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PHYSICS OF RADIOTECHNOLOGY
AND ION-PLASMA TECHNOLOGIES

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**STRUCTURE AND MECHANICAL PROPERTIES OF MULTILAYER
COATINGS (TiAlCrY)N/ZrN**

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Multiperiodic nitride coatings (TiAlCrY)N/ZrN with different layer thicknesses are formed by vacuum-arc evaporation in a nitrogen atmosphere (0.2...0.6 Pa) of two targets, TiAlCrY and Zr. The targets were located along one straight line at equal distances from the perpendicular axis on which the substrates were placed. The rotation of the axis with the substrates was carried out either continuously or with a fixed delay at the evaporators. The duration of the process was chosen so that the total thickness of the coating (total thickness of the bilayers) was 10...11 μm . The effect of nitrogen pressure and modulation period on the structural-phase state, elemental composition, and mechanical properties of multilayer coatings has been studied. An increase in the partial pressure of nitrogen and, consequently, its content in the coating leads to an increase in hardness. Reducing the thickness of the layers in the coatings increases the adhesive strength of the coatings and does not have a significant effect on the microstresses in the coating.

INTRODUCTION

The development of new coatings for cutting tools as well as for the protection of machine parts operating in conditions of intense wear, elevated temperatures and in aggressive environments is an important task of modern materials science. Currently one of the important directions for improving the performance of coating materials is the creation of multilayer structures with a nanoscale size of layers.

A significant increase in microhardness with an increase in the number of layers in multilayer TiN/NbN, TiN/ZrN, and TiN/CrN nanostructured coatings with the total film thickness of about 2 μm was found earlier [1]. A similar hardening effect in multilayer coatings was found also in the ZrN/CrN [2, 3] and MoN/CrN [4] systems.

In this case, the volume fraction of the interfaces increases in the structure of the coating material. It predetermines their high hardness simultaneously with the increase in wear resistance. Nanostructured components significantly increase the strength properties of the coating as a whole.

The creation of multilayer coatings with a nanoscale size of layers, the elucidation of the laws governing the formation of structural phase states and the nature of their unique strength properties is an important scientific and technological task.

The paper presents the results of experimental studies of the laws governing the formation of the phase composition and structural state of multilayer nitride coatings based on the (TiAlCrY)N and ZrN system, obtained by vacuum arc evaporation from a material of

two targets deposited on a rotating substrate in a reactive nitrogen atmosphere. Studies have also been conducted on the effect of technological parameters of coating on their mechanical properties.

METHODS OF PREPARATION AND EXAMINATION OF THE SAMPLES

Coatings were obtained by the vacuum-arc method from two targets obtained by the EBT method. The first one was $\text{Ti}_{0.57}\text{Al}_{0.36}\text{Cr}_{0.06}\text{Y}_{0.01}$, the second one was Zr. Samples of the size (15x15x2.5 mm) of 12X18H9T steel ($R_a = 0.09 \mu\text{m}$) were selected as substrates for the deposition of coatings. The technological parameters of the deposition are shown in Table 1. 5 Series of coatings were applied: 1 series – deposition was carried out from two sources with continuous rotation of the fixed samples at a speed of 8 rpm, which made it possible to obtain a layer about 12...15 nm thick with a total coating thickness ~ 10...11 μm ; 2–5 series – multilayer coatings obtained by evaporation of two materials with a fixed substrate stopping time near the target for 10, 20, 40, and 80 s (for each of the two targets). A constant negative potential of $U_b = -200 \text{ V}$ was applied to the substrates during the process of layer deposition.

The study of the elemental composition of the samples was carried out by analyzing the spectra of characteristic X-ray radiation, the surface morphology was studied by SEM (FEI Nova NanoSEM 450). The phase-structural state was studied using DRON-4-07 diffractometer in $\text{Cu-K}\alpha$ radiation.

The Revetest scratch tester (CSM Instruments) was used to determine the adhesion/cohesive strength of the

coatings and the resistance to scratching. Scratches were applied to the sample surface with a coating using a Rockwell C-type diamond spherical indenter with a radius of 200 μm under continuously increasing load and physical parameters like acoustic emission, friction

coefficient, and indenter penetration depth were recorded. Microhardness measurements of the coatings were carried out by a 402MVD Instron Wolpert Wilson Instruments hardness tester ($\text{HV}_{0.1}$, $P = 100 \text{ g}$).

Table 1

Physical and technological parameters of (TiAlCrY)N/ZrN coating deposition

Material	I_A , A	I_{fc} , A	U_b , V	P_N , Pa	τ , h	Note
1. (TiAlCrY)N/ZrN	85/85	0.4/0.4	-200	0.58	1.5	Continuous rotation
2. (TiAlCrY)N/ZrN	85/85	0.4/0.4	-200	0.58	1.5	Interval 80 s, 67 layers
3. (TiAlCrY)N/ZrN	85/85	0.4/0.4	-200	0.21	1.5	Interval 10 s, 528 layers
4. (TiAlCrY)N/ZrN	85/85	0.4/0.4	-200	0.39	1.5	Interval 40 s, 134 layers
5. (TiAlCrY)N/ZrN	85/85	0.4/0.4	-200	0.39	1.5	Interval 20 s, 266 layers

Legend: I_A – arc current; I_{fc} – focusing coil current; U_b – potential displacement supplied to the substrate; P_N – the partial pressure of the reaction gas – nitrogen; τ – deposition time.

RESULTS AND DISCUSSION

Fig. 1 shows images of the surface (above), as well as cross sections of samples from series 1, 2, and 5. Electron microscopy data indicate that coatings based on (TiAlCrY)N/ZrN are characterized by a dense structure and alternating layers have a high degree of

laminary. The modulation period (total thickness of two alternating layers) for samples of different series is: 1 series – 30 nm, 2 series – 400 nm, 3 series – 35 nm, 4 series – 195 nm, 5 series – 95 nm. The total thickness of the coatings was for all samples 10...11 μm .

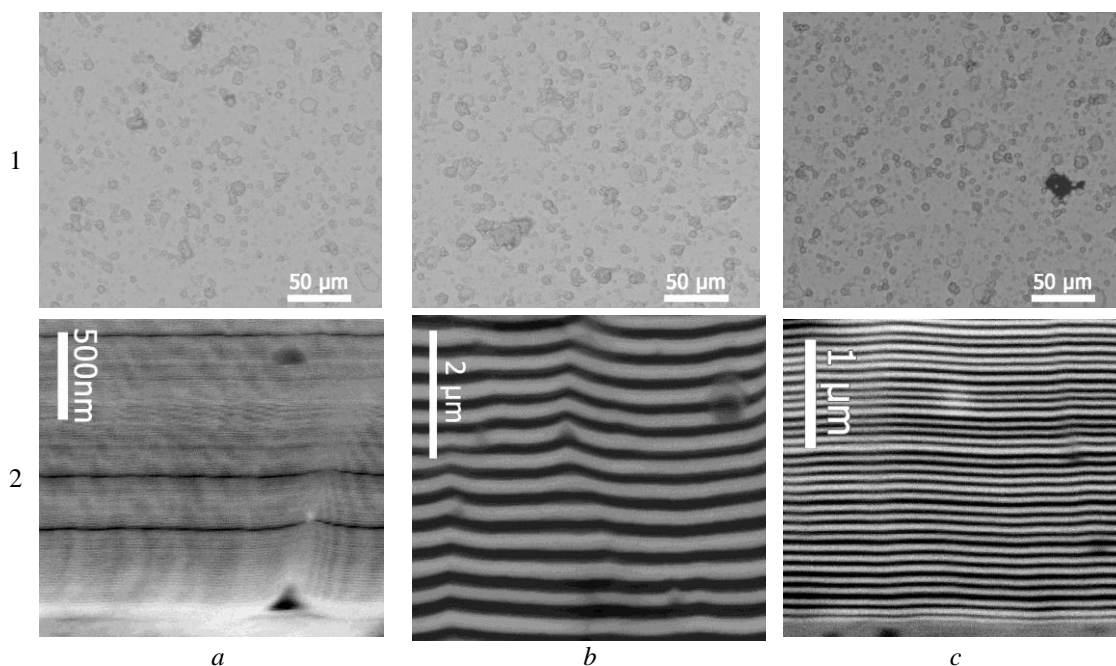


Fig. 1. The structure (SEM) of the multilayer coating (TiAlCrY)N/ZrN: a – series 1 (continuous rotation), b – series 2 (67 layers), c – series 5 (266 layers); 1 – surfaces, 2 – side sections

Fig. 2 shows the energy dispersion spectra of (TiAlCrY)N/ZrN nitride coatings.

The results of the elemental analysis of single-layer and multilayer coatings are also shown in Tabl. 2.

It is seen that for all series of coatings obtained at $U_b = -200 \text{ V}$, all the elements that are part of the cathode except Y are detected in the composition, and the nitrogen content varies depending on the coating parameters from 38 to 50%. Elemental analysis shows a strong difference in the composition of the coatings from the composition of the target, especially in

elements such as Cr and Y. This is due to the fact that for these elements, which are the most refractory of the target, the partial vapor pressure during the spraying process is much less than for Al and Ti. Therefore, their concentration in coatings is lower than in the target. Given that the concentration of Y in the target was about 1%, this element is not observed in the spectrum of coatings, since its concentration is most likely lower than 0.1%, which is the detection limit of this technique. The observed depletion of Ti coatings may be due to

ballistic sputtering, in which light weakly bound atoms are predominantly removed from the surface.

The results of X-ray studies of the structural and phase composition of the samples are shown in Figs. 3 and 4.

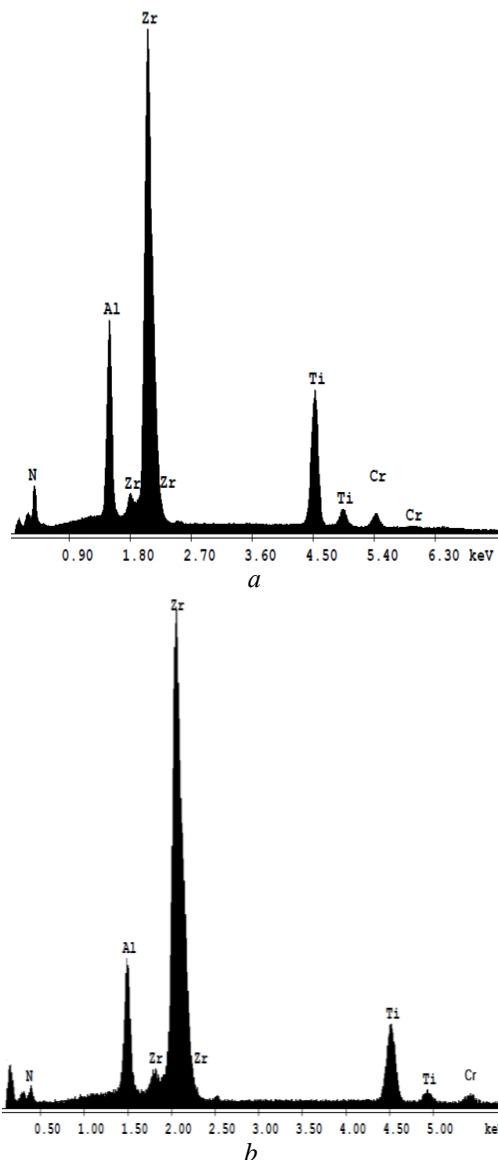


Fig. 2. Energy dispersive spectra of (TiAlCrY)N/ZrN coatings obtained under the following deposition modes: a – $P = 0.58$ Pa, $U_b = -220$ V; b – $P = 0.39$ Pa, $U_b = -220$ V

Table 2

Elemental analysis data of coated samples (in accordance with Tabl. 1)

No.	Elements included in coatings, at.%				
	N	Al	Zr	Ti	Cr
1	50.1	12.8	22.7	13.0	1.4
2	38.7	13.6	33.3	12.5	1.9
3	43.3	13.6	22.2	19.5	1.4
4	44.0	13.3	22.0	19.4	1.3
5	44.9	11.7	27.9	13.7	1.8

Analysis of coated samples obtained with continuous rotation (series 1) showed the presence of two phases – TiAlCrYN and ZrN nitrides with an FCC lattice; lines from the substrate are also present. The

lattice parameter of the ZrN nitride is $a = 4.590$ Å, the CSR size of this phase is $D = 5.4$ nm at the level of microdistortion $\epsilon = 4.79 \cdot 10^{-3}$. The lattice parameter of the complex nitride (TiAlCrY)N is $a = 4.203$ Å. The substructural characteristics of this phase could not be determined. The intensity distribution of diffraction lines from both phases corresponds to a weakly textured state.

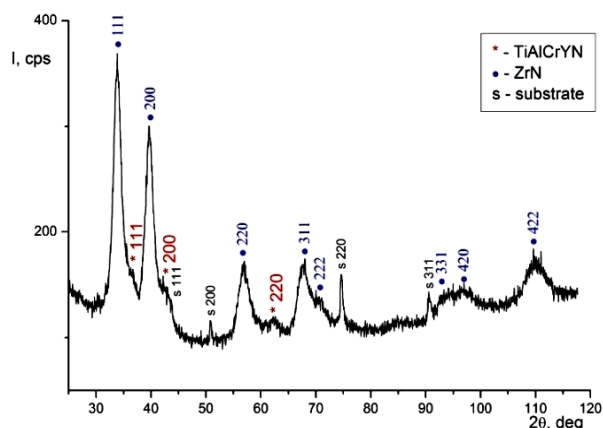


Fig. 3. Plot of the diffraction spectrum (TiAlCrY)N and ZrN obtained by continuous rotation (series 1)

Analysis of samples (TiAlCrY)N/ZrN with layer-by-layer sputtering and different numbers of layers (Fig. 4) showed the presence of two nitrides with an FCC lattice (ZrN and TiAlCrYN) in all samples.

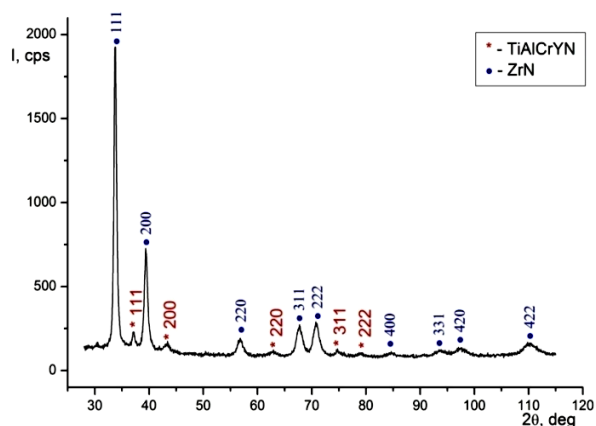


Fig. 4. Plot of the diffraction spectrum (TiAlCrY)N and ZrN obtained by rotating the substrate with a stopping time near the target is 40 s (series 4)

The intensity distribution of lines in the diffraction patterns of these samples indicates the presence of the (111) texture, that is, the grains of both nitrides has preferential orientation {111} crystallographic planes parallel to the surface of the coatings. It is also worth noting that with an increase in the number of layers, the size of OCD of nitrides decreases (as for ZrN nitride, the size of OCD in sample No. 2 (67 layers) was $D = 20.2$ nm, and in sample No. 3 (528 layers), the size of OCD decreased to $D = 13.6$ nm). It is also worth noting that the change in the number of layers has practically no effect on the lattice parameters of nitrides (within the limits of measurement error, Tabl. 3).

The effect of nitrogen concentration in the coating on the hardness is confirmed by the data of Tabl. 4.

Table 3
Phase composition and structural characteristics
of (TiAlCrY)N and ZrN coatings

No. series	Phase	Lattice parameter, nm	OCD size D , nm	Microdistortions, ϵ
1	ZrN	0.4590	5.4	$4.79 \cdot 10^{-3}$
	(TiAlCrY)N	0.4203	–	–
2	ZrN	0.4607	20.2	$3.91 \cdot 10^{-3}$
	(TiAlCrY)N	0.4175	24.1	$3.4 \cdot 10^{-3}$
3	ZrN	0.4607	13.6	$4.09 \cdot 10^{-3}$
	(TiAlCrY)N	0.4183	9.1	$2.46 \cdot 10^{-3}$
4	ZrN	0.4609	18.2	$4.39 \cdot 10^{-3}$
	(TiAlCrY)N	0.4183	19.9	$3.28 \cdot 10^{-3}$
5	ZrN	0.4607	17.0	$4.21 \cdot 10^{-3}$
	(TiAlCrY)N	0.4183	12.2	$3.26 \cdot 10^{-3}$

Table 4
The effect of nitrogen concentration
on the microhardness of the coating

No. series	Nitrogen content, at. %	Microhardness HV, GPa
1	50.1	49.0
2	38.7	31.0
3	43.4	27.3
4	45.8	45.0
5	44.9	45.7

The results of the study of the microhardness of the coatings indicate that the partial pressure of nitrogen, which affects the formation of the phase composition, has a significant effect on its hardness.

To determine the adhesive/cohesive strength of coatings, resistance to scratching and used the method of scribing. To interpret the results of testing the coatings, we analyzed the values of critical loads of L_C , which allow us to trace the entire process of destruction of coatings: L_{C1} denotes the moment of the first chevron crack appearance; L_{C2} – the moment of chevron cracks formation on the bottom of the scratch; L_{C3} – destruction is cohesive-adhesive in nature; L_{C4} – local peeling of the coating areas; L_{C5} – plastic abrasion of the coating to the substrate, loss of adhesive strength. Tabl. 5 shows the results of adhesive tests of coating samples based on (TiAlCrY)N and ZrN.

Table 5
The results of the adhesive testing of nitride coatings

No. series	P_N , Pa	L_{C1}	L_{C2}	L_{C3}	L_{C4}	L_{C5}
1	0.58	29.96	38.44	48.72	63.54	79.08
2	0.58	28.17	45.36	52.3	57.33	74.33
3	0.21	24.73	35.09	43.22	63.79	81.46
4	0.39	25.77	38.21	46.34	56.36	71.67
5	0.39	27.21	35.59	45.61	58.76	81.7

As can be seen from the results of studies of adhesive strength, the maximum load at which full wear of the coating occurs (L_{C5}) increases with decreasing layer thickness. The value of the load at which the first chevron cracks are formed depends on the following factors: nitrogen content, as well as Zr content. With an increase in the zirconium content, the viscosity of the coatings increases, which leads to an increase in the load required for the formation of the first cracks. In coatings containing more nitrogen and less Zr, the formation of the first cracks occurs at a lower load, while complete abrasion occurs at a higher one.

CONCLUSION

Multilayer nitride coatings (TiAlCrY)N/ZrN with different thickness of alternating layers were obtained by vacuum-arc evaporation from a material of two targets with deposition on a rotating substrate in a reactive nitrogen atmosphere.

Investigations of elemental composition of the coatings were carried out. It was found that with an increase in the partial pressure of nitrogen, its content in the coating increases up to 50 at.%, which leads to an increase in hardness up to 49 GPa.

Reducing the thickness of the layers in the coatings leads to a decrease in the size of the OCD, which, in turn, increases the adhesive strength of the coatings (the beginning of the destruction – with a load of 30 N). Changing the thickness of the layers, however, does not significantly affect the parameters and the level of microstrain of the crystal lattices of the coating material.

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СТРУКТУРА И МЕХАНИЧЕСКИЕ СВОЙСТВА МНОГОСЛОЙНЫХ ПОКРЫТИЙ (TiAlCrY)N/ZrN

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Многопериодические нитридные покрытия (TiAlCrY)N/ZrN с различной толщиной слоев сформированы вакуумно-дуговым испарением в среде азота (0,2...0,6 Па) двух мишеней – TiAlCrY и Zr. Мишени располагали вдоль одной прямой на равных расстояниях от перпендикулярной оси, на которой располагали подложки. Вращение оси с подложками осуществляли либо непрерывно, либо с фиксированной задержкой у испарителей. Длительность процесса выбирали так, чтобы общая толщина покрытия (суммарная толщина слоев) составляла 10...11 мкм. Проанализировано влияние давления азота и периода модуляции на структурно-фазовое состояние, элементный состав и механические свойства многослойных покрытий. Увеличение парциального давления азота и вследствие этого – его содержания в покрытии приводит к увеличению твердости. Уменьшение толщины слоев в покрытиях увеличивает адгезионную прочность покрытий и не оказывает существенного влияния на микронапряжения в покрытии.

СТРУКТУРА І МЕХАНІЧНІ ВЛАСТИВОСТІ БАГАТОШАРОВИХ ПОКРИТТІВ (TiAlCrY)N/ZrN

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Багатоперіодичні нітридні покриття (TiAlCrY)N/ZrN з різною товщиною прошарків сформовані вакуумно-дуговим випаровуванням в азоті (0,2...0,6 Па) двох мішеней – TiAlCrY і Zr. Мішені розташовували на одній прямій на рівних відстанях від перпендикулярної осі, на якій кріпилися підкладки. Обертання осі з підкладками здійснювали або безперервно, або з фіксованою затримкою у випарників. Тривалість процесу вибирали так, щоб загальна товщина покриття (сумарна товщина подвійних прошарків) становила 10...11 мкм. Проаналізовано вплив тиску азоту і періоду модуляції на структурно-фазовий стан, елементний склад і механічні властивості багатошарових покриттів. Збільшення парціального тиску азоту і внаслідок цього – його вмісту в покритті призводить до збільшення твердості. Зменшення товщини шарів у покриттях збільшує адгезійну міцність покриттів та істотно не впливає на микронапруження в покритті.