Formation features of composite coatings based on titanium nitride by method of vacuum-arc evaporation and magnetron sputtering

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Abstract. The paper studies the structure and properties of TiN and TiN-Cu coatings obtained by a hybrid technology of vacuum arc evaporating of a titanium target and ion-plasma sputtering of a copper target. The experiments were carried out in a plasma-chemical reactor of new-design with the possibility of injecting copper vapor into the region of TiN synthesis through a separating diaphragm with a variable metering aperture.

1. Introduction
In recent years, a new class of coatings based on TiN – nanocomposite ones with the grain size less than 100 nm has been developed. The effect of extreme improvement of physical and mechanical characteristics of the coatings of binary systems (TiN, ZrN, AlN, etc.) was discovered when some alloying components (Si, Cu, Al, Cr, etc.) [1-3] were added into their composition. For example, in [4-8] promising results were obtained in the synthesis of two-phase nanoscopic composites by alloying TiN coatings with copper. This shows that adding copper makes it possible to obtain multicomponent nitride coatings of a TiN-Cu composition with a nanocrystalline structure. In this case the Cu atoms with forming an amorphous layer [9] are located along the boundaries of TiN crystallites and block up the growth of a columnar structure which leads to nanostructuring of superhard TiN-Cu coatings with an average grain size of about 20 nm. The hardness of the coatings increases from 20 to 49 GPa with the increase in the copper content to 3.5 at. % [10].

For a number of reasons, processes based on vacuum arc discharges or magnetron discharges (planar arrangement) and the impact on the structure of the coating with plasma-forming gas ions (ion support, ion assist, ion bombardment), by applying a voltage displacement of 100-200 V occupy a certain place among the known low-temperature vacuum technologies of surface hardening. In this paper a new approach [11] for creating composite TiN-Cu coatings by injecting copper vapor into the TiN synthesis region based on coupling of two gas-discharge processes: arc evaporating of Ti and magnetron sputtering of Cu in the construction of a plasma-chemical reactor [12] is proposed. The possibility of introducing the Cu impurity component in the required concentration up to 3.5 at. % is very important, because the further increasing the copper content to 20 at. %, accompanied by a decrease in the crystallites of the nitride phase, is characterized by reducing its hardness to 14-15 GPa [10]. The decrease in hardness is due to the influence of soft plastic metal and the appearance of porosity in the coating. It is important to note the design features of the installation [12] and the influence of technological
parameters on the physical and mechanical properties of the coatings received. Some investigations were carried out to study the composition, structure and strength characteristics received at various TiN layers’ deposition regimes and different TiN-Cu composite modes with taking into account the design features of the installation. The optimally matched coating composition (TiN-at % Cu) will increase the hardness of the carbide cutting tools several times.

2. The experimental technique
The structural scheme of the plasma-chemical reactor [12] for depositing a TiN–Cu composite coating by an arc evaporation of titanium in nitrogen-containing plasma and ion-plasma sputtering of a copper target in a magnetron discharge is shown in figure 1.

Figure 1. The schematic diagram of the plasma-chemical reactor: (1) compartment of chemical reaction between Ti and N, (2) compartment of Cu vaporization, (3) arc evaporator of Ti, (4) planar magnetron with the copper cathode, (5) substrate holder, (6) shield, (7) diaphragm, and (8) metering orifice.

Compartment 1 (for TiN synthesis) and compartment 2 (Cu vaporization) are separated by diaphragm 7. The diaphragm seal 7, firstly, eliminates the mutual effect of different discharge types (vacuum-arc and magnetron discharges) on their stable stationary burning and, secondly, prevents the penetration of titanium vapor into the magnetron’s copper cathode. The copper vapor penetrates through metering orifice 8 in diaphragm 7 (figure 1) into compartment 1 to the substrate where a chemical reaction between Ti and N takes place. 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 20×250mm. up to 100×250mm. (figure 1). For more efficient magnetron target’s sputtering and creating a gas mixture a separate inlet for a gas supply process in the vacuum chamber is made. The share of argon was no more than 20% of the total volume of the working gas.

The TiN-Cu coatings were deposited in the copper vapor in the mode of titanium evaporation in a nitrogen-containing plasma, dissociation of molecular nitrogen \( N_2 \rightarrow 2N \), and chemical reactions between Ti and N. Plates made of 2-mm-thick fused silica (amorphous SiO\(_2\)) with a size of 15x15 mm were used as substrates. The X-ray phase analysis was carried out at a Bruker Phaser 2D diffractometer
(CuKα radiation). The microstructure of the layers was investigated with the help of a METAM PB-22 microscope. The microhardness of the formed layers was determined by a PMT-3 microhardness meter.

3. Results and discussion

Table 1 shows the process parameters used in the experiments. Initially, the experiments on obtaining copper layers (Cu) on fused silica substrate (SiO₂) were made by magnetron sputtering of a copper cathode when the electric arc evaporator was powered off. To obtain a sufficiently good copper layer, it is important to take into account the distance to the substrate relative to the magnetron cathode H, the magnetron discharge current I, the pressure in the chamber P (argon) and the sputtering time t [13]. Sufficiently a good result has been achieved with sample a (table 1). A uniform copper layer Cu with thickness from 0.4 to 0.5 μm has been obtained. Figure 2 shows photographs of the surface of a copper layer on a fused silica substrate.

| Number | Distance magnetron cathode-substrate, mm | Distance evaporator cathode-substrate, mm | Arc current, A | Magnetron discharge current, A | Pressure in a chamber, Torr | Deposition time, min |
|--------|----------------------------------------|------------------------------------------|----------------|-------------------------------|---------------------------|---------------------|
| a      | 190                                    | 230                                      | 1,1            | 2x10⁻³                        | 25                        |                     |
| b      | 190                                    | 230                                      | 80             | 0,9                           | 2x10⁻³                    | 10                  |
| c      | 190                                    | 230                                      | 80             | 0,9                           | 4x10⁻³                    | 10                  |
| d      | 190                                    | 230                                      | 80             | 1,1                           | 8x10⁻³                    | 10                  |

Figure 2. Photographs of the surface of a copper layer (Cu) on fused silica substrate (SiO₂), mode (a), table 1.

Then, experiments on depositing the TiN-Cu composite layers were carried out, during which the composition of the reaction gas (nitrogen+argon mixture), the pressure in the chamber, the deposition time varied. The optimum arc current and the magnetron discharge current were determined during the previous studies so their values remained unchanged [14]. Proceeding from the design features the optimal distances between the evaporator cathode and the substrate and between the magnetron cathode and the substrate (table 1) were determined and that allowed to achieve a uniform distribution of the deposited layers on the substrate [13]. The layers’ thickness was from 2–3 μm to 5–7 μm depending on the duration of the depositing time.
Figure 3. XRD patterns for coatings: a) TiN (80 A, 0.9 A, 2×10^{-3} Torr); b) TiN (80 A; 0.9 A, 4×10^{-3} Torr); c) TiN -Cu (80 A, 1.1 A, 8×10^{-3} Torr).
According to the X-ray phase analysis several samples contained a Ti$_2$N phase with a volume fraction ranging from 93.6% to 100% (figure 3). Besides, a small amount of a TiN phase (from 6.4% to 8%) was found in them. The presence of copper was not observed in the samples. The increase in the magnetron discharge current and the nitrogen pressure allowed to observe copper reflections with the intensity about 2% (table 1, mode (d)). The sample contained TiN with a tetragonal crystal cell as the main phase (about 99%).

The surface structure of TiN and TiN-Cu coatings and the average microhardness values are presented in table 2.

**Table 2.** 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](image1.jpg)                        |
|    |         | ![Photograph b](image2.jpg)                        |
| b  | 23665   | ![Photograph c](image3.jpg)                        |
|    |         | ![Photograph d](image4.jpg)                        |
| c  | 27259   | ![Photograph e](image5.jpg)                        |
|    |         | ![Photograph f](image6.jpg)                        |

In the case of sample c (mode d in table 1) 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 a and b (modes b and c table 2).

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 [12] 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. We assume that the microhardness values for the sample c (table 2) increased under the conditions of the experiment like in case [12], when during the Ti-N reaction in the Cu vapor, Cu is squeezed out towards the boundary between TiN grains. Copper suppresses the growth of the columnar structure of TiN crystallites, promoting nanostructuring of composite TiN–Cu coatings.

4. Conclusion

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. The deposition of coatings occurred at various technological parameters of the installation. The main difference from the studies we had earlier is in using a separation diaphragm with an adjustable metering hole in the installation and a mixture of working gases. The change in pressure of nitrogen is significantly affects on the chemical composition, cell parameters of the main phase, and the texture of crystallites of the formed coatings.

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