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Influence of Deposition Parameters on Physical and Mechanical Properties of Nitride High-Entropy Alloys (Ti-Zr-Hf-V-Nb)N

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Results of investigation of nitride high-entropy alloys (Ti-Zr-Hf-V-Nb)N are presented in current paper. Coatings were obtained using cathode vacuum-arc evaporation. Scanning electron microscopy with energy-dispersive analysis (SEM with EDS), X-ray diffraction analysis, "a $\sin^2\psi$" – measurement of a stress-strain state, microhardness and tribological tests were used for investigation of elemental composition, structure, mechanical and tribological properties. It was shown, that deposition parameters have complex influence on properties of nitride high-entropy alloys (Ti-Zr-Hf-V-Nb)N.

Keywords: High-entropy alloys, Cathodic-arc-vapor-deposition, Microhardness, Young's modulus, Friction coefficient, Wear factor.

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1. INTRODUCTION

Conventionally, transition metal nitrides were widely used as protective coatings (which have been examined in numerous studies (eg, TiN [1-3])) as well, as multicomponent compounds based on them (Ti-Hf-N (Fe) [4], Ti -Hf-Si-N [5], Zr-Ti-Si-N [6], Ti-Si-BN [7], [8, 9].) However, as it was proposed by Yeh J.-W. and others, the concept of high-entropy alloys (HEAs) [10] and later the concept of nitrides high-entropy alloy (e.g. systems (TiVCrZrHf)N [11], (TiVCrZrAl)N [12], (TiZrHfVNb)N [13, 14]), allowed the development of a new type of coatings, which have a stable structure and high performance [15 – 24].

Such type of alloys should consist at least of main elements (metals) with atomic concentrations from 5 to 40 at.%.The high entropy of mixing can stabilize the formation of a single-phase state in the form of a disordered solid solution and prevent the formation of intermetallic compounds during solidification. Thus, high-entropy alloys might demonstrate an enhanced strength in combination with good resistance to oxidation and corrosion. It follows that, in high-entropy alloys and nitrides based on it, preferably one stable phase is formed, and it contributes to improvment of physical and mechanical properties.

2. RESULTS AND DISCUSSION

Table 1 shows the deposition parameters of nitrides of high-entropy system (Ti-Zr-Hf-V-Nb)N, and the results of the elemental analysis, which were obtained by EDS. It is seen, that several modes of deposition were used. Some samples were obtained under the same substrate voltage bias, but under different gas pressure; and vice versa. It allows to investigate influence of one deposition parameter change, meanwhile the other one remains the same. Fig. 1 shows SEM images of nitride coatings' (Ti-Zr-Hf-V-Nb)N surface (sample №512 (Fig. 1a) and №523

Table 1 – Coating deposition parameters (Ti-Zr-Hf-V-Nb)N

№	U_b, V	P, Pa	Concentration, %						Lattice parameter, a, nm
			N	Ti	V	Zr	Nb	Hf	
505	110	5×10^{-1}	49.15	16.63	5.91	8.17	8.88	11.26	0.4405
506	100	2×10^{-1}	49.05	22.92	5.04	6.84	7.47	8.68	0.4380
507	50	5×10^{-1}	51.13	25.31	4.72	5.70	6.31	6.84	0.4362
509	100	3×10^{-2}	44.70	25.31	4.57	7.60	7.99	9.83	0.4376
510	50	2×10^{-1}	49.11	19.67	5.65	7.68	8.24	9.64	0.4395
512	200	8×10^{-2}	46.65	17.03	2.79	12.01	12.54	8.99	0.4435
513	40	8×10^{-2}	–	34.66	8.88	19.53	23.16	13.76	0.3371
514	200	2×10^{-1}	47.69	16.41	1.93	13.34	13.90	6.72	0.4435
515	200	3×10^{-2}	36.05	20.13	2.28	17.12	17.50	6.93	0.4433
523	200	2×10^{-1}	43.44	17.80	1.45	16.39	16.99	3.92	0.4408

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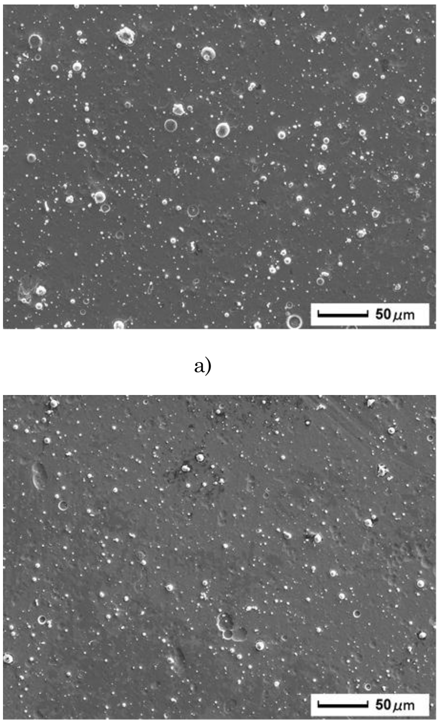
(Fig. 1b)) after the deposition. From the image we can observe that during the deposition of coatings, areas with dropping fraction with a size of several micrometers are formed. Coatings obtained under high N_2 pressure in the chamber, demonstrate partial reduction of dropping fraction. Presence of droplet fraction is sufficiently typical for coatings produced by cathodic arc deposition method, and a decrease of its size can be explained by the increasing of the pressure, and it causes the increasing of the intensity and density of the plasma. Therefore, the plasma flow is more intense and, correspondingly, the coating is more compacted. Thus, the number and size of macroinclusions on the surface of the coatings is reduced.



a)

b)

Fig. 1 – SEM images of the surface (Ti-Zr-Hf-V-Nb)N coatings, a) sample №512; b) sample №523

The results of X-ray diffraction analysis for all series of samples are shown in Fig. 2.

X-ray diffraction spectra of the TiZrHfVNb alloy (sample №513) demonstrate a strong texturing along the [110] direction.

However, analyzing the spectrum of nitride coatings, we can conclude that there is a formation of mild biaxial structure with the changing of N_2 pressure in the working chamber and the U_b bias potential in the samples №509, 512, 514, 515. This is evidenced by the strong peaks along the [111] axis, and [220] reflexes from [110] crystallographic axis, which are shown in X-ray diffraction spectra. In all other samples, of course, except for sample number 513, there is texturing of coatings along [111] axis, with the consequent increasing of the perfectness of this uniaxial texture. Also, fcc-crystalline lattice is the predominant.

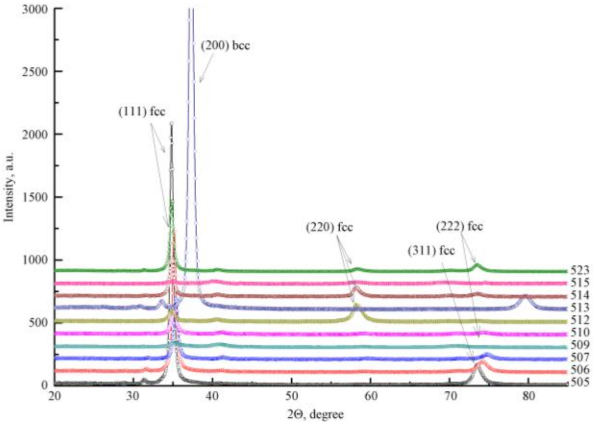


Fig. 2 – X-ray diffraction spectra of coatings of high-entropy Ti-Zr-Hf-V-Nb system and their nitrides

Mechanical tests of (Ti-Zr-Hf-V-Nb)N coatings demonstrates high values of hardness (from 19.34 to 29.94 GPa) anf Young's modulus (from 281 to 384.1 GPa), respectively. Fig. 3 shows hardness as a function of applied load for the samples №506, №507 and №514.

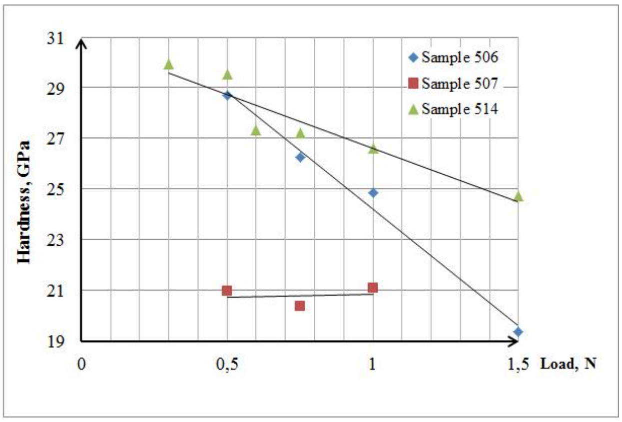


Fig. 3 – Hardness as a function of applied load of (Ti-Zr-Hf-V-Nb)N nitride high-entropy coatings

If we compare measured hardness with deposition parameters (Table 1), we can claim the following. Samples №506 and №514 show good correlation with each other, because dependence of measured hardness H value from deposition parameters is observed.

Thus, we can claim, that increasing of substrate voltage bias U_b from -50 V to -200 V causes increasing of hardness from 24.79 GPa to 27.56 GPa (these are average hardness values).

As for dependences of measured hardness from N_2 pressure in the vacuum chamber, we can say, that increasing of the pressure (from $2 \cdot 10^{-1}$ Pa to $5 \cdot 10^{-1}$ Pa) causes decreasing of coatings' hardness.

Table 2 shows results of wear resistance tests of (Ti-Zr-Hf-V-Nb)N coatings. As it can be seen from the shown data, there is increasing of wear resistance of steel after coating was deposited on the surface of the steel substrate.

This indicates that investigated high-entropy nitride alloys can be used as protective coatings for working parts of machining tools.

Table 2 – Tribological characteristics of the systems based on (Ti-Zr-Hf-V-Nb)N

Sample	Friction coefficient, μ		Wear factor,mm^3 × N^{-1} × mm^{-1}	
	initial	after test	counter solid (×10^{-5})	sample (×10^{-5})
Steel 45	0.204	0.674	0.269	35.36
(TiZrHfVNb)N	0.469	1.193	2.401	0.039

3. CONLUSIONS

Increasing of the negative potential on the substrate during the deposition of high-entropy nitride coatings of (Ti-Zr-Hf-V-Nb)N system leads to formation of the texture along the [111] axis, followed by the growth of its excellence.

Increasing of potential on the substrate also leads to increasing of the microhardness values of the coatings from 24.78 GPa to 27.36 GPa.

Results of tribological tests showed that after applying the test nitride coatings on steel disc, its durability significantly increased. This suggests high protective properties of (Ti-Zr-Hf-V-Nb)N coatings.

By varying the deposition parameters of high-entropy nitride (Ti-Zr-Hf-V-Nb)N alloy, one can define structure and influence on the physical and mechanical properties of the investigated coatings.

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