The effect of nickel on the high-temperature properties of multilayer ceramic coatings

A V Chernogor, I V Blinkov, A O Volkhonskiy and V S Sergevnin
NUST «MISiS», 119049, Moscow, Russia
E-mail: avchernogor@gmail.com

Abstract. The structure and composition of multicomponent TiCrMoN-Ni arc-PVD coatings with high nickel concentration (more than 8 at.%) are studied at bias potentials of 80 - 140 V. All coatings are characterized by a layered structure, the modulation period tends to decrease as increasing the bias potential. After annealing at 850 °C in vacuum, the coatings retain their layered structure without signs of dissolution of layers in each other. Nickel sublayers retain their polycrystalline structure, at the same time, the monolayer CrN are formed due to recrystallization.

1. Introduction
Nowadays, physical vapor deposition (PVD) is widely applied vacuum technology. High mechanical and unique physical properties of PVD coatings, which are provided not only by the nanocrystalline structure, but also by the nonequilibrium phase composition, have provided widespread use of such coatings in many industries since the 70s of the last century [1, 2]. First coatings obtained by this method were used to protect tools from wear, resulting in increase in the wear resistance of the tool by a factor of two or more. Currently, wear-resistant coatings also play a leading role in the development of PVD methods, although they have been supplanted by other modern trends. [3, 4]. However, over time, the requirements for protective coatings have increased dramatically. So, early works in this area focused on high hardness and adhesive strength as the only criteria in the development of coatings. Currently, it is necessary to take into account high temperatures up to 900 °C due to increased cutting speeds and the nature of the applied load [5]. This leads to the fact that the coatings must have high heat resistance, thermal stability of the structure, and high viscosity, while maintaining the hardness at the level of 25 - 40 GPa.

In previous studies we have shown that as coatings that satisfy such requirements, the coating system can be TiCrN-Mo2N-Ni [6, 7]. However, issues related to heat resistance and thermal stability were raised only indirectly and only for a system with a low nickel concentration (2.5 at.%) based on high temperature tribology [7]. In this work, the aim is to study the properties of coatings with a high concentration of nickel (≈10 at. %), as well as to study structural changes after annealing at temperatures up to 850 °C.

2. Methods
The coatings were prepared by the arc-PVD method on a setup equipped with two evaporators with magnetic droplet separators and one direct evaporator. A more detailed description of the installation scheme is presented in the works [7–9]. Coatings were prepared at bias potentials of 80, 100, 120, 140
and 160 V in argon atmosphere with pressure 0.8 Pa, substrate temperature equal to 450 °C on WC-6% Co substrates for 90 minutes. High purity chromium (99.99%), TiNi alloy and high purity molybdenum (99.9%) were used as cathode materials. The last two were evaporated through magnetic separators in order, firstly, to filter plasma flow from titanium droplets, and secondly, to ensure a low concentration of molybdenum nitride, which is characterized by destructive oxidation for coating at temperatures above 350-450 °C [10].

3. Results and discussion
The results of X-ray spectral analysis of the composition of the coatings are presented in table 1. The data show that all coatings are characterized by a high chromium content. The ratio between the concentrations of the elements Ti and Ni is approximately 1: 1, which corresponds to the composition of the TiNi cathode alloy. At the same time, at a significance level of 0.05, the dependence of Ti / Ni on the reciprocal of the modulus of the bias potential showed a significant linear correlation (F (11.7)> Fcr (5.05)). However, taking into account that the Ti / Ni ratio should reach a constant value as the concentration decreases, a logarithmic regression was performed to the approximation that at a bias potential of 0 V, the Ti / Ni ratio will be 1, that is, equal to the composition of the TiNi cathode material. According to the results obtained, in this case, the logarithmic regression is statistically significant (F (17.3)> Fcr (5.05)). Such a redistribution of concentrations is mainly due to the relatively low bond strength of nickel with a coating, which is in the metallic state, compared with the bond strength of transition metals in MeN [11].

| Bias, V | Ti (at.%) | Cr (at.%) | Mo (at.%) | Ni (at.%) | N (at.%) | Phase composition |
|---------|-----------|-----------|-----------|-----------|---------|------------------|
| -80     | 12.0±0.3  | 31.3±0.6  | 2.2±0.1   | 10.5±0.3  | 44      | TiCrN-Mo2N       |
| -100    | 13.8±0.3  | 32.2±0.6  | 1.2±0.1   | 11.8±0.3  | 41      |                  |
| -120    | 13.3±0.3  | 28.4±0.6  | 2.5±0.1   | 10.8±0.3  | 45      |                  |
| -140    | 14.7±0.3  | 27.8±0.6  | 2.0±0.1   | 11.5±0.3  | 44      |                  |
| -160    | 13.6±0.3  | 32.0±0.6  | 2.1±0.1   | 8.3±0.3   | 44      |                  |

*The error in measuring the concentration of light elements by X-Ray spectroscopy methods can be more than 5 atomic percent.*

The study of the structure of the coatings in the cross section was carried out by the TEM method on thin lamellas prepared from coatings on a hard alloy. Figure 1 shows images of the structure of coatings prepared at 80 and 120 V. All coatings are characterized by the presence of a layered structure formed because of planetary rotation of the substrates [8]. In this case, as the bias potential increases, the modulation period decreases from 62 nm to 44 according to a linear dependence with a coefficient of 0.93, which is associated with an increase in the sputtering coefficient of the growing coating by high-energy atoms.

According to XRD data, TiN-CrN-Mo2N nitrides with an FCC structure are formed in the coatings, while nickel could not be determined on any of the series of coatings, which indicates its X-ray amorphous nature [12]. Figure 2 shows the data of X-ray diffraction analysis, from which it can be seen that as the bias potential increases, the microstrains increase from 0.12 to 1.1% and the crystal lattice constant increases. Probably, this is due to an increase in the concentration of Schottky defects, Frenkel pairs, and dislocation clusters.

All samples were annealed at 850 °C. The data of X-ray structural analysis after annealing are shown in figure 2. After annealing for samples prepared at 140 and 120 V, the values of microstrains and lattice period remain approximately at the same level. However, for coatings prepared at 80 V, the values of microstrains, as well as the lattice period, increase. It is logical to assume that, after annealing, microdeformation should decrease because of recrystallization processes or remain at the same level if the temperature is insufficient to activate these processes.
According to the data of X-ray spectral microanalysis carried out on samples in the study of the TEM structure in the cross section, the depth of diffusion of W and Co atoms from the substrate into the depth of the coating increases from ~ 100 nm after preparation to 1 μm after annealing. Since cobalt and tungsten are characterized by a large atomic radius, their dissolution in the coating will lead to an increase in the crystal lattice period and microdeformations, which agrees with experimental data.

Figure 3 shows images of coatings after annealing at 850 °C. The layered structure of the coatings is retained, while the modulation period for all coatings after annealing approximately corresponds to the modulation period before annealing. This indicates the absence of processes of dissolution of layers in each other. Nevertheless, structural transformations occur within one layer, which consist in the formation of single-crystal sublayers. According to calculations of the plasma flow, these layers correspond to layers enriched in chromium, that is, formed by direct passage of the substrates opposite the evaporator with a chromium cathode [8]. These data clearly demonstrate the role of nickel in the thermal stability of coatings. It is known from previous studies that nickel is present only in sublayers formed by passing the substrates opposite the Mo evaporator and, to a greater extent, TiNi. Nickel tends to form an X-ray amorphous shell around nitride grains, which serves as a diffusion barrier during the recrystallization of coatings during the entire annealing [12].

4. Conclusions
As a result of this work, five series of TiCrMoNiN coatings were prepared at different bias potentials. It was found that at concentrations up to 13 at. %, the structure of the coatings corresponds to the...
matrix of X-ray amorphous nickel and the inclusion of titanium, chromium, and molybdenum nitrides with an FCC structure in the sublayers formed when the substrates pass opposite the Mo and TiNi evaporators. The chromium-enriched sublayer also has a pronounced polycrystalline structure; however, after annealing, it recrystallizes into single-crystal layers.

![Figure 3. TEM image of coatings cross section prepared at (a) 80 V and (b) 120 V after annealing at 850 °C.](image)

Since the effect of nickel on thermal stability is so pronounced, further studies of the thermal stability of coatings will be carried out with a uniform distribution of nickel over all sublayers of the coating.

Acknowledgments
The financial support by the Russian Science Foundation Program (Research Project No. 19-19-00555) is gratefully acknowledged

References
[1] PalDey S and Deevi S C 2003 Mater. Sci. Eng. A
[2] Randhawa H 1988 Thin Solid Films 167 175–86
[3] Selvakumar N and Barshilia H C 2012 Sol. Energy Mater. Sol. Cells
[4] Kelly P J and Arnell R D 2000 Vacuum
[5] Musil J 2012 Surf. Coatings Technol.
[6] Chernogor A V, Blinkov I V, Belov D S, Volkhonskiy A O and Sergevnin V S 2019 IOP Conf. Ser. Mater. Sci. Eng. 657 012045
[7] Chernogor A V., Klimashin F F, Volkhonskii A O, Blinkov I V. and Mayrhofer P H 2019 Surf. Coatings Technol. 377 124917
[8] Chernogor A V., Blinkov I V., Belov D S, Sergevnin V S and Volkhonskii A O 2019 Tech. Phys. Lett. 45 75–8
[9] Chernogor A V, Blinkov I V, Sergevnin V S and Demirov A P 2019 J. Phys. Conf. Ser. 1313 012011
[10] Solak N, Ustel F, Urgen M, Aydin S and Cakir A F 2003 Surf. Coatings Technol.
[11] Hanson D E, Stephens B C, Saravanan C and Kress J D 2001 J. Vac. Sci. Technol. A Vacuum, Surfaces, Films. 19 820–5
[12] Belov D S, Blinkov I V. and Volkhonskii A O 2014 Surf. Coatings Technol.