

INFLUENCE OF LAYER NUMBER AND THICKNESS OF CrAlYN/CrAlYO COATINGS ON PHASE COMPOSITION, STRUCTURE AND PROPERTIES

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The paper deals with CrAlYN/CrAlYO multilayer coatings obtained by the plasma-assisted vacuum-arc deposition onto a WC–8Co alloy substrate. It is investigated how the layer number and thickness of 16- and 32-layer coatings with the thickness of ~240 and ~120 nm, respectively, affect the phase composition, crystal structure parameters, roughness, surface morphology, and physical and mechanical properties. The X-ray diffraction analysis shows that the obtained multilayer coatings have a multiphase structure consisting of nitride CrN and AlN and oxide Cr₂O₃ and AlYO₃ phases. It is found that the roughness of the 32-layer CrAlYN/CrAlYO coating is almost 2 times lower than that of the 16-layer coating. It is shown that the larger number of layers and their lower thickness have a positive effect on physical and mechanical properties of the coatings. The hardness of the 32-layer coating increases by 52%. The synchrotron X-ray diffraction analysis of the 32-layer CrAlYN/CrAlYO coating shows its thermal stability up to ~1020°C during heating in air, while during heating in vacuum, its thermal stability keeps constant up to at least 1500°C.

Keywords: vacuum-arc deposition, multilayer coating, XRD analysis, physical and mechanical properties, synchrotron radiation.

INTRODUCTION

The development of nuclear, aviation, space, and chemical industries, requires the improvement of operational properties of groups of various materials [1, 2]. A special class of heat-resistant materials operate in severe conditions. For example, turbine blades in aircraft engines experience cyclic thermal loads with peak temperatures up to 1500°C in air and subjected to the influence of abrasive dust particles. In spite of the progress in developing heat- and corrosion-resistant materials and coatings [3, 4] for the aviation industry, operating at 1500°C, the range of issues to be solved does not decrease. The use of multilayer coatings with the different layer composition (soft and hard phases) allows to reduce internal stresses and brittleness at sufficiently high hardness [4–6]. As reported in [7], the alternation of layers with different physical and mechanical properties provides a significant change in the properties of multilayer coatings, such as stress concentration and crack propagation, resulting in an increase in the fracture toughness of the coating. In addition, the multilayer structure of coatings, which prevents the crack propagation, reduces the penetration of aggressive medium in the substrate, thereby decreasing wear rate and increasing corrosion resistance. According to Bobzin *et al.* [8], one of the promising multilayer systems is a combination of chromium- and aluminum-based nitrides and oxides. Chromium nitride exhibits a high thermal stability and has rather low coefficient of friction. It is shown that the introduction of chemically active yttrium into CrAlN coatings increases thermal stability and improves physical and mechanical properties [9, 10]. In these cases, yttrium is considered to be an effective inhibitor of diffusion processes

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during oxidation and corrosion attack, due to probably segregation along nitride grain boundaries [9]. Yttrium oxide is even more high-temperature phase than Cr_2O_3 and Al_2O_3 phases [11–13]. It is assumed that combined properties of Cr, Al and Y oxides allow creating composite layers with the higher heat resistance. This combination of nitrides and oxides provides the coating with high hardness and wear resistance along with the resistance to oxidation and other effects of aggressive environment.

The purpose of this work is to synthesize CrAlYN/CrAlYO multilayer coatings and study the influence of the layer number and thickness on their phase composition, crystal structure, roughness, surface morphology, and physical and mechanical properties, including the synchrotron X-ray diffraction analysis of thermal stability during heating in air and vacuum.

MATERIALS AND METHODS

The plasma-assisted vacuum-arc deposition was used for CrAlYN/CrAlYO multilayer coatings on the PPU-1 system (upgraded version of NNV6.6-II) [14] equipped with two electric-arc evaporators with the 80 mm cathode, additional nitrogen-containing plasma source “PINK” with a hot hollow cathode and the additional oxygen-containing plasma source “PIPK” with a cold hollow cathode. The PPU-1 system incorporated a planetary rotating holder with substrates, gas (N_2 and Ar) pumping system *via* the “PINK”, and gas (O_2 and Ar) pumping system *via* the “PIPK”. Electric-arc evaporators with Cr (purity: 99.5%) and AlY (1.5 wt.% Y) cathodes were installed on lateral sides of the working chamber. The “PINK” was placed on the door of the vacuum chamber, while the “PIPK” – on its upper wall. Internal chamber walls made of stainless steel served as the anode for metal and gas plasma sources. The “PINK” was used to clean the substrate surface by ion bombardment, substrate heating, and additional ionization of the gas plasma component, which affected the growing layers, and the metal plasma component. Cylindrical samples of a diameter 10 mm and 7 mm thick made of the WC–8Co alloy were used for the coating deposition. Prior to the coating deposition, the substrates were polished and cleaned ultrasonically in gasoline and acetone. During the deposition process, the substrate holder rotated around the central axis of the vacuum chamber at a 200 mm from it and around its axis. Prior to the experiment, the vacuum chamber was evacuated by a turbomolecular pump TMN-1000 to a limit pressure of 10^{-3} Pa. The working gas argon was fed through the “PINK” source; the working pressure was 0.3 Pa. In igniting the gas discharge and applying -600 V bias potential to the holder, substrates were heated up to $\sim 500^\circ\text{C}$. After the ionic-bombardment cleaning and chemical activation of the substrate surface, discharges were ignited in electric-arc evaporators, and the coating was deposited onto the substrate. Prior to the synthesis of the multilayer coating, the substrate was coated in argon with the adhesive chromium layer 100 nm thick. The obtained coatings consisted of 16 and 32 alternating layers CrAlYN and CrAlYO with the thickness of 240 and 120 nm, respectively. Such layers were obtained by a successive pumping of gaseous mixtures $\text{N}_2(80\%) + \text{Ar}(20\%)$ and $\text{O}_2(60\%) + \text{Ar}(40\%)$. The working pressure was 0.4 Pa for the synthesis of nitride layers and 0.6 Pa for oxide layers. The negative bias voltage was 50 V during the deposition of multilayer coatings. The “PINK” source current was 75 A for the CrAlYN layer deposition, and 25 A for the CrAlYO layer deposition. The “PIPK” source current was 55 A for the CrAlYO layer deposition. The current of the electric-arc evaporators with Cr and AlY cathodes was 90 and 55 A, respectively. The total deposition time and temperature were 128 min and 300 to 320°C . The thickness of as-deposited coatings was ~ 3.8 μm .

The phase composition of coatings was investigated on the XRD-7000S X-ray Diffractometer from Shimadzu. Measurements were conducted using copper radiation. The analysis of the phase composition was performed using PDF4+ database, PowderCell 2.4 software, and PowderCell Rietveld program. A contact profilometer (Tribotechnic, France) was used to measure the surface roughness. Nanohardness and elastic modulus of multilayer coatings were tested on an NHT-S-AX-000X Nanohardness Tester (CSEM, Switzerland) fitted with a Berkovich three-sided pyramid indenter, at the maximum indentation load of 10 mN. The NHT-S-AX-000X measured the hardness by Oliver and Pharr method. A DMI8M Inverted Microscope (Leica Microsystems, Germany) was used to investigate the coating surface. The thermal resistance was studied for the 32-layer CrAlYN/CrAlYO coating deposited onto the $12 \times 5 \times 0.5$ mm^3 substrate made of the WC–8Co alloy. The experiment was conducted on a diffractometer of the “Precise Diffractometry II” beamline mounted on channel No. 6 of the VEPP-3 storage ring in Siberian Synchrotron and Terahertz Radiation Centre of the Budker Institute of Nuclear Physics SB RAS, Novosibirsk, Russia. The substrate was heated in the HTK

TABLE 1. Phase Composition and Crystal Structure Parameters of CrAlYN/CrAlYO Multilayer Coatings

Coatings	Detected phases	Phase content, %	CSR size, nm	$\Delta d/d \cdot 10^{-3}$
16 layers	WC	18	46	1.2
	Cr ₂ O ₃	32	18	3
	AlN	<3	–	–
	CrN	49	15	2.2
	AlYO ₃	<3	–	–
32 layers	WC	10	64	2.2
	Cr ₂ O ₃	52	16	3.5
	AlN	11	15	4.2
	CrN	26	19	4.8
	AlYO ₃	<3	–	–

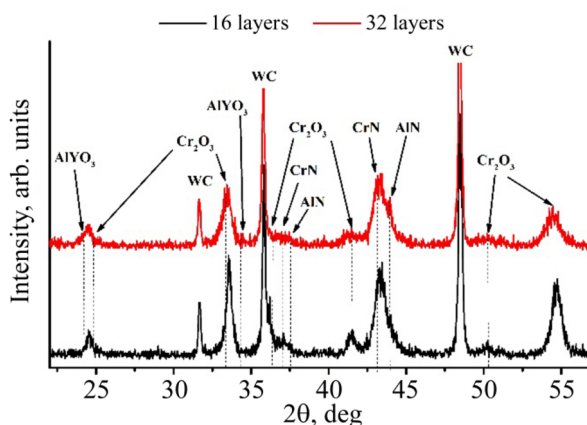


Fig. 1. XRD patterns for CrAlYN/CrAlYO multilayer coatings.

2000 (Anton Paar) high temperature chamber using a platinum heater also served as the substrate holder. The process parameters included 0.172 nm wavelength, 15°C/min heating rate, 30 to 1500°C temperature range. X-ray diffraction (XRD) patterns were recorded by the position sensitive detector OD-3M-350 at the exposure time of 1 min. Fityk (1.3.1) program was used for the obtained data processing.

RESULTS AND DISCUSSION

Figure 1 illustrates XRD patterns obtained for the CrAlYN/CrAlYO multilayer coating. Their phase composition and crystal structure parameters are presented in Table 1. Along with tungsten carbide (substrate), the structure of all coatings consists of CrN and AlN phases having the cubic crystal structure (see Fig. 1). As can be seen from Table 1, the CrN phase content in both coatings notably exceeds the content of the AlN phase. The rhombohedral Cr₂O₃ phase is also present in both coatings. The AlYO₃ phase is observed in much lower amount than the Cr₂O₃ phase. The content of Cr₂O₃ and AlN phases grows respectively from 32 to 52% and from 3 to 11% with increasing number of layers and decreasing coating thickness, while the CrN phase content reduces from 49 to 26%. The size of the coherent scattering region (CSR) ranges between 15 and 19 nm for all detected phases and does not depend on the coating architecture. Microstresses are observed in the crystal lattice of the CrN phase of the 32-layer coating, i.e., $\Delta d/d = 4.8 \cdot 10^{-3}$ according to Table 1.

TABLE 2. Parameters of CrAlYN/CrAlYO Multilayer Coatings

Parameters	16-layer coating	32-layer coating
Roughness R_a/R_z , $\mu\text{m}/\mu\text{m}$	0.063/1.043	0.034/0.433
Nanohardness H , GPa	11.3 ± 1.7	17.2 ± 4.1
Elastic modulus E , GPa	222.9 ± 32.6	257.6 ± 66.3
H/E	0.05	0.07
H^3/E^2	0.03	0.08

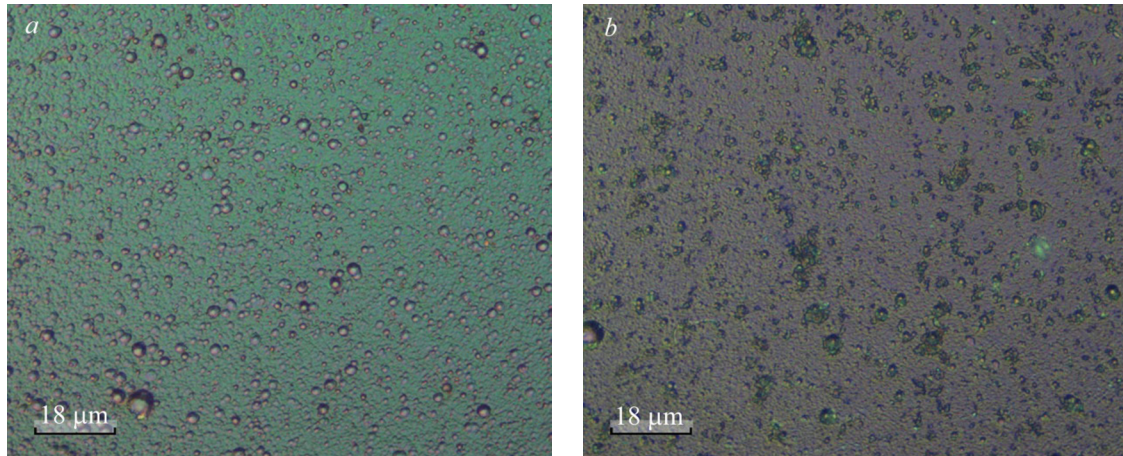


Fig. 2. Optical images of the coating surface: *a* – 16-layer coating, *b* – 32-layer coating.

Table 2 contains measurement results of the surface roughness and physical and mechanical properties of multilayer coatings. One can see that both R_a and R_z roughness parameters of the 16-layer coating are almost 2 times higher than that of the 32-layer coating. These data correlate with the surface of the respective coatings in Fig. 2. The droplet fraction for the 32-layer coating is significantly smaller than for the 16-layer coating. Moreover, not only the droplet fraction, but also the droplet size is smaller for the 32-layer coating than for the 16-layer coating.

Physical and mechanical properties of the coatings were investigated by nanoindentation. Using Oliver and Pharr method and specialized software, the nanohardness (H) and the elastic modulus (E) were determined and summarized in Table 2. The nanohardness of 16- and 32-layer coatings obtained at the same deposition parameters, was 11.3 and 17.2 GPa, respectively. This was due to a two-fold increase in the number of interface boundaries between the layers, which undoubtedly affects the hardness values [15, 16]. In addition, the reduced amount of the droplet fraction in the composition of the 32-layer coating, also affected this parameter. The ratios H/E and H^3/E^2 were considered to be closely related to the elastic and plastic resistance of the coatings [17–19]. From Table 2, one can see that the 32-layer coating possessed improved properties and manifested better tribological properties than the 16-layer coating.

Figure 3 presents a series of XRD patterns illustrating the structural changes across the CrAlYN/CrAlYO coating during heating in air and vacuum followed by cooling to room temperature. It is found that in the initial state, the CrAlYN/CrAlYO multilayer coating consists of WC, Al, CrN, AlN and Cr_2O_3 , AlYO_3 phases. During heating the coated substrate to $\sim 645^\circ\text{C}$ in air, the Al reflection disappears, while at $\sim 1020^\circ\text{C}$, it starts to intensively oxidate and fracture, change its geometry, and XRD patterns strongly distort at 1240°C and disappear at 1300°C . The subsequent cooling to room temperature does not recover XRD patterns. At the substrate heating to $\sim 950^\circ\text{C}$ in vacuum, the Al peak disappears, while in the range from ~ 1210 to 1220°C , the CrN and AlN peaks become more intensive and narrower. The phase composition of the coating does not change until 1500°C followed by successive cooling to room temperature.

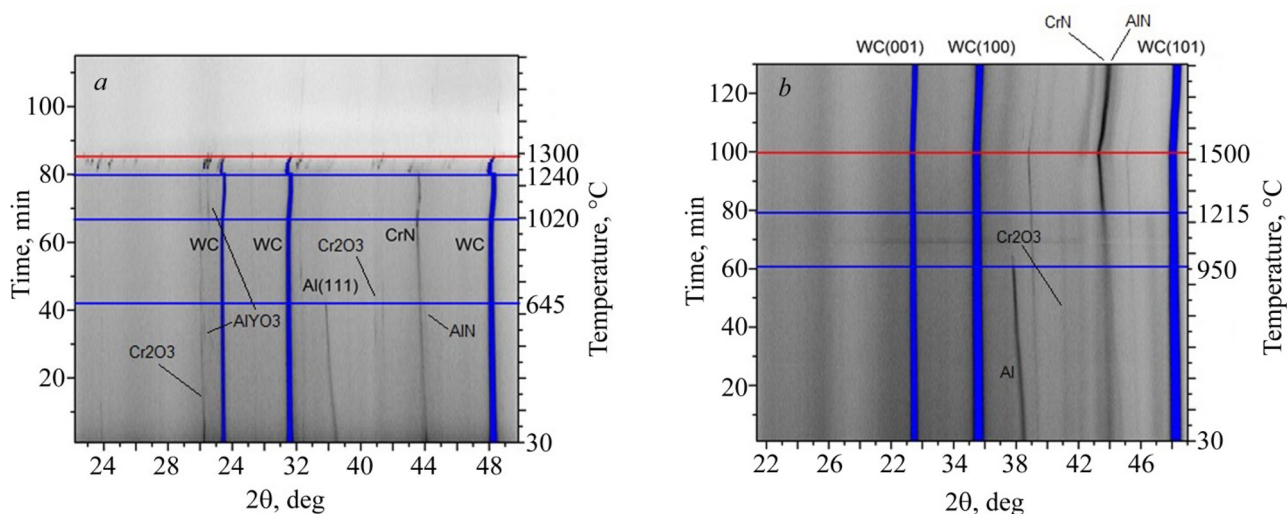


Fig. 3. A series of XRD patterns illustrating structural changes across the CrAlYN/CrAlYO coating during heating (a) in air up to 1300°C and (b) vacuum up to 1500°C followed by cooling to room temperature.

CONCLUSIONS

It was found that the number of layers (16 and 32) and the thickness (~240 and ~120 nm) of each alternating layer at the total thickness of ~3.8 μm of CrAlYN/CrAlYO multilayer coatings strongly affected their phase composition, crystal structure parameters, roughness, surface morphology, and physical and mechanical properties. With increasing number of layers and, consequently, decreasing thickness of each layer, the content of Cr₂O₃ and AlN phases grew from 32 to 52% and from 3 to 11%, respectively, while the content of the CrN phase reduced from 49 to 26%. The CSR size for all phases ranged from 15 to 19 nm and did not depend on the layer number and thickness. It was found that the roughness of the 32-layer CrAlYN/CrAlYO coating was almost 2 times lower than that of the 16-layer coating, that was associated with a decrease not only in the droplet fraction, but also the droplet size. It was also found that the large number of layers and their lower thickness had a positive effect on physical and mechanical properties. The hardness of the 32-layer coating increased by 52% (17.2 GPa) compared to the 16-layer coating. The synchrotron X-ray diffraction analysis showed that thermal stability of the obtained 32-layer CrAlYN/CrAlYO coating preserved during heating in air up to ~1020°C, whereas during heating in vacuum, it kept constant up to at least 1500°C.

COMPLIANCE WITH ETHICAL STANDARDS

Conflicts of interest

The authors declare no conflict of interest.

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Financial interests

The authors declare they have no financial interests.

Non-financial interests

None.

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