



Discrete Modified Nanostructural Wearproof Coatings TiN-Cu

D.S. Belov^{1,*}, I.V. Blinkov^{1,†}, A.O. Volkhonskiy^{1,‡}, J. Michalski²

¹ National University of Science and Technology "MISIS", Department of functional and high-temperature materials, 4, Leninskiy Ave., 119049 Moscow, Russian Federation

² Institute of Precision Mechanic, 3, Duchnicka St., 01-796 Warsaw, Poland

(Received 20 May 2013; revised manuscript received 05 June 2013; published online 31 August 2013)

Discrete modified nanostructural wearproof coatings Ti-N-Cu with crystallites size from 100 to 20 nanometers formed with ion-plasma vacuum-arc method. Copper amount in the received coatings made from 0 to 20 at. %, their hardness have considerably increased up to about 40-45 hPa in comparison with 20-22 hPa for Ti-N coverings. In this work, processes of structure and phase formation of Ti-N-Cu system coatings in a wide interval of copper concentration are investigated.

Keywords: Wearproof coating, Titanium nitride, Copper, Nanostructuring, Hardness, PVD method, Nanoindentation.

PACS numbers: 68.37. – d, 68.37.Hk, 68.55.Nq.

1. INTRODUCTION

Nanostructuring of nitride coatings (their preparation with a size of grains less than 100 nanometers) of various functional purpose makes it possible to implement in them high values of hardness combining with plasticity. This thereby provides the added performance of wear resistance in conditions of both constant, and fatigue loads [1, 2, 3].

One of the possible ways to limit growth of coating material grains during its deposition is implementation to the forming coating the components which will be spread over the surface of main coating phase nucleus and limit their growth [4, 5, 6]. The main criteria for choosing these modifying agents are lack of noticeable dissolution in a nitride phase and tendency to nitride formation.

This work includes researches on studying of structure and properties of TiN-Cu coatings with copper wide concentration range received by a method of ion-plasma vacuum-arc deposition on the hard-alloy cutting tool TT10K8B, including its tests for firmness conducted when cutting.

2. RESEARCH TECHNIQUE

Coatings were overlaid on an ion-plasma vacuum-arc unit of Bulat type, including three evaporative cathodes with separators of a drop phase in the atmosphere of reaction gas nitrogen ($PN_2 = 3 \times 10^{-3}$ Pa). Cathodes from VT-5 alloy, copper and combined from VT-5 alloy with insertion from Cu were used. The current of evaporative arc (I_d) was 120 A, the negative bias (U_c) energized to the substrate, changed from -80 V to -140 V.

Time of coating sputtering was about 90 minutes, their thickness was within 3.9–4.1 micrometers.

Morphology, structure of coatings was studied using a field raster electron microscope JSM-6700F with an add-on for energy-dispersive spectrometry JED-2300F,

JEOL.

To determine phase composition of a coating the imaging with DRON-4 diffractometer was carried out using CoK α emission and the graphite monochromator on the diffracted beam in asymmetric geometry (the angle between the incident ray and sample surface being $\alpha = 5^\circ$).

To carry out structural surveys of coatings the transmission electron microscope JEM 2100 of high resolution, JEOL, Japan was applied.

For sample thinning ion etching was used. Ion etching was carried out by means of the PIPS equipment (Precision Ion Polishing System, Gatan).

Coatings hardness (H) and elastic modulus (E) were measured by the method of continuous indentation at light loads. This test was performed using microindenter Micro-Hardness Tester (CSM Instruments) with fixed loading 300 mN. Indenter penetration depth was controlled so that it did not exceed 10 % of coating thickness to restrict substrate material influence.

3. RESULTS AND THEIR DISCUSSION

Appearance of the created coatings does not differ from appearance of the ion-plasma coatings which does not contain metal phase [7]. They have a cell structure with roughness (Ra) of about 0.3-0.2 microns (Fig. 1). Coatings containing 20 at. % of copper have rather porous structure which density increases with reduction in copper amount.

Copper amount at fixed I_d values = 120 A and $U_c = -120$ V varied in a coating from 0.6 to 20 at. % when using the respective cathodes, due to area ratio change of evaporating cathodes coatings - VT-5 and copper alloy from 5 to 1. U_c growth from -80 to -140 V, (bringing to energy increase of the sprayed ions bombarding the substrate) when preserving the identical area ratio of cathode surfaces from VT-5 and Cu (2.4), and also current of evaporating them electric arches

* LightningN4S@yandex.ru

† biv@misis.ru

‡ abwest@yandex.ru

(120A) led to reduction of copper amount in a coating from 9 to 1.7 at. % in case of its regular distribution on all substrate surface. Thus nitrogen amount in a coating in relation to a nitride composing element – titanium – also decreased (from 0.91 to 0.86). The increase in nonstoichiometry TiN is also supported by the lattice con-

stant equal to 4.239 and 4.207 Å respectively for the coatings received at Us-80 and – 140 B. This effect is connected with preferable spraying from a coating both the easiest element - nitrogen, and the copper, which bond energy is less than bond energy of titanium in nitride.

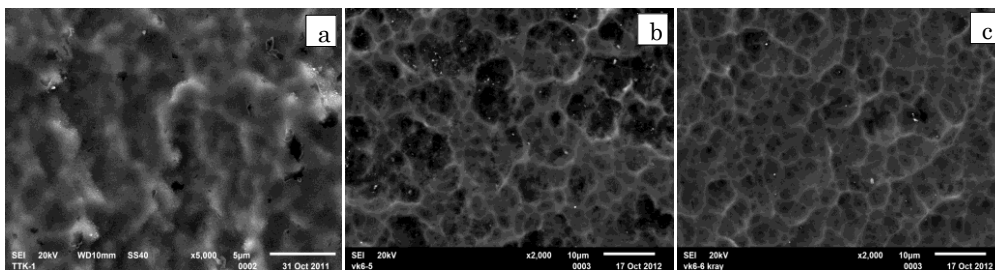


Fig. 1 – External appearance of Ti-Cu-N coatings with copper: a) 20 at. %; b) 9 at. %; c) 3 at. %

The x-ray phase analysis speaks for availability in all the samples the titanium nitride and copper if its amount in the coating is from 20 to 9 at. %. In case of smaller copper amounts, the lines of its x-ray diffraction are absent on roentgenograms. The level of nitride phase microdeformations of a coating because of copper amount (Figure 2) varied from 0.5 to 1.08 %.

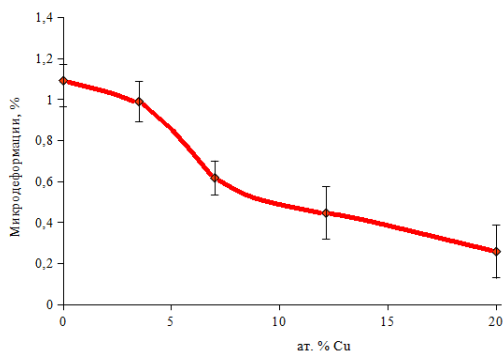


Fig. 2 – Change of microdeformations TiN level in TiN-Cu coating depending on copper amount

Reduction of their values with increase of copper amount in a coating can be connected with relaxed influence on them by plastic metal phase. Sizes of the stretching macrostresses in the received coatings, determined by the $\sin^2\theta$ method, made from 60 ± 40 to 90 ± 40 MPa that speaks for absence of stress in them. The sizes of composite nitride phase development are of about 15 nanometers and very little depend on coating copper amount.

In Figure 3, you see the images received by TEM method, crystallites of coatings TiN-Cu phases containing various amount of copper. The average size of titanium nitride crystallites, estimated according to dark-field images of coating structure and the images of separate particles received with use of TEM, varies from 20 to 100 nanometers in case of copper amount reduction from 20 to 0 at. % (pure titanium nitride) (Fig. 4). Comparison of their sizes with sizes of development shows that nitride phase grains are fragmented by low-angle borders on subgrains. Coatings consist of crystallites accidentally oriented relative to each other. The evidence of this are strongly marked rings on electron-

diffraction photograph (Fig. 3e). Absence of noticeable nitride phase texture is also supported by data of the X-ray diffraction analysis which speaks for bigger intensity of x-ray diffraction line TiN (200) in relation to (111). Reduction of the nitride phase crystallites size with increase in copper concentration gives evidence of its damping effect on growth process of TiN grains.

However, as it is seen from the diagram (Fig. 4), with increase of Cu concentration more than 7–10 at. % of noticeable coating structure refinement does not happen. This fact testifies that this very amount of copper provides complete covering of titanium nitride growing grains and its (copper) further introduction in a coating for the purpose of nitride phase structure refinement makes no sense.

This conclusion is also proved by results of created layers hardness measurement. Its average size on 12 measured values decreased from 46–49 to 14–15 hPa for the coatings containing from 3.5 to 20 at. copper %, respectively. It can mean that while increasing the copper amount in the coating more important for this characteristic is not the decreasing crystallites size, but the growing amount in a composite of soft plastic metal. Reduction in hardness of made coating can have a negative impact on its wear resistance.

To assess copper impact on titanium nitride coating operability one should take into account not only its modifying influence on coating structure, but also that it increasingly impacts coating heat conductivity. Increase of copper concentration increases the heat-removal from contact zone of tool nose with work material that leads to temperature reduction in the cutting zone. The performed analysis of TiN-Cu coatings heat conductivity (λ) by Kurnakov's [8] rule (connecting composite characteristics with components characteristics through their weight concentration), shows that λ for the nitride coating containing 20 at. % copper, increases to 116 W/(m²K) in comparison with 37 W/(m²K) - value, characteristic for TiN (λ for coating TiN-7 at. % of Cu is estimated by 65 W/(m²K).

Besides, soft plastic copper influences tribological properties of composite coating, in particular, reduces frictional coefficient by reducing friction force (Fig. 6).

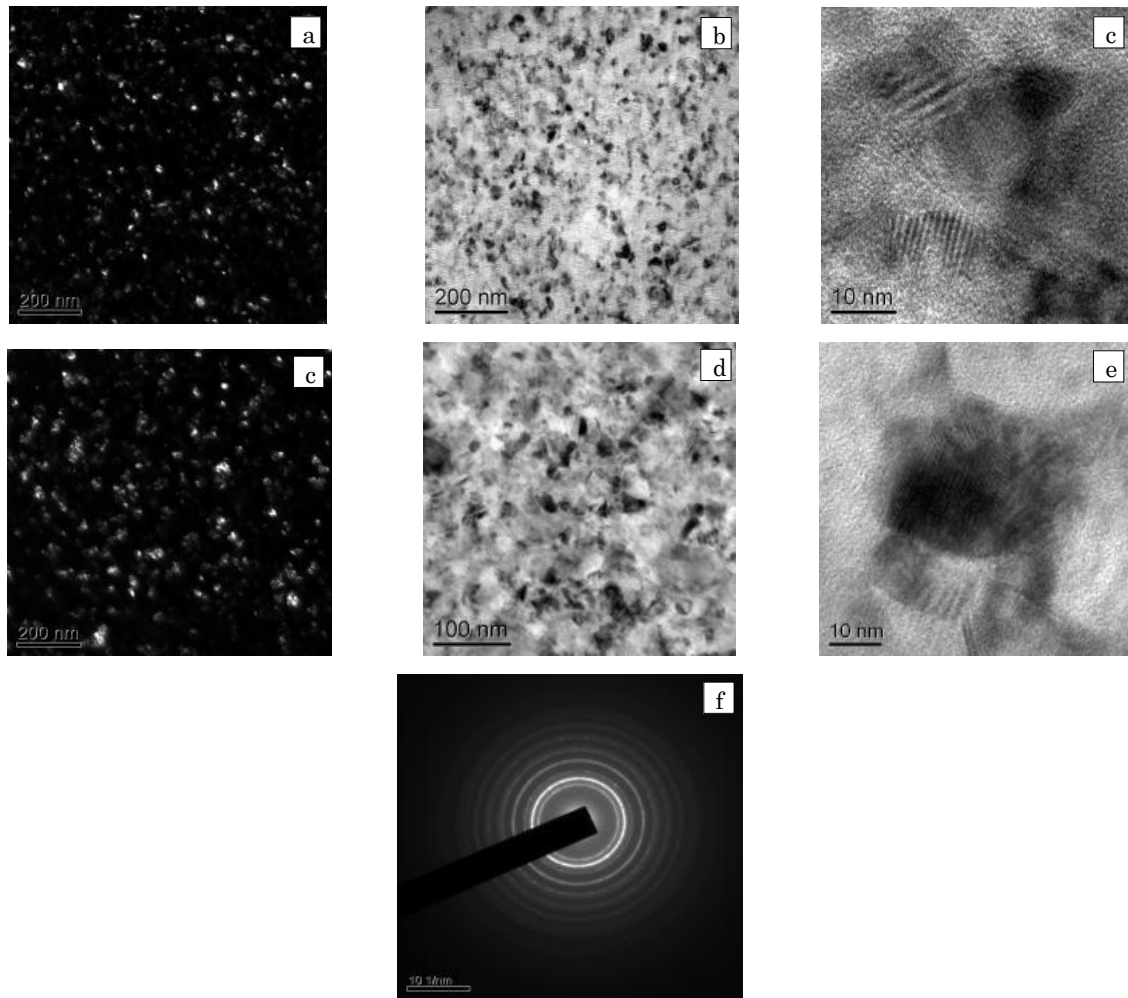


Fig. 3 – Electron microscope images of coatings Ti-Cu-N structure with copper: a, b, c)-20 at. % ; d, e, f)-7at. % ; a, d)- dark-field image; b, e)- bright-field image; c, f)- high-resolution images; g)- coatings electron-diffraction photograph

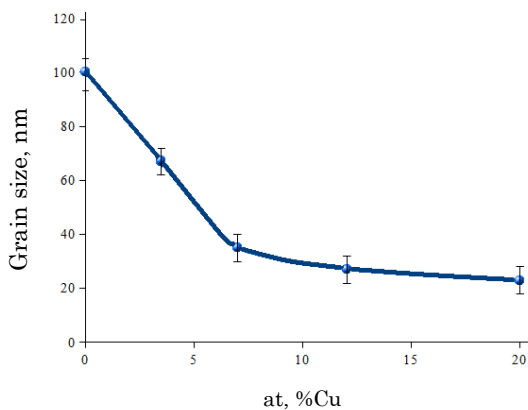


Fig. 4 – Dependence of TiN crystallites size in TiN-Cu coating from copper amount

The most important characteristic of any coating is its adhesive and cohesive durability in system "coating-substrate" which we investigated using measuring scratching method.

Results of FF, μ , AE, h measurements characteristic for the received coatings are given in Figure 7. Change from the interlocking contact to continuous when the indenter is sliding on a coating surface, if having Lc1 at about 10 H, leads to separation of microparticles from

the scratch edges. This process of separation is accompanied by sharp increase of AE level. It is proved by the optical image of coating damage area (Fig. 8). In process of load rise the coating has an intensive cohesive destruction which is expressed by formation of

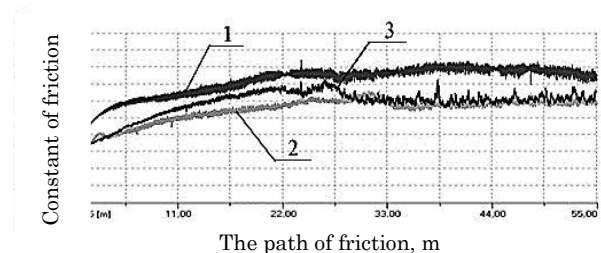


Fig. 6 – Experimental dependences of friction coefficient of friction on rubbing path for samples: 1) firm alloy VK-6; 2) firm alloy VK-6 with TiN coating – 3,5 at. Cu %; 3) firm alloy VK-6 with TiN coating – 7 at. Cu %

diagonal cracks set at the bottom of scratch, and also by coating fragmentation without its detachment from a substrate. In process of coating gradual wearing off, the friction coefficient increases a little, and in case of Lc3 loading > 55 N we can see its sharp growth. It is connected with covering full destruction and achievement by an indenter the material of substrate.

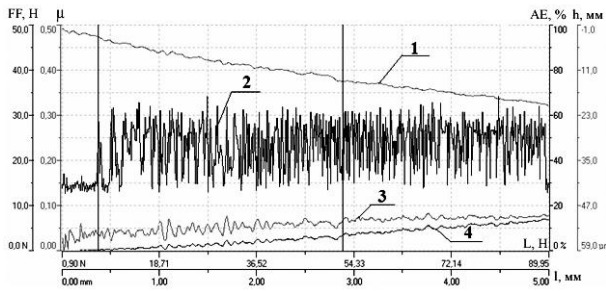


Fig. 7 – Results of measuring scratching of coating Ti-Cu-N with copper amount 9 at.% which has been carried out for studying of adhesive/cohesive durability: curves of h (1), AE (2), μ (3), FF(4) from applied load to the indenter and scratch length

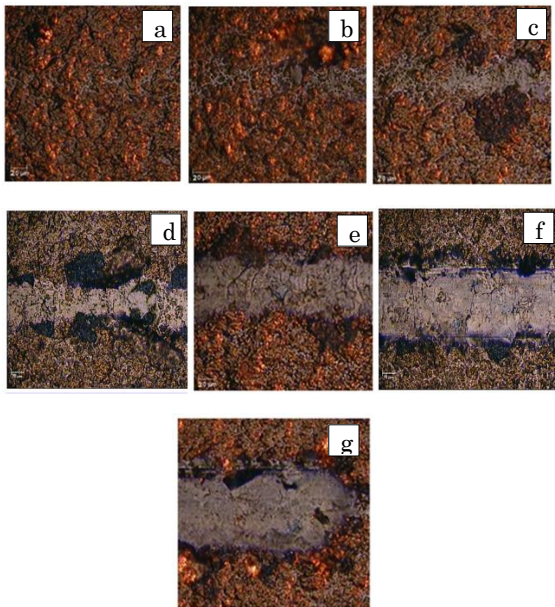


Fig. 8 – Image of scratch on the coating surface Ti-Cu-N c with copper amount 9 at.% with applied to the indenter loads: 0,9 N(a); 7 N (b); 9,3 N (c); 19 N (d); 29,7 N (e); 52,2 N (f); 60 N (g)

REFERENCES

1. V. Shtansky, S.A. Kulinich, E.A. Levashov, J.J. Moore, *Physics of rigid body* **45**, No. 6, 1122 (2003).
2. I.V. Blinkov, A.O. Volkhonskiy, A.G. Yudin, *Physics and chemistry of materials processing* **6**, 18 (2011).
3. A. Volkhonskiy, I.V. Blinkov, *Russ. J. Non-Ferr. Met.* **53**, No3, 259 (2012).
4. S. Veprek, M.G.J. Veprek-Heijman, P. Karvankova, J. Prochazka, *Thin Solid Films* **476**, 1 (2005).
5. Yu.F. Ivanov, N.N. Koval, O.V. Krysina et al, *Surf. Coat. Tech.* **207**, 430 (2012).
6. P. Patsalas, G. Abadias, G.M. Matenoglou et al, *Surf. Coat. Tech.* **205**, 1324 (2010).
7. I.V. Blinkov, V.N. Ankin, A.O. Volkhonsky, N.A. Sobolev, R.V. Kratochkvil, *HEI news. Powder metallurgy and functional coatings* **1**, 44 (2009).
8. G.N. Dulnev, Yu.P. Zarichnyak, *Heat conductivity of mixtures and composite materials* (L.: Energy: 1974).

4. CONCLUSION

Processes of structure and phase formation in Ti-N-Cu system were studied when forming ceramic-metallic coatings with copper amount from 0 to 20 at. % using ion-plasma vacuum-arc deposition method. These processes speak for availability in nitride coating titanium and copper, which before the moment of its concentration in a coating at the amount of 10 at. % is in X-ray amorphous condition.

Copper introduction in the coating structure leads to crystallites of a nitride phase refinement from 100 to 20 nanometers in case its concentration change within the interval stated above.

Coatings hardness thus grows from 20 to 49 hPa in case of copper amount increase in a coating to 3.5 at. %. Further increase of copper amount to 20 at.%, accompanied by crystallites of nitride phase refinement, is characterized by hardness reduction up to 14–15 hPa which is connected with influence on it soft plastic metal and appearing the porosity in a coating.

In the work the assumption was made on the influence on studied coatings wear resistance in comparison with coatings from titanium nitride their increased heat conductivity and improved tribological properties.