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EFFECT OF THE DEPOSITION CONDITIONS ON THE FORMATION OF THE MICROSTRUCTURE AND PROPERTIES OF (Ti, Zr)N COATING ON CHROMIUM CARBIDE STEELS

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A complex nitride (Ti, Zr)N coating on chromium carbide steels Kh13M2–30 vol.% Cr_3C_2 *and Kh17N2–30 vol.%* Cr_3C_2 *is obtained. The optimal deposition conditions are determined. The effect of deposition time on the hardness, structure, adhesion strength, and wear resistance of coatings during sliding friction (counterface—steel ShKh15) is investigated. It is established that annealing at 900–1200°C promotes an active interaction of the coating elements with the substrate accompanied by the formation of a transition zone. It is found that the (Ti, Zr)N coatings produced at nitrogen pressure* $P = 2$ *Pa, spray-off distance* $d = 230$ *mm, and deposition time 30–40 min possess the best mechanical and tribotechnical properties.*

Keywords: *carbide steel, complex nitride, coating, durability, deposition, tribotechnical properties.*

INTRODUCTION

One of the most effective ways to increase the performance of machine parts, machinery, and cutting tools is to deposit wear-resistant coatings on their friction surfaces. The coatings produced by plasma condensation with ion bombardment in vacuum (CIB) using a Bulat machine deserve a special attention [1].

Single-layer (TiN, TiC) and multi-layer wear-resistant coatings on the basis of carbon-nitride, nitride-oxide, or others are the most common in commercial use, because they allow increasing the performance of structural and tooling materials by a factor of 2–5 [2–4]. Further improvement of methods for depositing coatings and optimization of their structure are focused on creating new compositions of materials, primarily, multi-layered and nanostructured materials, which can better meet the requirements to modern ways of strengthening and re-facing of abraded surfaces [5, 6]. However, the small number of scientifically-based principles of their formation and application leads to the fact that the same multi-layer coatings are often recommended to use for products with different operating conditions and, vice versa, different multi-layer coatings are recommended for identical operating conditions. To be noted that the effect of the deposition conditions, the composition and structure of the coating on the properties of tool materials has not been studied adequately. Furthermore, the studies are complicated by the lack of scientifically-based methods for design of coatings for different operating conditions. A critical

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review of solid compounds allowed choosing one of the most promising materials: complex titanium–zirconium nitride (Zr, Ti)N. Coatings made of this material have hardly been studied. At the moment, such coatings are deposited as separate layers (TiN and ZrN); therefore, their benefits have not been clarified yet.

The purpose of the study is to investigate CIB-deposited coatings base on titanium–zirconium nitride and the effect of operating conditions on the formation of the structure and properties of chromium carbide steels.

MATERIALS, OBJECTS, AND EXPERIMENTAL PROCEDURE

The samples of carbide steels based on Kh13M2 and Kh17N2 with 30 vol.% Cr_3C_2 were produced by wet mixing-grinding in a ball mill for 70 h. The mixtures were pressed in closed die-molds under 800 MPa, and then the prismatic samples (6 mm × 6 mm × 40 mm) were sintered in vacuum furnaces at 0.01 Pa. After sintering, the porosity of the samples did not exceed 2%, the hardness was 75–80 HRA, and the bending strength was 1450–1470 MPa. The technology for producing carbide steel samples is detailed in [7].

The spray-off distance from the cathode to the substrate was 160–270 mm, the nitrogen pressure in the chamber was $P = 0.79$–1.99 Pa, current was 100 A, and the spraying time was 10–40 min. The deposition conditions were selected as recommended in [8].

The samples made from carbide steel were ground washed in an ultrasonic bath, and degreased just before deposition. The coating was deposited using a VU-1B machine for vacuum-plasma deposition with a 60 wt.% Ti–40 wt.% Zr cathode.

The determination of stresses that arise between the coating and the substrate and X-ray diffraction analysis were carried out by using an Ultima IV universal diffractometer (Rigaku, Japan). Electron microprobe analysis was performed using a REM106I microscope (Selmi, Ukraine). The chemical composition of samples coated was determined using an Expert 3L X-ray-fluorescence analyzer (Inam, Ukraine). Wear resistance and the coefficient of dry friction were investigated in pair with steel ShKh15 using an M-22m friction machine (load $P = 2$ MPa, sliding rate $V = 1.0$ m/sec, friction distance $L = 5$ km). The microhardness of the sample surface was examined using a PMT-3 unit and a standard 136-degree square-base diamond pyramid. Due to the high hardness of the surface, the load on the diamond pyramid was 2 N, and the holding time was 10 sec. Almost no indentation was seen at smaller loads and shorter holding.

The adhesion strength of the coating to the substrate was determined using a conical diamond indenter [8]. The sliding rate of the indenter was 0.75 mm/sec and the load at which the coating was completely torn off was 0.95 N. While scratching the films, we measured the horizontal force F corresponding to the vertical load under which no traces of the coating left on the substrate after scratching. It was assumed that the horizontal force F consists of three components:

$$F = F_1 + F_2 + F_3, \tag{1}$$

where F_1 is the force that occurs during scratching the film; F_2 is the force required to fully tear off the film from the substrate (adhesion strength); F_3 is the force acting on the indenter sliding over the substrate with no coating ($F_3 = 0.6$ N). The forces F_1 and F_2 can be determined by the formulas:

$$F_2 = 1/4 \cdot \sigma \cdot \pi \cdot D^2, \tag{2}$$

$$F_1 = DhH, \tag{3}$$

where σ is the adhesion strength per area unit, Pa; D is the width of the scratch, μm; h is the thickness of the film, μm; H is the hardness of the coating.

Then, the formula for the adhesion strength of the coating with the substrate reads as follows [3]:

$$\sigma = \frac{4\left(F - F_3 - dhH\right)}{\pi D^2}. \tag{4}$$

RESULTS AND DISCUSSION

General theoretical and experimental data have shown that the greater the spray-off distance, the higher the hardness of the coating deposited. This is because an increase in the spray-off distance from the cathode to the substrate causes metal ions to interact with the reaction gas (nitrogen) for a longer time. In turn, the longer the interaction, the higher the probability of collision of titanium and zirconium ions with nitrogen molecules and the higher the total content of nitride (Ti, Zr)N. This is due to the high average multiplicity and energy of titanium and zirconium ions in the range of low gas pressures, which increases the energy of ions that reach the surface of the samples.

Figure 1 demonstrates that the microhardness of the coating (Ti, Zr)N is strongly dependent on the deposition time. Thus, after deposition for 10 min, the hardness of the coating is the lowest because of the small number of (Ti, Zr)N particles that reached the surface of the sample. In general, the microhardness of the coating on the carbide steel Kh17N2–30 vol.% Cr_3C_2 is higher than that of the coating on the surface of Kh13M2–30 vol.% Cr_3C_2. The highest microhardness (>24 GPa) is observed after 30 and 40 min of deposition, which can be attributed to the formation of the maximum number of Ti–Zr nitride particles deposited on the sample surface.

The values of integral microhardness of the coating layers deposited for 30 and 40 min are almost the same, which indicates that the optimal deposition time falls into this interval. Further increase in the deposition time may lead to separations of the coating because of an increase in the thickness and stresses.

Table 1 shows that an increase in the pressure of the reaction gas in the chamber and spray-off distance leads to a decrease in the hardness of the coating. As the pressure is increased from 0.79 to 1.99 Pa, the deposition rate of particles increases significantly due to the high average multiplicity and the energy of titanium and zirconium ions in the range of high gas pressures.

Since the coefficient of condensation of nitride particles decreases with increase in their energy, this phenomenon causes (i) a decrease in the deposition rate in the range of low pressures and, consequently, (ii) an increase in the number of titanium–zirconium nitride bonds [6].

To reduce the stresses, the samples deposited for 30 min were annealed in vacuum at 900–1200°C (holding time $\tau = 2$ h), then their microhardness was determined (Fig. 2). After annealing, the microhardness of the coating significantly decreases. Therefore, after annealing at 900°C, the microhardness equals to 9.75 GPa, which slightly

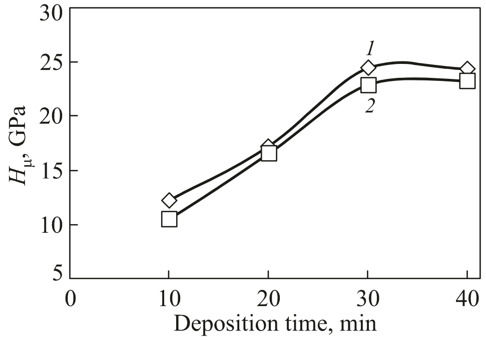


Fig. 1. Variation of integral microhardness H_μ of the coating (Ti, Zr)N with the deposition time for carbide steels Kh17N2–30 vol.% Cr_3C_2 (*1*) and Kh13M2–30 vol.% Cr_3C_2 (*2*)

TABLE 1. Effect of the Nitrogen Pressure in the Chamber and Spray-off Distance *d* on the Integral Microhardness of the (Ti, Zr)N Coating

Nitrogen pressure, Pa	*d*, mm	H_μ, GPa
0.79	160	23.53
1.99	200	11.33
0.79	230	24.45

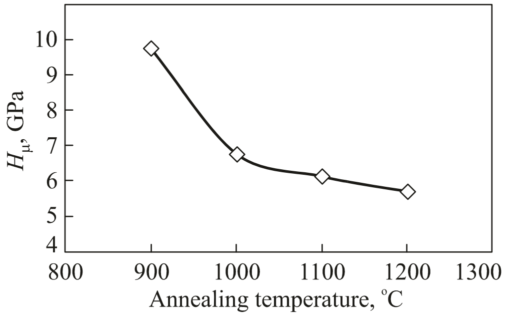


Fig. 2. Variation of microhardness of the coating with annealing temperature

exceeds the microhardness on the carbide steel with no coating (8.4 GPa). With further increase in the annealing temperature, the microhardness continues to decrease, which can be explained by the diffusion of substrate elements (Mo, Fe, Cr, Ni) into the coating and the enrichment of the latter with ductile metals. The microhardness of the samples annealed at 1000–1200°C decreased to 6 GPa.

The stresses between the coating and the substrate made of carbide steel Kh13M2–30 vol.% Cr_3C_2 have been determined. It is known that vacuum-plasma deposition of coatings induce residual compressive stresses that increase in absolute magnitude with the coating thickness [5]. Among the causes of the residual stresses in (Ti, Zr)N films are the difference in thermal expansion coefficients between the film and the substrate and to the stresses in the (Ti, Zr)N films induced by the ion bombardment of the coating during its growth. The decrease in the stresses with increase in the deposition time from 30 to 40 min proves the above (Fig. 3). The causes of formation of the residual stresses in thin films during ion bombardment can be displayed using the model of thermal peaks, which are areas where the energy of the bombarding ions is transferred to the coating. The coating atoms acquire energy from the bombarding ions through a number of elastic collisions and, as a result, become more mobile and can displace from their original position. The sample with coating deposited for 40 min has the lowest residual stresses ($\sigma = -2.3$ GPa), which can be explained by a partial separation of the (Ti, Zr)N coating from the substrate.

To analyze the effect of the annealing temperature on the adhesion of the coating layer, we investigated the adhesion strength of the coating to the substrate of the Kh17N2–30 vol.% Cr_3C_2 carbide steel samples annealed at $T = 900$°C for $\tau = 2$ h.

Figure 4 displays that the adhesion strength of annealed and non-annealed (Ti, Zr)N coatings on the carbide steel Kh17N2–30 vol.% Cr_3C decreases with increasing deposition time. This dependence can be explained by an increase in the thickness of the deposited layer or an increase in the concentration of structural defects at the film–substrate interface, which is promoted by the difference in thermal expansion coefficient between the film and the substrate. Thus, thicker films can separate from the substrate during operation.

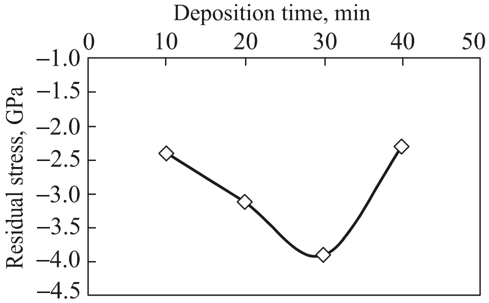


Fig. 3

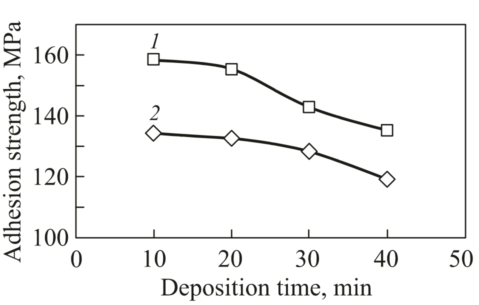


Fig. 4

Fig. 3. Variation of residual stresses with deposition time for carbide steel samples with nitride coating

Fig. 4. Variation of adhesion strength of the (Ti, Zr)N coating on the Kh17N2–30 vol.% Cr_3C_2 carbide steel with deposition time of annealed (*1*) and non-annealed (*2*) samples

TABLE 2. Study of the Wear Resistance of the (Ti, Zr)N Coating by Dry Friction

Deposition time, min	Friction coefficient f	Linear wear of friction pair I_L, μm/km	Mass loss I_m, mg/km		Temperature of sample, °C	Relative mass loss
			Sample	Counterface (ShKh15)		
Carbide steel Kh13M2–30 vol.% Cr_3C_2						
10	0.30	16	0.52	2.20	65	0.236
20	0.36	9.6	0.48	2.04	55	0.235
30	0.38	6	0.36	3.30	66	0.110
40	0.25	12	0.22	1.48	45	0.148
Carbide steel Kh17N2–30 vol.% Cr_3C_2						
10	0.32	9	0.42	2.78	52	0.150
20	0.30	8	0.32	2.12	60	0.150
30	0.36	7	0.22	3.94	62	0.058
40	0.22	7	0.20	2.92	55	0.068

Study of the wear resistance of the coating during dry friction against the counterface made of steel ShKh15 has demonstrated (Table 2; Fig. 5*a*) that the mass loss of samples decreases with increasing deposition time. In our case, this is due to an increase in the integral microhardness of the coating with increase in the deposition time to 30–40 min. Coated with (Ti, Zr)N, the samples of carbide steel Kh17N2–30 vol.% Cr_3C_2 have a greater wear resistance than those of carbide steel Kh13M2–30 vol.% Cr_3C_2, which can be explained by an increase in the microhardness of the coating on the samples made of carbide steel Kh17N2–30 vol.% Cr_3C_2 (Fig. 5*a*).

As the deposition time is increased from 10 to 30 min, the friction coefficient (Fig. 5*b*) first increases and then decreases, reaching the minimum after 40 min. This may be due to a partial separation of the coating from the substrate and sliding of the sample surface with no coating. The main factor that affects the wear resistance of the coatings is the presence of fine drip phase of titanium and zirconium rather than their hardness. The phase is a kind of lubricant that contributes to the significant improvement of tribological characteristics of the system [6]. Figures 6*a* and 6*b* show not only the microstructure of the sample surface after wear resistance tests, but also a partial separation from the substrate resulting from the friction against the couterface made of steel ShKh15. This indicates uneven wear and too thin coating. More even wear across the entire contact surface is typical for the samples with no coating.

Study of the microstructure of the carbide steel–coating interface of the Kh13M2–30 vol.% Cr_3C_2 and Kh17N2–30 vol.% Cr_3C_2 samples (Figs. 6*c* and 6*d*) has shown the formation of a transition zone between the coating layer and the substrate, i.e., partial interaction of its elements with the substrate (Table 3).

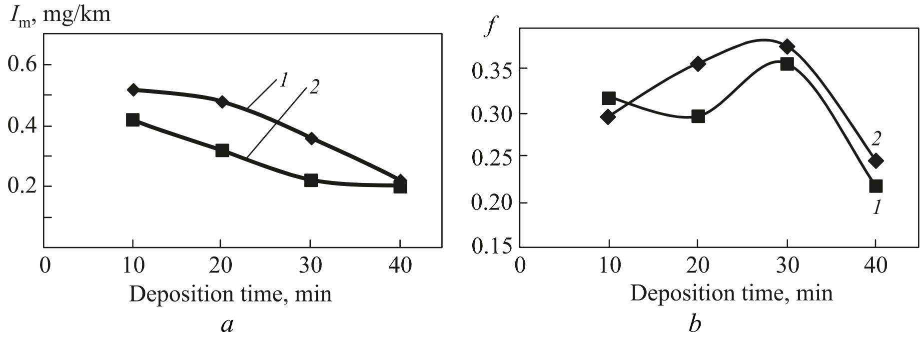
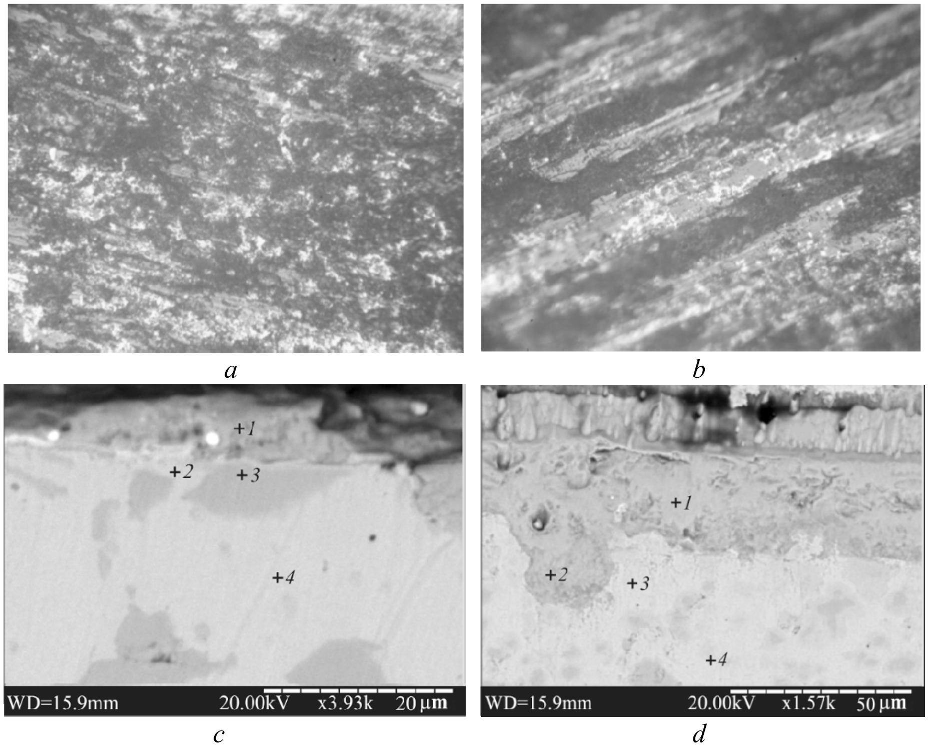


Fig. 5. Variation of mass loss I_m (*a*) and friction coefficient f (*b*) with deposition time for carbide steels Kh13M2–30 vol.% Cr_3C_2 (*1*) and Kh17N2–30 vol.% Cr_3C_2 (*2*) with coatings



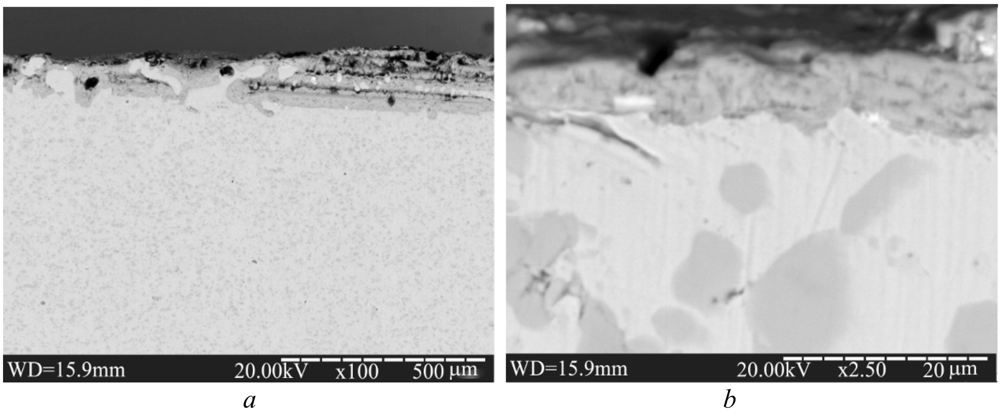
a *b*

c *d*

Fig. 6. Microstructure of the sample surface after wear resistance tests (*a*, *b*) and the carbide steel–coating interface (*c*, *d*): Kh17N2–30 vol.% Cr_3C_2 (*a*, *d*) and Kh13M2–30 vol.% Cr_3C_2 (*b*, *c*)

TABLE 3. Results of Chemical Analysis of Non-Annealed Carbide Steel Samples with (Ti, Zr)N Coating

Carbide steel, %	Content of element, wt.%									
	Substrate				Coated surface					
	Fe	Cr	Mo	Ni	Fe	Cr	Ti	Zr	Mo	Ni
Kh17N2–30 Cr_3C_2	64.5	32.30	1.67	0.53	50.55	31.70	11.44	2.59	1.72	0.44
Kh13M2–30 Cr_3C_2	64.9	31.73	1.62	0.52	9.06	5.10	59.34	24.12	1.49	0.12
70 Fe–27 Cr–3 C	70.02	28.10	0.38	0.37	38.61	17.04	31.29	10.84	0.33	0.20



a *b*

Fig. 7. Microstructure of the substrate–coating interface of the non-annealed Kh13M2–30 vol.% Cr_3C_2 sample (*a*) and annealed Kh17N2–30 vol.% Cr_3C_2 sample (*b*)

TABLE 4. Results of Electron Microprobe Analysis of the Phase Components in the Non-Annealed Samples of Carbide Steels Kh13M2–30 vol.% Cr_3C_2 and Kh17N2–30 vol.% Cr_3C_2 with the (Ti, Zr)N Coating

Phase	Content of element, wt.%					
	Ti	Zr	Fe	Cr	Mo	Ni
	Kh13M2–30 vol.% Cr_3C_2					
1	68.04	25.73	–	–	5.99	0.24
2	67.02	24.53	1.26	–	6.83	0.37
3	0.35	0.83	88.37	9.50	0.95	–
4	–	0.51	81.59	16.71	1.18	–
	Kh17N2–30 vol.% Cr_3C_2					
1	69.57	24.37	0.12	–	5.08	0.88
2	0.29	0.43	87.53	8.07	0.58	3.11
3	–	0.46	29.37	69.56	0.60	–
4	–	0.12	90.26	6.82	0.42	2.38

Note: The numbering of the phases corresponds to the points in Figs. 6*c* and 6*d*.

The microstructure of the substrate–coating interface of the non-annealed (Fig. 7*a*) and annealed (Fig. 7*b*) samples somewhat differ: the annealed sample has a more blurred boundary, which may be due to the diffusion of substrate elements into the coating (Table 4).

CONCLUSIONS

A complex nitride (Ti, Zr)N coating on chromium carbide steels Kh17N2–30 vol.% Cr_3C_2 and Kh13M2–30 vol.% Cr_3C_2 has been examined. It has been established that the maximum integral microhardness belongs to the coatings produced under a nitrogen pressure of 0.79 Pa for 30 min.

It has been demonstrated that the (Ti, Zr)N coatings on the Kh17N2–30 vol.% Cr_3C_2 carbide steel deposited for 40 min has the highest wear resistance: the mass loss totaled just 0.2 mg/km.

The microstructure and phase composition of the coating–substrate interface have been investigated. It has been revealed that the annealing in the 900–1200°C temperature range leads to the active interaction of the coating and substrate elements with the formation of a transition zone.

The adhesion strength of the coating to the substrate steadily decreases with increase in the deposition time from 10 to 40 min.

It has been established that the (Ti, Zr)N coatings deposited under nitrogen pressure $P = 0.79$ Pa and stand-off distance $d = 230$ mm for 30–40 min possess the best mechanical and tribotechnical properties.

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