

# DEPOSITION OF CHROMIUM NITRIDE COATINGS FROM VACUUM ARC PLASMA IN INCREASED NITROGEN PRESSURE

V.D. Ovcharenko<sup>1</sup>, A.S. Kuprin<sup>1</sup>, G.N. Tolmachova<sup>1</sup>, A. Gilewicz<sup>2</sup>, O. Lupicka<sup>2</sup>,  
J. Rochowicz<sup>2</sup>, B. Warcholinski<sup>2</sup>

<sup>1</sup>National Science Center „Kharkov Institute of Physics and Technology“, Kharkov, Ukraine;  
<sup>2</sup>Koszalin University of Technology, Koszalin, Poland

E-mail: bogdan.warcholinski@tu.koszalin.pl

The application of protective coatings on metal materials is the effective way to improve their durability. Chromium nitride coatings are applied mainly on tools due to good resistivity to oxidation compared to other metal nitride coatings and good wear resistance. Some characteristics of the coatings deposited in fixed position in regard of chromium cathode on the samples parallel directed to it and the other arranged opposite in the nitrogen pressure ranged from 0.5 to 3.0 Pa are investigated.

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## INTRODUCTION

Protective coatings based on transition metals nitrides are deposited mainly in nitrogen pressure specific for required stoichiometric composition. One of the most commonly deposition technique used is cathodic arc evaporation due to excellent characteristics of the coatings. The coatings are characterized by high hardness, good adhesion to the substrate, high density, homogeneity and show better properties than the coatings prepared by magnetron sputtering. The disadvantage of this deposition method is relatively high roughness of the coating' surface, resulting from a large number of macroparticles on the surface.

The absence of through pores and macroparticles in the condensates, usually achieved by the use of various designs of plasma filters [1]. A simpler decision is to deposit nitride coatings at high pressures of nitrogen  $\sim (2...4)$  Pa [2]. In this case, the deposition rate on the front and reverse sides congruent when a diameter of specimen  $\leq 40$  mm, and this ZrN coating shows higher mechanical properties than coatings obtained from the forward-flow [3].

The goal of this research is to assess the difference in deposition rates, statistics of macroparticles on the surface, roughness, chemical composition of the coatings deposited on samples placed in two different position - on the front and back side of samples during deposition Cr-N coatings. According to our the best knowledge it was not studied previously.

## 1. EXPERIMENTAL

The CrN deposition process was performed by unfiltered cathodic arc evaporation method using TINA 900M system. Samples (hardened HS6-5-2) polished to the roughness Ra about  $0.02 \mu\text{m}$ , after chemical cleaning process were placed within the 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  $1 \times 10^{-3}$  Pa. Prior to the deposition, the substrates were sputter cleaned by argon ( $\text{Ar}^+$ ) and chromium ( $\text{Cr}^+$ ) ions at argon pressure of 0.5 Pa under -70 V negative

substrate bias voltage for 10 min. The thin ( $\sim 0.1 \mu\text{m}$ ) chromium layer was also deposited onto the substrate to improve the adhesion [4]. A deposition process was performed on a heated to a temperature of  $300^\circ\text{C}$  substrates, at substrate bias voltage of -70 V with arc current of 80 A and three nitrogen pressures: 0.5, 1.8 and 3.0 Pa.

The coatings thickness was evaluated by means of the ball cratering test (Calotest). Chemical composition of the coatings was performed using energy dispersive X-ray spectroscopy - EDS (Oxford Link ISIS 300) at 20 kV. The surface morphology was completed using scanning electron microscopy (SEM - (JEOL JSM-5500LV). To define the size of macroparticles and the number of macroparticles on the unit of area on the surface of the coatings the metallographic microscope Nikon Eclipse MA200 equipped with NIS-Elements software was used. The measurement area was about  $(440 \times 330) \mu\text{m}^2$ . The surfaces of the coatings were recorded at the same magnification (400x) contrast and sharpness. For each sample five measurements in one line at equal distances from each other was carried out. The surface roughness was measured by profilometer Hommel Werke T8000.

## 2. RESULTS AND DISCUSSION

Deposition rates computed for the set of samples deposited are gathered in Fig.1. Dotted line is placed here and in next figures for eye guiding only.

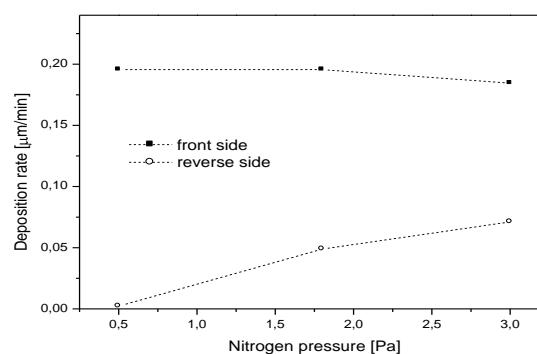
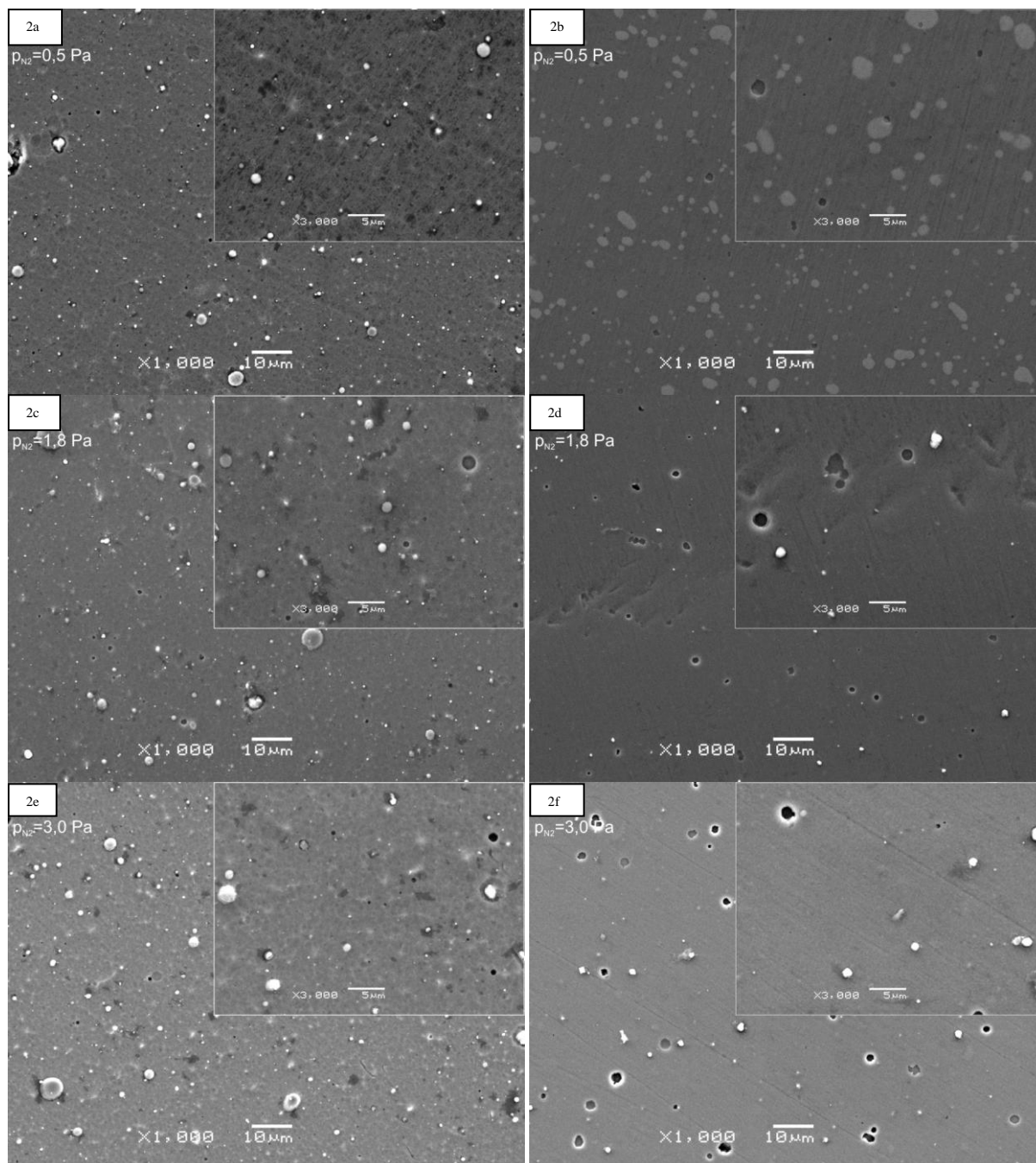


Fig. 1. Influence of nitrogen pressure on the deposition rate on the front and reverse side of samples



*Fig. 2. Surface morphology of CrN coatings deposited on the front (left) and reverse (right) side of samples at different nitrogen pressure*

The deposition rate of chromium coatings on the front of the samples is independent of pressure of nitrogen in all investigated range and is about  $0.2 \mu\text{m}/\text{min}$ . In the case of deposition on reverse side of samples the change of deposition rate is roughly similar as in ZrN coatings [3] at increasing of nitrogen pressure to 3 Pa and reaching  $\sim 0.07 \mu\text{m}/\text{min}$ .

The surface quality (the number of macroparticles, roughness) play important role in wear processes. The durability of the coating is greater for smaller amount of surface defects [5, 6], weakly bound to the coating.

Macrodefects observed on the coatings on the samples obtained at all range of pressure are identified, according EDS investigations, to be droplets of cathode material. On the surface of the coatings deposited on the

front side of the substrates the macroparticle sizes varies from less than  $0.5 \mu\text{m}$  to more than a few  $\mu\text{m}$ , Fig. 2.

Number of droplets increases with nitrogen pressure raises. On a front side samples is about 4 times higher than on back side and depends on the nitrogen pressure, Table. This effect is comparable with data presented by Wan et al. [7] for CrN coatings obtained by arc ion plating method.

Number of particles of a small size ( $0...1 \mu\text{m}$ ) is much greater than the large-sized particles, more than  $3 \mu\text{m}$ . Their number decreases for higher nitrogen pressures during the deposition process in case of coatings obtained on the reverse side, but number of the particles of larger dimensions increases.

The number of macroparticles on the coatings' surface and its dimensional fractions

Nitrogen pressure [Pa]	Number of macroparticles			
	Total	0...1 μm	1...3 μm	3...8 μm
Front side of sample				
0.5	4192	2555	1481	156
1.8	3410	2012	1185	213
3.0	4889	2430	2115	344
Reverse side of sample				
0.5	1325	1001	302	22
1.8	1969	829	981	159
3.0	1424	464	731	229

The reduction of the small particles with increase of nitrogen pressure is more evident and the proportion of particles with dimensions greater than 3 μm is higher, Fig. 2,b. In these coatings can also be observed a large number of craters. In some of them are located visible particles. These craters probably resulted from the shadowing by droplets on surface during deposition. It is also possible other interpretation. According to the [3], some of the particles of high melting point and a low electron work function  $e_{\phi}$  (for chromium  $T_{melt} = 2180$  K and  $e_{\phi} = 4.5$  eV) can heat up to a temperature even 5000 K and get positive potential due to thermionic emission. Acceleration (substrate bias voltage -70 V) in the plasma of positively surface-charged particle leads, due to thermal and mechanical stresses, to the formation of craters.

A large and growing amount of macroparticles on the surface of the coatings causes an increase in the fraction of samples covered by the macroparticles, with the increase of the nitrogen pressure. It depends both on the sample position (front, reverse) and the nitrogen pressure, Fig. 3. On the front surface (up to 8%) is approximately two times higher than the reverse side.

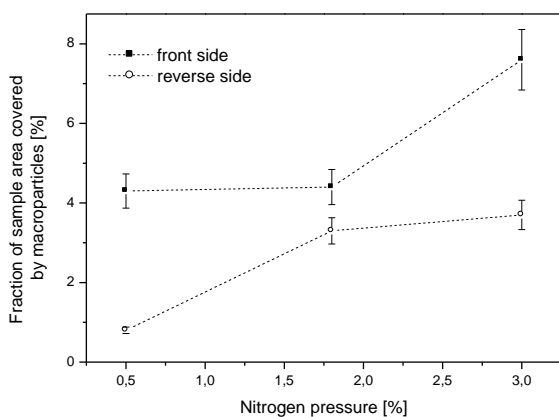


Fig. 3. Fraction of samples covered by the macroparticles versus nitrogen pressure

The large amount of macroparticles on the coatings' surface changes the initial substrate roughness from about 0.02 to above 0.1 μm (front side) and higher up to 0.025 μm reverse side, Fig. 4. This effect is comparable with area covered by macroparticles (see Fig. 3). Generally it can be stated that with increasing nitrogen pressure during coatings' deposition increases the quantity of the surface defects, and consequently the surface roughness.

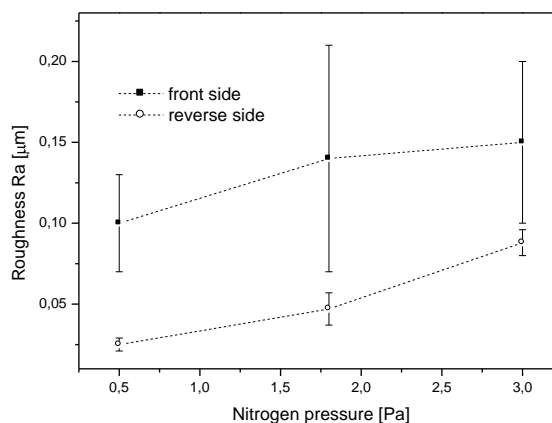


Fig. 4. Roughness Ra of CrN coatings as a function of nitrogen pressure

The chemical composition, determined using EDX spectroscopy, of Cr-N coatings deposited at different nitrogen pressures are shown in Fig. 5 – for coatings deposited on front side of samples and in Fig. 6 – for coatings deposited on reverse side of samples.

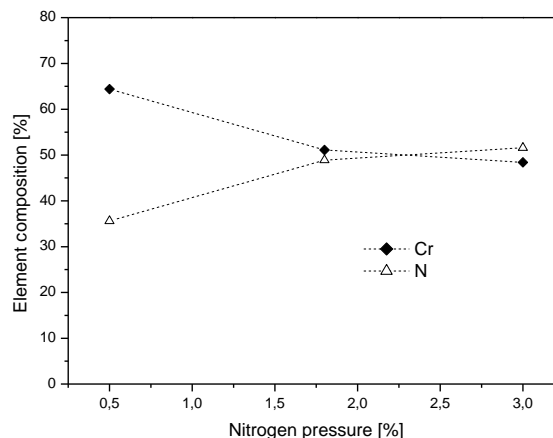


Fig. 5. Chemical composition of the coatings deposited on the front side of samples

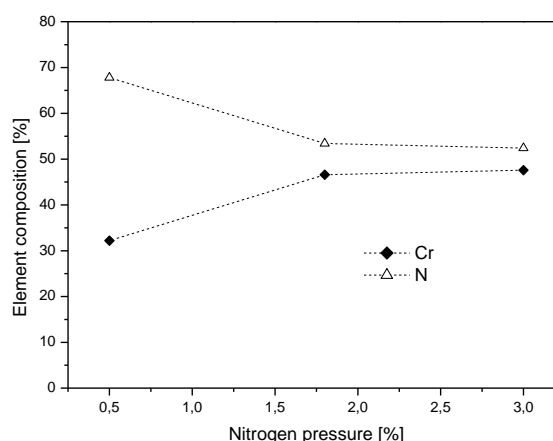


Fig. 6. Chemical composition of the coatings deposited on the reverse side of samples

It can be seen that the nitrogen concentration increases and chromium concentration decreases when nitrogen pressure increases from 0.5 to 1.8 Pa. Above this pressure the composition of the coatings keeps nearly unchanged. The coatings deposited at nitrogen pressure 0.5 Pa on the front side of samples show Cr<sub>2</sub>N

structure and at higher nitrogen pressure CrN structure both for front and reverse side of samples.

## CONCLUSIONS

Cathodic arc evaporation method at different nitrogen pressure during the process allowed to obtain two groups of the coatings deposited on the front and reverse side of the steel substrates. As a result of tests of the thickness and the chemical composition of the coatings and the surface morphology was found that:

1. The deposition rate of coating on the front side is almost constant regardless of the pressure of nitrogen. The coatings obtained on the reverse side of the substrates are characterized by a lower deposition rate, rising with an increase of nitrogen pressure.
2. With increase of nitrogen pressure increases the amount of macroparticles on the surface of the coatings, wherein the amount on the front side is 2...3 times greater than the reverse side and rises the fraction of larger particles. Most of the particles (over 60%) is small, to 1  $\mu\text{m}$ .
3. The fraction of the surface covered by the macroparticles is the smallest at the reverse side resulting at pressure 0.5 Pa, and is approximately 1%, and the largest for the coating obtained on the front side and at a pressure of 3.0 Pa - about 8%.
4. The surface roughness of front side deposited coatings rises of about 0.1 to about 0.15  $\mu\text{m}$  and in reverse side from about 0.03 to 0.09  $\mu\text{m}$  with increase of nitrogen pressure.
5. For low nitrogen pressure (0.5 Pa) the coating deposited on the front side of sample shows Cr<sub>2</sub>N structure. For higher nitrogen pressure (1.8 and 3.0 Pa) the coatings deposited both on the front and reverse side of samples show stoichiometric CrN structure.

## ACKNOWLEDGEMENTS

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## ОСАЖДЕНИЕ НИТРИД-ХРОМОВЫХ ПОКРЫТИЙ ИЗ ВАКУУМНО-ДУГОВОЙ ПЛАЗМЫ ПРИ ПОВЫШЕННЫХ ДАВЛЕНИЯХ АЗОТА

*В.Д. Овчаренко, А.С. Куприн, Г.Н. Толмачёва, А. Гилевич, О. Луницка, Я. Рохович, Б. Вархолинский*

Применение защитных покрытий на металлических материалах является эффективным способом улучшения их прочности. Покрытия из нитрида хрома применяются в основном на инструменте благодаря хорошему сопротивлению окислению, по сравнению с другими нитридными покрытиями, и хорошей износостойкости. Были исследованы некоторые характеристики покрытий, осажденных в фиксированном положении на лицевую и обратную стороны образцов, установленных в плоскости, параллельной по отношению к хромовому катоду, в диапазоне давлений азота от 0,5 до 3,0 Па.

## ОСАДЖЕННЯ НІТРИД-ХРОМОВИХ ПОКРИТТІВ ІЗ ВАКУУМНО-ДУГОВОЇ ПЛАЗМИ ПРИ ПІДВИЩЕНОМУ ТИСКУ АЗОТУ

*В.Д. Овчаренко, О.С. Купрін, Г.М. Толмачова, А. Гілевич, О. Луницка, Я. Рохович, Б. Вархолінський*

Застосування захисних покриттів на металевих матеріалах є ефективним способом поліпшення їх міцності. Покриття з нітриду хрому застосовуються в основному на інструменті завдяки гарному опору окисленню, в порівнянні з іншими нітридними покриттями та добрій зносостійкості. Були досліджені деякі характеристики покриттів, осаджених у фіксованому положенні на лицьову і зворотну сторони зразків, встановлених в площині, паралельній по відношенню до хромового катода, в діапазоні тисків азоту від 0,5 до 3,0 Па.