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Nanostructural TiN/Cu coatings deposited from the separated plasma flows

Abstract. *The results of the structural and physical-mechanical properties investigation of TiN/Cu coatings, deposited from multicomponent separated vacuum arc plasma are shown in this paper. The characteristics of the nanosized TiN-based coatings generation alloying by the element not forming chemical compounds with titanium and nitrogen under the chosen technological parameters are examined. The regularities of the microhardness and friction properties of TiN/Cu coatings changing under different elemental composition are determined.*

Abstrakt. *W pracy przedstawiono wyniki badań strukturalnych oraz właściwości fizyko-mechanicznych powłok TiN/Cu, otrzymanych łukową metodą próżniowo-plazmowego osadzania warstw ze złożonych odrębnych źródeł. Zbadano charakterystyki nanorozmiarowych powłok na bazie TiN generowanych dopingowaniem elementu nie tworzącego związki chemiczne z tytanem i azotem przy wybranych parametrach technologicznych. Ustalono, że prawidłowości mikrotwardości oraz właściowści tarciowe powłok TiN/Cu zmieniają się przy różnym składzie pierwiastkowym* ***(Nanostrukturalne warstwy TiN/Cu osadzane z osobnych przepływów plazmy)****.*

Keywords: wear resistance coatings, vacuum-arc deposition, separation, nanostructure, friction factor.
Słowa kluczowe: powłoki odporne na zużycie, łukowe osadzanie próżniowe, separacja, nanostruktura, współczynnik tarcia.

Introduction

Nanostructural films and coatings possess unique physical-mechanical properties and the determining factors are the synthesis condition and the alloying element choice.

The fracture processes in the nanocrystalline materials are realized by the interatomic bond breakage with high energy barriers, which are typical for high-melting nitrides compounds. Hence, the scientifically-technological fundamentals of the multicomponent nanosized TiN-based coatings deposition, alloyed by B, C, Al, Si, Cu and Cr, which make it possible to increase the resistance and service products properties are dynamically developed [1-3]. The application of the vacuum-arc techniques of the surface engineering are the most promising nowadays. Thus, the application of the high-ionized low-temperature plasma flow during vacuum-arc deposition under ion bombardment leads to coatings generation of the complex compound with nanosized structure [4, 5]. Besides, the control of the temperature conditions allows to deposit protective coatings both carbides and high-speed steel tools.

It's known, the structure and physical-mechanical properties control of the generated condensates during multicomponent coatings deposition are realized by means of the different strengthening mechanisms, namely, solid solution, grain-boundary and dispersion strengthening [6]. While alloying, the strengthening of the coating material is caused by both the chemical bond type changing and grain size refinement, leading to the intergranular boundary extension in the coating [7]. At the same time the alloying elements can generate compounds with different solubility with titanium nitride or can not interact with it.

The problem of the optimal components concentrations proportions choice in the coating and the generation conditions is still opened and stipulate the carrying out of the further investigations, as far as the necessity of serial reproduction of the nanocomposite coatings with the required properties.

In this paper, it is suggested to investigate the vacuum-plasma multicomponent TiN-based coatings generation characteristics, alloyed by Cu, the element not forming chemical compounds with titanium and nitrogen under the chosen technological parameters, to determine the optimal alloying element concentration, providing the protective coating properties increasing.

Material and methods

The modernized vacuum-arc plant, equipped by Y-shaped macroparticles separator was used in this work to generate multicomponent TiN/Cu coatings (Fig.1).

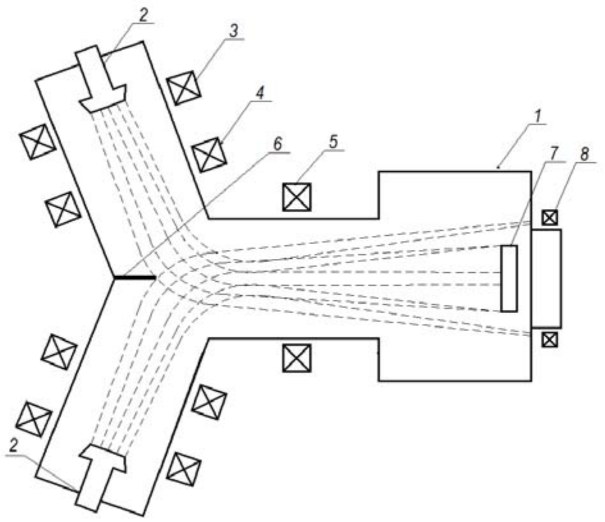

Fig.1. Scheme of multicomponent coatings deposition from the separated plasma flows: 1 – vacuum camera; 2 – arc evaporators; 3, 4, 5, 6 – electromagnetic coils; 6 – screen for droplets withdrawal; 7 – substrate

Two opposite arc evaporators ((2) are placed symmetrically at an angle of 120º degrees relative to the incidence axis of the total plasma flow. The ionized components of plasma flows are deflected by 120º by means of electromagnetic coils (5, 8) and mixed plasma flows are deposited onto substrate. The focusing of the different plasma flows is controlled by the electromagnetic coils (3, 4). The screen (6) provides the droplet phase withdrawal from plasma flows and its deposition on the plasma-guide walls.

The coatings were generated by means of simultaneous two cathodes sputtering (titanium and copper) under the partial pressure $6.0 \cdot 10^{-3}$ Pa. The phase composition of the coating was controlled by the arc current changing on the complementing cathode (copper) in the current range 40 –80 A.

X-ray diffraction and X-ray phase analysis were carried out in the measuring range between 30° and 120° using CuK_α characteristic X-Ray radiation. By using the main characteristics of the diffraction maximum allowed estimating the lattice parameter (d), coherent-scattering region size (L). The morphology and structure of the deposited coatings were studied by means of transparent electron microscope S-4800 Hitachi. The coatings composition was determined by electron microprobe EPMA; JEOL, JXA 8500-F Microhardness was measured by nanoindenter Duramin under load 0.25 N. The tribological investigations were carried out using «ball-on-disc» test in the open air without any lubricant (counterbody – HB = 200 MPa, running time – 30 min). The specific volume wear was chosen as a parameter, characterizing the coatings wear, and it was estimated according to [8].

Results and discussion

Due to the physical laws characteristics of the arc discharge existence, the generated coatings have the macroparticles in the condensates, and it has a negative influence on their protective properties. So it's effective to use separators to decrease the heterophase of the plasma flow, interacting with protecting products surfaces [9-11].

The scanning electron microscope investigations showed, the morphology of the TiN/Cu coatings, deposited from the multicomponent separated plasma flow, was characterized by the absence of the drops (Fig.2).

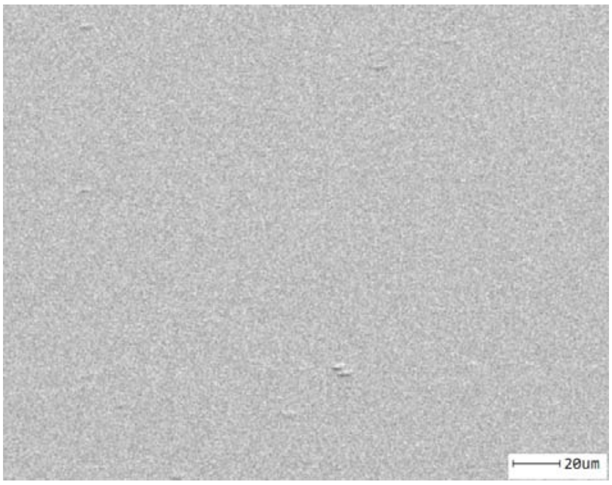

Fig.2. Surface morphology of the TiN/Cu coatings

The addition of the alloying element leads to the columnar structure changing typical to the mononitride coatings onto globular (Fig.3).

It's found from the X-ray investigations, that TiN/Cu coatings deposited under different arc currents of the copper evaporator, are characterized by the diffraction peaks of cubic TiN (structure B1 NaCl) (Fig.4). There were no reflections, attributed to copper or its compounds under low concentrations (2-4 at.%). Apparently, the copper atoms don't generate the own crystalline phase in this case and are in the amorphous condition on the grain boundary [12]. The additional copper peak is just registered when the concentration of the alloying element in the coating is about 16 at. %. At the same time the calculations showed, the increasing of the copper concentration in the coating from 2 to 16 at. % had no influence on the grain size.

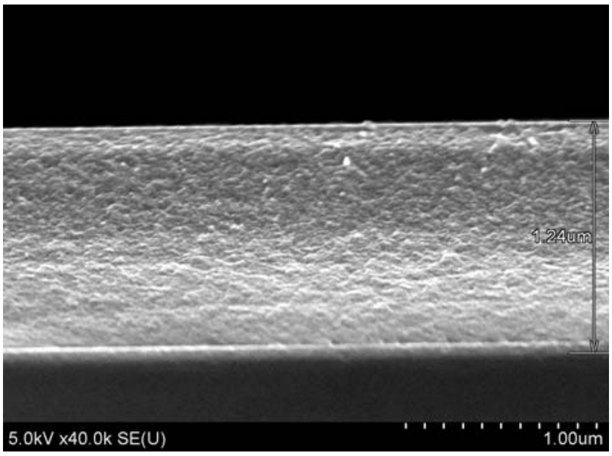

Fig.3. Fractograph of the TiN/Cu coatings with copper concentration 2 at.%

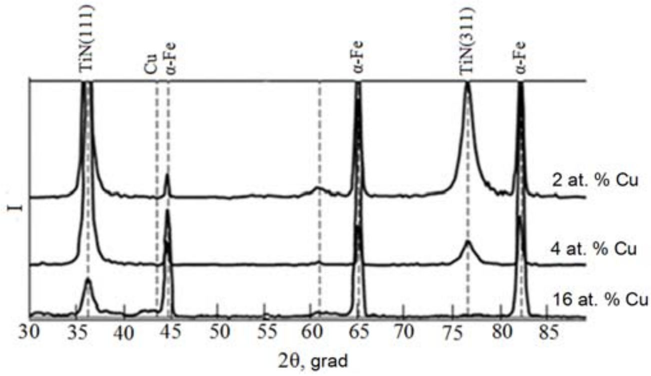

Fig.4. TiN/Cu coatings X-ray diffraction patterns with different copper concentration

The determined effect of the microhardness growth in the TiN/Cu coatings with copper concentration 2-4 at.% agrees with modern concepts about the important role of the large-scale factor while generating the structural-sensitive mechanical properties within the grain-boundary strengthening model (table 1).

Table 1. Structural and mechanical characteristics of the TiN/Cu coatings under different deposition parameters

$P \cdot 10^{-3}$, Pa	I_{Ti}, A	I_{Cu}, A	Ti, at. %	Cu, at. %	d, Å	L, nm	H, GPa
6.0	55	40	97.93	2.07	4.3046	7.5	40.3
		50	95.73	4.21	4.3056	6.9	39.8
		60	92.17	7.83	4.3048	8.2	26.5
		70	88.66	11.34	4.3045	8.1	24.3
		80	84.28	15.72	4.3044	7.6	17.6

The grain size limitation and intergranular boundary extension are caused by the thermodynamically controlled segregation insoluble components at grain boundaries. The grains boundaries are appeared to be both an intensive energy dissipation zone and the cracks stopping and it leads to the material strengthening.

According to the obtained results, the addition of 2 at.% of copper leads to the significant microhardness increase, at the same time even the partial coat of the nitride titanium grains by copper stops their growth, stimulating the appearance of the new TiN phase nuclei during the deposition. When the copper concentration is over 5 at.%, the coatings microhardness decreases, but the grain size remains the same (7-8 nm). Apparently, the increasing of volume copper content at TiN grain boundaries reduces the level of interatomic bond between the crystalline phase atoms, and due to the grain-boundary sliding mechanism microhardness of the generated coatings decreases [7].

The local damage in the frictional contact zone takes place in highly nonequilibrium condition and the intensive plastic deformation of the coating material, the focal temperature rise or oxidation and etc can occur. As can be seen from the tribological investigations with different copper concentration in the coatings, the minimum values of the dry friction factor are for the coatings with copper concentration (2-4 at.%) and it's 2.5 times lower in comparison with TiN (Fig.5). It should be noted, the minimum wear rate is also for the coatings with given copper concentrations in the coating.

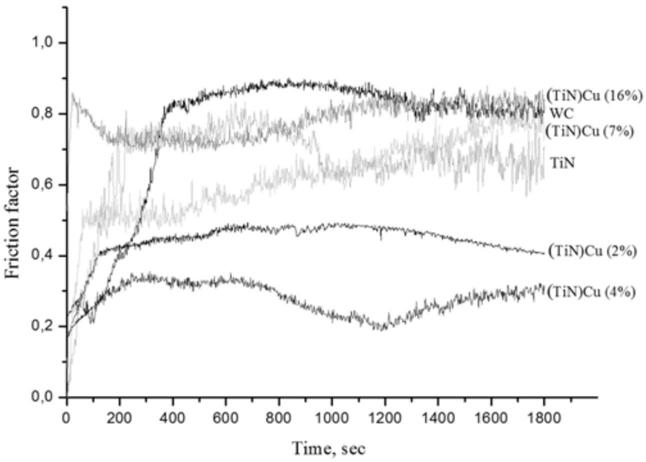

Fig.5. Friction factor of the vacuum arc coated cutting plates

The copper concentration increasing in the coating leads to specific volume wear increasing of the tested coatings, and it's mainly connected with lower microhardness of the generated coatings (Fig.6).

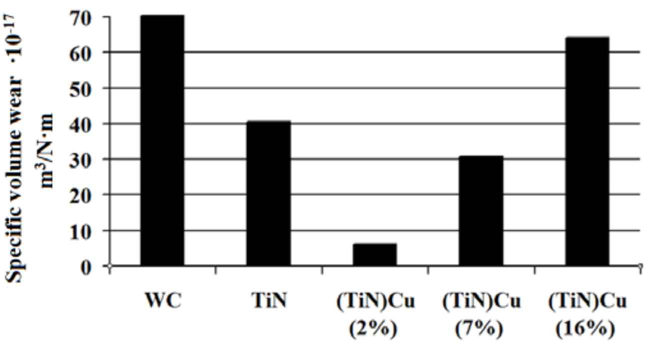

Fig.6. Specific volume wear of the carbides

Thus, the main factors, determining the high wear resistance of the TiN/Cu coatings are:
- crystal grain size is lower than 10 nm;
- the presence of the damping plastic copper interlayer between the hard nitride titanium grains;
- in order to suppress the grain-boundary sliding mechanism the volume copper content in the coating should be less than 4 at.%.

Conclusions

The carried out investigations showed, that the application of the multicomponent plasma of vacuum-arc discharge allowed to control the structure and physical-mechanical properties of the generated TiN/Cu coatings, and it should provide the operational properties increase of the harden products.

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