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Deposition of TiN-Cu coatings on T15K6 alloy by hybrid plasma technology

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Abstract. The deposition of TiN-Cu composite coatings in a vacuum plasma-chemical reactor by injection of copper vapor into the TiN synthesis area based on the coupling of gas-discharge processes of vacuum-arc evaporation of Ti and magnetron sputtering of Cu is considered. According to X-ray phase analysis, reflections are identified that belong to tungsten and titanium carbides, titanium nitride with different crystal lattice and unusual intensities. Copper reflections are not observed, although X-ray microanalysis of the coating structure confirms the presence of copper in the coatings under study throughout the entire coating profile. It is shown that in the proposed mode of TiN-Cu coatings deposition, the copper content is 5.57 at. %. The microhardness and uniformity of the surface structure of TiN-Cu coatings significantly depend on the vacuum-arc discharge current, magnetron discharge current, the composition of the mixture of argon and nitrogen gases, and the pressure of the working gas mixture in the plasma-chemical reactor.
Keywords: gas-discharge plasma, vacuum-arc evaporation, ion-plasma sputtering, composite coatings, synthesis, structure, structure, properties.

1. Introduction

TiN-Cu composite coatings with a nanocrystalline structure in the synthesis of TiN coatings with the addition of copper have high hardness and ductility [1–4]. Moreover, Cu atoms, when localized to form a layer [1, 5] along the boundaries of TiN crystallites, block the growth of the columnar structure of TiN crystallites and lead to the nanostructuring of superhard TiN-Cu coatings with an average grain size of ~20 nm. Along with the processes of synthesis of TiN-Cu coatings by sputtering in a magnetron discharge and an ion beam [6], particular interest is the synthesis of TiN-Cu composite coatings by injection of copper vapor into the TiN synthesis area based on the coupling of two gas-discharge processes, arc evaporation of Ti and magnetron sputtering of Cu, in the design of a plasma-chemical reactor [7]. Thus, the coupling of evaporation and ion sputtering processes potentially opens up the possibility of controlled management of the sizes of TiN crystallites in a buildable TiN-Cu coating.

This work examines the synthesis of TiN-Cu nanocomposite coatings on the principle of combining the processes of vacuum-arc evaporation of Ti and magnetron sputtering of Cu. Such processes potentially open up the possibility of controlled management of crystallite sizes in the growing coating, which is extremely important, since the nanostructure and, as a consequence, the microhardness of coatings, to a certain extent depend on the concentration of the impurity component, copper.

2. Experimental technique

The synthesis of TiN-Cu composite coatings was carried out in a vacuum chamber of a plasma-chemical reactor [8]. Structurally, the vacuum chamber contains a vacuum-arc evaporator 1 and a planar magnetron 2, Fig. 1. The areas of TiN synthesis and Cu vaporization are separated by a metal diaphragm (not indicated in Fig. 1) with a slotted dosing hole. The separating diaphragm does not allow the mutual influence of different forms of discharges - vacuum-arc and magnetron on their stable stationary combustion and prevents copper vapor from entering the titanium cathode of the vacuum-arc evaporator 1 and titanium vapor from entering the copper cathode of the planar magnetron 2. Vacuum arc evaporator 1 is installed horizontally Fig. 1 and contains a welded body cooled by running water, a cathode with a diameter of 60 mm, made of titanium grade BT-1-0, an anode, an ignition device, a magnetic coil that ensures uniform evaporation of the cathode by the cathode spot of a vacuum-arc discharge. Arc discharge current 60–90 A, nitrogen working gas

pressure $2.6 \cdot 10^{-1}$–12 Pa, combustion voltage 35–45 V. The distance from the evaporator cathode to the substrate is 230 mm. Planar magnetron 2 is installed vertically on the side wall of the vacuum chamber [8]. The power of the magnetron power supply is ~3 kW, the output voltage is up to 10^3 V. Water cooling of the permanent magnets ensures stable operation of the magnetron. Using the magnetron discharge control unit, the discharge power and, as a result, the sputtering speed of the copper target are adjusted. The magnetron ensured stable operation in the nitrogen gas pressure range of $2.6 \cdot 10^{-1}$–12 Pa. The magnetron discharge current is 0.2–0.7 A, the discharge voltage in the experiments was 340–450 V and depended on the pressure of the nitrogen gas or a mixture of nitrogen and argon gases.

In the mode (Fig. 1) of dissociation in nitrogen-containing plasma 3 of molecular nitrogen $N_2 \leftrightarrow 2N$ by plasma electrons, vacuum-arc evaporation of titanium vapor by a cathode spot and ion-plasma sputtering of copper vapor injected through a 5×100 mm^2 slot dosing hole in the diaphragm, a chemical reaction of titanium vapor and atomic nitrogen in copper vapor occurs on the substrate 4. The deposition time of TiN-Cu coatings is 15–25 minutes.

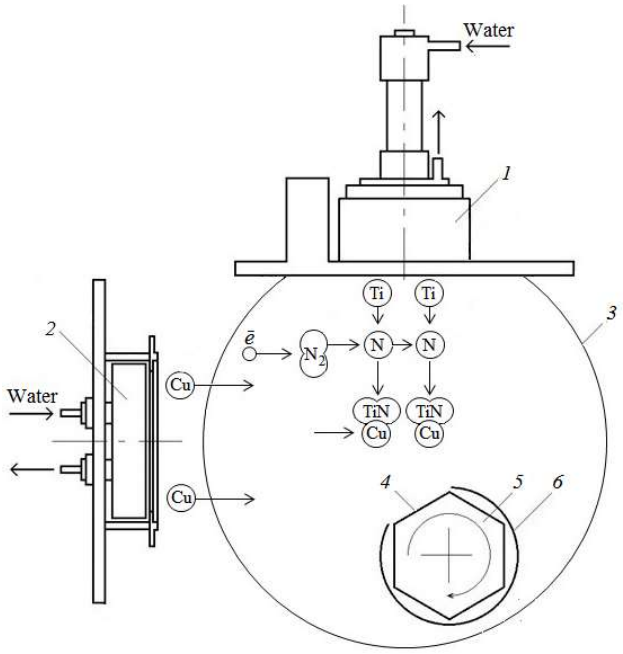

Fig. 1. Block diagram of the synthesis of TiN-Cu composite coatings: 1 – vacuum-arc evaporator, 2 – planar magnetron, 3 – vacuum-arc discharge plasma, 4 – substrates, 5 – substrate holder, 6 – screen.

Fig. 2. General view of the plasma chemical reactor.

Replaceable hexagonal plates type 11114 (HNUM) GOST 19068-80 made of hard alloy T15K6 are used as substrates, usually used for through cutters and end mills. The drum-type substrate holder 5 provided fastening of six substrates. When growing TiN-Cu coatings, the growth surface of the initial substrate is oriented at an angle of 45° to the normals of the mutually perpendicular planes of the evaporated titanium cathode and the sputtered copper cathode of the magnetron. In this case, the reserve substrates are covered with screen 6. As the coating growth stops, the substrate holder is rotated at an angle of 60° and the next substrate is removed from the screen, opening the growth surface for coating growth. The distance from the magnetron cathode to the substrate is in the range of 120–140 mm. A reference voltage of 160–180 V supplied to the substrate holder ensures ionic cleaning of the growth surface from gas inclusions, surface preparation time is 4–10 minutes. The

plasma-chemical reactor is pumped out to a residual pressure of $6.6 \cdot 10^{-3}$ Pa using an H400 diffusion pump. Preliminary rarefaction is provided by an AVZ-20D forevacuum pump.

A general view of the plasma-chemical reactor is shown in Fig. 2. X-ray phase analysis of the coatings was carried out on a D2 Phaser Bruker diffractometer using a linear detector for powder diffraction LYNXEYE and interpretation of X-ray patterns using the DIFFRAC.EVA software package with the international database ICDD PDF2. X-ray microanalysis of the coating structure was performed using a JSM-6510LV JEOL electron microscope (Japan) with an INCA Energy 350 microanalysis system from Oxford Instruments (UK). Metallographic analysis of the surface structure of the TiN-Cu composite coating was performed with a METAM PB-21 optical microscope equipped with a VEC-335 digital camera and the NEXSYS ImageExpert Pro 3.0 software package. The microhardness of the formed layers was measured using a PMT-3 M microhardness tester equipped with a digital camera with the NEXSYS ImageExpert MicroHardness 2 fingerprint image processing program in accordance with GOST 9450-76 (Knoop fingerprint reconstruction method).

3. Results and discussion

First, we tested the synthesis mode of TiN coatings using a vacuum-arc evaporator in the absence of copper vapor (the planar magnetron was turned off). The growth surface of the substrates was preliminarily cleaned in a glow discharge by applying a high voltage of ~1 kV in a vacuum of 6.8 Pa for 5 minutes. Next, the TiN coating deposition process is carried out, the main parameters are: arc discharge current 90 A, nitrogen gas pressure in the vacuum chamber 0.37 Pa, synthesis time 10 min, bias voltage 180 V, cathode-substrate distance 230 mm.

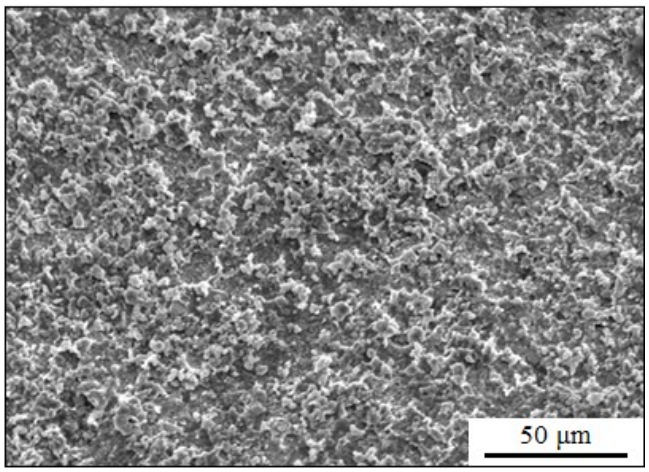

Fig. 3. Microstructure of the TiN coating surface (magnification x500).

The study of the surface microstructure and determination of the elemental composition was carried out using scanning electron microscopy and X-ray microanalysis. Fig. 3 shows the microstructure of the surface of the TiN coating, Table 1 presents the elemental composition of TiN coating. The coating surface is quite uniform and does not contain microdroplets, thanks to optimally selected values of the vacuum-arc discharge current. The coating has a dense structure, no porosity is observed, and grain boundaries are clearly visible. Fig. 4 shows an X-ray diffraction pattern of the TiN coating deposited on the surface of the T15K6 alloy. According to X-ray phase analysis, along with reflections of WC (001), (100), (101), (110), (002), (111), (200), (102), (201) and Ti_2C (111), (200), (202), (311), (222), belonging to the are observed. Crystallites of the TiN coating, usually having a columnar structure, are partially textured along the (111) plane, although reflection

reflections can be identified that belong to other planes (200), (202) and (222) with intensities unusual for them. The microhardness of the TiN coating is 19 GPa.

Table 1. Elemental composition of the TiN coating.

Chemical element	N	O	Ti	Co	W
Atomic percent	4.2	2.65	34.66	3.92	54.57

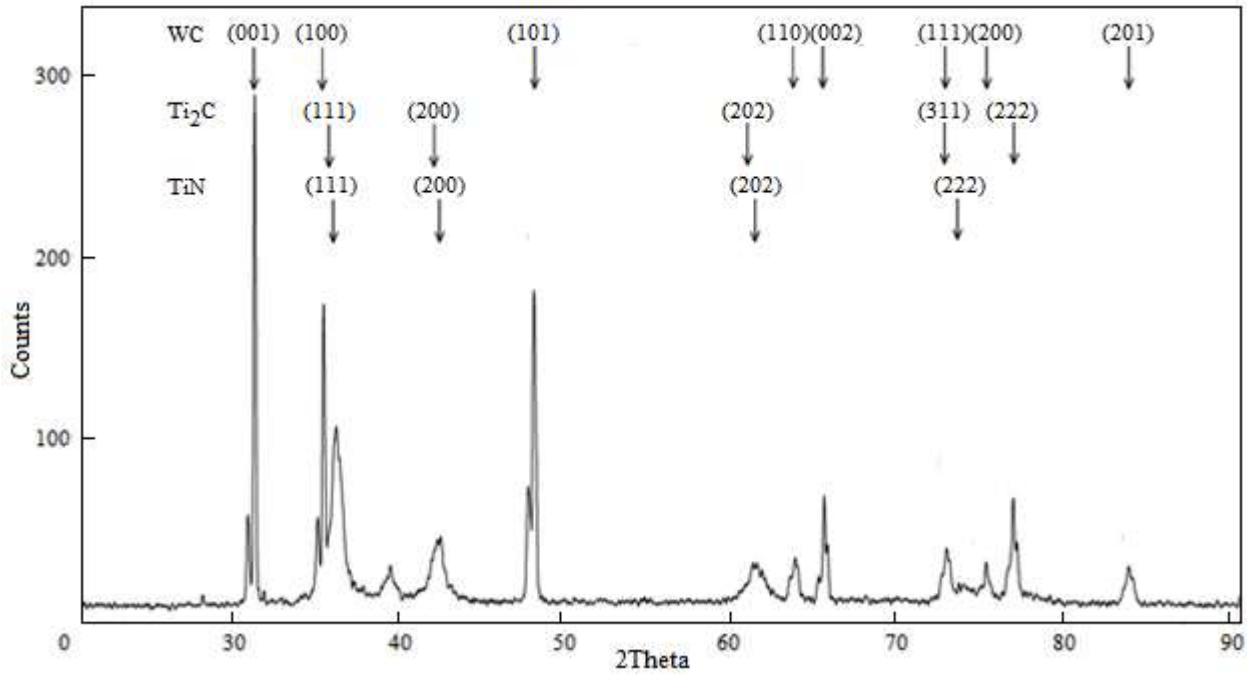

Fig. 4. X-ray diffraction of the TiN coating.

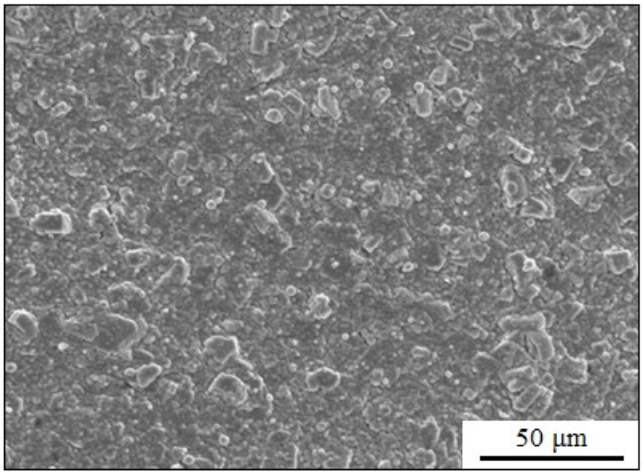

Fig. 5. Microstructure of the TiN-Cu coating surface (magnification x500).

After testing the synthesis modes of TiN coatings, the synthesis (Fig. 1) of a TiN-Cu composite coating was carried out in the vacuum chamber of a plasma-chemical reactor [7]. For more efficient sputtering of the magnetron cathode, nitrogen 80% and argon 20% were mixed in the total volume of the mixture of working gases in a gas mixer. Technological parameters for deposition of TiN-Cu coatings: cleaning time 10 minutes, bias voltage 160 V, arc discharge current 90 A, magnetron discharge current 0.5 A, discharge burning voltage 400 V, gas mixture pressure in the vacuum

chamber 2.4 Pa, substrate temperature 473 K, synthesis time 15 minutes. The coating thickness is ~6 μm. The surface microstructure of TiN-Cu composite coatings is shown in Fig. 5. The layer is uniform, with clear grain boundaries. The grain size is on average 10-15 μm. The characteristic columnar structure of TiN coatings changes to globular [7].

Fig. 6 shows an X-ray diffraction pattern of the TiN-Cu coating deposited on the surface of the T15K6 alloy. According to the X-ray phase analysis, along with reflections of WC (001), (100), (101), (110), (002), (111), (200), (201), (112) and Ti_2C (111), (200), (202), (311), (222), (422) belonging to the T15K6 alloy, reflections of the TiN coating (111), (200), (202), (222), (311) with different crystal lattice and volume fraction are observed. According to X-ray phase analysis, there are no copper reflections in the composite layer, Fig. 6. At the same time, X-ray spectral microanalysis of the structure of the coatings confirms the presence of copper in the coatings under study throughout the entire profile of the coatings, Table. 2.

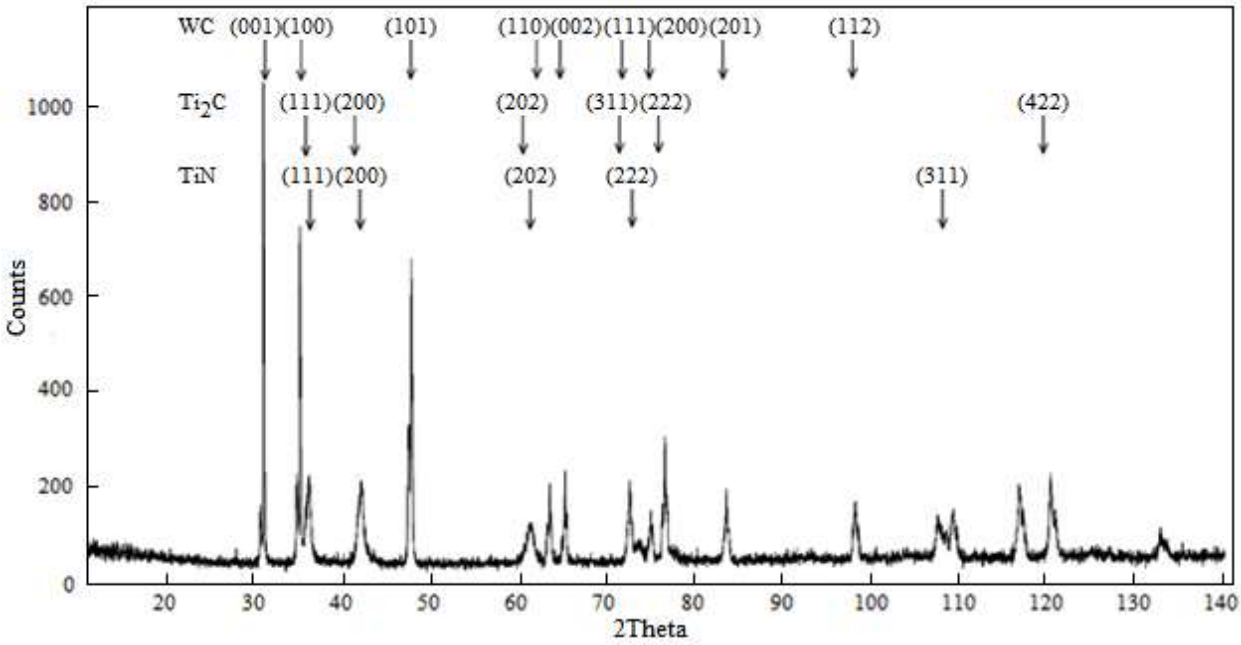

Fig. 6. X-ray diffraction of the TiN-Cu coating.

Table 2. Elemental composition of the TiN-Cu coating.

Chemical element	N	Al	Ti	Cu	W
Atomic percent	8.91	0.23	79.81	5.57	5.48

Probably, copper, without forming its own crystalline phase and not being in the crystal lattice of other phases, is located at the boundaries of crystallites in an amorphous or X-ray amorphous state. As in [2, 9, 10], during the reaction of Ti and N in Cu vapor, copper is displaced to the boundary between TiN grains. Copper blocks the growth of the columnar structure of TiN crystallites, promoting the nanostructuring of TiN-Cu composite coatings. This is evidenced, on the one hand, by the low affinity of Cu for N; nitrogen does not form compounds with Cu (copper does not directly combine with nitrogen; it is impossible to obtain nitrogen nitride Cu_3N). On the other hand, the phase diagram of the Ti-Cu system shows [11] that at low contents of atomic percent of copper intermetallic compounds are not stably formed, moreover, intermetallic compounds TiCu, Ti_2Cu, Ti_2Cu_3, $TiCu_3$ are formed at high atomic percent of copper and temperatures ~ 1073–1173 K. The time during which copper atoms form a closed shell around a growing TiN crystallite determines the growth time of

nanosized TiN crystallites and, as a consequence, the size of the crystallites. The microhardness of the coatings is 38–42 GPa.

The general view of a T15K6 hard alloy plate with TiN–Cu coating is shown in Fig. 7.

Fig. 7. Image of a hexagonal replaceable plate made of T15K6 hard alloy with the TiN-Cu coating.

4. Conclusion

Synthesis of TiN coatings in Cu vapors on alloy T15K6 on the basis of gas-discharge processes of vacuum-arc evaporation of Ti in nitrogen-containing plasma and magnetron ion-plasma sputtering of Cu is considered. According to X-ray phase analysis, reflections are identified that belong to tungsten and titanium carbides, titanium nitride with different crystal lattice and unusual intensities. Copper reflections are not observed, although X-ray microanalysis of the coating structure confirms the presence of copper in the coatings under study throughout the entire coating profile. In the proposed mode of TiN-Cu composite coating application copper content is ~ 5.57 at.%. The coating thickness is ~6 μm. Microhardness of coatings, 38-42 GPa. The wide possibilities of simplified technology for changing the structure and phase composition favor the creation of nanostructured composite superhard TiN-Cu coatings.

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