Nanostructured ceramic-metal coatings obtained by ion-plasma vacuum arc method

I V Blinkov, D S Belov, A O Volkonskii, A V Chernogor and V S Sergevnin
National University of Science and Technology MISIS, 119049, Leninskiy prospect, 4, Moscow Russia
E-mail: biv@misis.ru

Abstract. Ceramic-metal coatings (Ti,Al)N-Cu and (Ti,Al)N-Ni were obtained by Arc-PVD method. Metal components content in the coatings was regulated by varying the ratio between the surface area of the evaporated cathodes and the arcs current evaporating them. Concentration ranges of the metal components content in coatings which ensure the formation of an isomorphous nanocrystalline structure with a grain size of 15-20 nm, have been established. These coatings are characterized by superhardness of 43-51 GPa with preservation of viscosity (relative work of plastic deformation during nanoindentation ~65-70%). At the same time, the coatings obtained are characterized by a low level of macrostresses.

1. Introduction
Nanostructuring is the one of the work areas to improve the properties of multifunctional coatings. A possible way to limit the growth of grains of the ceramic-metal coating during its formation according to the principle of multiphase [1] is to introduce into the composition of the formed material a metal phase distributed over the surface of the nuclei of the main ceramic phase and limit their growth. To select these modifying additives, the criterion should be the absence of a noticeable interaction with the nitride phase and a tendency to nitride formation. Such metals can be copper and nickel [2–4]. The work is devoted to the study of the structure and phase formation of arc-PVD coatings based on complex Ti-Al-N nitride, copper and nickel.

2. Experimental
The deposition of coatings was carried out on the ion-plasma vacuum-arc sputtering equipment type "Bulat-NNV 6.6-I1". In the work, both two and three cathode evaporation systems were used. Combined cathodes (Ti, Al) - Cu were used as evaporating systems for producing (Ti, Al) N-Cu coatings with varying metal content. At the same time, the ratio of the areas of each component of such a cathode, VT5 alloy and copper, varied from 5: 1 to 1: 1 to obtain a certain concentration of copper in the gas phase and, accordingly, in coatings from 1.6 to 23 at.%. To obtain coatings (Ti, Al) N-Ni, an evaporative system was used from cathodes made of Ti-Ni alloy (50 at.%). The Ni content in the coatings varies from 1.5 to 26 at.%. Varied by changing the current of the evaporating arcs from 80 to 140 A. The reaction gas used was VCh6.0 brand nitrogen. The partial pressure of nitrogen (P_N2) was maintained at 0.5 Pa. The deposition time was 60 minutes. The coating thickness was 4-4.5 μm. Carbide plates VK6 (WC – 6%Co), VK6NTC (WC – 6%Co – 2%TaC) and TT10K8B (WC – 3%TiC – 7%TaC – 8%Co) were used as substrates. The changing parameters of the deposition process were...
the arc current (I) at the cathodes from 80 to 120 A, the bias potential (Us) on the substrate from -80 to -140 V. The X-ray analysis analyzed the phase composition and structure characteristics of the coatings. The binding energies of elements in the coating material were studied using X-ray photoelectron spectroscopy (XPS). The structure of the investigated coatings was studied on a transmission electron microscope (TEM). The physicochemical properties of ceramic metal coatings were determined by the method of measuring nanoindentation. The determination of macrostresses was carried out in 2 ways: by the sin²ψ method and through the determination of the radius of curvature of the sample of the substrate coated by the Stony method [5].

3. Results and discussion

The morphology of the formed coatings with a copper content up to 10 at.% (figure 1(a)) and nickel up to 12 at.% (figure 1(b)) is characterized by a cellular surface structure with a roughness (Ra) of the order 0.1 μm. The grain structure of the coatings is equiaxial; pores, cracks and other discontinuities are absent.

Figure 1. Characteristic frontal and end images of the surface and fracture of Ti-Al-Cu-N coatings with copper content: (a) up to 10 at.%, (c) more than 10 at. % and Ti-Al-Ni-N coatings with nickel content: (b) up to 12 at.%, (g) more than 12 at.%.

In coatings with copper and nickel content above 10 and 12 at. % (figure 1(c), (d)) respectively, porosity appears, which is associated with poor wettability of titanium nitride by these metals. The average crystallite size of the nitride phase with increasing content of Cu and Ni varies from 100 to 20-15 nm, which indicates the blocking effect of the metal phase on the grain growth process of the nitride phase (figure 2). With an increase in the concentration of Cu more than 7 and Ni more than 3.5 at. % of the noticeable refinement of the ceramic phase does not occur (figure 3), which indicates a complete blockage of the growing (Ti, Al) N grains. The dimensions of the coherent scattering regions of the nitride phase in the coatings of the Ti – Al – Cu – N and Ti – Al – Ni – N systems are of the order of 15–20 nm and 12–25 nm, respectively, and depend little on Cu and Ni content in the coatings.
These values are of the same order of magnitude as the corresponding crystallites. The microstrain values ($\varepsilon$) of the Ti-Al-Cu-N and Ti-Al-Ni-N coatings decreased from 1.08 and 1.3% to 0.3 and 0.22%, respectively, with increasing Cu up to 10 at.% and Ni up to 12 at.%. X-ray diffraction patterns indicate the presence in Ti-Al-N-Cu and Ti-Al-N-Ni coatings with a copper content of ~ 10 and nickel and ~ up to 12% (at.) only complex nitride (Ti, Al) N. Analysis of the photoelectron spectra of Cu2p and Ni2p of these coatings showed that the peak maxima of Cu2p3/2 and Ni2p3/2 correspond to 933 and 853 eV, which indicates the presence of copper and nickel in metallic states [6]. Comparison of X-ray analysis and XPS data indicates that the metal phases are X-ray amorphous. With an increase in the content of copper and nickel in the coatings on diffractograms, diffraction lines of metal-containing phases Ti (1-x) Cux and Ni (1-x) Ti x appear.

The study of the stress state of the Ti – Al – Cu – N and Ti – Al – Ni – N coatings as compared to the Ti – Al – N coating (table 1) indicates a decrease in the absolute values of macrostresses by more than 20 times.

![Figure 2](image1.png)

**Figure 2.** High-resolution electron microscopic images of the Ti-Al-Cu-N coating structure with a copper content of ~7 at.% (a) and a Ti-Al-Ni-N coating with a nickel content of 2.8 at.% (b).

![Figure 3](image2.png)

**Figure 3.** Dependence of crystallite size (Ti, Al) N (a) and hardness (b) of (Ti, Al) N-Cu and (Ti, Al) N-Ni coatings on the content of Me-components.

Relaxation of both thermal stresses arising due to the difference in the coefficients of linear thermal expansions of the coating and the substrate, and structurally phase, the appearance of which is determined by the structural and phase heterogeneity in the coatings that appear during their growth, is associated with the preservation of copper and nickel in the metallic state in the composition coatings. Its mechanism can be associated both with the dissipation of stress fields in the plastic phase, and with the cross connection destruction (screeds of the viscous phase) in the stress field in the bridge structure of ceramic metal coatings [7].
Table 1. The composition and properties of the investigated coatings Ti-Al-Cu-N and Ti-Al-Ni-N and reference sample Ti-Al-N.

| Researched Coatings Systems | chemical composition, at. % | H, GPa | E, GPa | $\sigma(1)$, GPa$^a$ | $\sigma(2)$, GPa$^b$ |
|----------------------------|-----------------------------|--------|--------|---------------------|---------------------|
| Ti-Al-Cu-N                 | 51,2 2,1 3,1 -              | 43,6   | 43±3   | 649±31              | +0,19 +0,32         |
| Ti-Al-Ni-N                 | 48,2 1,9 - 8,0              | 41,9   | 51,5±5 | 680±25              | +0,17 +0,25         |
| Ti-Al-N                    | 52,8 2,0 - -                | 45,2   | 29,1±1 | 561±16              | -4,3 -4,7           |

$^a$\(\sigma(1)\), GPa – macrostresses measured by X-ray diffraction.

$^b$\(\sigma(2)\), GPa – macrostresses measured from the curvature of the coated substrate.

It has been established that with an increase in the concentration of Me-components in coatings, their hardness varies according to the dependences shown in figure 3(b). The nature of its initial growth is correlated with the type of dependences of the change in the crystallite size of the ceramic phase. The maximum hardness values are in the range of Cu concentration from 1.5 to 7 at.% and Ni from 1 to 12 at.%. Its noticeable decrease at high concentrations of copper and nickel is due to the effect on the hardness values of the increasing content of the plastic metal phase and the appearance of the porosity of the coatings. At the same time with superhardness in the corresponding range of concentrations of metal components, these coatings are characterized by a high level of viscosity. This is evidenced by the values of the relative work of their plastic deformation (65-70%), measured by nanoindentation of samples, which was used as an indicator of the crack resistance of the coating material [8].

4. Conclusions
1. It was established that the introduction of copper and nickel into the composition of ion-plasma vacuum-arc coatings (Ti, Al) N up to 10–11 at.% and 12–13 at. %, respectively, when this occurs, the crystallites of the nitride phase are crushed from 100-120 to 15-18 nm with a transition from a columnar structure to an equiaxial grain. At these concentrations, the metal phase in the ceramic metal coatings is in the X-ray amorphous state. The excess of the content of Ni and Cu above the specified values is accompanied by the formation of porosity in the structure of the deposited layers, with the simultaneous appearance of intermetallic compounds TiNi and TiCu in the coating composition.

2. The hardness of the (Ti, Al) N-Cu (Ti, Al) N-Ni coatings increases from 20–22 to 49 GPa with increasing copper to 3.5 at. % and up to 54 GPa with an increase in the nickel content to 12 at. % Coatings are characterized by high viscosity. An increase in the copper content to 20 at.% And nickel to 26 at.% Leads to a decrease in the hardness of the coatings to 14-15 and 23-25 GPa, respectively. The relative work of their plastic deformation of 65-70%, measured by nanoindentation, indicates a high level of viscosity of ceramic-metal coatings.

Acknowledgments
The study was carried out by a grant from the Russian Science Foundation (Project No. 19-19-00555).

References
[1] Blinkov I V, Volkhonskii A O and Yudin A G 2012 Inorganic Materials: Applied Research 231–8
[2] Musil J, Zeeman P, Hruby H and Mayrhofer P H 1999 Surface and Coatings Technology 120–121 179–83
[3] Ivanov Yu F, Koval N N and Krysina O V 2012 Surface and Coatings Technology 207 430–4
[4] Akbari A, Riviere J P, Templier C and Bourhis E L 2006 *Surface and Coatings Technology* **200** 6298–302

[5] Blinkov I V, Volkonskii A O, Belov D S, Sergevnin V S, Chernogor A V, Kiseleva T V and Bondarev A V 2018 *Pis’ma v ZHTF* **44** 4 80–5

[6] Crist B V 1999 *California: LLC XPS International* 5 11

[7] Wang Y X and Zhang S 2014 *Surface and Coatings Technology* **258** 1–16

[8] Zhou Y, Asaki R, Soe W-H, Yamamoto R, Chen R and Iwabuchi A 1999 *Wear* **236** 159