

EFFECT OF CARBON ON THE PROPERTIES OF CrN COATINGS FORMED BY CATHODIC ARC EVAPORATION IN STATIONARY SYSTEM

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Due to good resistance to oxidation and wear chromium nitride coatings are widely used in industry. The works aimed at further improving, for example by carbon doping, the properties of the coatings. The goal of this study was to assess effect of carbon addition to CrN coatings deposited without substrates rotation on the deposition rate, roughness, structure, hardness, adhesion, wear and comparison with properties of CrN coating.

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INTRODUCTION

Deposition of coatings using vacuum arc plasma under an atmosphere of nitrogen is one of the most common methods of obtaining the transition metal nitride coatings. The process of forming such coatings in nitrogen pressure range ~ 0,001...10 Pa was the subject of many papers [1–5]. Due to the good mechanical, tribological and chemical properties, they are widely applied in industry [6]. The advantage of this method is the high deposition rate and ability to change their properties in a wide range [2, 3].

Chromium nitride coatings are most commonly used. A great effect on the properties of coatings CrCN has the technological conditions of their formation, including the composition and pressure of the atmosphere and the substrate bias voltage. The increase in nitrogen pressure changes the phase structure of Cr-N coatings according to the relation: $\text{Cr} \rightarrow \text{Cr} + \text{Cr}_2\text{N} \rightarrow \text{Cr}_2\text{N} \rightarrow \text{Cr}_2\text{N} + \text{CrN} \rightarrow \text{CrN}$. Due to the different chemical composition of these phases they exhibit different physical properties [7, 8]. The addition of carbon atoms changes the mechanical properties of such coatings. Low carbon amount in CrN coating improves mechanical and tribological properties: increases the adhesion and hardness and reduces coefficient of friction and wear rate [9]. The increase in carbon content leads to a refinement of the structure and results in amorphization of the coating [9].

The application of the coatings on substrates of small dimensions has been the subject of several studies [2–5]. The results indicate that with increasing diameter of the substrate the deposition rate was reduced on their front and reverse side. In the case of circular substrates having a diameter of 50 mm film formation on the reverse surface of the disc is reduced considerably and it is almost two times lower than at its front surface [2].

A disadvantage of cathodic arc evaporation is the large number of macroparticles embedded in the surface of the coating, and thus the relatively high roughness. It can be reduced by plasma filters of different principle operations. This reduces the number of surface defects of coatings [1], but also the deposition rate of the coating.

In case of TiN coatings deposited at nitrogen pressure of 1.5...5 Pa they showed an increased deposition rate [2, 3]. For ZrN coatings formed at nitrogen pressure of

2...4 Pa [3], the deposition rate on the front and reverse side of substrates are similar, if their diameter is less than 40 mm. Additionally, ZrN coating obtained on the reverse side of the substrate exhibits better mechanical properties than the coating obtained on the front side.

The aim of the study was the comparison of mechanical properties of CrN and CrCN coatings formed in a stationary system on the front and reverse side of the substrate under the same technological conditions and to determine the effect of carbon addition on the properties of CrN coating.

EXPERIMENTAL

The CrN and CrCN coatings were deposited using unfiltered cathodic arc evaporation method (TINA 900M system). The steel substrates (HS6-5-2 steel, hardened at 1210 °C, quenched in oil and tempered at 560 °C with hardness 63 HRC) polished to the roughness Ra of about 0.02 μm, after chemical cleaning process were mounted at a distance of 16 cm from the cathode in vacuum chamber. Two substrates were used for evaluation the properties of the coatings deposited on the front and reversed side of the samples.

The chamber was evacuated to a pressure of $1 \cdot 10^{-3}$ Pa. Prior to the deposition, the substrates were ion etched by argon (Ar^+) and chromium (Cr^+) ions at argon pressure of 0.5 Pa under 70 V negative substrate bias voltage for 10 min. A deposition process of CrN coatings was performed on a heated to a temperature of 300 °C substrates, at substrate bias voltage of -300 V with arc current of 80 A and nitrogen pressure 3.0 Pa. To improve the adhesion of the coating to the substrate a thin (~ 0.1 μm) chromium layer was deposited onto the substrate [8]. CrCN coatings were deposited under the same parameters with addition acetylene flow (10 sccm).

The coating thickness, surface morphology, phase and chemical composition, roughness, hardness and adhesion were determined using methods and devices described in [5] and friction and wear in [10].

RESULTS AND DISCUSSION

The investigations of chemical composition of CrCN coatings formed on the front side of substrate indicate on presence of approx. 11 at.% of carbon. The coatings formed on reverse side of the substrate show about 2 at.%

of carbon less. The ratio of chromium to nitrogen in CrCN and CrN coatings deposited on both sides of the substrates is approx. 1:1. This ratio is characteristic for cubic CrN phase [8]. It should be also be noted that in all coatings confirmed the presence of about 0.5 at.% of oxygen.

It has been found that thickness of CrN and CrCN coatings (Table 1), formed on the front side of the substrate are almost two-three times greater than on the reverse side of the substrate. This finding confirms the studies described in [2–5].

Table 1
The thickness and roughness of the coatings

Coating	Thickness, μm		Roughness Ra, μm	
	Front	Reverse	Front	Reverse
CrN	7.7	2.4	0.05	0.03
CrCN	6.0	2.9	0.11	0.03

The morphology of CrN and CrCN coatings deposited on the front and reverse side of the substrate is shown in Fig. 1. Larger amount, particularly small

particles on the surfaces of the coatings formed on the front side of both coatings are visible (Table 2). The coating formed on the front side shows surface structure called “honeycomb” typical for CrCN coatings obtained at higher substrate bias voltages [7, 11]. It is interesting that on reverse side of the coatings greater macroparticles dominates, although it appears that in the case of CrCN coatings number of large macroparticles is greater.

Table 2
The dimensional fractions of macroparticles on the coatings surface, and their roughness Ra

Coating	Particle distribution, %		
	0...1 μm	1...3 μm	3...8 μm
Front side of sample			
CrN	58	38	4
CrCN	62	33	5
Reverse side of sample			
CrN	36	47	17
CrCN	31	50	19

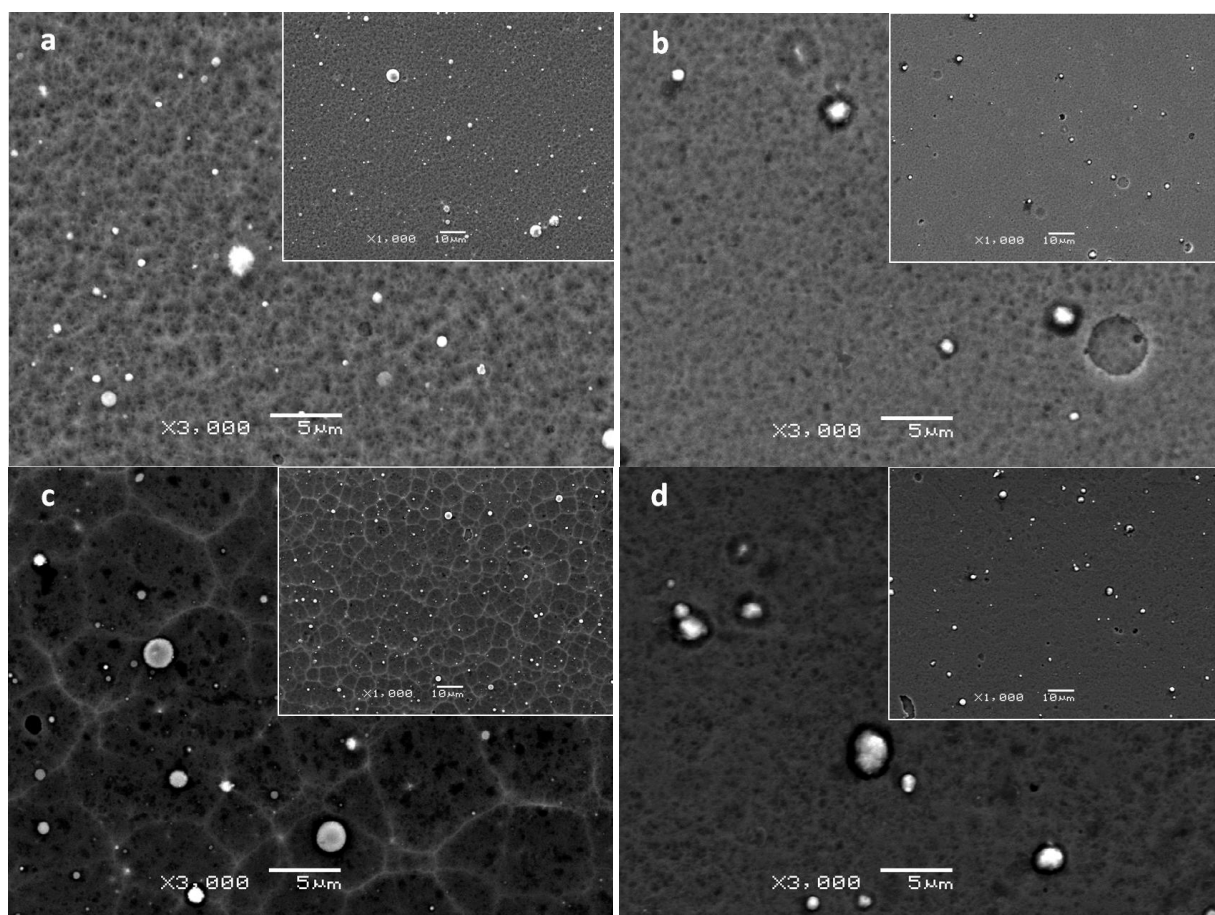


Fig. 1. Surface morphology of CrN (a, b) coatings and CrCN (c, d) coatings deposited on the front (left) and reverse (right) side of samples at nitrogen pressure of 3.0 Pa and substrate bias voltage -300 V

It can be also found that the surface roughness of CrCN coating formed on the front side of the substrate is about 0.11 μm , about two times more than for the front side of the substrate and 0.03 μm for the rear side. The surface roughness of the CrN coating formed on the front side of the substrate is much smaller than in the case of coatings and CrCN is 0.05 μm , and the surface roughness of the CrN coating on the back side of the substrate is the

same as for the coatings CrCN. The higher roughness of CrCN coatings compared with CrN was previously reported [11].

The diffraction patterns of the coatings tested are shown in Figs. 2 (front) and 3 (reverse). The analysis of diffraction lines was conducted based on ICDD reference data: 11-0065 (CrN), 035-0803 (Cr_2N), 06-0694 (Cr) and 06-0696(Fe). The presence of iron (from steel substrate),

hexagonal Cr₂N phase and cubic CrN phase is observed. Due to the reduced thickness of the coating deposited on the reverse side of the substrate the intensity of the diffraction lines of iron is greater. The diffraction pattern coatings tested indicates that they are highly textured. It should be noted that according ICDD 11-0065 diffraction lines intensity is as follow: (111) – 80%, (200) – 100%, (220) – 80%, (311) – 60%, (222) – 30%, (400) – 30%, (420) – 50%.

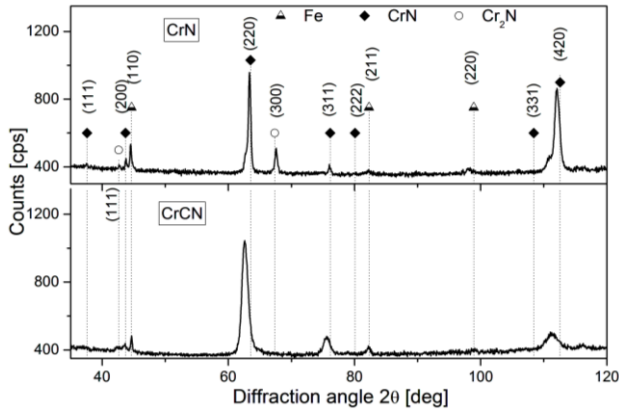


Fig. 2. X-ray diffraction patterns of the CrN and CrCN coatings deposited at front side of the substrates

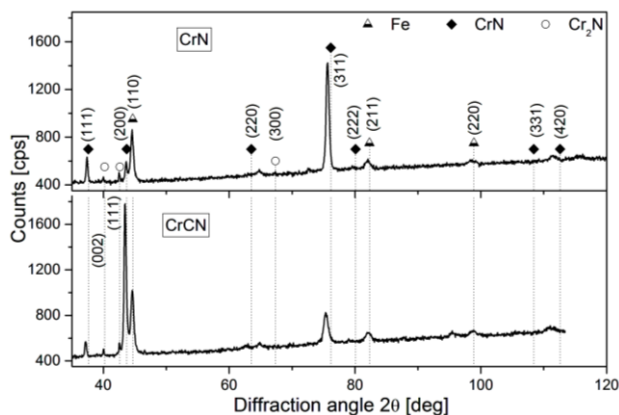


Fig. 3. X-ray diffraction patterns of the CrN and CrCN coatings deposited at reverse side of the substrates

The coatings deposited on the front side of the substrate show much greater thickness compared to the coatings formed on the reverse side. Despite this the intensity of the diffraction lines registered in the second case are more intense, which may indicate the presence of higher number of the crystallites in the coating.

Investigations made by Almer et al. [12] indicate that even a small amount of carbon in CrN coating significantly changes the microstructure and mechanical properties. The crystal structure observed is cubic δ-Cr(C,N), the intensity of the diffraction lines decreases, the diffraction lines are broadened. The latter results point to the refinement of grains and/or amorphization of the coating. The stress in the coating is also reduced. XPS analysis shows that 25...50% of the carbon atoms substitute nitrogen in the lattice and the remain part was identified as amorphous carbon [12]. The parameters of structure of CrN and CrCN coatings are gathered in Table 3.

Table 3

The parameters of CrN and CrCN coatings structure

Parameter	CrN		CrCN	
	Front	Reverse	Front	Reverse
Lattice parameter, nm	0.4148	0.4174	0.4186	0.4220
Average grain size, nm	–	80	61	86
Microstrain, %	–	0.17	0.63	0.30

It should be noted that the grain size of the coating deposited to the reverse side of the substrate is greater. Similar results were obtained in our previous work [5]. The microstrain of the coating formed on the reverse side of the substrate is lower compared to the coating formed on the front side probably due to lower deposition rate.

The hardness of the CrN coatings is considerably lower than CrCN coatings formed under the same conditions, Table 4. The modulus of elasticity is also higher for CrCN coatings. Interesting was that these values (H, E) for the coatings formed on both sides of the substrate were similar. Only in the case of CrCN coating formed on the reverse side of the substrate the hardness is lower about 25%. H/E ratio can be a more suitable parameter for predicting wear resistance than is hardness alone [13]. The higher the ratio, the deformation resistance of the coating is higher. All deposited coatings show similar, according this ratio, wear resistance. The adhesion of the coatings, indicated as Lc₂ critical load at which the observed total delamination of the coating is generally high. Lower values for CrCN coatings are typical for CrCN coatings. It was published elsewhere [12, 14].

Table 4

Mechanical properties of CrN and CrCN coatings

Parameter	CrN		CrCN	
	Front	Reverse	Front	Reverse
Hardness, GPa	15.5	15.9	26.5	20.5
Elastic modulus, GPa	319	300	363	331
H/E	0.05	0.05	0.07	0.06
Lc ₂ , N	101	101	66	93
Wear rate, μm ³ /Nm	1600	3000	200	4400

CONCLUSIONS

The findings of investigations are as follow:

1. X-ray studies showed that, depending on a method of placing the substrates, it is possible to produce coatings with different dominant crystallographic orientation. The addition of carbon to the CrN causes broadening of diffraction lines in the diffraction pattern. It indicates the refinement of grain size and increases the hardness of the coating formed on both sides of the substrates.

2. Larger value of the lattice parameter of chromium carbonitride in relation to the chromium nitride is probably connected with incorporation of the carbon atoms in interstitial positions. All investigated coatings are highly textured.

3. Roughness parameter Ra, and the hardness of the coatings formed on the front side of the substrate is larger than the coatings formed on the reverse side. CrCN

coatings have a lower adhesion to the substrate but higher hardness and wear resistance compared with CrN.

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ВЛИЯНИЕ УГЛЕРОДА НА СВОЙСТВА CrN-ПОКРЫТИЙ, ФОРМИРУЕМЫХ КАТОДНО-ДУГОВЫМ ИСПАРЕНИЕМ В СТАЦИОНАРНОЙ СИСТЕМЕ

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Покрyтия из нитрида хрома широко используются в промышленности благодаря хорошей стойкости к окислению и износу. Выполняются работы, направленные на дальнейшее совершенствование свойств покрyтий, например, путем легирования углеродом. Цель данного исследования состоит в том, чтобы оценить влияние легирования углеродом CrN-покрyтий, наносимых без вращения подложки, на скорость осаждения, шероховатость, структуру, твердость, адгезию и износ, а также сравнить со свойствами CrN-покрyтия.

ВПЛИВ ВУГЛЕЦЮ НА ВЛАСТИВОСТІ CrN-ПОКРИТТІВ, СФОРМОВАНИХ КАТОДНО-ДУГОВИМ ВИПАРОВУВАННЯМ У СТАЦІОНАРНІЙ СИСТЕМІ

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Покриття з нітриду хрому широко використовуються в промисловості завдяки хорошій стійкості до окислення і зносу. Виконуються роботи, спрямовані на подальше вдосконалення властивостей покриттів, наприклад, шляхом легування вуглецем. Мета даного дослідження полягає в тому, щоб оцінити вплив легування вуглецем CrN-покриттів, що наносяться без обертання підкладки, на швидкість осадження, шорсткість, структуру, твердість, адгезію і знос, а також порівняти з властивостями CrN-покриття.