Wear Resistant Coating on Tungsten Carbide Hard Alloy

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Abstract. The article reveals new knowledge about the role of zirconium in the composition of (Ti, Zr)N ion-plasma coating applied on WC10KS alloy. It is determined that when zirconium is introduced into ion-plasma coating TiN (50%) wear resistance and adhesion strength grow, nanohardness increases by 23 % (up to 38500MPa), Yung’s modulus rises by 67 %, friction coefficient reduces to $\mu = 0.07$ and performance characteristics of a carbide alloy improve.

Introduction
Development of many industries such as metalworking, machine building, mining, wood processing involves application of sintered tungsten carbide hard alloys which are widely used as tool materials. A promising trend of improving hard alloys is developing reinforcing technologies which provide better performance characteristics. Among these technologies there is quenching of carbide alloys in water solutions of polymers [1], modification of alloy surface with refractory carbides and borides and some others [2 – 4].

Increasing wear resistance without sacrificing viscosity provides durability of any tools which undergo intensive loads during machining, pressing or rock drilling. In this context great attention is being paid to working out reinforcing technologies for tungsten carbide alloys in Russia and abroad. Using new methods of surface hardening with the help of concentrated energy flows is a priority trend in increasing durability of carbide alloys [5 – 7]. Russian industry produces WC-Co carbide plates with TiC and TiN ion-plasma coatings. These coatings are widely spread due to their satisfactory performance characteristics and adopted production technology. Nevertheless TiC and TiN have some drawbacks, low heat resistance being the main one. In this connection it can be useful to test introducing zirconium into the composition of TiN ion-plasma coating and to study its properties on WC10KS carbide alloy.

Results and discussion
For this research we used carbide alloy plates of WC10KS alloy produced by open stock company “Kirovograd Hard Alloys Plant” (Russia). The plates were covered with (Ti, Zr)N ion-plasma coating from separate cathodes of titanium and zirconium (50 % Ti + 50 % Zr). Nitrogen was used as a reaction gas. Two cathode made of titanium alloy were placed in front of each other in a chamber, and a cathode of zirconium alloy was placed between them.

The structure of the carbide alloy with ion-plasma coating was studied with the help of scanning electronic microscope «Philips XL-30».

Metallographic research of cross-sections (Fig. 1) showed that 15mmk thick (Ti, Zr)N ion-plasma coating applied on carbide plates WC10KS do not cause micro-cracks in the coating or on its border.
with the main metal. Two phases of TiN and ZrN prove microlaminated structure of the coating (Fig. 2) which improves performance characteristics. In spite of the microlaminated structure of the coating its elements are uniformly distributed without microspores between layers. (Fig. 3).

![Figure 1. Microstructure of WC10KS alloy with ion-plasma coating (Ti, Zr)N](image1)

![Figure 2. Fragment of diffraction pattern of WC10KS alloy with ion-plasma coating (Ti, Zr)N](image2)

To determine surface hardness of alloys with ion-plasma coating a method of nanoidentation (kinetic hardness) by means of «Nano Hardness Tester» was used, the results were processed with the help of Mountains Map Universal, 2.0.13 software.

The results of nanoidentation of a carbide alloy with (Ti, Zr)N ion-plasma coating proved that this coating is superhard with nanohardness 38500MPa (Fig. 4).
Introduction of zirconium alloying element into the composition of TiN coating improves its mechanical properties: nanohardness increases by 22 -23%, Young's modulus grows by 66 -67% (See the Table). The growth of Young's modulus means increasing energy of atomic links and thus increasing the strength of the coating.

| Properties               | Coatings      |
|--------------------------|---------------|
| Nanohardness, MPa        | TiN           | (Ti, Zr)N     |
|                          | 31450         | 38499         |
| Young's modulus, GPa     | 307.00        | 511.67        |

Tribological testings of coated samples in original sintered state at room temperature were carried out with the help of high-temperature tribometer programmed «PC-Operated High Temperature Tribometer». A degree of wearing was determined by means of measuring the depth and the area of the track made by an unmoving diamond indenter on a rotating sample under the load of 3H, linear speed 2.5 cm/s, with rotating speed 4000 for uncoated samples and 12000 for coated samples. The
analysis was carried out with the help of Mountains Map Universal, 2.0.13 software.

Tribological testings of samples with ion-plasma coating showed that wear track depth on WC10KS alloys is 76.6nm and that on the original sample is 58mkm (Fig. 5).

Track cross-section area on worn out coated samples makes up 4.2 mkm$^2$ and on uncoated samples it is 12921mkm$^2$ (Fig. 6). Friction coefficient ($\mu$) of WC10KS alloy with (Ti, Zr)N ion-plasma coating after treatment is fixed at 0.07 which differs from friction coefficient of the original sample equaling 0.41.

![Figure 5. View of tracks after tribological tests](image1)

![Figure 6. Profiles and areas (in grey color) of wear tracks cross-sections of (a) coated samples, (b) uncoated samples](image2)
High wear resistance of \((\text{Ti, Zr})\text{N}\) ion-plasma coating can be explained from a perspective of atomic concept by V.F. Moiseev which claims that nitrides of metals from the fourth group of Mendeleev’s table provide less intensive wearing because chemical compounds with the highest atomic binding energy (maximal hardness and heat of atomization) are to provide the highest wear resistance.

Ion-plasma spraying is the finishing operation and it does not require any other perfections. After spraying a part can be used for intended purpose. Thus surface roughness is a very important characteristics of the part quality.

It is known that a tool with great roughness has short service life, that is why when a part is being designed an admissible value of surface microgeometry is set to provide the part durability. According to State Standard \(\text{TU 48-19-367-92}\), the admissible value of surface finish is \(R_a = 2.5\text{mkm}\). The surface microgeometry of a carbide alloy before and after applying \((\text{Ti, Zr})\text{N}\) ion-plasma coating was studied with the help of «Micro Measure 3D station». Profilometric research showed that the ion-plasma coating improves the samples surface. The surface roughness of an original sample is \(R_a = 1.32\text{mkm}\). After applying the\((\text{Ti, Zr})\text{N}\) ion-plasma coating on WC10KS alloy the roughness makes up 0.97mkm (Fig. 7).

![Figure 7. Microgeometry of WC10KS alloy with (Ti, Zr)N (a) coating; (b) original sample](image)

The coating fully performs its functions when it is strongly adhesive to the main material. Adhesion considered as binding between of surface layers of dissimilar bodies and phases when they contact is
one of the main characteristics the obtained thin hard coatings. It characterizes the contact strength of the coating with the base material. It is suggested that it depends greatly on energy of a particle falling on the base plate: the higher is the energy, the greater is the adhesion. During ion-plasma spraying due to the impulse received from an ion knocked-on atoms cross a striking distance and settle down on the base plate. The energy of the atoms which approach the base plate is considerably higher than that during thermal vacuum spraying. It let us suggest that the adhesion of ion-plasma coatings with carbide alloy base plate will be satisfactory.

For this research adhesion tests of ion-plasma coating on WC10KS alloy were carried out with the help of Micro Scratch Tester using a method of scratching with diamond indenter which undergoes linear increasing loads.

To analyse thin hard coatings it is not enough just to increase the speed of load growth. That is why one of the possible solutions is using swing module which allows to prolong multifold the device track and to use high coefficient of normal strength growth. One of the advantages of oscillating sample action is a greater length of the scratch in comparison with a usual scratch. In the case of progressing loads it leads to smoother load growth between the minimal and maximal values.

Load strength at the moment when coating starts peeling off is an important characteristics of adhesive strength. It is called critical load strength and is determined with great accuracy with the help of acoustic sensor, tangential load sensor, penetration depth and normal strength sensors, and build-in optical microscope (Fig. 8).

Within our research the adhesion tests of ion-plasma coating on WC10KS alloy were carried out at the following modes: diamond indenter speed – 7.97 mm/min at constantly growing load beginning with initial value of 0.1H to the final ones of 150.0H; signal level from acoustic emission sensor – 9; scratch length – 8mm.

The test showed that at normal loading of 22.3H (Fig. 8, a) a scratch is formed on the coating. As the load grows up to 46.8 H the scratch becomes wider (Fig. 8, b, c). When the load reaches 55.6 H (Fig. 8, d) a simultaneous leap of acoustic emission and fraction signals takes place. This value is critical because it concurs with the moment when the layer begins separating.

In a whole we can conclude that viscosity of (Ti, Zr) N ion-plasma coating with hard base metal is high. In fact high viscosity of (Ti, Zr) N ion-plasma coating with hard base metal is explained by microlamination which is characteristic for coatings produced by separate electrodes. A boundary between microlayers of the coating prevents crack growth and thus increases crack resistance.
Conclusion
Superhard 10 ÷ 15 mkm thick (Ti, Zr)N ion-plasma coating with nanohardness 38500MPa characterized by high wear resistance and adhesion strength was obtained on the surface of carbide alloy WC10KS. It was determined that extra alloying of ion-plasma coating TiN with zirconium leads to increasing nanohardness by 22 ÷ 23 %, Yung’s modulus by 66 ÷ 67 %. Growth of Tung modulus means increasing atom links and thus rising the strength of the coating.

This research is done within a state order by Ministry of Education and Science of Russia № 11.153.2014/K

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