A plasma-chemical reactor of coupled vacuum-arc and ion-plasma processes for protective coatings formation based on titanium nitride

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Abstract. A plasma-chemical reactor based on the principle of coupling of gas-discharge processes in a VU-1B vacuum installation has been developed. This plasma-chemical reactor combine vacuum-arc evaporation of titanium in a nitrogen-containing plasma and ion-plasma sputtering of copper with the formation of copper vapor. The basis of this method of coatings deposition is the principle of dosing the injection copper vapor into the region of TiN synthesis through a separating diaphragm with a variable metering aperture, which prevents penetration of a titanium vapor into the copper cathode of the magnetron. The synthesis of TiN coatings in copper vapors has been carried out with the formation of nanostructured composite TiN-Cu coatings.

1. Introduction
Deposition of special coatings considerably improves the physical and mechanical properties of the surfaces of cutting tools, parts, assemblies, and outfits of manufacturing equipment [1–3]. Titanium nitride (TiN) coatings are widely used today in machine building and metal processing. These coatings are characterized by high hardness indices (20–30 GPa) and low coefficients of friction (≤ 0.1). Their main drawback is the significant impact brittleness, which sharply constricts the field of their application [4]. Promising results on the synthesis of two-phase nanostructured composites by alloying TiN coatings with copper were obtained in [5–10]. The investigations on the development of new technologies for obtaining composite layers with high plasticity and hardness [11–14] are a matter of special interest. Nanocrystalline protective composite nitride coatings and, in particular, TiN–Cu coatings, were obtained by arc evaporation of composite cathodes sintered from Ti and Cu powders and by synthesis of TiN under the conditions of a gas-discharge nitrogen plasma of an auxiliary arc discharge that affect the properties of coatings [15]. It has been shown that addition of copper allows one to obtain multicomponent nitride coatings of a TiN–Cu composition with a nanocrystalline structure. In this case, under conditions of localization of Cu atoms with the formation of an amorphous layer [15], they suppress the growth of a columnar structure of TiN crystallites around the TiN boundaries and result in nanostructuring of TiN–Cu coatings with a mean grain size of approximately 20 nm. The coatings in [16] possess a hardness of up to 45 GPa, a low coefficients of friction (0.2), a high adhesion strength with respect to metal and hard-alloy substrates (> 30 N), an elevated degree of elastic reduction (< 50%), a high wear resistance (< 2600 μm·N·m⁻¹), high temperature stability (up to 1373 K), and an increased oxidation resistance (up to 1073 K).
The use of composite cathodes complicates metered, monitored, and controlled addition of Cu to a coating that is being grown. In this connection, a new approach is proposed for creating composite TiN-Cu coatings by injecting copper vapor into the TiN synthesis region based on coupling of two gasdischarge processes: arc evaporation of Ti and magnetron sputtering of Cu, in the construction of a plasma chemical reactor. For execution the process of composite TiN-Cu coatings deposition a new type of plasma chemical reactor [17, 18] based on the reconstruction of standard chamber of the serial installation VU-1B is developed.

2. The design of installation and experimental technique
A plasma chemical reactor based on the principle of coupling gas-discharge processes that combine arc evaporation of titanium in nitrogen-containing plasmas and ion-plasma sputtering of a copper to form copper vapor is shown in figure 1. General view of the VU-1B installation is presented in figure 2.

**Figure 1.** The design of the plasma-chemical reactor: 1 – compartment of chemical reaction between Ti and N, 2 – compartment of Cu vaporization, 3 – arc evaporator, 4 – planar magnetron with the copper cathode, 5, 9 – cathodes, 6, 10 – anodes, 7 – Ignition electrode, 8 – magnetic coil, 11 – magnetic system, 12 – substrate holder, 13 – shield, 14 – diaphragm, 15 – metering orifice.

**Figure 2.** General view of the installation.

The installation has a chamber with dimensions of 550 mm in width and height of 530 mm which by means of a water jacket can be cooled or heated. The vacuum chamber is equipped with a planar magnetron and an electric arc evaporator. The planar magnetron (4) was mounted upright on a sidewall of the vacuum chamber. The power supply of the magnetron has a power of approximately 3 kW and an output voltage of up to $10^3$ V. Water cooling of the permanent magnets (11) provides stable operation of the magnetron. The discharge power and, consequently, the rate of copper-target (9) sputtering, are regulated using the magnetron-discharge (figure 3) control unit. The magnetron provided stable operation at nitrogen-gas pressures ranging from 0.26 to 12 Pa with discharge currents of 0.4–1.2 A.
The 60-mm-diameter cathode (5) is made of VT-1-0-grade titanium and is cooled with running water. The power supply of the evaporator has a power of approximately 2 kW. The characteristics of the arc discharge (figure 4) are as follows: the discharge current is 60–100 A, the working-gas (nitrogen) pressure is 0.26–12 Pa, and the arcing voltage is 35–45 V.

The drum-shaped substrate holder (12) is enclosed inside the vacuum chamber. Compartment 1 (for TiN synthesis) and compartment 2 (Cu vaporization) are separated by a diaphragm (14). The diaphragm seal (14), first, eliminates the mutual effect of different discharge types (vacuum-arc and magnetron discharges) on their stable stationary burning and, second, prevents penetration of a titanium vapor into the copper cathode (9) of the magnetron.

Copper vapor penetrates through the metering orifice (15) in the diaphragm (14) into compartment 1 to the substrate on which chemical reaction between Ti and N proceeds. The diaphragm is made in such a way so that to change the gap size and regulate the copper vapor’s injection process. The gap size can vary from 20×250 mm$^2$ up to 100×250 mm$^2$ (figure 1). The H400 diffusion pump is used for high vacuum pumping. The rough vacuum is provided by an AVZ-20D backing pump.

Plates made of 2-mm-thick fused silica (amorphous SiO$_2$) with a size of 15×15 mm$^2$ are installed in the vacuum chamber on the holder of substrates (figure 1). The chamber with the samples is pumped out to a residual gas pressure of $1\times10^{-3}$ Pa and gas nitrogen or a mixture of argon and nitrogen is injected through the needle-leaks to the compartments 1 and 2 of the plasma chemical reactor. When a voltage was applied from electric power supply between the cathode and the anode in compartment 1 using the ignition electrode (7) a vacuum arc discharge with a cathode spot is initiated. The magnetic field of the magnetic coil (8) provides uniform evaporation of the titanium cathode by the cathode spot of the arc discharge. As the vacuum-arc evaporator enters in to stationary burning mode of the arc discharge, a stationary magnetron discharge is ignited. The discharge current was regulated by the power source. The planar magnetron provided stable performance at nitrogen- gas pressures ranging from 0.26 to 12 Pa. The discharge voltage in the experiments was 350–480 V and depending on the nitrogen pressure. A toroidal magnetic field with an induction of 0.2–0.8 T keeps the gas-discharge plasma above the cathode surface. As a result of physical sputtering of copper cathode by plasma ions accelerated in the near-cathode potential fall a copper vapor penetrates through the metering orifice in the diaphragm into compartment where TiN synthesis proceeds with the formation of nanostructured TiN-Cu composite coatings. Besides for control of process of growth of coverings work on studying of the gas plasma generated vacuum and also arc evaporator and different distance (from 45 to 300 mm) from output apertures of sources. Measurements of parameters of plasma are taken in the environment of nitrogen. For each chosen mode probe characteristic by which the floating potential,
potential of plasma and temperature of electrons will be determined by a graphic method is removed. In the future, results of researches will be presented.

Table 1. Photographs of the surface of a TiN and TiN-Cu layers on a fused silica substrate (SiO₂)

| № | HK (MPa) | Photographs of the surface of a TiN and TiN-Cu layers |
|---|----------|------------------------------------------------------|
| a | 22300    | ![Photograph a](image)                                |
| b | 23665    | ![Photograph b](image)                                |
| c | 27259    | ![Photograph c](image)                                |

3. Results and discussion

Some results on the composite coatings TiN-Cu synthesis at different values of arc current and magnetron discharge current have been received [21]. The layers’ thickness of TiN and composite TiN-Cu was from 2–3 to 5–7 μm depending on the duration of the depositing time. Using a Bruker Phaser 2D diffractometer (CuKα radiation) X-ray phase analysis was performed according to which samples contained a Ti₂N, TiN phase with different crystal cell and volume fraction. In addition, copper reflections were recorded with the intensity about 2%. By means of a METAM PB-22 microscope the microstructure of TiN and TiN-Cu coatings was investigated. The surface structure of TiN and TiN-Cu coatings and the average microhardness values determined by a PMT-3 microhardness meter are presented in table 1 [21]. In the case of sample c the coating has a fairly homogeneous structure with small inclusions of the drop phase. And a more heterogeneous structure...
with inclusions of titanium droplets up to 12 μm in a cross section is observed in the case of samples \( \text{a} \) and \( \text{b} \).

A microhardness measurement showed a fairly uniform distribution of it over the surface of the samples. But the microhardness of the samples was different and varied from 22 to 27 GPa. The previous studies [19] have allowed to achieve a higher copper content in the coating and to reduce the size of the TiN crystallites to 100 nm. We didn’t have a success to achieve similar values in this work. It is likely because of the impossibility to control accurately the quantitative content of the injected argon and nitrogen at this stage of research to achieve the optimum proportion of the gas mixture. It is proposed by installing an automated gas inlet system to upgrade the installation. This will solve the problem of achievement the optimum proportion of the gas mixture.

4. Conclusion

A new plasma-chemical reactor based on combination of the properties of arc and magnetron discharges was developed. The main methods of nanostructured coatings deposition that can be implemented by means of this installation:

- combined vacuum-arc deposition and magnetron spraying with the use of reaction gases and the reference voltage supply on the substrate for composite coatings production;
- separate vacuum-arc deposition and magnetron spraying with the use of reaction gases for multilayer coatings of different composition production.

With the help of a plasma-chemical reactor by conjugating the operating modes of a vacuum arc evaporator and a planar magnetron, some coatings based on TiN of different phase composition including TiN-Cu, were formed.

Acknowledgments
The work was performed within the State task of Russian FARO (project No. 0336-2016-0005).

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Tsyrenov D B-D, Semenov A P, Smirnyagina N N and Semenova I A 2018 IOP Conf. Series: Journal of Physics 1115 032060