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Comparing the Tribological Properties of the Coatings (Ti-Hf-Zr-V-Nb-Ta)N and (Ti-Hf-Zr-V-Nb-Ta)N + DLC

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The paper compares the tribological characteristics of the coatings (Ti-Hf-Zr-V-Nb-Ta)N and (Ti-Hf-Zr-V-Nb-Ta)N + DLC obtained by means of vacuum-arc deposition method. Coefficients of friction for nitride coatings (Ti-Hf-Zr-V-N-Ta)N have an average value of 1.06; for nitride coatings with DLC the value was 0.5 in the beginning, and then decreased to 0.14. To achieve high performance for functional coatings consisting of two layers - the bottom - and top-nitride DLC it is necessary to ensure the formation of a layer of solid lubricant in the areas of actual contact while retaining the structure of the coating.

Keywords: HEA, Multielement coatings, Wear resistance, Protective coatings, Friction, DLC.

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INTRODUCTION

To improve the protective characteristics of cutting tools and friction pairs, one of the promising areas of study is using multielement coatings based on carbides, nitrides and silicides of transition metals [1, 2]. Multielement coatings based on nitrides of two or more metals differ from the single-element ones with higher physical and mechanical characteristics, higher thermal stability, and are widely used as wear-resistant surface layers in mechanical engineering.

As a material to obtain such coatings, high entropy alloys (HEA) are used [3-5]. Such multicomponent alloys contain at least 5 major metal elements, with the atomic percentage of each in the range of 5 to 35 %. The main feature of HEAs is in forming a single-phase stable substitutional solid solution (mainly fcc- or bcc-lattices), which is has both thermodynamic stability and high strength properties [6].

However, the obtained coatings, based on multicomponent systems have a very high coefficient of friction while performing friction tests in the air [7]. One promising area in tribology is the development and application of diamond-like films [8, 9]. Diamond-like coatings obtained under nonequilibrium conditions by means of ion-plasma methods depending on physical and technological deposition parameters may have different carbon modifications, in particular with *sp*2-bonds between the carbon atoms – graphite, which under the conditions of friction forms a solid lubricant layers [10]. Therefore, our task was to examine and compare the tribological characteristics of the coatings (Ti-Hf-Zr-V-Nb)N and (Ti-Hf-Zr-V-Nb-Ta)N + DLC.

1. EXPERIMENTAL PART

The coatings were obtained by means of vacuum-arc deposition method. As the vaporized materials (cathodes) high entropy alloy based on (Ti + Hf + Zr + V + + Nb + Ta) and graphite have been used. The working gas (molecular nitrogen) was used to obtain nitride coatings. The coatings were deposited on the "Bulat 6" installation. The thickness of the coatings in the experiments was 4.0 microns.

Multielement coatings with high hardness were chosen for tribological tests. Deposition modes are given in paper [11].

Carbon coatings were obtained on the installation UVNIPA 1-001 with ion gas source, with a help of which cleaning and heating the substrates was done. Pulsed plasma source with a cathode made of graphite has also been used [12]. As a cathode material specific pure graphite MPG-6 has been used. The vacuum chamber was evacuated to a pressure of not greater than $P = 2 \times 10^{-3}$ Pa. Buffer unit with capacity of 2000 microfarads was charged to a voltage of 300 V. Discharge pulse duration was 1.0 ms. The pulse repetition rate was 5 Hz. The deposition rate of the carbon coating was 0.5-0.7 nm per pulse.

Before depositing the diamond-like coating, the cleaning of the surface of a substrate with a coating (Ti-Hf-Zr-V-Nb-Ta) with argon ions with an energy of 3.0 keV and an ion current density ≈ 25 A/m^2 at $P = 2...3 \times 10^{-2}$ Pa has been done. The thickness of the coating was 1.2 microns.

The surface morphology was investigated by means on scanning electron microscope FEI Nova NanoSEM 450. The study of the elemental composition of the coatings was conducted by means of analyzing the spectra of the characteristic X-rays generated by an electron beam in a scanning electron microscope.

The samples of steel 45 with a size of 45 mm in diameter and 5.0 mm thickness were used as substrates for coatings depositing ($Ra = 0.09$ microns). The tribological tests were performed in air by "ball-disk" scheme. High temperature "Tribometer", CSM Instruments, has been used as a friction machine. The balls with a diameter of 6.0 mm, made of sintered certified material – Al_2O_3 were

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used as counterbodies. The load was 6.0 N, the sliding speed – 15 cm/s. The tests conform to international standards ASTM G99-959, DIN50324 and ISO 20808. The roughness and the volume of removed material were determined by the section of wear track on the surface of the coating with a help of automated precision contact profilometer of Surtronic 25 model.

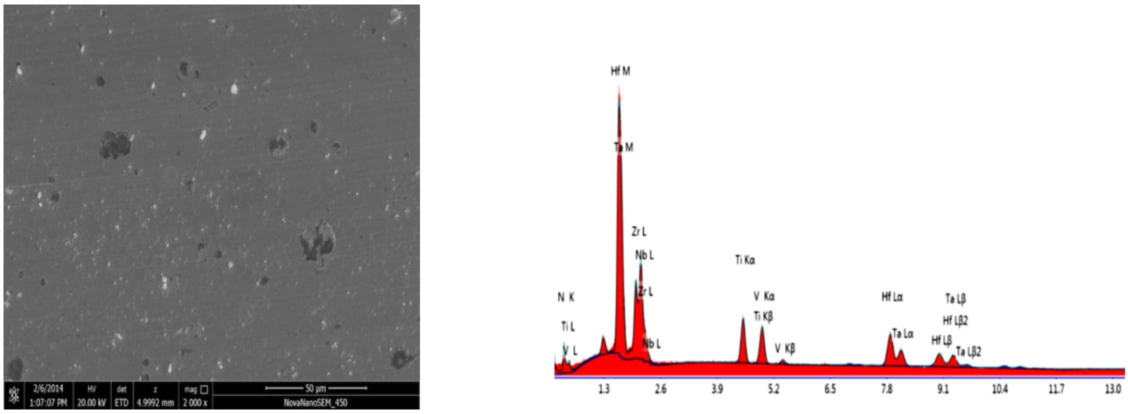
The hardness of the coatings was measured by means of durometer of DM 8 by micro-Vickers method.

2. RESULTS AND DISCUSSION

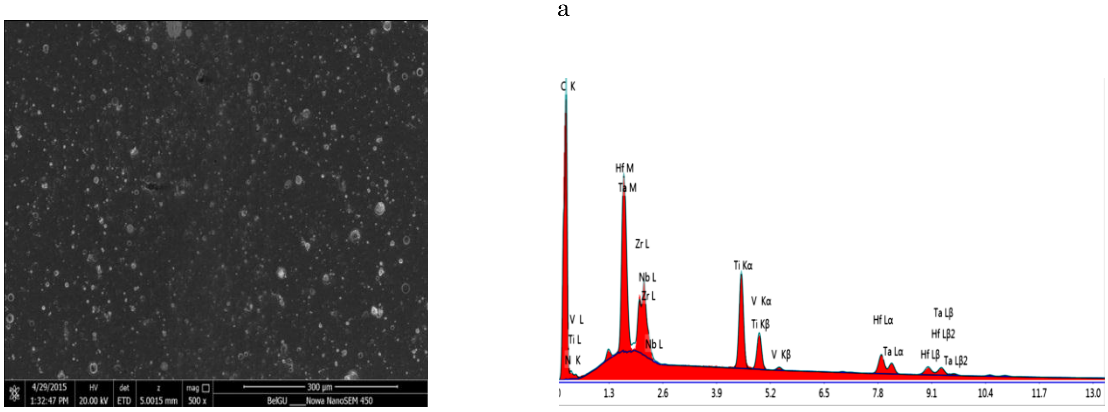
Figure 1 shows surfaces of the coatings (Ti-Hf-Zr-V-Nb-Ta)N and (Ti-Hf-Zr-V-Nb-Ta)N + DLC obtained by means of vacuum-arc deposition, as well as their energy-dispersive spectra.

Table 1 shows the results of elemental analysis. It was found that the coatings, formed by the evaporation of multi-element cathode, have a number of morphological features. In particular, part of the elements is in the form of individual insertions of up to 150 nm, but there is a good agreement between the elemental composition of the coating and the evaporated target (excluding nitrogen).

Depositing nitride diamond-like coating (DLC) on the surface results in a change of morphology and elemental composition, which is associated with a change in the roughness due to the escape of mircoparticles from graphite and their deposition on the surface of nitride multi-component coating, as well as with spraying the surface due to the radiation component [13,14]. The ion bombardment during the deposition of diamond-like coating leads to high compressive stresses in the coating, the consolidation of the condensate, increase of hardness, which thus leads to the formation the coatings with different content of sp^3 phase [15].



a



b

Fig. 1 – Image of the surface and elemental composition of the coating: a- (Ti-Hf-Zr-V-Nb-Ta) N; b- (Ti-Hf-Zr-V-Nb-Ta) N + DLC

Table 1 – The elemental composition of multi-component coatings

Coatings	Concentration of the elements in the coating. at. %							
	N	C	Zr	Nb	Ti	V	Hf	Ta
(Ti-Hf-Zr-V-Nb-Ta)N	54.85	–	8.52	8.37	7.67	6.1	9.29	5.2
(Ti-Hf-Zr-V-Nb-Ta)N + DLC	5.41	88.54	0.65	0.73	2.68	0.79	0.75	0.44

Table 2 – Mechanical and tribological characteristics of the coatings

Coatings	Coefficient of friction, μ		Intensity of wear mm³/N/m		Hardness, GPa	*Ra*, microns
	Initial	During the tests	Counterbody	coatings		
(Ti-Hf-Zr-V-Nb-Ta)N (25 °C)	0.683	1.063	3.84×10^{-6}	4.1×10^{-5}	42.2	1.32
(Ti-Hf-Zr-V-Nb-Ta)N + DLC (25 °C)	0.556	0.14	4.2×10^{-6}	0	68.1	1.28
(Ti-Hf-Zr-V-Nb-Ta)N + DLC (420 °C)	0.639	0.618	2.22×10^{-6}	5.21×10^{-6}	51.2	

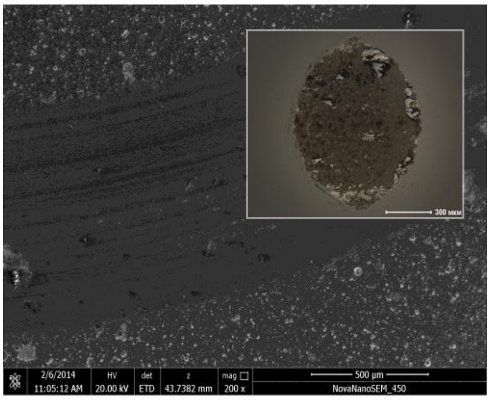
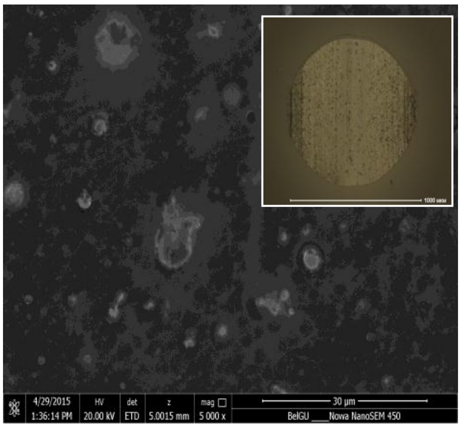
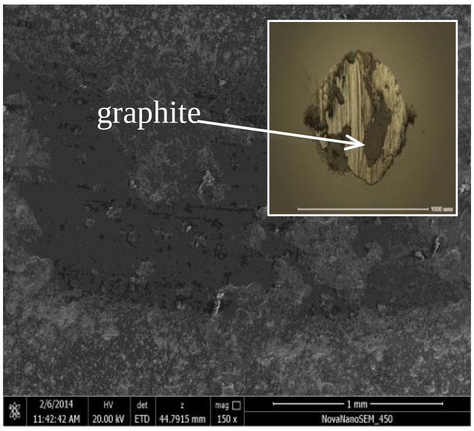


Fig. 2 – Image of the wear groove of the coating (Ti-Hf-Zr-V-Nb-Ta)N and the counterbody of Al_2O_3 at a temperature of $T = 25$ °C



a



b

Fig. 3 – Image of the wear groove of the coating (Ti-Hf-Zr-V-Nb-Ta)N + DLC and the counterbody of Al_2O_3 a – at $T = 25$ °C; b – at $T = 420$ °C

Mechanical and tribological characteristics are shown in Table 2. In the first stage we studied tribological characteristics of multielement nitride coating at room temperature. These experiments are needed to obtain information on the nature of wear of the coatings. Analysis of friction tracks indicates that multi-element nitride coatings are worn by abrasive mechanism (Fig. 2).

In the second stage tribological characteristics of (Ti-Hf-Zr-V-N-Ta)N + DLC at the temperatures of 25 °C

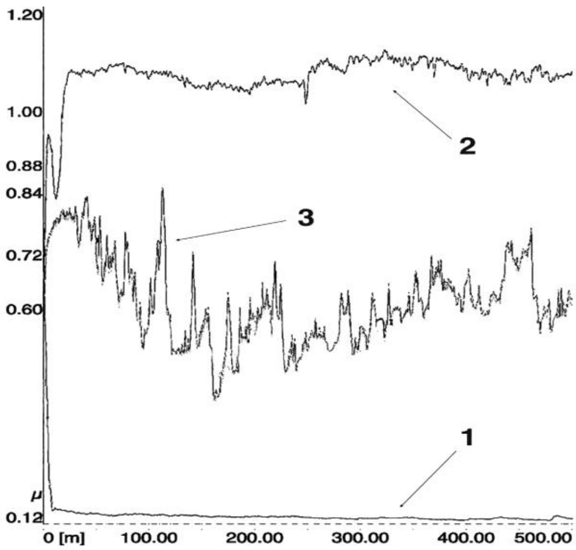


Fig. 4 – Change in the coefficient of friction of the coatings depending on the friction path: 1 – (Ti-Hf-Zr-V-Nb-Ta)N (25 °C); 2-(Ti-Hf-Zr-V-Nb-Ta)N + DLC(25 °C); 3-(Ti-Hf-Zr-V-Nb-Ta)N + DLC (420 °C)

and 420 °C. The results of research of wear grooves and counterbody are shown in Figure 3. Comparison of the coefficients of friction of multielement coatings are shown in Fig. 4.

In the case of nitride coating with a surface layer of DLC, the wear of counterbody sintered from Al_2O_3 takes place (see. Table 2). The obtained results of wear of the counterbody are slightly higher (4.2×10^{-6}mm^{3}N^{-1}m^{-1} in comparison with the nitride coatings 3.84×10^{-6} mm^{3}N^{-1}m^{-1}, however, they have a very high wear resistance (Figure 3a). It is known that on the surface of DLC, obtained by means of ion-plasma methods, there is a large number of active centers, which actively adsorb the molecules of the medium, including oxygen and thereby form CN phase, which serves as a solid lubricant.

At high temperature tests the wear of the counterbody is low in comparison with wear at room temperatures for nitride coating and the coating with DLC layer; the wear of the coatings is also lower in comparison with the nitride coating. This seems to be related to the structure reconstruction of the diamond-like coating, which leads to the formation of layers of graphite (see. Fig. 3b, counterbody).

Coefficients of friction (see Fig. 4): for nitride coatings (Ti-Hf-Zr-V-N-Ta)N have an average value of 1.06; for nitride coatings with DLC the value was 0.5 in the beginning, and then decreased to 0.14 maintaining this value all the way of friction during these testing conditions; in the case of temperature tests, some kind of fluctuations of the friction coefficient at all the friction way occur, which is apparently related to the structural reconstruction in the surface layers of the coating.

The obtained results confirm the available data in literature regarding the dependence of tribological properties of diamond-like coatings on a variety of factors, including the material of the substrate and the counterbody, and the pressure on the contact. During the dry friction some of them, in particular, coating on steel

95X18 dopped by silicon, are operable with no lubricant at pressures on the contact ≤ 390 MPa, and more than 6000 cycles before the failure. Use of lubricants and, thus, a significant decrease of the friction coefficient may significantly improve their tribological properties. This improvement can be especially notable if the coating will be able to provide an orienting effect on the molecules of lubricating layers [9].

In conclusion, it should be noted that to achieve high performance for functional coatings consisting of two layers - the bottom - and top-nitride multi - diamond (DLC) it is necessary to ensure the formation of a layer of solid lubricant in the areas of actual contact while retaining the structure of the coating.

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