Influence of bias voltage on structure and mechanical properties of TiCrN-Mo$_2$N-Ni coatings

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Abstract. In this work, the influence of bias voltage on the structure, composition and physical properties of TiCrN-Mo$_2$N-Ni arc Physical Vapor Deposition (arc-PVD) coatings were studied. Multilayer structure formed at all applied bias voltage due to planetary rotation of substrates. Thickness of sublayers range from 1 to 32 nm and defined by the plasma flow intensity from evaporators. Monte-Carlo calculation was used to study structure of prepared coatings. According to calculation and analysis of TEM images, sublayers composed by nitrides mixture. All coating characterized by high hardness, which correlated with residual stress of coatings.

1. Introduction
Nowadays, surface engineering methods are widely used in many industries [1-8]. In particular, they are used to increase the service life of the cutting tool by applying wear-resistant coatings. These coatings should be characterized by high hardness, increased adhesion strength with the substrate, resistance to oxidation, low friction coefficient. To create such coatings, methods of magnetron deposition [7] and arc-PVD deposition [8] are widely used. In contrast to magnetron, arc Physical Vapor Deposition (arc-PVD) is characterized by a higher deposition rate and increased adhesive strength of the coating with the substrate.

Refractory and transition metals frequently used as material for coatings, due to their high hardness (titanium nitrides with hardness more than 25 GPa [9]), low the coefficient of friction (coatings base on molybdenum described as self-lubricant [10]), and oxidation resistance (chromium nitrides can be applied up to 700°C [11]). At present time, studies of multicomponent coatings based on these elements are being actively conducted [12-15]. It was shown that the coatings of the Ti-Cr-N and Cr-Mo-N systems are characterized by high wear resistance, and due to Cr, the oxidation resistance of such coatings reaches 700°C [12]. Additionally, Cr prevents the process of evaporation of the molybdenum oxides up to 900°C [13]. Nickel addition into coatings based on nitrides of these metals leads to the refinement of nitride grains and an increase in the wear resistance [6,16]. To achieve the high mechanical and tribological properties, multicomponent coatings are used. In this paper, system TiCrMoN-Ni were proposed, in which a high concentration of chromium is designed to provide high oxidation resistance, molybdenum to reduce the coefficient of friction, and nickel to increase hardness, due to the grinding of nitride grains.

2. Methods
The arc-PVD method was used to prepare three series of coatings with a bias potential of 80, 120 and 140 V. All depositions were carried out for 90 min and electric currents on cathodes are listed in table...
1. The values of electric current applied to the cathodes were chosen so that the plasma flow density corresponded to the maximum values, at which the processes of the droplet formation are insignificant. TiNi evaporated through the droplet magnetic separator, since titanium is tend to intensive formation of large droplets, up to several micrometers in diameter. The inclusion of such droplets in the structure of the coating, whose thickness is about 2.5 microns, leads to a dramatically decrease of tribological properties of the coatings. Also, a high content of molybdenum in the coating can reduce the oxidation resistant due to the avalanche-like oxidation of molybdenum-based compounds, known as molybdenum pest [17]. Therefore, it was decided to evaporate molybdenum through a magnetic separator, which reduces the density of the plasma flow [18]. Thus, it was possible to reduce the concentration of molybdenum to 5 atomic percent.

| Table 1. Deposition parameters. |
|----------------------------------|
| Bias (V) | Cathode current, A |
|---------|--------------------|
| TiNi    | Cr     | Mo     |
| -80     | 140    | 120    | 130    |
| -120    |        |        |
| -140    |        |        |

The morphology and elemental composition were studied using a field emission scanning electron microscope (SEM) JSM-6700 equipped with an energy dispersive spectrometer (EDS, JEOL, Japan) at acceleration voltage of 20 kV. Structural transformations and the phase composition were studied by means of transmission electron microscopy (TEM). Structure of the coatings was studied by Monte-Carlo calculation, as reported in [19,20]. Thin lamellas of the coatings were prepared by ion beam etching. Mechanical properties were studied using a Micro-Hardness Tester (CSM, Switzerland) equipped with a diamond Berkovich indenter in the continuous multi-cycle (CMC) indentation mode. The unloading was limited to 5% of the corresponding maximum load (50 µN). The duration of a single loading–unloading cycle was 60 s. From the analysis of the resulted load–displacement curves, hardness and elastic modulus (as well as the degree of elastic and plastic strain were determined. Phase analysis was performed on a D8 Discover apparatus by means of glancing angle X-ray diffraction utilizing copper radiation. The macrostresses were measured by means of sin2ψ using an angle of incidence of 2°. The wear resistance and friction coefficient were measured with Pin-On-Disk tribometer (Nano, USA). The wear tests were performed under 25 and 550°C, Al2O3 ⌀6 mm, sliding speed of 20 m/s and an applied load of 5 N. The wear track after tests was studied using optical profilometer and X-ray Photoelectron Spectroscopy (XPS).

3. Results

3.1. Elemental composition and surface morphology

The EDS results are presented in table 2. It can be seen that the main element of the coating is chromium, whose high concentration is provided primarily by sputtering the chromium cathode through a direct-flow evaporator. While the deposition of titanium and molybdenum leads to a decrease in plasma flow by more than two times. Is should be noted, that the concentration of nickel in the coating is directly proportional to the bias voltage applied to the substrates. This is because the presence of elements with a high nitrogen affinity, such as chromium, molybdenum and titanium, completely suppresses the formation of nickel nitrides. As a result, nickel presents in the coating is either in the form of a solution in nitrides (with a solubility limit of less than 0.5%) or in the metallic state [21]. The cohesive energy of metallic nickel is significantly lower than the cohesive energy of transition metal nitrides; therefore, in the deposition process, nickel is re evaporated by plasma ions with an energy of more than 150 eV [22].
Table 2. Chemical composition of coatings.

| Bias (V) | Ti (at. %) | Cr (at. %) | Mo (at. %) | Ni (at. %) | N (at. %) |
|----------|------------|------------|------------|------------|----------|
| -80      | 9.6        | 35.2       | 5.7        | 5.4        | 44       |
| -120     | 8          | 42         | 7          | 1.4        | 41.6     |
| -140     | 7.5        | 42         | 7.5        | 2.5        | 40       |

According to SEM (figure 1), it can be seen a droplet fraction on the coatings surface. Evaporating titanium through a droplet phase separator reduces the fraction of the micro-droplet fraction in the coating structure, as well as their average size. However, as a result of elastic collisions of drops with the walls of the chamber \[23\], some of them still reach the surface of the coating. In general, the surface is characterized by continuity and cellular structure, which is a replica of the surface of the substrate.

Figure 1. SEM images of coating morphology, prepared at – 80 V (a), - 120 V (b) and -140 V (c).

3.2. Phase composition and coating structure

Table 3. Binding energies of elements.

| Bias, (V) | Cr/Ti ratio | Binding Energy, (eV) | Cr-2p\(\frac{3}{2}\) | Ti-2p\(\frac{3}{2}\) | Mo-3d | Ni-2p\(\frac{3}{2}\) |
|----------|-------------|----------------------|----------------------|----------------------|-------|----------------------|
| -80      | 22.4        | 575.5                | 454.8                | 228.2                | 852.3 |
|          | 2.9         | 574.3                | 455.3                | 228.1                | 852.3 |
| -120     | 21.5        | 575.4                | 454.9                | 228.2                | 852.1 |
|          | 2.5         | 574.2                | 455.3                | 228.1                | 852.2 |
| -140     | 18.8        | 575.6                | 454.8                | 228.1                | Below the limit of detection |
|          | 4.1         | 574.4                | 455.2                | 228.1                |          |

The study of the phase composition of multicomponent coatings entails a number of difficulties. In the case of the TiCrMo-N systems, the only presented phase is the \textit{fcc} solid solution of nitrides of the corresponding metals. And taking into account the similarity of the lattice parameters, as well as the unlimited solubility of the components in each other, it is not possible to take an accurate conclusion about the phase composition based on the diffraction patterns. In addition, the high value of microstrain, leads to the broadening of diffraction lines, which also complicates the analysis. Therefore, to study the phase composition, an X-ray photoelectron spectroscopy (XPS) analysis was also carried out, the results of which are presented in table 3. In all coatings, a change in the binding energy of titanium and chromium depending on the concentration of these elements is detected. At the same time, taking into account X-ray diffraction analysis (XRD), the formation of nitrides or metals with a structure other than fcc is excluded. Consequently, this behavior is caused primarily by the redistribution of ionic-metal-covalent bonds, which is observed in the case of the formation of solid solutions Ti\(_1-x\)Cr\(_x\)N with different concentrations \(x\) \[24\]. Taking into account that the planetary rotation of the substrates in the plasma flow propagating in space according to a law close to sinusoidal \[19\], it is possible to form a number of solid solutions with different concentrations. Interestingly that the binding energy of molybdenum...
remains constant for all coatings and corresponds to $\gamma$-Mo$_2$N and does not depend on the elemental composition of the studied areas of the coatings. Despite the fact that molybdenum is also characterized by unlimited solubility in TiN and CrN, its dissolution does not occur. Nickel in the coatings is present in a metallic state.

The planetary rotation of the substrates leads to the formation of a layered structure, the model of which is shown in figure 2. According to the TEM, the planetary rotation of the substrates leads to the formation of layers with a thickness equals to 45, 51 and 62 nm for coatings prepared at -140, -120 and -80 V respectively. Each such layer consists of sublayers formed as a result of the rotation of the substrate around its own axis. The thickness of the sublayer ranges from ~1 to 32 nm. At the same time, as the bias potential increases, the average sublayer thickness decreases. Examination of these sublayers by TEM and XPS methods with layer-by-layer etching does not give an idea of their composition due to the insufficient accuracy of these methods [20]. To investigate the distribution of elements in the coating, numerical calculations were performed, the results of which are presented in figures 2(a)-2(c).

As can be seen from the calculated composition of coating layer, one sublayer consists of a mixture of nitrides CrN/TiN/$\gamma$-Mo$_2$N, while, as mentioned above, CrN/TiN form a complex solid solution TiCrN. Also, all coatings are characterized by the presence of a single-phase CrN sublayer with a thickness of up to 25 nm, the formation of which is caused by the evaporation of the chromium cathode through a direct-flow evaporator. As the concentration of nickel in the coating increases, the nitride grains are refined, which is associated with Ni segregation on the surface of the growing grains.

It should be noted that with an increase in the bias voltage, the level of compressive residual stress decreases. As a rule, the dependence of the bias voltage and the level of compressive residual stress is directly proportional [25]. But in this case, nickel leads to refinement of nitride grains [26], which
reducing the probability of relaxation processes of residual stress by plastic deformation. This is also confirmed by the results of microindentation presented in table 4. It can be seen that coatings with a high level of compressive stresses correspond to greater resistance to plastic deformation and its share in the total work of deformation, despite the plasticity of nickel.

Table 4. Mechanical properties of coatings.

| Bias (V) | Stress (GPa) | Hardness (GPa) | Elastic Module (GPa) | Plastic Deformation (%) | Temperature, (°C) | Wear, (m²/N) | CoF |
|----------|--------------|----------------|----------------------|-------------------------|-------------------|--------------|-----|
| -80      | -4.4         | 42             | 440                  | 43                      | 25, 550           | 25, 550      |     |
| -120     | -0.6         | 32             | 450                  | 57                      | 25, 550           | 25, 550      |     |
| -140     | -1.2         | 32             | 400                  | 63                      | 25, 550           | 25, 550      |     |

3.3. Mechanical and tribological properties
All coatings are characterized by high hardness, at the same time, the influence of residual stresses on the coating’s hardness is pronounced, as can be seen from table 4.

![Figure 3. Wear track of coating prepared at -80 V (a), -120 V (b) and -140 V (c) and SEM images of wear track of coating, prepared at -140 V (d).](image)

It can be seen that despite the increase of nickel concentration, which should contribute to an increase in plasticity and a decrease in hardness, residual stress plays a dominant role in mechanical properties. The coating prepared at -140 V is characterized by greater hardness and wear resistance at room temperature. However, as the temperature of tribological tests increases up to 550°C, the wear resistance of highly stressed coatings begins to be significantly inferior to coatings with low values of residual stress. Taking into account the fact that after annealing there is a complete relaxation of macrostresses (according to XRD analysis the level of residual macrostresses reduce to -0.1 GPa), a possible reason for the reduced wear resistance of such coatings is more active diffusion processes, leading to degradation of the multilayer coating structure and growth nitride grains. However, the wear of all coatings after friction consists only in the abrasion of the protruding irregularities of the coating without opening the substrate, as evidenced by the optical profilometer of the friction track and the SEM image presented in figure 3. According to XPS data, molybdenum oxides (Mo3d 231.6 eV) are present in the
wear track at 550°C, as opposed to tribological tests at 25°C. The formation of Mo containing oxide film leads to a decrease in the friction coefficient to values about 0.45 at high temperatures.

4. Conclusions
TiCrMoN-Ni coatings were prepared at a bias potential of 80, 120 and 140 V by the arc-PVD method. All coatings are characterized by a multilayer structure with sublayer thicknesses from 1 to 32 nm, consisting of a mixture of complex solutions Ti₆₋₉Cr₂N and γ-Mo₂N. As the bias increases, the thickness of the coatings decreases from 2.7 to 2.4 μm as a result of an increase in the re-evaporation of adatoms of the growing coating. An increase in nickel in coatings prepared at a bias potential of 80 V leads to the grinding of nitride grains and an increase in residual stress. This contributes to the growth of mechanical properties, including hardness up to 42 GPa, but in the process of heating there is a complete relaxation of compressive stress, and highly stressed coatings are characterized by lower wear resistance.

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