of a plasma flow from droplets fraction [10]. On the door of the vacuum chamber an original extended source of gas-discharge plasma with thermionic and hollow cathodes and the extended arc evaporator of personal construction are located [6, 9]. The installation is equipped with power supply system of negative bias voltage (up to 1000 V) for the treated details. It can operate, as in the stationary, and pulsed modes with smooth adjustment of frequency of pulse repetition (10–50 kHz) and pulse duty factor (10–90%), and the device of microarcs cancellation [11].

The vacuum system of the installation provides creation in the working chamber of residual pressure of ~ 10⁻³ Pa. Pumping occurs by the backing sliding vane rotary pump (AVPR-90D pump) with the pump speed of 25 l s⁻¹, and the AB-1500 turbomolecular pump providing the maximum pump speed of 720 l s⁻¹. A two-channel system with RRG-10 leaks of working gases provides the range of working pressures from 0.01 to 2 Pa with automatic maintenance of a pressure value and the set ratio of working gases.

The control of the QUINTA installation is exercised by means of the automated control system based on the personal computer and the ADAM 5000 industrial controller. Two COM-ports are used for the control of peripheral devices, one of them interacts directly with power supplies, the second one – with the industrial controller which manages vacuum and water systems. The communication is carried out according to RS-485 standard.

The program of the automatic system control (ASC) of QUINTA installation represents the window application implemented in the Delphi-7 Professional. The functions executed by the software of ASC:

- displaying the current state of the equipment;
- representation of equipment operation parameters changes;
- monitoring the system for the presence of erroneous states of equipment operation;
- blocking of prohibited operating states of the system;
- automatic realization of technological processes;
- displaying the dynamics of physical values changes;
- recording of event log;
- automatic operation mode of vacuum system;
- automatic correction of the working pressure and the volume ratio of the gases.

It should be noted that in the automatic mode the control program is capable to carry out independently the technological process on the technological process list (TPL) entered by the operator, carrying out the hundreds of steps in a single technological cycle.

For convenience of the user, an interface of the program is divided into the several thematic blocks, which are issued in the form of tabs: main, vacuum, water and options (figure 3).

The main window of the program shows the parameters required to control the setup and to monitor its operation: power supply parameters, pressure values, temperature, gas supply system control, access to the control panel of all power supplies, access to the control panel of the TPL.

For management of a vacuum system three modes are used (figure 3a). They are selected by an operator and can be automatic, manual and service. In the automatic mode all control is realized by the control program, the operator can select only procedures: pumps on, pumping of the chamber, pumps off, opening of the chamber door. In the manual mode, the operator independently can manage all devices of a system, however, at the same time, the program blocking remains for the purpose of faults prevention due to wrong actions of the operator. In the service mode all program blocking are turned off, there are only electric blocking which protect a system from serious accidents.

To control of water supply in the cooling system and its discharge, the separate window of the program is provided (figure 3b).
In order to automate the process according to a pre-known algorithm with an arbitrary number of stages, a TPL is provided. The main window of the TPL is a table with rows, which correspond to the process parameters, and the number of columns is equal to the number of process steps. Each step is characterized by its own set of parameters, which can be set using the control menu of process steps. The TPL allows to carry out the technological processes completely in the automatic mode, to keep records of experiments. Thus the repeatability of experiments, excluding the errors of the operator is provided.

For generation of the gas plasma on the QUINTA installation, the extended PINK-P-0.4M plasma source based on non-self-sustained arc discharge with thermionic and hollow cathodes is used [6–8]. It is mounted on a rectangular seat in a chamber door with aperture sizes of $120 \times 460$ mm$^2$ and the fixing sizes of $140 \times 480$ mm$^2$ on ten M6 pins with a vertical step of 120 mm. The gas plasma source has two channels of the thermionic cathodes, which is made from a tungsten wire with a diameter of 1.5 mm and length of 175 mm. Each channel consists of two thermionic cathodes and three current leads. It is made for the purpose of reliability augmentation of plasma source during prolonged processes. In the case of emergency fusion of one thermionic cathode there is an automatic switching to the second one without stopping of technological treatment of products. The length of the work area of the hollow cathode is 400 mm. The maximum discharge current of gas plasma source is 150 A. The average density of an ion saturation current from the plasma in the center of the chamber reaches 3 mA·cm$^{-2}$. The main working gases are argon and nitrogen. In the construction of gas plasma source the possibility of work with active gases, such as oxygen, acetylene, etc. occurs. The view and construction of a gas plasma source is presented in figure 4.

The work principle of gas plasma source with thermionic and hollow cathodes is following. Through the gas inputs, a flow of working gas enters to the internal volume of plasma source. The thermionic cathodes are warmed up to the temperature of thermoemission and emit the electrons from its surface. Between the hollow cathode and the anode (walls of vacuum chamber) is voltage up to 200 V. The electrons from thermionic cathodes in the field of applied voltage get the directed movement. The electrons trajectory is extended due to imposing of outside longitudinal magnetic field (up to 6 mT) and their oscillations in the hollow cathode. Therefore, the electrons make the effective ionization of gas that leads to ignition of the non-self-sustained arc discharge without the cathode spot. The formed gas plasma fills the space of the hollow anode. To change filament current, and consequently, of electrons emission from the thermionic cathode, it is possible to regulate easily the discharge current from several to hundreds of amperes at discharge voltage of several tens of volts (10–100 V). This arc discharge
allows to generate effectively low-temperature plasma in large volumes ($\geq 0.1 \text{ m}^3$) with its concentration of $n_e \sim 10^9$–$10^{11} \text{ cm}^{-3}$ and uniformity of $\pm 15\%$ of average value. The placing of a details in this plasma and giving them the negative or positive bias voltage, it is possible to retrieve ions or electrons from the plasma and to carry out the modification of products surface layer. The processes of ion cleaning, heating and activation of a surface, nitriding and ion-plasma assistance of vacuum arc deposition or magnetron sputtering of coatings are realized on the QUINTA installation by means of PINK-P-0.4M gas-plasma source.

**Figure 4.** The view (a) and construction (b) of PINK-P-0.4M gas plasma source: 1 – housing; 2 – hollow cathode; 3 – current lead; 4 – thermionic cathode; 5 – gas inputs; 6 – magnetic coil; 7 – clamp; 8 – insulator.

In order to obtain the metal and composite coatings, four electric arc evaporators of different design are used on the QUINTA setup. That allows to adapt the setup and its technological modes for realization of a wide range of objects of ion-plasma treatment of the products surface layer.

DI80 electric arc evaporator represents arc evaporator based on self-sustained arc discharge with integral-cold cathode, magnetic retention of cathode spot and focusing of plasma flow [12, 13]. Its design is shown in figure 5.

For the arc evaporator of the presented construction the discharge voltage is 20–40 V and its value remains almost constant in the operating range of currents of 50–150 A. The cathode arc evaporator allows to work steadily with a maximum current of discharge up to 150 A. That provides the average density of an ion current on a substrate of $\sim 1 \text{ mA cm}^{-2}$ and the maximum rate of coating growth up to $5 \mu\text{m h}^{-1}$, if the substrate is located in the center of the working chamber at the distance of 300 mm from an output aperture of the arc evaporator in the mode with rotation of specimens.

The separation of a plasma flow from the droplet fraction at evaporation of the metallic cathode by DI80 is realized by a curvilinear plasma guide, which represents a part of the toroid, which is made of magnetically inert material with the water-cooled walls and a flow turning angle in $120^\circ$ [10]. Due to turn of ion plasma components in longitudinal magnetic field there is a separation of a plasma flow from macroparticles which settle on ridge walls of the magnetic filter. It allows to obtain more homogeneous and qualitative coatings. The "DI80 arc evaporator – magnetic filter" system provides the growth rate of droplet-free coatings up to $4–6 \mu\text{m h}^{-1}$ in the center of the vacuum chamber on the rotating specimens and details.
Figure 5. The scheme of electric arc evaporator 1 – housing; 2 – focusing magnetic coil; 3 – stabilizing magnetic coil; 4 – cathode; 5 – igniter electrode; 6 – cathode holder; 7 – cathode flange; 8 – ignition lead.

The DI100 arc evaporator was developed as a replacement of that for the NNV6.6-I1 setup and it has improved cathode cooling combined with a more process-oriented design. That allows to improve the coating quality and to increase its growth rate.

The QUINTA installation is equipped with two DI100 arc evaporators which provide steady ignition and stationary functioning of an arc low-pressure discharge with current of 45–250 A at a discharge voltage of 20–40 V. The cathode diameter of the DI100 evaporator is 100 mm. The growth rate of coatings is 6–8 μm·h⁻¹ in the center of the vacuum chamber on the rotating details. Due to the improved cooling of the cathode and optimization of cathode device construction of the evaporator the share of droplet fraction is decreased by 2–5 times depending on the cathode material in the comparison with the use of standard arc evaporators of NNV6.6-I1 installation.

Figure 6. 3D model (a) and view (b) of the DI100 arc evaporator.

The arc evaporator consists of the water-cooled housing and the cathode holder which are electrically isolated from each other, and from the grounded vacuum chamber. The cathode holder was made in the form of the water-cooled flange to which negative potential from the inverter power source is applied.
It provides the discharge current up to 250 A at a discharge voltage of 20–40 V. The replaceable cathode is installed in the cathode device; the material of the cathode serves as the substance deposited as a thin-film layer on different substrates. The cathode is fixed on a cathode holder by means of the cap flange, through rubber sealing. The housing of the arc evaporator is made in the form of the water-cooled cylinder; on its face end the cathode holder is fixed through the electrically isolated flange. On the housing the magnetic coils for creation of magnetic field are installed. For initiation of discharge the ignition device based on the breakdown on the surface of dielectric is used. In figure 6 the 3D model and view of the cathode device of the DI100 arc evaporator are shown. The distinctive constructional feature of the DI100 arc evaporator is the possibility of application the porous materials as the evaporated cathodes materials (e.g., silumin or materials, obtained by SHS-method), that is impossible in the case of the use of standard arc evaporator. At the same time between the evaporated cathode and the system of its water cooling there is the copper diaphragm with thickness of 0.5 mm; that provides rather good cooling, preventing direct contact of a cooling water with the cathode material.

It should be noted that the DI100 source is intended for productive technological processes of coating synthesis: diameter of the working cathode is 100 mm, height of \( h = 50\text{–}60 \text{ mm} \), i.e. the volume of working material of the cathode is 2–4 times more, than that for standard cathodes for the NNV6.6-I1 or BULAT installations. The maximum discharge current is increased up to 250 A, that allows to reach the growth rate of coatings to \( \sim 10 \mu\text{m}\cdot\text{h}^{-1} \).

The extended DP400 arc evaporator which operation principle is similar that described in [9]. It provides high uniformity of coating deposition within the flat cathode which square is 80×400 mm\(^2\). The coating growth rate reaches 6 \( \mu\text{m}\cdot\text{h}^{-1} \) in the center of the working chamber. The range of working arc discharge currents of DP400 evaporator is 50–200 A. The view and construction of the DP400 arc evaporator are presented in figure 7.

![Diagram of arc evaporator](image)

**Figure 7.** The view and construction of extended DP400 arc evaporator: 1 – cathode; 2 – housing; 3 – flange; 4 – shield; 5 – igniter electrode.

The arc evaporator has the consumable squared cathode with the sizes of 400×80×15 mm\(^3\) installed on the water-cooled housing. Water inputs of the housing at the same time are the current leads for discharge current. The initiation of discharge is carried out by giving of a pulse voltage on an igniter electrode and by breakdown on the surface of dielectric. The movement of the cathode spot on the surface of the cathode is carried out by consecutive switching of current leads, and the cathode spot moves to each time-point towards the connected current lead. Due to selection the switching frequency
of current leads, it is possible to achieve uniformity of coating growth rate at the level of ± 5% on length of all square of evaporator cathode. The distribution of coating growth rate at the distance of 350 mm from the evaporator cathode is presented in figure 8.

Due to the low thickness (15 mm) and large dimensions (400×80 mm²) of the cathode, it remains integrally cold during operation, therefore the amount of macroparticles in the metal plasma flow is reduced to 10 times compared to that in the case of the standard evaporator of the NNV6.6-I1 setup.

Figure 8. The distribution of the coating growth rate along the length of the DP400 electric arc evaporator.

3. Synthesis and properties of ZrN-based coatings
As a successful example of application of the vacuum ion-plasma equipment described above the wear-resistant coating based on zirconium nitride is presented. The deposition of ZrN coatings was carried out in the modes with plasma assistance during the simultaneous work of DI80 source of metal plasma with magnetic filtering of a plasma flow from droplet fraction and a PINK-P-0.4M source of gas plasma. The synthesis was carried out in gas mixture of Ar/N₂ at partial nitrogen pressure of 0.04 Pa and total mixture pressure of p = 0.2 Pa. The argon and nitrogen leak was divided: through curvilinear guide of the DI80 evaporator and through PINK-P-0.4M gas plasma source, respectively. The duration of coating growth was selected so that the nitride layer with thickness of (2–5) μm was formed on the substrate. The material of substrates was WC – 8% Co hard alloy (HV0.5 = 13.5 GPa). Before the deposition the surface of specimens was cleaned, heated and activated by bombardment of argon ions at bias voltage \( U_b = -990 \) V and gas pressure of 0.01 Pa. For the increase of uniformity of elemental composition on the depth coating the equipment with the fixed specimens rotated with a speed of 3 rpm. The varied parameters at ZrN coating deposition were the parameters of pulse bias voltage regulated by original power supply of bias voltage [11]. The coatings were deposited at the constant average power put per one pulse, but at different parameters of bias voltage (the increase of bias voltage value at reduction of pulse duty factor). For the identification of influence of bias parameters at the invariable average power on ZrN coatings properties the following modes were selected. The first mode: bias voltage amplitude \( U_b = -150 \) V, pulse duty factor \( \gamma = 85\% \) [14], frequency of pulse repetition \( f = 50 \) kHz; the second mode: \( U_b = -990 \) V, \( \gamma = 12\% \), \( f = 50 \) kHz.

It was found that at maintaining the average power delivered in the one pulse, but at different parameters of the pulse bias voltage, the nitrogen concentration in the ZrN coating decreased (table 1). A slight decrease of nanohardness is observed, at the same time the friction coefficient and the wear parameter decreased by 1.5 and 4.8 times, respectively (table 2). The roughness of the coating decreased slightly. The degree of elastic recovery remained unchangeable.
Table 1. The elemental composition of ZrN coatings obtained at different parameters of pulse bias voltage, but constant average power in the pulse.

| Mode | Zr (wt.%) | N (wt.%) | Zr (at.%) | N (at.%) |
|------|-----------|----------|-----------|----------|
| 1    | 81.66     | 18.34    | 40.61     | 59.39    |
| 2    | 86.28     | 13.72    | 49.14     | 50.86    |

Table 2. The properties of ZrN coatings obtained at different parameters of pulse bias voltage, but at the constant average power in the pulse.

| Mode | HV_{0.03} (GPa) | E (GPa) | W | R_a (μm) | R_z (μm) | μ_{av} | V (mm³·N⁻¹·m⁻¹) |
|------|-----------------|---------|---|----------|----------|--------|-----------------|
| 1    | 30.5            | 385.3   | 0.50 | 0.045    | 0.327    | 0.62   | 14.27·10⁻⁵     |
| 2    | 29.1            | 369.5   | 0.52 | 0.036    | 0.308    | 0.42   | 2.97·10⁻⁵      |

It should be noted that the changes of the properties are primarily caused by changes in elemental and phase composition, as well as changes of the structural characteristics of ZrN coatings (table 1, table 3, figure 9). Both types of coatings consist mainly of crystallites of zirconium nitride with cubic lattice. The size of the region of coherent scattering (CSR) of the coatings obtained under the mode 1 (50 nm) is twice more [14], than that of coatings deposited on the mode 2 (24 nm). It can be caused by difference in the size of crystallites and different state of coatings with residual compressive stress in the conditions of the second mode (Δd/d = 9.4·10⁻³), in the comparison with the that in the case of the mode 1 Δd/d = 0.78·10⁻³). In the addition, the preferred orientation of the base phase crystallites (ZrN) changed from [111] to [220] (figure 9, table 3). In ZrN coating, synthesized on the mode 2, the existence of other phases besides ZrN with a cubic crystal lattice is observed: Zr_{0.5}Nb_{0.5}N with a cubic crystal lattice (8 wt.%) and Zr with a hexagonal crystal lattice (6 wt.%).

Figure 9. X-ray diffraction patterns for ZrN coatings on hard alloy substrate from WC-8%Co, formed in the plasma of arc discharges at the following parameters: 1) U_b = -150 V, \( \gamma = 85\% \), \( f = 50 \) kHz; 2) U_b = -990 V, \( \gamma = 12\% \), \( f = 50 \) kHz.
Table 3. The results of X-ray analysis of ZrN coating deposited by vacuum arc plasma-assisted method with plasma separation from macroparticles under different modes of bias voltage supply to the specimens with growing coating

| Mode | Phase, type of crystal lattice | Phase content (wt.%) | Crystal lattice parameter (Å) | CSR (nm) | Δd/d |
|------|--------------------------------|----------------------|-------------------------------|----------|------|
| 1    | WC, hexagonal                  | 10                   | a = 2.905 c = 2.836            | 60       | 7.3·10⁻³ |
|      | ZrN, cubic                     | 90                   | a = 4.600                      | 50       | 0.8·10⁻³ |
| 2    | WC, hexagonal                  | 13                   | a = 2.9040 c = 2.8350          | 70       | 0.1·10⁻³ |
|      | ZrN, cubic                     | 73                   | a = 4.6374                     | 24       | 9.6·10⁻³ |
|      | Zr₀.₅Nd₀.₅N, cubic             | 8                    | a = 4.4798                     | 30       | 0.9·10⁻³ |
|      | Zr, hexagonal                  | 6                    | a = 3.2256 c = 5.2470          | 20       | 2.9·10⁻³ |

4. Conclusion
Thus, the development and created QUINTA ion-plasma equipment allows to optimize processes of synthesis of the composite coatings, both due to their elemental composition, and due to purposeful formation of structure by automated control of such process parameters as pressure of working gases, currents of gas plasma source and arc evaporators, the characteristics of bias voltage power supply and speed of substrate rotation. This realizes the engineering of the materials and products surface with pre-predicted functional and service properties.

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