THE EFFECT OF UNINTENTIONAL OXYGEN INCORPORATION INTO Cr-CrN-DLC COATINGS DEPOSITED BY MePIIID METHOD USING FILTERED CATHODIC VACUUM ARC CARBON AND METAL PLASMA

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The multilayer Cr-CrN-DLC coatings deposited by MePIIID method on substrates made of high speed steel HS 6-5-2 were studied. The streams of filtered carbon and metal arc plasma were used in both ion implantation and deposition phases. Investigation of the chemical composition of Cr-CrN-DLC coatings revealed considerable amount of oxygen in deposited DLC film. Additional alloying of DLC films with chromium reduced the concentration of oxygen. The presence of oxygen affects the properties of DLC coatings, which was confirmed by the investigation of the hardness and adhesion.
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1. INTRODUCTION

Metal Plasma Immersion Ion Implantation and Deposition (MePIIID) is a hybrid process, widely used for simultaneous implantation and deposition of metallic and ceramic films in reactive and non-reactive environments [1]. Most of papers on the MePIIID method report the use of curved magnetic filters for removing microdroplets from metallic plasma flow used for implantation and deposition of metallic components of coatings, and methane or acetylene as a carbon carrying media for DLC films deposition.

In this paper, the modification of hybrid MePIIID process is presented, which consists in the use of combined techniques of filtering cathodic arc plasma flows – carbon plasma flow by T-shape magnetic filter and chromium plasma flow by electrostatic filter.

2. EXPERIMENTAL TECHNIQUES

The synthesis of Cr-CrN-DLC coatings was carried out using the modernized vacuum arc device developed especially for MePIIID technology. The coatings were deposited on the substrates made from high speed steel HS 6-5-2 mounted in the zone where carbon and chromium plasma flows mixed (Fig. 1).

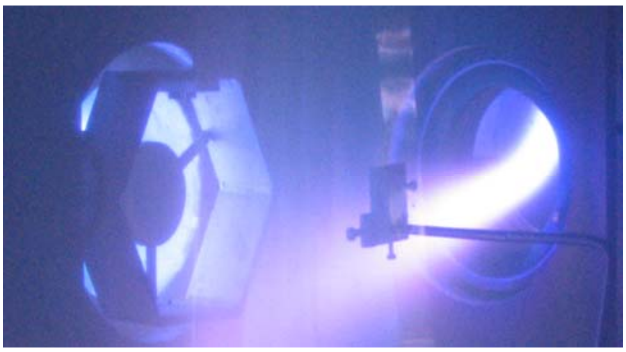

Fig. 1. The substrate immersed in the flows of chromium plasma (from the left) and carbon plasma (from the right) passing through the separators during the MePIIID process

Before the placement in the vacuum chamber the substrates were ground and polished to the roughness of Ra = 0,06 μm and then washed and degreased in trichloroethylene. The initial vacuum in the chamber was at the level of 1×10^{-5} mbar. As source materials for deposition of Cr-CrN-DLC coatings a pure chromium (Cr 99.999%) and a pure carbon (C 99,999%) cathodes were used. Arc currents of 75A for chromium and 90A for carbon were applied. The magnetic flux density along the T-shaped filter axis amounted to 16 mT, the electrostatic filter was biased with the positive potential of 27 V.

All experiments consisted of four stages of technological process:

1. substrate etching and heating by the bombardment with argon ions in arc enhanced glow discharge (AEGD),
2. ion implantation and deposition of chromium sublayer from filtered vacuum arc plasma,
3. deposition of CrN coating from filtered chromium arc plasma in nitrogen atmosphere,
4. deposition of DLC coating from filtered carbon arc plasma in argon atmosphere.

The parameters of deposition of multilayer Cr-CrN-DLC coatings are shown in the Table below. The substrate temperature during the experiments was measured by the infared pyrometer Raytek Termalert 4. The hardness of the coatings was measured using nano-hardness tester CSEM with a Berkovich pyramid. Quantitative analysis of the coatings composition was carried out using radio frequency glow discharge optical emission spectrometer (RF GDOES) JY10000RF produced by the company Jobin Yvon Horiba. Analysis of the sample surfaces composition was also performed by the X-ray Photoelectron Spectroscopy (XPS) using the spectrometer produced by the company Vacuum Systems Workshop Ltd. (VSW) England. The surface morphology of the coatings and their roughness parameters were studied using an atomic force microscope (AFM) Q-Scope 250 produced by the company Quesant Instrument Corporation.

Parameters of deposition of multilayer Cr-CrN-DLC coatings

Stage of the process	Gas, pressure p [mbar]	Substrate BIAS U_{BIAS} [kV]	Pulse duration τ [μs]	Pulse frequency f [kHz]	Substrate temp. T [°C]	Process time t [min]
Substrate etching (AEGD)	Ar $5{,}0\times10^{-3}$	2	20	2	90	15
Cr implantation and deposition	Without gas $1{,}0\times10^{-5}$	2	20	2	100	10
CrN coating deposition	N_2 $4{,}0\times10^{-3}$	2	20	2	115	20
DLC coating deposition	Ar $1{,}2\times10^{-4}$	2/4/6	20	1/2/2,5	165…200	30

3. RESULTS AND DISCUSSION

The total thickness of Cr-CrN-DLC coatings obtained was about 2,2 μm. Investigation of surface morphology of Cr-CrN coatings showed that the electrostatic separator does not remove completely droplet phase from the plasma flow (Fig. 2).

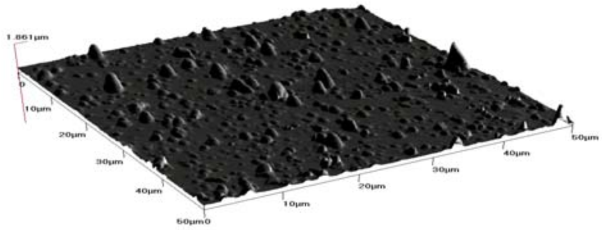

Fig. 2. The surface morphology of Cr-CrN coating deposited with the use of the electrostatic separator

The presence of droplets on the substrate surface shows that part of the droplets pass through a filter to the substrate, spreading over its surface, stick on it and are immured by the deposited flux.

The surface morphology of the investigated DLC coatings deposited using the T-shaped magnetic filter confirms high effectiveness of cleaning carbon plasma from the microparticles in this system (Fig. 3).

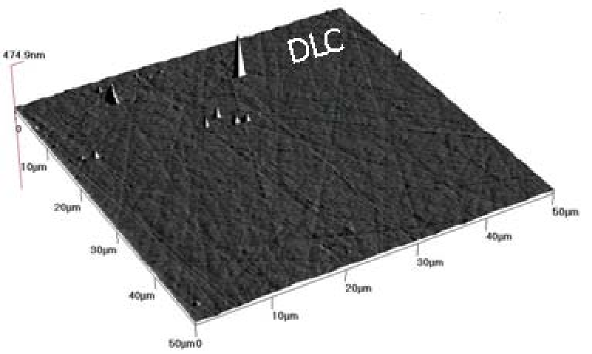

Fig. 3. Surface morphology of DLC coatings deposited with the use of the magnetic separator

The presence of a small number of defects on the surface shows that most of the carbon particulates remains inside the filter and only the smallest microparticles can pass due to the rebounding inside plasma guide [2]. Using the RF GDOES method the distribution of the concentrations of Cr-CrN-DLC coating components throughout the coating thickness was determined (Fig. 4).

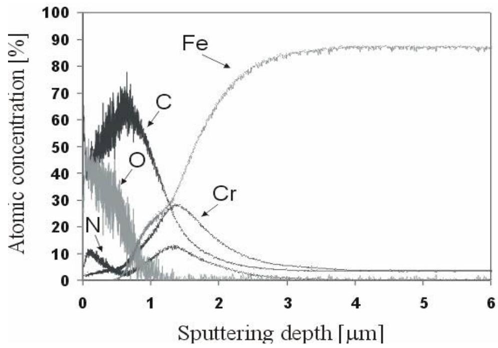

Fig. 4. Concentration profiles of Cr-CrN-DLC coating components

In the investigated samples with Cr-CrN-DLC coatings a high concentration of oxygen of 38…45 at. % was observed on the surface of DLC film. The infiltration of oxygen during the experiment was excluded because vacuum of 1×10^{-5} mbar was reached before each stage of the process and high purity gases (99,9999%) were used. Local maximum of nitrogen concentration coinciding with the maximum of oxygen concentration suggested that most likely, oxygen penetrated into the vacuum chamber and the coating when the chamber was open to the atmosphere, despite the fact that the substrates were previously cooled to the temperature of 50°C and the chamber was heated with warm water.

In order to prevent oxygen infiltration into the coating two additional stages of the process were included:

- pre-sputtering of the carbon cathode by arc discharge,
- doping of deposited DLC coating with chromium.

Pre-sputtering of the cathode did not yielded significant results, but doping of DLC coating with Cr allowed the oxygen concentration to be significantly reduced (Fig. 5).

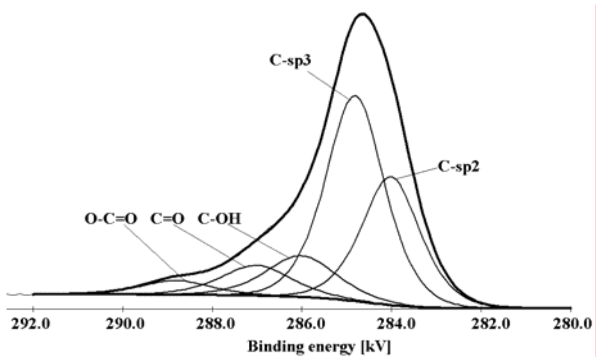

Fig. 5. C1s peaks of XPS spectrum of DLC coating doped with chromium

The analysis of C1s peaks of XPS spectrum of DLC film doped with Cr indicates predominant occurrence of sp^3 and sp^2 carbon bonds. Energy shift from 285 eV to 284 eV indicates the $sp^3 \rightarrow sp^2$ phase transformation in the DLC film due to the temperature rise caused by its bombardment with Cr ions.

Increasing the substrate temperature to 200°C and an increase in ion energy up to 6 keV decreases the microhardness and the Young modulus, and thus internal stresses [3], of the film (Fig. 6).

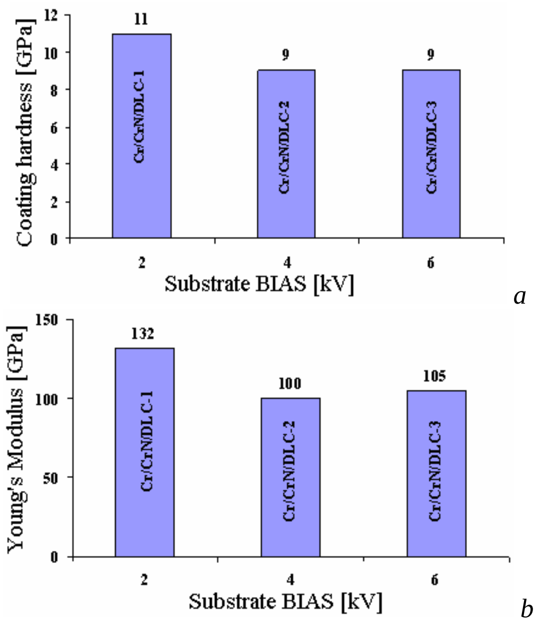

Fig. 6. Dependence of hardness (a) and Young modulus (b) of Cr-CrN-DLC coatings on the substrate BIAS

It is also noticed that the maximum critical load has increased from 15 to 26 N, with substrate BIAS increase from 2 kV to 6 kV, and was consistent with low internal stress at high accelerating potential on the substrate of 6 kV (Fig. 7).

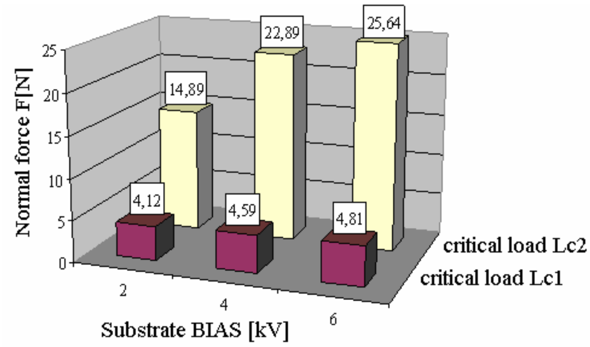

Fig. 7. Changes in the critical load of adhesion with substrate BIAS for Cr doped Cr-CrN-DLC coatings

4. CONCLUSIONS

The paper presents research on the properties of Cr-CrN-DLC coatings. GDOES spectra showed the presence of oxygen impurity in the film, but doping of DLC coatings with Cr reduced the oxygen amount. It was also shown that the adhesion of the Cr-CrN-DLC coatings obtained by the MePIIID method, can be improved with increasing substrate BIAS, and respectively, internal stresses of the coatings will decrease, but the hardness of the films will also decrease.

REFERENCES

1. A. Anders. Energetic deposition using filtered cathodic arc plasmas // *Vacuum*. 2002, v. 67, p. 673-686.
2. I.I. Aksenov, V.E. Strel'nitskij, V.V. Vasilyev, D.Yu. Zaleskij. Efficiency of magnetic plasma filters// *Surface and Coatings Technology*. 2003, v 163-164, p. 118-127.
3. X. Zhang, Z. Wu, X. Wu, L. Qin, X. Yu, Y. Xu, H. Zhang. Structure and properties of tetrahedral amorphous carbon films implanted with Ti ion// *Surface and Coatings Technology*. 2007, v. 201, p. 5219-5222.

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ЭФФЕКТ НЕПРЕДНАМЕРЕННОГО ВНЕДРЕНИЯ КИСЛОРОДА В Cr-CrN-DLC-ПОКРЫТИЯ, ОСАЖДЕННЫЕ МЕТОДОМ MePIIID, С ИСПОЛЬЗОВАНИЕМ ФИЛЬТРОВАННОЙ ВАКУУМНО-ДУГОВОЙ УГЛЕРОДНОЙ И МЕТАЛЛИЧЕСКОЙ ПЛАЗМЫ

Я. Валькович, Я. Буяк, В. Завалеев

Изучаются многослойные покрытия Cr-CrN-DLC, осажденные методом MePIIID, на подложках из быстрорежущей стали HS 6-5-2. Отфильтрованные потоки углеродной и металлической плазмы использовались в ионной имплантации и осаждении покрытий. Исследование химического состава Cr-CrN-DLC-покрытий показало значительное количество кислорода в осажденных DLC-пленках. Дополнительное легирование пленок DLC хромом сократило концентрацию кислорода. Присутствие кислорода влияет на свойства покрытий DLC, которые были подвержены исследованиям на твердость и адгезию.

ЕФЕКТ НЕНАВМИСНОГО ПРОНИКНЕННЯ КИСНЮ У Cr-CrN-DLC-ПОКРИТТЯ, ОСАДЖЕННІ МЕТОДОМ MePIIID, З ВИКОРИСТАННЯМ ФІЛЬТРОВАНОЇ ВАКУУМНО-ДУГОВОЇ ВУГЛЕЦЕВОЇ ТА МЕТАЛЕВОЇ ПЛАЗМИ

Я. Валькович, Я. Буяк, В. Завалєєв

Вивчаються багатошарові покриття Cr-CrN-DLC, осадженні методом MePIIID, на підкладках з швидкорізальної сталі HS 6-5-2. Відфільтровані потоки вуглецевої та металевої плазми використовувались в іонній імплантації та осадженні покриттів. Дослідження хімічного складу Cr-CrN-DLC-покриттів виявило значну кількість кисню в осаджених DLC-плівках. Додаткове легування плівок DLC хромом зменшило концентрацію кисню. Присутність кисню впливає на властивості покриттів DLC, які були досліджені на твердість та адгезію.