# The optical-mechanical properties of alloyed carbon coatings

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***Abstract* — Collisional activation spectroscopy is a rather elementary, quick, and non-destructive method of defining the properties of carbon coatings. The collisional activation spectra contain the information about quantitative content of $sp^3$ and $sp^2$ bonds. Macroscopic properties of metal alloyed carbon coatings (e.g. hardness, wear resistance, friction factor, and refractive index) are in close ties with the parameters received from the corresponding collisional activation spectra. It has been stated that for Cu-C coatings the intensity ratio of G- and D-peaks is defined by the changes in Cu concentration in a coating. The concentration of diamond $sp^3$ phase considerably decreases while increasing the concentration of copper, which during the synthesis process of an alloyed carbon coating works as a catalyst advantaging graphitization of a growing coating. This fact is proved by low values of friction factor and low wear resistance of the coating if copper concentration is increased with more than 3 %.**

***Keywords* – cathode-arc evaporation, alloyed carbon coatings, microhardness, internal stresses, friction.**

## I. INTRODUCTION

One of the main synthesis directions of diamond-like coatings (DLC) with high mechanical properties (high hardness, low friction coefficient, high thermal conductivity and very high optical transparency in infrared (IR) region) is the production of systems that are optimal in their construction and chemical composition [1,2]. It is stated that metal and nitrogen alloying of diamond-like carbonic coatings considerably influences their structure, $sp^2/sp^3$ ratio of hybridized atoms, leads to significant modifications of mechanical properties, electro conduction, optical, tribo-technical and other characteristics [3-4]. Depending on the nature of a metal, method and conditions of alloying, the metal in coating volume stays either in the state of an independent implantation micro- or nanophase or in the state of a carbide [5, 6]. Correspondingly, in such systems the influential character of alloying metal nature on the properties of coatings considerably varies.

In such systems one can expect the formation of specific structures which combine the mechanisms of disperse hardness and chemical interaction.

As the variant of active influence on the properties and structure of DLCs we should take into account their multicomponent doped by metal and nitrogen atoms [5, 6]. In such heterogeneous systems on particular conditions and synthesis rates, besides carbide, in the disperse phases it is possible to form metal containing compounds with the participation of nitrogen (nitrides, carbonitrides) which influence the mechanical properties of carbon coatings. It also should be pointed that the structure, properties, compound processes which take place while synthesizing such systems, their variations, e.g. during friction and wear processes, have not been studied yet.

Several characteristics and mechanical properties of the films were investigated in this study.

In the given paper titanium (forms carbides [6]), copper (chemically does not interact with carbon [6]), nitrogen (dissolves in carbon coatings well and can produce chemical compounds with metals [7]) and other elements are chosen as main ingredients which are used while multicomponent alloying.

## II. EXPERIMENTAL PROCEDURE

The unit of vacuum sputtering PVM-D is used for the production of alloyed carbon coatings. It includes: a gas ion source (helps clean and heat a substrate, introduce nitrogen growing coating into a composition); a plasma source of stationery cathode-arc discharge with a metal cathode; a plasma source of impulse cathode-arc discharge with a graphite cathode (used for carbon coatings). The carbon coatings have been applied at discharge voltage 250–300 V and impulse frequency from 1 to 35 Hz. The given rates have been chosen in accordance with earlier recommendations [8].

Copper alloying of a carbon coating has been produced from plasma of impulse cathode-arc discharge formed by the compound cathode of graphite and an alloying metal. Titanium introduction into the coating has been produced by a separate electro arc evaporator. X-ray spectroscopic microprobe analysis has been used to determine the concentration of alloying elements.

Values of micro-hardness, level of internal mechanical stresses, and tribo-chemical characteristics have been chosen as main features which determine the mechanical properties of coatings.

Tests for coatings micro-hardness have been produced at constant load of 10 g to an intender for all samples with loading duration 7 s at the durometer Leica VMHT MOT (Knoop).

X-ray diffraction analysis has been used to estimate internal stresses in a film on a silicon substrate [8]. The

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method is based on the recording of X-ray radiation reversed by two different points of a crystal at the Wolf-Bragg angle.

Tribo-technical testing has been produced at the tribometer MMT. The tribological tests were performed using the ball-on-plane testing geometry. The estimation peculiarities of friction coefficient and wear resistance with the help of the micro-tribometer MMT are given in [5].

The morphology analysis of thin film systems by the AFM method shows that a surface of alloyed coatings formed by the cathode-arc evaporation method is characterized by a considerable level of heterogeneity. The coatings having dripping phase are formed while DLC alloying by titanium, precipitated on the surface of a substrate from a separate current formed by an arc evaporator. While DLC alloying by copper, coatings having micro particles of spherical form with diameter above 0,15 µm. It can also be explained by the presence of copper micro drops in the current.

The measuring results of mechanical properties of alloyed diamond like coatings are given in Table 1.

As it is shown at the table 1, the copper introduction into a coating leads to a considerable drop in micro-hardness of a coating. It also should be pointed that high values of hardness are observed at alloying of a carbon coating by titanium up to 49-50 %. It can be determined by the formation of hard carbide phases of penetration to the volume of a coating [6, 7].

The nature and concentration of alloying particles produce particular influence on the character and values of internal mechanical stresses, appearing in the layers during the process of their synthesis. One-component carbon coatings formed by the vacuum-plasma method are characterized by high hardness and high modulus of elasticity as well as high internal stresses. These properties are explained by $sp^3$ bonds of carbon atoms in a coating [9]. High values of internal stresses of compression are the main factor leading to the destruction of adhesive conjugation of the system "surface-substrate". It has been stated that their values drop considerably while being alloyed. E.g., the introduction of 2,7 % cooper into a coating causes more than two times internal stresses drop. It should be pointed that relatively high hardness retains.

The most interesting fact is the change in internal stresses character while introducing copper and nitrogen into a coating. Tension internal stresses in such systems are varying (10-55 GPa) and can cause the destruction of a coating. Tension internal stresses effect negatively on wear resistance of a coating while being fractioned [9].

The following points have been stated: kinetic peculiarities of friction and wear resistance of alloyed DLC, the influence of conditions and rates of synthesis of carbon coating alloyed by metals on the value of friction coefficient (Fig. 1).

The lowest values of friction coefficient (f = 0,2 - 0,3) are registered while introducing copper into a DLC. Carbon coatings containing titanium are characterized by instability while being fractioned and by higher values of f.

The tests have revealed that the copper-alloyed DLC possess the maximum wear resistance (Table 2). Compared with non-alloyed DLC they last over $2 \cdot 10^3$ times longer. It should be pointed that wear resistance of the coatings depends strongly on the nature of the substrate material to which they are applied.

High tribo-technical properties of copper alloyed DLC can be explained by the formation of a dispersed copper film in the area of friction which functions as a dry-film lubricant (Fig.2, b). In wear process, DLC alloyed by titanium, defects have a local character in the contact area, and the surface structure formation does not take place (Fig.2, a).

A copper particles removes heat from spots of a factual contact, thus lowering the velocity of graphitization process of a diamond like coating and its further oxidation that in

TABLE I
MICROHARDNESS AND INTERNAL STRESS VALUES OF ALLOYED DLC

| Method | Coating composition | Micro-hardness ($H_K$),MPa | Internal stresses type σ, GPa |
|---|---|---|---|
| Impulse cathode-arc discharge | $C_{100\%}$ | 1947,25 | compression 68,3 |
| | $C_{97,6\%} + Cu_{2,4\%}$ | 1611,08 | compression 47,9 |
| | $C_{97,3\%} + Cu_{2,7\%}$ | 1743,62 | compression 33,0 |
| | $C_{97,26\%} + Cu_{2,74\%}$ | 1477,63 | compression 31,2 |
| Impulse cathode-arc discharge in $N_2$ environ-ment | $[C+N_2]_{97,49\%} + Cu_{2,51\%}$ | 1829,74 | tension 54,4 |
| | $[C+N_2]_{96,17\%} + Cu_{3,83\%}$ | 1637,61 | tension 21,7 |
| | $[C+N_2]_{94,72\%} + Cu_{5,28\%}$ | 1294,27 | tension 11,1 |
| Impulse cathode-arc discharge + electro arc evaporation of a metal | $C_{50\%} + Cu_{0,575\%} + Ti_{49,425\%}$ | 1766,34 | compression 16,0 |
| | $C_{50\%} + Cu_{0,85\%} + Ti_{49,15\%}$ | 1556,87 | compression 17,6 |
| | $C_{50\%} + Cu_{0,815\%} + Ti_{49,185\%}$ | 1622,15 | compression 15,2 |

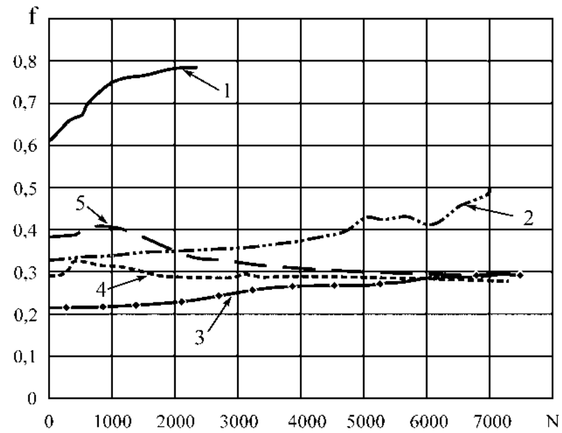
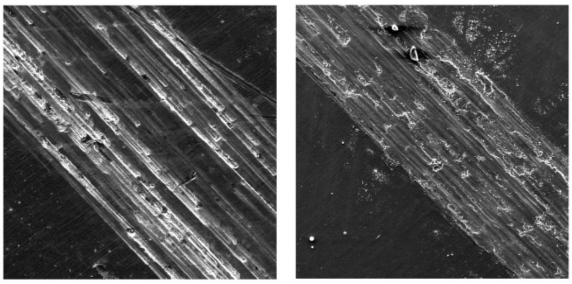



Fig. 1. Dependence of friction coefficient from the number of coatings abrasion cycles: 1 – a substrate without a coating; 2 – $C_{50\%} + Cu_{0,85\%} + Ti_{49,15\%}$ 3 – $C_{97,26\%} + Cu_{2,74\%}$ ; 4 – $C_{100\%}$; 5 – $C_{51,76\%} + Ti_{48,24\%}$

TABLE II
WEAR RESISTANCE OF ALLOYED DLC SPUTTERED ON A STEEL SUBSTRATE

| Coating | Number of abrasion cycles before full failure of the coatings | Friction coefficient at the moment of full failure of the coatings |
|---|---|---|
| DLC | ≈ 1500 | 0.28 |
| Ti + DLC | ≈ 2000 | 0.3 |
| Cu +Ti+DLC | > 3800 | 0.2 |



(a) (b)

Fig. 2. Electronic micro photographs of a friction area of a coating C+Ti (a), C + Ti +Cu (b)

accordance with [5, 6] can be regarded as the main stages of wear of a carbon matrix.

While synthesizing diamond-like coatings alloyed titanium it is possible to observe the definite concentration influence of the alloying element on $sp^3/sp^2$ ratio. But the dependence of mechanical properties from titanium concentrations has a completely different character. Titanium comes into the chemical interaction with carbon, which is in $sp^2$ condition, thus considerably decreasing the content of graphite phase in the coating. ID/IG ratio gradually decreases while increasing titanium carbide phase.

The reduction of tribochemical activity is characteristic for the coatings doped by titanium, and, as a result of this, more stabile work during the friction process occurs, which happens due to the activity decrease of carbon-oxygen interaction in the friction zone. This process can be explained by the minimal content of $sp^2$ phase which intensively interacts with oxygen and forms surface oxides.

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