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REGULAR ARTICLE

Structure and Properties of Wear-Resistant Nanostructured Coatings Based on W, Cr and N

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The effect on the structural phase state and mechanical properties of the composition of the parameters of obtaining nanocomposite and nanolayer wear-resistant coatings based on Cr, W, and N, obtained by the method of magnetron sputtering was investigated in this work. CrWN nanocomposite coatings were precipitated by the magnetron method with DCMS permanent magnets from a complex target consisting of Cr and W with different ratios of components by area. Electron microscopic studies of the obtained CrWN coatings showed a nanocrystalline finely dispersed structure with a grain size of up to 30 nm. From the analysis of the elemental composition of the coatings, a clear correlation can be observed between the composition of the target and the composition of the resulting coating. For CrN/WN nanolayer coatings, two metal targets of pure Cr and W were used, and coatings of chromium nitride and tungsten nitride were applied sequentially by magnetron sputtering. A dense and smooth microstructure of multilayer coatings was obtained. The presence of a nanolayer structure was confirmed and the sequential change of CrN and WN layers was shown. Smooth and clear interfaces between the CrN and WN layers were observed, indicating a dense and well-packed configuration of the multilayer coating. The CrN/WN nanolayer coatings showed a high hardness of about 30 GPa, which was higher than that of the CrWN nanocomposite coating, where the hardness was about 23 GPa.

Keywords: Nanostructured coatings, Microhardness, Surface strengthening

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1. INTRODUCTION

Studies of wear-resistant coatings based on Ti-N, Zr-N, Mo-N and Cr-N coatings show their high hardness and excellent tribological characteristics. Such coatings are promising materials for wide application, for example, as protective coatings against rapid tool wear [1-11]. Along with this, the structure and tribological properties of W-N coatings have not been studied much. All of the above coatings based on Ti-N, Zr-N, Mo-N, Cr-N and W-N phases are sensitive to the N_2 partial pressure used during deposition. If the partial pressure of the reactive gas in the deposition chamber is insufficient, the formation of interatomic bonds with low chemical and thermal stability is possible. Oxidation resistance can be significantly improved due to the formation of a dense oxide layer on Cr-N [12].

A wide range of scientific research is devoted to the study of the material properties of nanostructured coatings with universal [13] and high wear-resistant characteristics [3, 14-16]. Among various coatings, nitride nanocomposite or nanolayer systems are studied quite widely [5, 7, 9, 11, 13, 14]. Transition metal nitrides are considered as a protective coating due to their excellent properties in terms of hardness, wear resistance and corrosion resistance. Chromium nitride (CrN) systems are promising for coatings with high hardness, excellent antioxidant properties, and good resistance to corrosion and wear [5, 12, 13]. Tungsten, in its metallic form, is another material that is often used because of its high melting point and high hardness [17-20]. Tungsten nitride coatings are used in optical and microelectronic devices, such as barrier layers and electrodes. However, limited literature on its mechanical properties can be found. It was concluded that coatings with a nanolayer configuration with pure metal and metal nitride have higher mechanical properties than single-layer coatings.

Nitride coatings with a complex elemental and phase composition have been increasingly used recently [5, 6, 9, 15, 16, 20, 21]. In such coatings, it is possible to improve a number of functional parameters due to the appropriate selection of components and concentrations that are part of the coating or individual layers.

A particularly important task is the study of the physical and mechanical properties and the structural-phase state of a nanostructured composite or multilayer coating depending on the conditions of deposition and the different composition of the coatings, which gives relevance to the topic of the work.

The purpose of the work is to study the impact on the structural phase state and mechanical properties of the composition and parameters of obtaining nanocomposite and nanolayer wear-resistant coatings based on Cr, W and N, obtained by magnetron sputtering.

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2. MATERIALS AND METHODS

Samples of P6M5 high-speed steel were used as substrates for applying nanocomposite CrWN and nanolayer CrN/WN coatings (the chemical composition of the substrate corresponds to the SSU values within the permissible error) and polished Si plates. The substrates were polished using a mechanical method combined with a diamond grinding wheel.

After that the substrates were cleaned with ultrasound for 10 minutes, sequentially in acetone and ethyl alcohol. CrWN nanocomposite coatings were deposited by the magnetron method with DCMS permanent magnets from a complex target consisting of Cr and W with different area ratios: 95:5, 75:25, 50:50. The discharge power was 500 W. For CrN/WN nanolayer coatings, two metal targets of pure Cr and W were used. The targets were pre-cleaned in a chamber under an argon atmosphere for 10 minutes. Before the coating deposition process, the chamber was evacuated to a pressure of $10^{-3} \div 10^{-4}$ Pa, then Ar and N_2 were introduced. The deposition of the coating took place in an atmosphere of two gases, Ar and N_2, the ratio of which was 10 to 1. The thickness of the applied coating was monitored in-situ by the quartz resonator method. The deposition time of individual layers of multilayer nitride coating CrN/WN during sequential sputtering was modified from 100 to 240 seconds. The two-layer period of the CrN/WN nanolayer coating was monitored at 10 and 24 nm modulation.

X-ray analysis using X-ray spectrometer Dron 4.07 (with CuKα radiation - wavelength 0.154 nm) is used for qualitative and quantitative analysis of the coating composition. Hardness was measured by the microindentation method with a Vickers square diamond pyramid with an angle of 136°, which is used as an indenter at a load of 50 grams. The CrN/WN nanolayer microstructure was evaluated using scanning (SEM on a Tescan VEGA 3 scanning electron microscope) and transmission (TEM-125K) electron microscopy. Energy dispersive spectra were obtained with the help of additional detectors on a Tescan VEGA 3 microscope. The surface topography of CrWN nanocomposite samples of different compositions was investigated using atomic force microscopy (AFM), based on the registration of changes in the force of attraction of the needle-probe to the sample surface from point to point. AFM allows obtaining surface images with extremely high accuracy, up to several angstroms.

3. RESULTS AND DISCUSSION

The main factors affecting the hardness and wear resistance of coatings based on Cr, W and N are the condensation parameters, such as the voltage applied to the substrate, the temperature of the substrate, the concentration of the gases in which the deposition occurs, their pressure, and the composition of the target.

Using magnetron sputtering of Cr and W with reactive gas N_2, a CrWN nanocomposite coating was condensed. Fig. 1 shows the TEM image and the diffraction pattern of the CrWN nanocomposite coating.

The TEM research of the obtained CrWN coatings showed a nanocrystalline finely dispersed structure with grain size up to 20-30 nm and their uniform distribution on the surface, which corresponds to the results of other authors [12, 17, 19]. The diffractogram also confirmed the nanocrystalline microstructure of CrWN pores with randomly distributed grains in it. In addition, CrN phases with (111) and (200) orientations were identified from electron diffraction, while no significant WN phases were observed. This was a confirmation that co-precipitation of W and Cr with the reactive gas N_2 tends to form a CrN crystal structure, and with W, nitrogen is part of the solid solution.

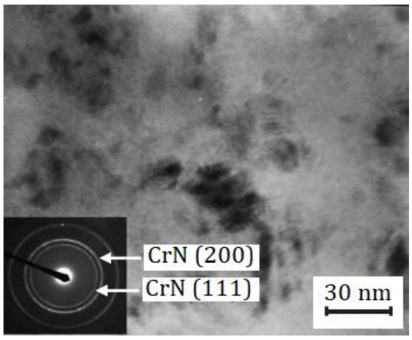

Fig. 1 – Structure and diffraction pattern of the nanocomposite coating CrWN

SEM analysis revealed that the obtained coatings were homogeneous, demonstrating perfect adhesion to the substrate without defects or voids; cracking or delamination was also not observed.

From the data analysis of the elemental composition of coatings (Table 1), we can observe a clear correlation between the composition of the target and the composition of the obtained coating.

Table 1 – Comparison of the target composition and the composition of the obtained coating

	Cr:W	Cr:W	Cr:W
Target composition, weight %	95:5	80:20	50:50
Coating composition, at%.	99:1	93:7	78:22

The correlation between the indicators of the effectiveness formation of the corresponding coating with the ratio between the content of Cr and W on the target and the corresponding content of materials in the applied coating is presented in Fig. 2.

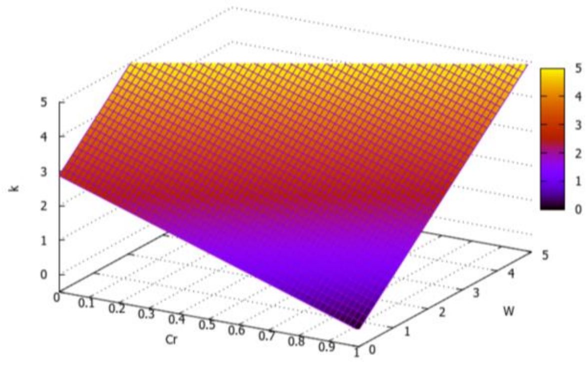

Fig. 2 – Results of simulation of indicators of the efficiency of coating formation depending on the content of Cr and W in the

target when obtaining CrWN nanocomposite coatings

The simulation results allow us to predict the quantitative composition of the target material, taking into account the coefficient of performance *k* of the coating operation based on the given elemental composition of the coating material.

The energy dispersive spectra obtained for coatings based on Cr, W, and N were taken for different fragments and characterize their stoichiometry (Fig. 3).

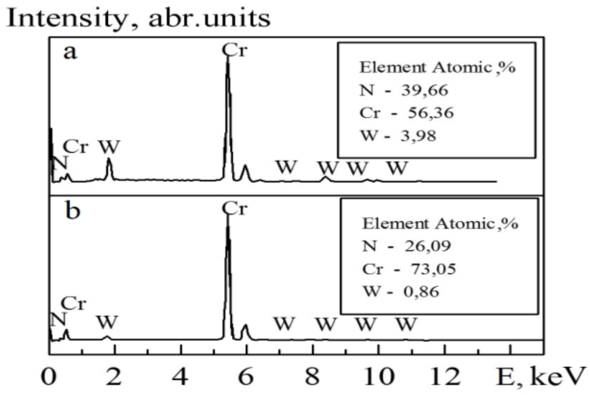

Fig. 3 – Energy dispersive spectra for samples with coatings: $Cr_{40}W_{56}N_4$ (a) and $Cr_{26}W_{73}N_1$ (b)

The energy dispersive spectra further confirm the increase in the content of tungsten nitrides in the coating with the increase in the content of tungsten in the target, as indicated by the increase in the peaks for the elements W and N.

The conducted X-ray researches show that the obtained coatings consist of phases such as WN, W_2N, CrN (with an information layer depth of approximately 200 nm), with a cubic (NaCl-type structure) crystal lattice without a clearly defined grain orientation axis. As an example, X-ray patterns obtained from samples with $Cr_{75}W_1N_{24}$ and $Cr_{56}W_4N_{40}$ coatings are presented in Fig. 4.

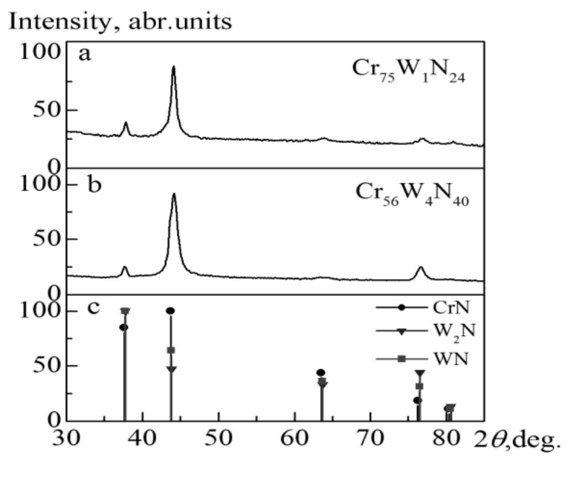

Fig. 4 – X-ray diffraction spectra of $Cr_{75}W_1N_{24}$ (a) $Cr_{56}W_4N_{40}$ (b) coatings and table values of chromium and tungsten nitrides (c)

Fig. 4, also shows tabular values corresponding to CrN - 01-076-2494, W_2N 00-025-1257, WN - 01-075-1012. As can be seen from the figures, there is a modification of the spectrum with a change in the concentration of components in the coating. Thus, for the coating with a higher content of W, the peaks corresponding to the phases of tungsten nitrides become substantially significant.

To visualize the CrN/WN multilayer coating of successively deposited CrN and WN layers with a controlled modulation period, a cross-sectional SEM image of CrN/WN multilayer coatings with a total thickness of approximately 650 nm was used (Fig. 5).

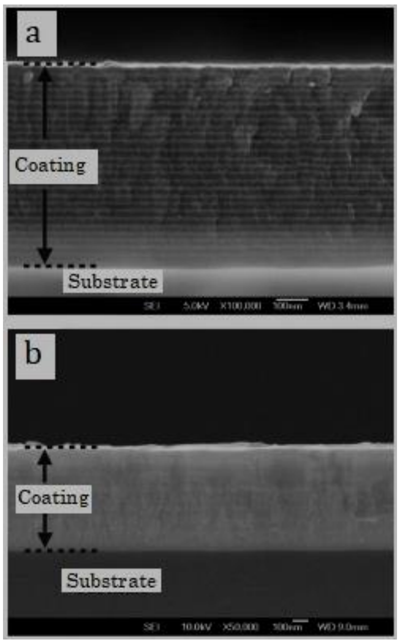

Fig. 5 – Cross-sectional SEM images of (a) 51- and (b) 121-layer CrN/WN nanolayer coatings

Using the magnetron sputtering method a dense and smooth microstructure of multilayer coatings was obtained by. It can be seen that the 51-layer CrN/WN coating has a layered configuration consisting of darker and lighter nanolayers placed sequentially. The thickness of the bilayer periods in the 51-layer CrN/WN coating, which was 24 nm, is specified in Table 2. Control of the layer thickness in the nanolayer coating was achieved by adjusting the deposition time. An SEM image of the cross-section of the 121-layer CrN/WN coating is shown in Fig. 5, b.

Table 2 – Characteristics of CrWN and CrN/WN nanostructured coatings

Type coating	Coating thick-ness, nm	Number of layers	Modu la-tion, nm	Micro-hard-ness, GPa
CrN/WN 51-layer	650	25-WN 26-CrN	24	30.5
CrN/WN 121-layer	640	60-WN 61-CrN	10	28.8
CrWN	650	-	-	22.3

It has a similar smooth and uniform configuration as the 51-layer coating. The coating thickness was approximately 640 nm. Unlike the 51-layer multilayer coating, the nanostructure of the 121-layer CrN/WN coating could not be well shown because the thickness of one layer was too thin for SEM resolution.

The detailed configuration of the layer of the nanolayer CrN/WN coating was checked using transdermal electron microscopy (Fig. 6).

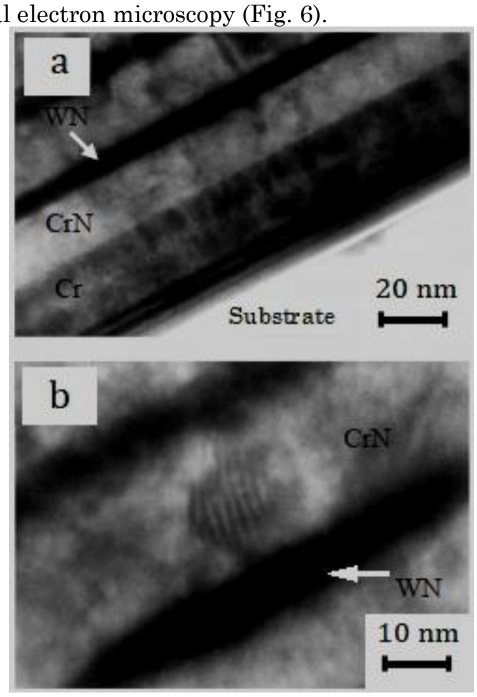

Fig. 6 – Microstructure of 51-layer CrN/WN coating

The darker bands corresponded to tungsten nitride layers, whereas the chromium nitride layers had lighter bands. The presence of a nanolayered structure has been confirmed, showing how the layers of CrN and WN were successively changed. Moreover, smooth and clear interfaces between the CrN and WN layers were also observed, indicating a dense and well-packed configuration of the multilayer coating.

The crystal image of the nano-layered 51-layer coating CrN/WN is shown in Fig. 6, b. The visible grain of CrN is clearly observed precisely between two adjacent WN layers. The layer thickness can be changed by adjusting the deposition time for each nitride layer, thereby controlling the crystallite (or grain) size in the nanolayer structure.

When conducting X-ray studies for nanolayer CrN/WN coatings, two extended peaks corresponding to CrN (111) and (200), which is due to the formation of CrN, WN and W_2N.

The results of phase identification revealed that CrN and an amorphous/nanocrystalline phase of WN/W_2N were observed in the CrN/WN nanocoatings.

Characteristics of nanostructured coatings based on Cr, W and N are summarized in Table 2.

The microhardness of nanolayer coatings reached 30 GPa, and for the CrWN nanocomposite coating it is about 23 GPa, which corresponds to literature data [19, 22]. That is, the CrWN nanocomposite coating in this study showed lower hardness compared to the CrN/WN nanolayer coating.

Limiting the crystallite size to a few nanometers by the interface layers became the dominant factor leading to an increase in the hardness of the CrN/WN coating.

AFM image of the surface of the studied samples of CrWN nanocomposite coatings is shown in Fig. 7.

It is shown that with a lower chromium content, a more uniform and fine-grained surface topography is observed.

The analysis of studies of the structural phase state of coatings based on Cr, W and N, conducted through by X-ray analysis methods, depending on the composition of the target, showed that regardless of the composition of the target, the use of reactive magnetron sputtering allows to obtain a coating with a uniform density of the structure, good adhesion and low roughness coating.

The crystallite size in one nitride layer was fixed within two adjacent interfaces. The CrWN coating exhibited a CrN phase with incorporated W solid solution, while the CrN/WN nanolayer structure possessed CrN phases and amorphous/nanocrystalline WN and W_2N phases.

Limiting the size of the crystallites to a few nanometers by the interface layers became the dominant factor leading to an increase in the hardness of the coating. The nanolayer structure with limited nitride grains in the nano-range was favorable for improving the mechanical characteristics of nanocomposite and nanostructured coatings.

4. CONCLUSIONS

Based on the data obtained by the X-ray method and determination of microhardness, the structural and mechanical properties of wear-resistant coatings based on Cr, W and N were analyzed in the work, depending on the conditions of production.

CrWN nanocomposite coatings were obtained from a complex target, which consisted of Cr and W with different ratios of components by area, and multilayer nanostructured CrN/WN coatings were obtained by the method of sequential deposition under magnetron sputtering.

The analysis of studies of the structural phase state of coatings based on Cr, W and N, carried out by X-ray analysis methods, depending on the composition of the target, showed that regardless of the composition of the target, the use of reactive magnetron sputtering allows to obtain a coating with a uniform density of the structure, good adhesion and low roughness coating.

X-ray studies show that the resulting coatings include phases such as WN, W_2N, CrN with a cubic crystal lattice and an average grain size of up to 30 nm.

Analysis of the mechanical properties of the CrN/WN nanolayer coating revealed a relatively higher hardness of about 30 GPa compared to the CrWN nanocomposite coating, where the hardness was about 23 GPa. Limitation of the crystallite size to a few nanometers behind the interface layers became the dominant factor leading to an increase in hardness. The nanolayer structure with restricted nitride grains in the nanorange was favorable for increasing the mechanical characteristics of the multilayer CrN/WN coating.

It was determined that the surface morphology of the coating obtained by atomic force microscopy depends on the values of the shear stresses on the substrate, the composition of the obtained coatings, temperature and deposition time. It is shown that with a lower chromium content, a more uniform and fine-grained surface topography is observed.

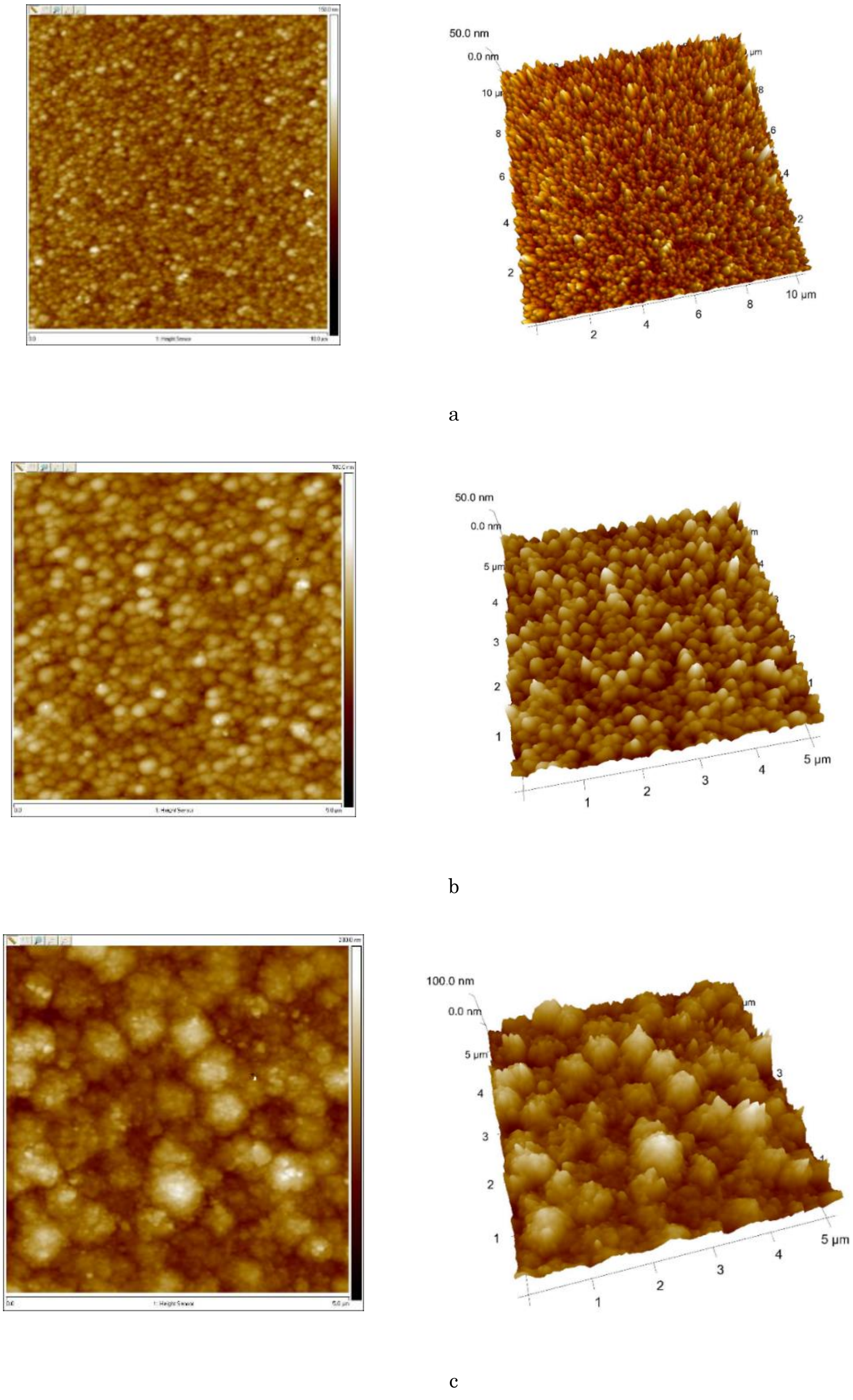

Fig. 7 – AFM images of CrWN nanocomposite coatings applied to P6M5 steel samples obtained with different composition of the target and composition of the obtained coating: composition of the target, wt.% Cr:W – 50:50 (a), Cr:W – 80:20 (b) and Cr:W – 95:5 (c)

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Структура і властивості зносостійких наноструктурованих покриттів на основі W, Cr та N

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В роботі було досліджено вплив на структурно-фазовий стан і механічні властивості складу параметрів отримання нанокомпозитних та наношарових зносостійких покриттів на основі Cr, W та N, отриманих методом магнетронного розпилення. Нанонкомпозитні покриття CrWN осаджувались магнетронним методом із постійними магнітами DCMS з комплексної мішені, яка складалася з Cr та W з різним співвідношенням компонентів по площі. Елетронно-мікроскопічні дослідження отриманих CrWN-покриттів показали нанокристалічну дрібнодисперсну структуру з розміром зерна до 30 нм. Із даних аналізу елементного складу покриттів можна спостерігати чітку кореляцію між складом мішені та складом отриманого покриття. Для наношарових покриттів CrN/WN використовували дві металеві мішені з чистого Cr та W і покриття з нітриду хрому та нітриду вольфраму наносили послідовно методом магнетронного розпилення. Була отримана щільна і гладка мікроструктура багатошарових покриттів. Підтверджено наявність наношарової структури і показано послідовну зміну шарів CrN і WN. Спостерігались плавні та чіткі інтерфейси між шарами CrN та WN, що вказує на щільну і добру упаковану конфігурацію багатошарового покриття. Наношарові покриття CrN/WN демонстрували високу твердість близько 30 ГПа, що було вище, ніж для нанокомпозитного покриття CrWN, де твердість становило близько 23 ГПа.

Ключові слова: Наноструктурні покриття, Мікротвердість, Поверхневе зміцнення