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MECHANICAL CHARACTERISTICS AND STRUCTURE OF VACUUM ARC Ti-Cr-N COATINGS

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The elemental composition, mechanical properties and structure of Ti-Cr-N coatings deposited in a wide range of nitrogen pressures from unfiltered and filtered vacuum arc plasma flows from Ti-Cr alloy cathodes containing 23 and 32 wt.% Cr have been investigated. It was found that for different deposition modes, the dependence of the Cr content in the coatings on the nitrogen pressure has a minimum near $1 \cdot 10^{-3}$ Torr, which correlates with the maximum hardness H_μ. When plasma filtration or a cathode with a lower Cr content is used, the hardness maximum shifts to lower nitrogen pressures. The mechanisms that determine the elemental composition of the coatings are discussed. In the coatings deposited at a pressure of $9 \cdot 10^{-4} \ldots 5 \cdot 10^{-3}$ Torr, the main phase is a nanocrystalline cubic solid solution of (Ti,Cr)N with a NaCl-type structure. Increasing the chromium content in the cathode contributes to the formation of an amorphous crystalline structure. Filtration effectively separates the droplet component from the plasma stream and produces coatings with reduced surface roughness. Nanostructured Ti-Cr-N coatings with high mechanical properties (H_μ ~ 35 GPa) containing ~ 20 wt.% Cr, which can be used to protect structural materials in power engineering and other nuclear industries.

INTRODUCTION

A modern direction for producing hard nanostructured coatings is vacuum arc synthesis using multicomponent cathodes [1]. Vacuum arc coatings based on transition metal nitrides using Cr as an alloying element are characterized by enhanced mechanical, corrosion and erosion resistance, as well as oxidation resistance at high temperatures, and can be used to protect nuclear reactor fuel elements [2–4]. TiCrN-coated Ti6Al4V also showed moderate antibacterial ability and excellent biocompatibility compared to uncoated Ti6Al4V and CoCr alloys [5]. The deposition rate of (Ti-Cr)N coatings is highly dependent on the parameters of the vacuum arc process and can range from 1 to 19 μm/h [5, 6].

The method of manufacturing alloyed cathodes affects the surface morphology, the number of macroparticles, and the properties of the coatings when they are used in the vacuum arc deposition process [7, 8]. For example, even for pure chromium cathodes, increasing the grain size of the Cr cathode slightly increases the droplet density of the Cr-N coatings, while decreasing the hardness of the Cr-N coatings deposited in the stationary mode at 2 Pa nitrogen pressure [9]. The deposition rate, elemental composition, internal stresses and properties of CrN and TiN coatings are strongly dependent on the reaction gas pressure and the bias voltage on the substrate [10, 11].

It is possible to reduce the number of macroparticles in the metal plasma stream by using filtering devices to prevent droplets from falling onto the substrate [12]. A well-known advantage of deposition in a separated flow is the production of homogeneous coatings that do not contain macroparticles; the disadvantage is the low deposition rates. However, in publications on this topic, insufficient attention has been paid to analyzing the effect of filtration on the composition and properties of Ti-Cr-N coatings compared to coatings obtained from unfiltered plasma streams.

The aim of this work is to study the elemental composition, mechanical properties and structure of Ti-Cr-N coatings deposited in unfiltered and filtered vacuum arc plasma flows from Ti-Cr alloyed cathodes at different nitrogen pressures.

MATERIALS AND METHODS

The Ti-Cr-N coatings were deposited on a Bulat type vacuum arc unit using plasma sources with magnetic cathode spot retention and plasma flow focusing [11]. Samples of 12X17 steel with dimensions of 20×10×1.5 mm were placed in a vacuum chamber on a substrate holder in both unfiltered and filtered plasma flows. A negative bias voltage U, V was applied to the samples, the v alue of which was selected in the range from 150 to 350 V. The vacuum arc sources had an arc current of I = 90 A. A linear filter [13] with a Ø 60 mm shutter was used to filter the plasma flow. This filter was located at a distance of 150 mm from the cathode surface.

We used one-component Ti cathodes of VT1-0 alloy, cathodes with Cr (99.9%), and two-component Ti-Cr cathodes obtained by vacuum arc melting with 23 wt.% (Ti-23Cr) and 32 wt.% (Ti-32Cr) chromium impurity for the synthesis of the coatings. The cathode-substrate distance was 350 mm. During the nitride coating process, the vacuum chamber was filled with nitrogen gas using an automatic injector. The working gas pressure was adjusted from 10^{-5} to 10^{-2} Torr.

The elemental composition of multicomponent cathodes and coatings was controlled by X-ray fluorescence analysis on a crystal diffraction vacuum spectrometer SPRUT-VM. According to the intensity of the corresponding characteristic lines, the values of the concentration of metal components (excluding nitrogen)

were calculated, which allows us to estimate the degree of reproducibility of the composition of the cathode in the coatings. In addition, the elemental composition of the multicomponent coatings, taking into account the concentration of nitrogen in them, was measured using a JSM 7000-1F scanning electron microscope equipped with X-ray energy dispersive microanalysis.

The microhardness of the coatings was measured on a PMT-3 microhardness tester at loads of 0.5 and 1 N and coating thicknesses of ~10 μm. The surface roughness was measured with a profilometer and the coating thickness was measured with an MII-4 microinterferometer.

The phase composition of the coatings was investigated by X-ray diffraction (XRD, DRON-3) using Cu Kα radiation at 30 mA and 20 kV in the Bragg/Brentano mode. The International Center for Diffraction Data (JCPDS) database was used to interpret the results obtained. The lattice parameters of the nitride phase were determined from the XRD patterns taking into account the angular position of all detected diffraction peaks. The crystallite size (coherent scattering zone) in the coatings was calculated from the (111) or (200) full width at half maximum (FWHM) peak broadening using the Scherrer equation.

RESULTS AND DISCUSSION

The main process parameters that can be used to conveniently change the properties of the resulting coatings when using vacuum arc deposition are the gas (nitrogen) pressure P_{N2}, Torr injected into the working chamber and the bias voltage U, V applied to the substrate. The search for optimal deposition modes was carried out according to the following scheme: 1) fixing the working pressure and changing the bias voltage within 150…350 V and 2) fixing the voltage and changing the working gas pressure within $P_{N2}= 10^{-5}…10^{-2}$ Torr. At the same time, other deposition parameters (arc current, cathode-substrate distance, heat dissipation conditions on the substrate, etc.) were kept constant in the experiment. Excessive internal stresses, which are characteristic of multi-component coatings, usually manifest themselves in ultra-high hardness and brittleness [14]. Such factors not only do not provide protective properties, but may also lead to a loss of mechanical properties of the working surface of the hardened part. Therefore, the criteria for assessing the quality of the obtained Ti-Cr-N coatings were: the presence of excessive internal stresses in the coatings together with an assessment of their microhardness. The result of a visual inspection of the surface of coatings of a certain thickness (10 μm), in which the appearance of chip centers on it was observed, served as a criterion for the presence of these stresses. Based on the results of these studies, the optimal range of bias voltages to obtain coatings without excessive internal stresses was determined to be between -250 and -350 V. In further experiments on the deposition of Ti-Cr-N coatings, the negative voltage applied to the substrate was U = -320 V in the direct flow deposition regime and U = -270 V in the separated flow deposition regime.

The Ti-Cr-N coatings deposited by direct flow had a developed surface topography due to the presence of a significant number of microparticles. A linear filter was used to reduce the roughness of the Ti-Cr-N coating. The roughness of the samples, measured by the Ra parameter, indicates the high filtering characteristics of the device used: in the direct flow – Ra = 0.99 μm, in the filtered flow – Ra = 0.28 μm. According to the results of the experiment, the deposition rates for Ti-Cr-N coatings obtained from the direct flow and filtered from macroparticles were ~ 15 and ~ 5 μm/h, respectively.

For the unfiltered plasma flow deposition regimes, the relative Cr content in Ti-Cr-N coatings obtained from Ti-23Cr (1) and Ti-32Cr (2) cathodes was studied as a function of nitrogen pressure (Fig. 1). From Fig. 1, it can be seen that at low nitrogen pressure, the metal content of the coatings corresponds quite well to the composition of the cathodes. With increasing N_2 pressure, the dependences of Cr = f (P_{N2}) have a slowly decreasing character, and starting from approximately $P_{N2} = 5\cdot10^{-4}$ (1) and $1\cdot10^{-3}$ Torr (2), the slope of the curves increases, indicating a more significant depletion of Ti-Cr-N coatings with chromium. For both dependencies (1, 2), in general, a constant difference in the Cr concentrations in the coatings is maintained, which is equal to 10 wt.% incorporated in the cathode materials during their manufacture. For curve (1), which refers to the Ti-23Cr cathode, a minimum is recorded at a pressure of $5\cdot10^{-3}$ Torr. As can be seen from the figure, the differences in the behavior of curves (1) and (2) are only associated with a shift of the minimum for curve (2) with higher chromium content towards higher pressures. One of the factors affecting the position of the minimum chromium concentration may be the scattering of a significant amount of chromium ions on nitrogen atoms.

A similar character of the dependence of the silicon concentration in Ti-Si-N coatings was observed by the authors of [15]. In order to substantiate the reasons for such an extreme dependence, the following main mechanisms were identified in the work: 1) “depletion” of the plasma flux with less energetic metal ions as a result of collisions with a gas target; 2) selective sputtering of nitride coating components by an incoming particle stream; 3) formation of nitride compounds with different resistance to sputtering. It is known that the charge composition of chromium ions and titanium ions is very close (about 2/3 of the composition of both plasma streams belongs to doubly ionized atoms); the average energy per unit charge also differs slightly, in both cases it is close to 70 eV [16]. Nevertheless, a decrease in the relative concentration of chromium in Ti-Cr-N coatings is observed in the specified range of nitrogen pressures, and the reason for this phenomenon apparently depends less on the energy characteristics of the ionic components of the plasma stream than on the set of mechanisms operating during the plasma chemical synthesis at the substrate surface.

Fig. 2 shows the dependence of microhardness on the N2 pressure of nitride coatings deposited from Ti-23Cr (1), Ti-32Cr (2), Cr (3), and Ti (4) cathodes from an unfiltered plasma stream. The Ti-Cr-N films were deposited at a bias voltage of U = - 320 V, and the CrN and TiN films were deposited at U = - 250 V.

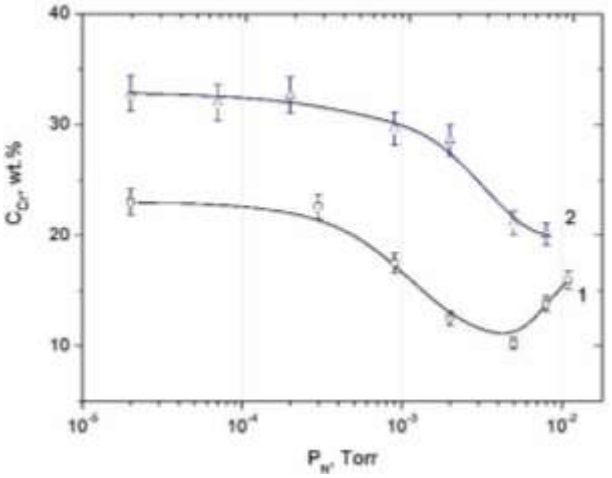

Fig. 1. Relative chromium content in Ti-Cr-N coatings obtained from Ti-23Cr (1) and Ti-32Cr (2) cathodes without plasma filtration as a function of N_2 pressure

The curve for TiN coatings (4) shown in Fig. 2 generally follows the classical dependence $H_\mu = f(P_{N2})$ with two maxima [12, 17]. The curve for CrN (3) has a similar character to TiN, but its first maximum is shifted toward high pressures by almost an order of magnitude.

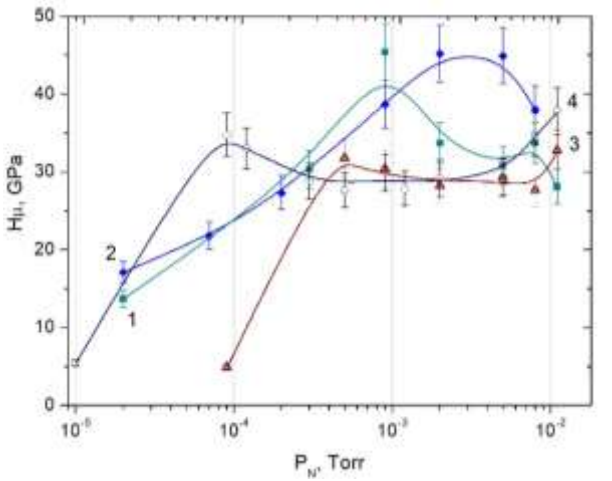

Fig. 2. Effect of N_2 pressure on the hardness of nitride coatings deposited from Ti-23Cr (1), Ti-32Cr (2), Cr (3) and Ti (4) cathodes from an unfiltered plasma stream

From Fig. 2 it can be seen that the course of the dependence $H_\mu = f(P_{N2})$ for Ti-Cr-N coatings with lower Cr concentration (1) correlates with the dependence (3) for CrN, but with a significant difference in the amplitudes of the microhardness at the maximums: ~ 30 GPa (CrN) and ~ 40 GPa (Ti-Cr-N). For curve (2), with an increase in the concentration of chromium in the cathode to 32 wt.%, an even higher value of microhardness is recorded at the maximum (up to 45 GPa), which occupies a wider pressure range (from $1 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$ Torr). It should be noted that for coatings with higher Cr content, the microhardness maximum is shifted to higher pressures, as is the dependence of Cr concentration on pressure (see Fig. 1). Thus, the addition of Cr to TiN-based coatings leads to a significant increase in microhardness over a wide pressure range from $5 \cdot 10^{-4}$ to 10^{-2} Torr. At the same time, when comparing the microhardness curves (1) and (2) (see Fig. 2) for Ti-Cr-N coatings with the corresponding curves of the relative concentration of Cr (1) and (2) (see Fig. 1), it is clear that the microhardness maxima occur in the areas of depletion of the coatings with chromium.

Fig. 3 shows the dependence of the relative Cr content on the nitrogen pressure in Ti-Cr-N coatings obtained from the filtered plasma stream. As can be seen from Fig. 3 (1, 2), the nature of the relative chromium concentrations in the filtered flow is not very different from the unfiltered flow (see Fig. 1). That is, the same extreme behavior of the concentration curves versus nitrogen pressure $C_{Cr} = f(P_{N2})$ is observed, where two characteristic areas are revealed: 1) a rather sharp depletion of the coating with chromium (for Ti-32Cr – $(0.2\ldots1)\cdot10^{-3}$ Torr) and 2) a gradual enrichment of the coating with chromium ($(1\ldots5)\cdot10^{-3}$ Torr). However, for the coatings obtained from the Ti-32Cr cathode in the filtered flow (see Fig. 3 (2)), in contrast to the direct flow, the minimum on the curve is determined with a shift towards low nitrogen pressure of almost one order of magnitude. For the Ti-23Cr cathode (see Fig. 3 (1)), the same minimum is less pronounced, but, as in the case of the unfiltered flow, it is shifted even further toward low nitrogen pressure.

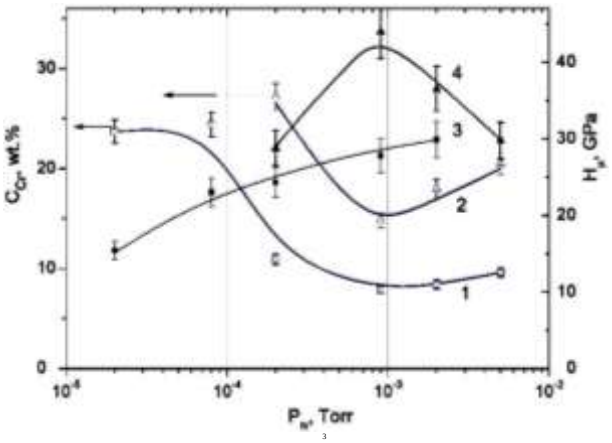

Fig. 3. Relative chromium content (1, 2) and microhardness (3, 4) of Ti-Cr-N coatings obtained from Ti-23Cr (1, 3) and Ti-32Cr (2, 4) cathodes using a filter as a function of N_2 pressure

As can be seen in Fig. 3, the microhardness curve (4) also has an extreme character, where the position of the maximum (~ 40 GPa) corresponds to the minimum of the chromium concentration (2). For coatings with a lower Cr content (3), the microhardness versus pressure has a monotonically increasing character, which corresponds to a prolonged minimum for the Cr concentration curve (1).

Thus, a significant increase in microhardness H_μ up to ~ 40 GPa for Ti-Cr-N coatings obtained from the filtered flow, which is manifested with an increase in nitrogen pressure in the range of $3 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ Torr, is due, as for the direct flow, to the depletion of the Cr component of the coating. When the pressure is increased in the range from $1 \cdot 10^{-3}$ to $5 \cdot 10^{-3}$ Torr, there is a gradual increase in C_{Cr} accompanied by a decrease in H_μ to a value of ~ 30 GPa. Such changes in microhardness are obviously due to the restructuring of the structure and/or phase composition of the coatings.

The extreme nature of the $C_{Cr} = f(P_{N2})$ and $H_\mu = f(P_{N2})$ is determined by the mechanisms operating during the plasma chemical synthesis on the substrate surface: the selective sputtering of nitride coating components by an incoming particle stream and the formation of nitride compounds with different resistance to sputtering.

As can be seen from Table 1, the values of Cr concentration measured by X-ray energy dispersive microanalysis for different nitrogen pressures agree with the result shown in the graph of Fig. 3 (2) within the error of the methods. With an increase in nitrogen pressure in the operating range from $9 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ Torr, the concentration of Cr in the coating increases by about 6.5 wt.%, Ti decreases by 7.5 wt.%, and N_2 increases by 1 wt.%. Thus, the table shows that titanium sputtering is preferred over chromium sputtering as the pressure increases.

Table 1

Elemental concentrations in Ti-Cr-N coatings deposited at different nitrogen pressures (cathode Ti-32Cr, filtered)

No.	Coating	C_{Ti}	C_{Cr}	C_{N2}
		wt.%	wt.%	wt.%
1	$P = 9 \cdot 10^{-4}$ Torr	70.9	17.4	11.7
2	$P = 5 \cdot 10^{-3}$ Torr	63.3	23.9	12.8

The phase composition of Ti-Cr-N coatings deposited from cathodes with different chromium additive contents at two fixed nitrogen pressures ($P_{N2} = 9 \cdot 10^{-4}$ and $P_{N2} = 5 \cdot 10^{-3}$ Torr) was investigated by XRD analysis. The diffractograms of the coatings are shown in Fig. 4, and Table 2 shows the results of their analysis. The data presented in the figure correspond to the coatings obtained both in the direct flow (left column) and with the use of plasma filtration from the droplet component (right column).

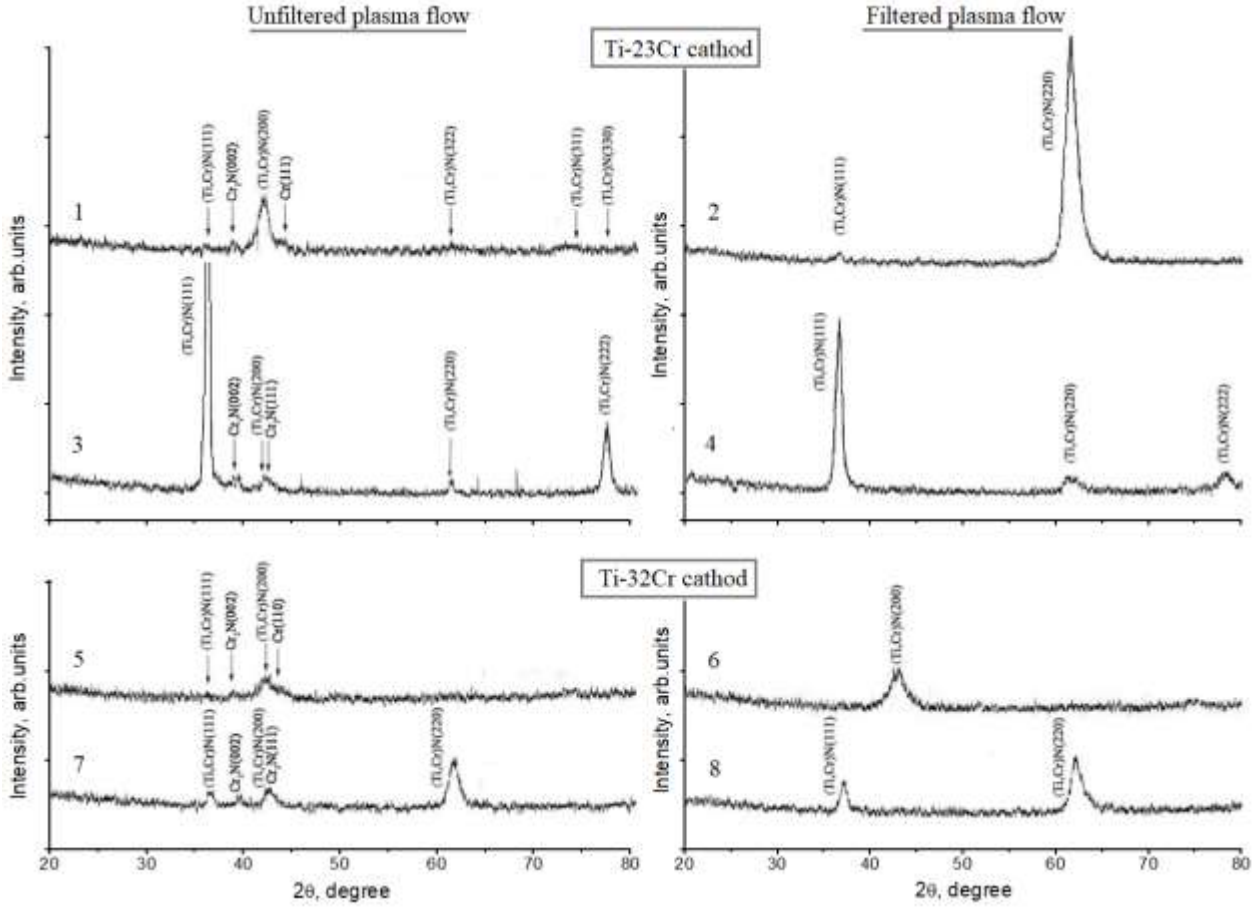

Fig. 4. Diffractograms of Ti-Cr-N coatings deposited in direct and filtered plasma flows at different nitrogen pressures: 1–4 – Ti-23Cr cathode; 5–8 – Ti-32Cr cathode; 1, 2, 5, 6 – $P_{N2} = 9 \cdot 10^{-4}$ Torr; 3, 4, 7, 8 – $P_{N2} = 5 \cdot 10^{-3}$ Torr

In all the coatings studied (see Fig. 4 and Table 2), the main crystalline phase is a cubic solid solution of (Ti,Cr)N with a NaCl-type structure. Furthermore, in the diffractograms of the coatings deposited from the direct flow, in addition to the (Ti,Cr)N lines, weak and broad lines are detected near 40 and 43 degrees. These are most likely lines (002) and (111) of the $(Cr,Ti)_2N$ solid solution, a phase with a lower nitrogen content based on a Cr_2N compound with a hexagonal lattice (JCPDS [35-0803]). In addition, the diffractograms of the coatings obtained at a low pressure of $9 \cdot 10^{-4}$ Torr show a weak line near 44.5 degrees. This is most likely the line of chromium – (110) Cr (JCPDS [19-0323]). Since the $(Cr,Ti)_2N$ and Cr lines are not detected in the diffractograms of the coatings obtained by filtration, these phases should be attributed to the droplet fraction of the coatings.

Table 2

Results of X-ray diffraction analysis of Ti-Cr-N

No.	Composition of the cathode	P_{N_2}, Torr	Filter	Lattice parameter (Ti,Cr)N, nm	Crystallite size, nm	Orientation	Traces of other detected phases
1	Ti-23Cr	$9\cdot10^{-4}$	-	0.424	9	[100]	$(Cr,Ti)_2N$; Cr
2			+	0.429	7	[110]	
3		$5\cdot10^{-3}$	-	0.424	25	[111]	$(Cr,Ti)_2N$
4			+	0.426	14	[111]	
5	Ti-32Cr	$9\cdot10^{-4}$	-	0.423	8	[100]	$(Cr,Ti)_2N$; Cr
6			+	0.426	6	[100]	
7		$5\cdot10^{-3}$	-	0.424	9	[110]	$(Cr,Ti)_2N$
8			+	0.426	8	[110]	

As can be seen from Table 2, the values of the lattice parameter of (Ti,Cr)N nitride are in the range 0.423…0.429 nm, which is close to the value of the parameter characteristic for the stoichiometric TiN phase – 0.4242 nm (JCPDS [38–1420]) and slightly higher than the value for the CrN phase – 0.4140 nm (JCPDS [11–0065]). Chromium has unlimited solubility in the TiN crystal lattice and forms a continuous series of solid solutions. The period of the crystal lattice of the (Ti,Cr)N solid solution in the coatings varies between the values of the TiN and CrN parameters depending on the ratio of metal components according to the Wegard rule, as observed in [18]. In these experiments, slightly overestimated values of the (Ti,Cr)N lattice parameters were obtained, since the influence of residual compressive stresses formed in the coatings is not taken into account [19]. It can be seen that the value of the period of the (Ti,Cr)N lattice is higher in the case of filtration than in the case of direct flow, which is mainly due to the lower chromium content and the higher stress level caused by the more intense ion bombardment of the growth surface. The size of the crystallites in the coatings is in the range of 6…25 nm, and filtration leads to crushing of the structure

An important fact characterizing the structural state of the coatings is the number and intensity of the lines of the (Ti,Cr)N phase. For samples No. 3 and 4, obtained using a Ti-23Cr cathode at an elevated nitrogen pressure of $P = 5\cdot10^{-3}$ Torr, the lines are the most intense and narrow, indicating a well-formed crystal structure. In direct flow deposition (sample No. 3), the crystallite size for nitride is 25 nm. A strong axial texture is formed in the films with the [111] axis in the direction normal to the film surface. The use of separation (sample No. 4) does not lead to dramatic changes in the structure. The predominant orientation of [111] remains unchanged but is less pronounced and the size of the crystallite is reduced to 14 nm.

When using a cathode with a higher chromium content, Ti-32Cr (samples No, 5–8), the intensity of the (Ti,Cr)N lines in the diffractograms decreases and their width increases, indicating a decrease in the quantity and quality of crystalline cubic nitride and a high probability of the presence of X-ray amorphous phases in the coatings. A similar effect is observed for the Ti-23Cr cathode when the nitrogen pressure is reduced to $9\cdot10^{-4}$ Torr (sample No. 1). Apparently, this is due to the fact that the affinity of chromium for nitrogen is much lower than that of titanium, and the increased chromium content in the deposition stream or the low nitrogen pressure in the working volume leads to conditions where the amount of nitrogen in the coating is insufficient to form a sufficiently perfect single phase crystal structure. In these coatings, a change in the predominant orientation of the nitride grains to [100] or [110] is observed. The use of plasma filtration, even at low pressure, favors crystallization (sample No. 2) and the formation of a nanostructure with a strong texture [110]. It is known that for coatings based on Ti-N and Ti-Al-N systems, this structure provides high resistance to various types of wear [14, 20].

The results obtained from the study of Ti-Cr-N coatings are in good agreement with the existing literature data on the effect of deposition parameters on the composition, structure and hardness of vacuum arc coatings based on transition metal nitrides. With increasing nitrogen pressure in the vacuum chamber, changes in elemental composition and transitions between amorphous and nanocrystalline structures have also been observed for Ti-Si-N, Ti-Al-N, and Ti-Al-Si-N coatings [19, 21, 22]. For each system, there are intervals of nitrogen pressure in the vacuum chamber that, depending on the potential, ensure the synthesis of coatings with nanocrystalline cubic structure (such as NaCl) and close to stoichiometric nitrogen content, which have high hardness and thermal stability. However, it should be noted that the combination of components in the composition of coatings based on Ti-Cr-N and Ti-Si(Al)-N systems has fundamental differences. Chromium has unlimited solubility in the TiN crystal lattice and forms a continuous series of solid solutions. The ability of Si and Al to dissolve in the TiN lattice depends largely on the synthesis conditions. In such coatings, a nanocomposite structure with nanocrystalline grains and strong thin amorphous layers between them is formed under certain conditions due to the decomposition of the supersaturated solid solution. For Ti-Cr-N coatings, the structural changes between the amorphous crystalline and nanocrystalline structure are largely due to the lack of nitrogen in the coatings, both at low and too high nitrogen pressure in the vacuum chamber, similar to Ti-N coatings [19]. In addition, under deposition conditions that ensure the formation of crystalline TiN, Cr-N coatings may have a less perfect crystal structure [18] or contain phases with lower nitrogen content [23]. Under such conditions, a higher titanium content in the cathode facilitates the

interaction with nitrogen and stabilizes the crystalline phase.

The formation of texture in coatings deposited from streams of energetic ions is considered in the context of stresses and is related to the desire to minimize the free energy of the system, which consists of strain energy and surface energy [24]. An important factor in determining the axis of preferred orientation in coatings is not only the energy of the ions forming the coating, but also the ratio of the deposition temperature to the melting point of the nitride (homologous temperature). This is particularly important for Ti-Cr-N coatings because the melting points of TiN and CrN nitrides are significantly different – 2945 and 1720 °C, respectively. The combination of relatively high ionic energy and low homologous temperature leads to texture formation [111]. Increasing the temperature can change the texture to [110] or [100]. The low energy combined with low homologous temperature favors the formation of amorphous phases.

The peculiarity of filter deposition is a sharper dependence of structure on pressure, and a shift of the intervals at which a well-formed crystal structure and texture are formed to lower pressures. These differences are due to the lower deposition rate from the filtered stream, the increased nitrogen activation, and the greater impact of ion bombardment on the growth surface. As the nitrogen pressure increases, the energy of the deposited particles decreases due to scattering off the gas molecules, resulting in a weakening of the bombardment effect [12, 16].

The nature of the dependence of relative chromium concentrations in Ti-Cr-N coatings on nitrogen pressure during deposition is also related to ion bombardment, but the interaction of plasma components with nitrogen is no less important. This is especially true for the selective sputtering of nitride coating components. Since the affinity of titanium for nitrogen is higher than that of chromium, the optimum nitrogen pressure range that promotes the formation of stoichiometric nitride for TiN is shifted to lower values compared to CrN. A gradual decrease of the Cr concentration in the coatings in the range of nitrogen pressures 10^{-4}…10^{-3} Torr may be due to the more active formation of Ti-N bonds. A part of the chromium component, which does not have strong bonds in the nitride compound, is sprayed more actively. With an increase in pressure in the range of $(1…5)\cdot10^{-3}$ Torr, the increase in Cr concentration in coatings is due to the preferential atomization of the titanium component under conditions where Cr-N bonds are better formed. In this case, the resistance to sputtering of Cr in the coating is higher than that of Ti. It should be noted that the chromium content in coatings deposited from filtered plasma at a pressure of 10^{-3} Torr under conditions of high-voltage pulsed bias potential on the substrate is 1.5 times higher than in the cathode and practically does not change with increasing potential amplitude [18]. This result differs from the data for Ti-Al-N coatings, where a good agreement between the element content in the cathode and the coatings is obtained [14].

The effect of Cr content on the hardness of Ti-Cr-N coatings is not clear. It is known that the hardness of coatings depends on many factors, including not only the ratio of metal components, but also the nitrogen content, the substructure, the density of crystal defects, and the level of residual stresses [25]. Changes in pressure and potential parameters alter the entire range of coating properties to which hardness is sensitive. The high hardness of the obtained Ti-Cr-N coatings (> 30 GPa) is mainly due to the nanostructure, and an additional increase in hardness of the coatings deposited using a cathode with a higher Cr content is associated with the effect of solid solution hardening.

CONCLUSIONS

1. The elemental composition, mechanical properties, and structure of Ti-Cr-N coatings deposited at a wide range of nitrogen pressures from unfiltered and filtered vacuum arc plasma streams from Ti-Cr alloy cathodes containing 23 and 32 wt.% chromium were investigated.

2. It was found that the dependence of $C_{Cr} = f(P_{N2})$ in the obtained nanostructured Ti-Cr-N coatings is characterized by extreme behavior with a minimum near $1\cdot10^{-3}$ Torr, which correlates with the extreme behavior of microhardness $H_\mu = f(P_{N2})$, but with a maximum at this pressure. The maximum microhardness is shifted to lower nitrogen pressures when using plasma filtration or a cathode with a lower Cr content.

3. The decrease of the Cr concentration in the coating in the pressure range up to $1\cdot10^{-3}$ Torr is due to the selective sputtering of nitride layers by an incoming ion stream. Since the affinity of titanium for nitrogen is higher than that of chromium, the formation of Ti-N compounds occurs first in the condensation zone under nitrogen-deficient conditions. Most of the chromium, which does not have strong bonds in the nitride compound, will sputter more.

4. With an increase in nitrogen pressure in the range of $(1…5)\cdot10^{-3}$ Torr, an increase in the concentration of Cr in the coatings is observed, which is due to the predominant sputtering of Ti. An increase in C_{N2} affects the rearrangement of the orientation and the formation of a polycrystalline structure. Under these deposition conditions, the resistance to sputtering of Cr in the nitride compound is higher than that of Ti.

5. In the coatings deposited at a pressure of $9\cdot10^{-4}$…$5\cdot10^{-3}$ Torr, the main phase is a nanocrystalline cubic solid solution of (Ti,Cr)N with a NaCl-type structure. Coatings deposited from unfiltered vacuum arc plasma contain a small amount of Cr and $(Cr,Ti)_2N$ phases. Increasing the chromium content in the cathode from 23 to 32 wt.% leads to a decrease in the quantity and quality of nanocrystalline (Ti,Cr)N nitride and to the formation of amorphous phases. The use of a filter allows to effectively separate the droplet component from the plasma stream and to obtain coatings with reduced surface roughness. It should be noted that filtration helps to reduce the chromium content and the size of nitride crystallites due to more intense ion bombardment of the growth surface.

6. Deposited nanostructured Ti-Cr-N coatings with 20 wt.% chromium content and high mechanical properties (up to 35 GPa) can be used to protect

structural materials in power generation and other nuclear industries.

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МЕХАНІЧНІ ХАРАКТЕРИСТИКИ ТА СТРУКТУРА ВАКУУМНО-ДУГОВИХ Ti-Cr-N-ПОКРИТТІВ

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Досліджено елементний склад, механічні властивості та структуру Ti-Cr-N-покриттів, осаджених у широкому діапазоні тисків азоту з потоків нефільтрованої та фільтрованої вакуумно-дугової плазми сплавних катодів Ti-Cr, що містять 23 та 32 ваг.% Cr. З'ясовано, що для різних режимів осадження залежності вмісту Cr у покриттях від тиску азоту мають мінімум поблизу $1\cdot10^{-3}$ Торр, що корелює з максимумом твердості H_μ. При застосуванні фільтрації плазми або катода з меншим вмістом Cr максимум твердості зміщується у бік менших тисків азоту. Обговорюються механізми, що визначають елементний склад покриттів. У покриттях, осаджених при тиску $9\cdot10^{-4}$…$5\cdot10^{-3}$ Торр, основною фазою є нанокристалічний кубічний твердий розчин (Ti,Cr)N зі структурою типу NaCl. Збільшення вмісту хрому в катоді сприяє формуванню аморфно-кристалічної структури. Фільтрація дозволяє ефективно виділяти з плазмового потоку крапельну складову і отримувати покриття зі зниженим рівнем шорсткості поверхні. Отримано наноструктурні Ti-Cr-N-покриття з високими механічними характеристиками (H_μ ~ 35 ГПа), що містять ~ 20 ваг.% Cr, які можуть бути використані для захисту конструкційних матеріалів у енергетичному машинобудуванні та інших галузях атомної енергетики.