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Synthesis of TiN coatings in Cu vapor on T15K6 alloy using the hybrid plasma technology

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The synthesis of TiN coatings on T15K6 alloy in Cu vapor based on gas-discharge processes of vacuum-arc evaporation of Ti in nitrogen-containing plasma and magnetron ion-plasma sputtering of Cu is described. The following process parameters of the synthesis of TiN-Cu composite coatings have been determined: arc discharge current of 90 A, magnetron discharge glowing current of 0.5 A and voltage of 400 V, gas mixture pressure in the vacuum chamber of 2.4 Pa, growth surface temperature of 473 K, the synthesis time ~of 15 min, cleaning time of the substrate growth surface of 10 min, bias voltage of 160 V. Electron probe microanalysis of the structure confirms the copper content of ~5.57 at.% in the coatings under study over the entire coating profile. The microhardness of coatings is 38-42 GPa.

Keywords: gas discharge plasma; vacuum arc evaporation; ion-plasma sputtering; composite coating.

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Introduction

When synthesized with copper added, composite TiN-Cu coatings having a nanocrystalline structure exhibit high hardness and plasticity [1, 2]. Cu atoms, when localized to form coating [1] along the boundaries of TiN crystallites, prevent the columnar structure of TiN crystallites from growing and lead to nanostructuring of superhard TiN-Cu coatings with an average grain size of ~20 nm. The dependence of the coating hardness on the copper content has a non-monotonic pattern. The maximum hardness value is achieved at relatively low copper concentrations [1] ~ (1–2) at. %, with a nanocomposite structure formed in the TiN coatings being synthesized.

Among the most advanced processes that allow high precision copper filling during synthesis of composite nanostructured TiN-Cu coatings, there are gas-discharge devices combining two gas-discharge processes: arc evaporation of Ti and magnetron sputtering of

Cu, designed as a plasma-chemical reactor [3]. This combination has a potential enabling the controlled sizing of crystallites in a coating being built-up, which is extremely important because the nanostructure and, consequently, the microhardness and crack resistance of coatings are dependent on the concentration of an impurity component, the copper, to a certain extent. Controlling the parameters of vacuum arc and magnetron discharges while building up coatings [4, 5] facilitates controlling the ratio of evaporated and sprayed components.

This paper discusses the synthesis of TiN-Cu composite coatings based on combination of the Ti vacuum-arc evaporation process and Cu magnetron sputtering process [3, 6, 7] and describes the surface microstructure of TiN-Cu composite coatings, their X-ray diffraction analysis, electron probe microanalysis and microhardness.

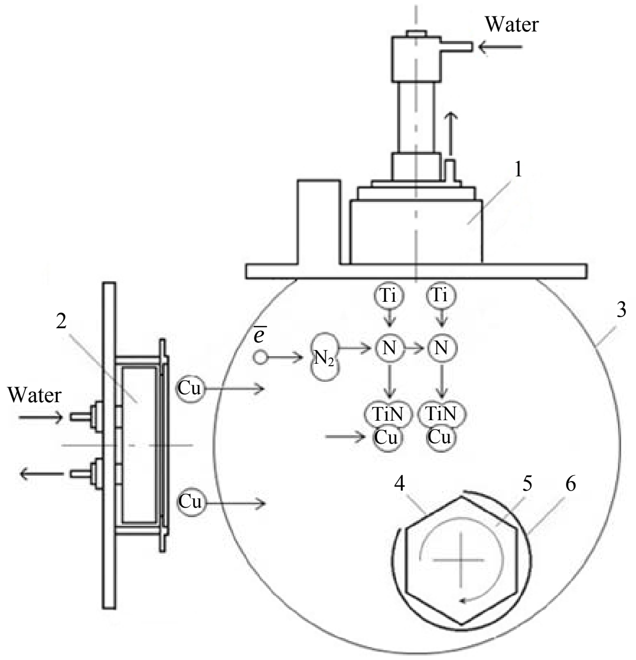

Fig. 1. Schematic diagram of the synthesis of TiN-Cu composite coatings: 1 – vacuum-arc evaporator; 2 – planar magnetron; 3 – vacuum-arc discharge plasma; 4 – substrates; 5 – substrate holder; 6 – screen

Experiment procedure

TiN-Cu composite coatings were synthesized in the vacuum chamber of the plasma-chemical reactor [3]. The vacuum chamber comprises vacuum-arc evaporator 1 and planar magnetron 2 (see Fig. 1). Vacuum-arc evaporator 1 is positioned horizontally and provides the evaporation of the water-cooled cathode by a cathode spot of vacuum arc discharge. The cathode has a 60-mm diameter and is made of titanium grade BT-1-0. The arc discharge current is 60-90 A, the pressure of working gas, nitrogen, is 2.6×10^{-1}–12 Pa, glowing voltage is 35-45 V. Planar magnetron 2 is positioned vertically. The magnetron power supply capacity is ~3 kW, the output voltage is up to 10^3 V. Water cooling of permanent magnets ensures stable operation of the magnetron.

The sputtering rate of the copper target is controlled by the magnetron discharge power. The sputtering efficiency is controlled by adding ~20 % of argon to the total volume of the working nitrogen and argon mixture in the gas mixer. The magnetron supported the stable operation within the plasma-forming gas pressure range of 2.6×10^{-1}–12 Pa. The magnetron discharge current is 0.2–0.7 A. The discharge glowing voltage during the experiments was 340–450 V. The discharge glowing current and voltage depend on the pressure of the nitrogen and argon gas mixture. The distance from the evaporator cathode to the substrates 4 is 230 mm. Replaceable hexagonal plates of type 11114 (HNUM) as per GOST 19068-80 made of T15K6 hard alloy are used as substrates. Generally, they are used for straight-turning tools and end cutters. Drum-type substrate holder 5 allowed fastening up to six substrates. During building up of 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 sputtered copper cathode. Spare substrates shall be covered with screen 6. When the coating building-up is finished, the substrate holder rotates to an angle of 60° and the next substrate is extended out of the screen, opening the growth surface for building up a coating. The distance from the magnetron cathode to the substrate is within the range of 120–140 mm. The reference voltage of 160–180 V supplied to the substrate holder enables ion cleaning of the growth surface to remove gas inclusions; the surface preparation time is 4–10 min.

Findings and discussion

TiN-Cu composite coatings of ~6 μm in thickness were synthesized on substrates 4 (see Fig. 1) by initiating a chemical reaction between titanium vapor and atomic nitrogen in copper vapor, in conditions of dissociation in nitrogen-containing plasma 3 of molecular nitrogen $N_2 \leftrightarrow 2N$ by plasma electrons, vacuum-arc evaporation by a cathode spot of titanium vapour and ion-plasma sputtering of copper vapor. Process parameters of the synthesis: arc discharge current of 90 A, magnetron discharge glowing current of 0.5 A and voltage of 400 V, gas mixture pressure in the vacuum chamber of 2.4 Pa. At first, the hard alloy surface is cleaned, activated and heated up to ~473 K for ~10 minutes with metal-containing ions and plasma-forming gas ions, the bias voltage equaling to 160 V. The surface temperature of T15K6 hard alloy is measured with TXA thermoelectric transducer (chromel-alumel). After that, under the synthesis process parameters, the achieved surface temperature of the hard alloy is steady-state, and the TiN-Cu coating is synthesized for 15 minutes at a constant temperature of ~473 K.

Fig. 2 shows the surface microstructure of TiN-Cu composite coatings. The metallographic analysis of the TiN-Cu composite coating surface structure was performed using METAM PB-21 optical microscope equipped with VEC-335 digital camera and NEXSYS ImageExpert Pro 3.0 software package. The coating is uniform wit clear grain boundaries.

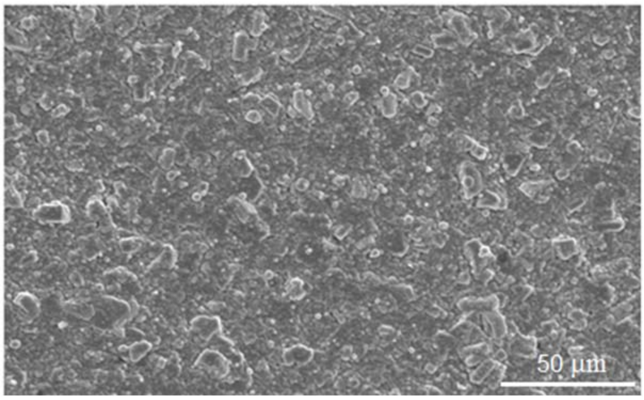

Fig. 2. Surface microstructure of TiN-Cu coating (500× magnification)

Fig. 3 shows the X-ray pattern of the TiN-Cu coating synthesized on the surface of T15K6 alloy. The X-ray phase analysis of the coatings was carried out by means of D2 Phaser Bruker diffractometer using a LYNXEYE linear detector for powder diffractography and decoding of X-ray patterns with DIFFRAC.EVA software package with the ICDD PDF2 international database. According to the X-ray phase analysis completed, reflections of the TiN coating (111), (200), (202), (222), (311) having different crystal lattices and volume fractions are observed along with the WC reflections (001), (100), (101), (110), (002), (111), (200), (201), (112) and Ti_2C (111), (200), (202), (311), (222), (422) belonging to T15K6 alloy. According to the X-ray phase analysis, there are no copper reflections in the composite layer. Whereas the electron probe microanalysis (electron probe microanalysis of the coating structure was performed using JSM-6510LV JEOL electron microscope (Japan) with INCA Energy 350 Oxford Instruments microanalysis system (Great Britain)) of the coating structure confirms that there is copper in the coatings under study throughout the entire coating profile (see the table).

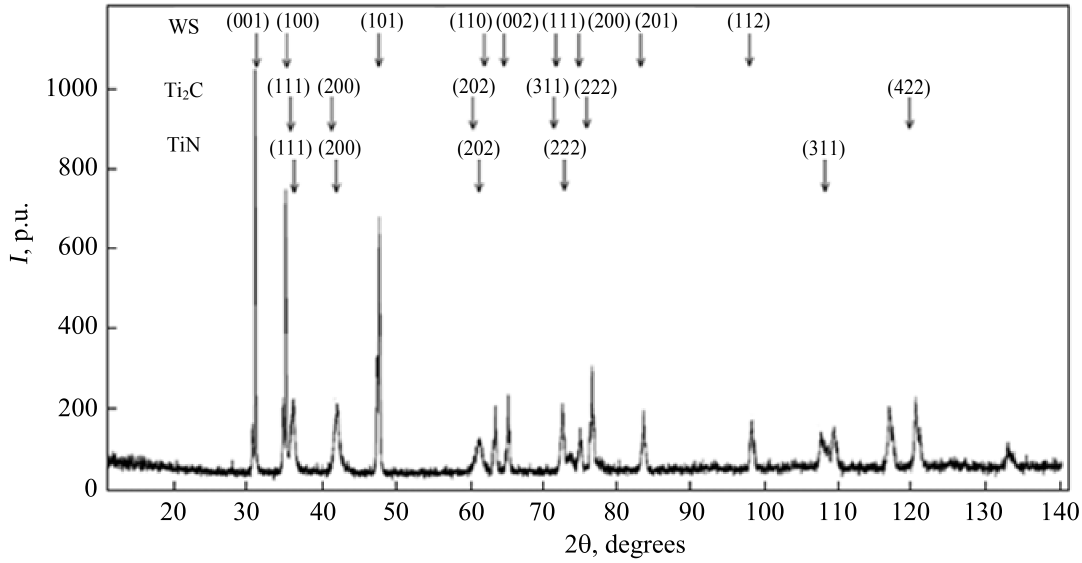

Fig. 3. X-ray pattern of TiN-Cu coating

Table

Elemental composition (in at.%) of TiN-Cu coating

No.	Al	Ti	Cu	W
8.91	0.23	79.81	5.57	5.48

Since copper does not form its own crystalline phase and is not part of the crystal lattice of other phases, it is probably located at the boundaries of crystallites in an amorphous or X-ray-amorphous state. As in [2, 5, 6], during the reaction of Ti and N in Cu vapor, copper is displaced to the boundary between TiN grains. Copper prevents the columnar structure of TiN crystallites from growing, thus contributing to the nanostructuring of TiN-Cu composite coatings. On the one hand, it is shown by the low affinity of Cu for N. Nitrogen does not form compounds with Cu (copper does not directly combine with nitrogen; nitrogen nitride Cu_3N cannot be produced). On the other hand, the phase diagram of the Ti-Cu system shows [8] that intermetallics are not formed steadily at low atomic percentages of copper; moreover, TiCu, Ti_2Cu, Ti_2Cu_3, $TiCu_3$ intermetallics are formed at high atomic percentages of copper and at temperatures of ~1073–1173 K. The time needed for copper atoms to form a closed shell around a growing TiN crystallite determines the growth duration of nanosized TiN crystallites, and, as a consequence, the size thereof.

The microhardness of the formed layers was measured using ПМТ-3 M microhardness tester equipped with a digital camera and NEXSYS ImageExpert MicroHardness 2 program for indentation image processing as per GOST 9450-76 (using the Knoop indentation restoration method). The microhardness of coatings is 38–42 GPa.

Conclusion

TiN-Cu composite coatings of ~6 μm in thickness were synthesized on replaceable hexagonal plates of type 11114 (HNUM) as per GOST 19068-80 made of T15K6 hard alloy by initiating a chemical reaction between titanium vapor and atomic nitrogen in copper vapor, in conditions of dissociation in nitrogen-containing plasma of molecular nitrogen by plasma electrons, vacuum-arc evaporation by a cathode spot of titanium vapor and ion-plasma sputtering of copper vapor. The following process parameters of the synthesis of TiN-Cu composite coatings have been determined: arc discharge current of 90 A, magnetron discharge glowing current of 0.5 A and voltage of 400 V, gas mixture pressure in the vacuum chamber of 2.4 Pa, growth surface temperature of 473 K, the synthesis time ~of 15 min, cleaning time of the substrate growth surface of 10 min, bias voltage of 160 V. According to the X-ray phase analysis, there are no copper reflections in the composite layer. Electron probe microanalysis of the structure confirms the copper content of ~5.57 at.% in the coatings under study over the entire coating profile. The microhardness of coatings is 38–42 GPa.

According to the results of testing TiN-Cu coatings in real operating conditions under critical loads on replaceable hexagonal plates made of T15K6 and fixed on the straight-turning tool for cutting structural steel 40X on 16K20 screw-cutting lathe, the coatings did not fail (chips, peeling) in the contact area of the cutting tool, which is a clear evidence that the TiN-Cu coating strongly adheres to T15K6 hard alloy applied using the hybrid plasma technology. The test results confirmed that TiN-Cu coatings can be used as wear-resistant ones. In addition, the following pattern was established in [9]: TiN-Cu coatings with the Cu concentration of ~12 at.% and microhardness of up to 45 GPa feature a low friction coefficient (0.2), high adhesive strength to the metal and hard alloy substrate (> 30 N), higher degree of strain recovery (< 50 %), high wear resistance (< 2600 μm^3/N·m), good thermal stability (up to 1373 K), and higher oxidation resistance (up to 1073 K).

Thus, the diverse applicability of the simplified technology for changing the structure and phase composition make allows creating composite superhard TiN-Cu coatings that significantly increase the surface microhardness of straight-turning tools and end cutters made of T15K6 hard alloy.

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