

Impact of Ion Nitriding on Phase Composition, Structure and Properties of Carbon Films Doped with Metals

A.S. Rudenkov, D.G. Piliptsou, A.V. Rogachev, N.N. Fedosenko
and Xiaohong Jiang

Abstract The main modification laws of properties, phase composition and mechanical properties of single component and metal alloyed (Cr, Ti, Cu) carbon coatings subjected to ion nitriding are defined. It is stated that ion nitriding gives rise to the fraction of sp^2 -phase while reducing the cluster size in the surface layers. The formation of CN_x compounds with dominating bonds of $N-Csp^2$ type is determined at ion nitriding of carbon containing coatings. The single component carbon coatings being ion nitrided are characterized by more dispersed structure, bigger content of $N-Csp^3$ bonds in comparison with the structure and composition of coatings formed at the conditions of ion assistance or with the appearance of molecular nitrogen.

Keywords Carbon coatings · Alloying · Nitriding · Phase composition · Morphology · Hardness · Friction

1 Introduction

A wide range of properties of carbon coatings, their dependence on conditions and the modes of synthesis are caused by the variety of structural conditions of carbon, the modification of their structure and chemical activity of carbon [1–5]. While forming carbon coatings alloyed by metals and/or nitrogen, the main factors taken into consideration are their nature and concentration of the alloying elements, the way of their chemical interaction with carbon, the distribution nature on layer thickness, the existence of transitional layers. All these factors define the phase, structural condition of a carbon matrix, chemical composition of interphase layers

A.S. Rudenkov · D.G. Piliptsou (✉) · A.V. Rogachev · N.N. Fedosenko · X. Jiang
International Chinese-Belarusian Scientific Laboratory by Vacuum-Plasma Technologies,
Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing 210094, China
e-mail: pdg_@mail.ru

A.S. Rudenkov · D.G. Piliptsou · A.V. Rogachev · N.N. Fedosenko · X. Jiang
Gomel State University named after F. Skorina, Sovetskaya, 104, 246019 Gomel, Belarus

and, respectively, the property of coatings [1–3]. Such layers are characterized by higher thermo- and wear resistance, a lower level of internal mechanical tension in comparison with single component coatings, while preserving high values of microhardness.

The modification of physical and chemical parameters of carbon coatings while introducing metals into their composition is explained by the chemical interaction processes with formation of carbides [1], catalytic influence of metals on synthesis processes and sp^3 - and sp^2 -clusters dispersion [2, 4]. The formation of CN_x compounds is defined at the alloying of carbon coatings by nitrogen carried out at a deposition stage by treating the growing layer by nitrogen ions (the ion assistance mode) [5, 6] or deposition of a coating in the environment with high concentration of molecular nitrogen [7–9], and the formation of carbonitrides and nitrides of metals is stated during the alloying process of metal-containing carbon coatings [8]. At the same time the dispersion and volume of the formed phases, the nature of their distribution along the layer thickness are substantially determined by the technological parameters of alloying, nitrogen ions energy, the degree of activation processes of chemical interaction [7, 9]. It should be noted that the given results characterize the coatings which alloying is carried out as a result of simultaneous surface deposition of carbon atoms generated in plasma, and the evaporated atoms of metal. There are no data of the nitriding influence carried out by nitrogen ions treatment of previously besieged layers on the chemical composition, structure and properties of single component and composite metal-containing carbon coatings.

In this regard, the main objective of the research is to establish the composition peculiarities, structure and phase condition, mechanical properties (hardness, wear resistance) of surface layers of single component and alloyed by metals of various nature carbon coatings subjected to ion nitriding.

2 Experimental

The research object are the single component and composite carbon coatings alloyed by Cr, Ti, Cu metals which produce various chemical activity in relation to carbon and nitrogen. The deposition of carbon coatings is produced from pulse cathodic plasma by the technique introduced in [3]. The deposition a-C:Me coatings is produced by the co-deposition of carbon atoms and metal atoms generated by magnetron dispersion (discharge power at dispersion of Cr, Ti is 400 W, at dispersion of Cu—200 W). At the same time the atomic content of metal in a coating is approximately identical 2.2 ... 2.65 %.

Ionic nitriding is carried out by means of a high-energy ionic source at the following parameters: gas pressure $P = 10^{-1}$ Pa; current—0.2 A; the accelerating voltage 2 kV.

Studying of morphology of the alloyed carbon coatings is carried out by method of atomic force microscopy (AFM) in the modes of topography and phase contrast measuring with the help of the Solver Pro device of NT-MDT (Moscow, Russia).

The determination of phase structure of carbon coatings is carried out by the analysis of the combinational dispersion spectra gathered at Senterra spectrometer with the wavelength of the exciting radiation of 532 nm, power 10 mW. The decomposition of the registered spectra at D- ($\sim 1400 \text{ cm}^{-1}$) and G-peaks ($\sim 1550 \text{ cm}^{-1}$) is produced the Gauss method. The chemical composition and structure of carbon bonds are defined by the method of x-ray photoelectronic spectroscopy (XPES). The measurements are produced by the PHI Quantera device at aluminum substance activation by K α -radiation with quantum energy 1486.6 eV and with 250 W power.

The DM-8 microhardness tester (AFFRI, Italy) is used to measure the microhardness according Knoop. The load on a diamond pyramid is equal to 245 mN, the duration of the test is 10 s.

The tribotechnical tests are carried out according to the scheme “sphere-plane” (a ball with 5 mm radius from the tempered ShH15 steel, the coating is applied on a flat silicon substrate). The load is 0.98 N, the average speed of movement -0.0087 m/s . After rubbing, we determined the contact patch diameter using an optical microscope. The rider’s wear rate was calculated as $j = V/FL$, where F is a load (N); L is the friction length (m); V is the worn volume of the spherical segment of the rider (m^3). The friction coefficient and wear rate were calculated by averaging the data of three independent experiments.

3 Results and Discussion

It is established that at ionic nitriding the morphology of coatings considerably changes due to etching. The roughness and the amount of particular structural formations of single component and composite carbon coatings decrease after ionic nitriding (Table 1).

At the same time the most considerable roughness reduction is observed at single component carbon coating treating. Such coatings, as it is noted in [10], contain graphite microdrops, and their primary etching occurs in the ionic nitriding course, what defines roughness decrease of a coating. In metal-containing carbon layers at their nitriding the new firm phases of introduction can be formed possessing the lower etching speed in comparison with graphite, and, as a result of it, the changes of surface topography are less expressed.

Table 1 Roughness parameters of carbon coatings to/after ionic nitriding on the AFM data basis

Coatings	Average height (nm)	Rms (nm)	Grain density ($\text{grain}/\mu\text{m}^2$)	Average grain size (nm)
a-C	81/26	22.8/8.5	54/78	164/128
a-C:Cr	20/10	7.8/3.9	49/62	93/82
a-C:Cu	18/21	5.0/4.2	98/76	87/89
a-C:Ti	11/16	2.4/3.4	44/47	118/118

Table 2 The results of Raman-spectroscopy of the alloyed carbon coatings to/after ionic nitriding

Coating	D-peak		G-peak		I_D/I_G ratio
	Centre (cm^{-1})	Width (cm^{-1})	Centre (cm^{-1})	Width (cm^{-1})	
a-C	1438.2/1434.4	275.3/282.1	1562.8/1563.8	197.2/189.2	0.50/0.58
a-C:Cr	1395.5/1377.4	336.4/358.5	1549.1/1546.0	167.0/147.9	1.15/1.64
a-C:Cu	1406.4/1401.4	307.2/319.1	1551.8/1555.6	165.9/156.8	1.04/1.21
a-C:Ti	1404.4/1399.9	323.5/328.9	1554.8/1554.6	169.8/169.2	1.01/1.07

Ionic nitriding of carbon coatings also leads to the change of their phase state. According to the results of Raman spectroscopy presented in Table 2, after ionic nitriding of the single component and alloyed by metal carbon coatings the increase in D-peak width, decrease in G-peak width, increase of the relation of I_D/I_G are observed.

As it is stated in research [3], narrowing of G-peak width is caused by the order increase of sp^2 -clusters, the increase in a ratio of I_D/I_G can be caused by the reduction of their size and growth of the number of sp^3 bonds. The broadening of D-peak and its shift to the area of low wave numbers can demonstrate the disorder and reduction of sp^3 -clusters number. Such changes can be caused by the destruction of grains borders and substrate heating under the influence of the subsequent ionic bombing that correlates with AFM data and the results of experiments on formation of carbon coatings in the conditions of ionic bombing stated in research [10].

The formation of carbon coatings in the conditions of ionic assistance (irrespective of the assisting ions energy) has more significant effect on their phase structure [11]. At assisting the I_D/I_G ratio increases from 0.5 to 1.38, and G-peak width decreases to 166.6 cm^{-1} . After ionic nitriding the I_D/I_G ratio equals to 0.58, and G-peak width equals to 189.2 cm^{-1} . Such changes are explained by various mechanisms of phase transitions $\text{sp}^3 \rightarrow \text{sp}^2$ of carbon coatings. At ionic assistance, the main cause for the change of phase structure are inelastic impacts of ions of nitrogen and carbon in plasma, while the subsequent ionic nitriding has a superficial character, the processes of etching, implantation and local heating of the top coat layers prevail.

It should be noted that the introduction of metal in a carbon coating a little reduces graphitization degree, and in the case of an alloying copper ionic nitriding even reduces the surface area of the substrate occupied by sp^2 -clusters (Fig. 1).

The change of a chemical composition of the coatings subjected to ionic nitriding is defined according to the change of location and the N1s form of peak of XPS of the spectrum (Fig. 2).

It is stated that both the single component and alloyed by metals carbon coatings contain chemically bonded atoms of nitrogen in a surface layer. The decomposition of N1s peak of single component carbon coatings allows to allocate N-C sp^3 bonds with $\sim 398.2 \text{ eV}$ energy, N-C sp^2 (399.9 eV) and N-O (401.7 eV). At N1s peak of the coverings alloyed by titan there is a component with 397.3 eV energy, corresponding to titan nitride N-Ti [12]. N1s peak of the carbon coatings alloyed by

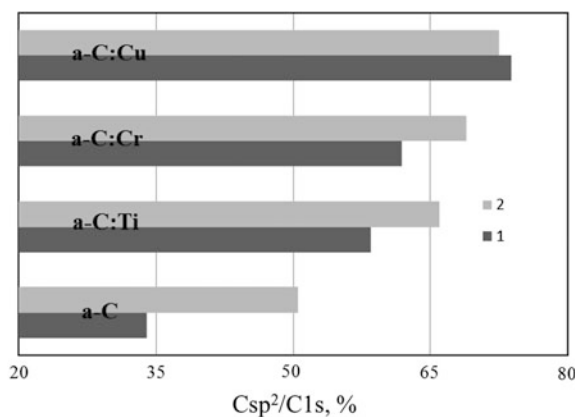


Fig. 1 The content of a sp^2 -phase in a coating before (1) and after (2) ionic nitriding

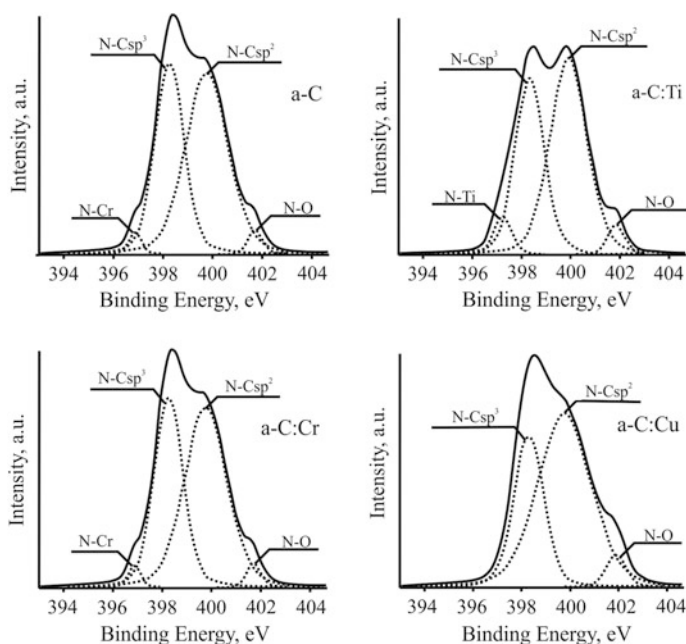


Fig. 2 N1s-peak XPS of carbon coatings subjected to ion nitriding

chrome is displayed on the following components: N-Cr with binding energy 396.7 eV [13], N-Csp³ with binding energy ~ 398.3 eV, N-C sp² (399.8 eV) and N-O (401.7 eV). It is difficult to reveal the presence of copper nitride by the XPS method as the binding energy of copper nitride equals to ~ 932.7 eV for Cu2p, that is very close to Cu-O component with spin-orbit orbital modification 2p_{3/2} with a

priori higher intensity [14]. The subsequent ionic processing of the single component and alloyed by carbide-forming metals carbon coatings leads to the growth of the contents of the sp^2 -hybridized atoms of carbon that is partly confirmed by the data of Raman-spectroscopy confirming the insignificant growth of I_D/I_G ratio. It is difficult to judge about the modification of a sp^3 -phase as at the decomposition Csp^3 and C–N, C=N bonds are meant of the component with the binding energy ~ 285.4 eV. However, even taking into account the intensity contribution of the given component of C=N and C–N bonds it is possible to conclude that the share of the integrated area slightly decreases in all cases.

From the analysis of N1s it becomes obvious that at ionic processing of the deposited carbon coating CN_x bonds with the prevailing content of N– Csp^2 bonds are formed. Besides, after ionic nitriding for the coatings alloyed by carbide forming metals, the decrease in content of carbides of metal and formation of nitrides are fixed. Also the insignificant increase in content of the sp^2 -hybridized atoms of carbon is observed. The above mentioned modifications prove that at nitriding of the already formed carbon coatings the implantation of nitrogen ions in a near-surface layer takes place with the subsequent formation of chemical compounds of nitrogen and carbon.

Table 3 introduces the results of the XPS spectra analysis of single component carbon coatings after the ionic nitriding and the coatings formed in the conditions of ionic assistance or in the environment of molecular nitrogen with its pressure in a vacuum chamber of 0.1 Pas [11].

It is stated that in all exploded ways of carbon coating nitriding nitrogen forms chemical bonds mainly with Csp^2 carbon (the ratio of bonds number of N– Csp^3 and N– Csp^2 is less than one), it can be connected with higher adsorptive activity and diffusive permeability of a graphite phase. At ionic nitriding of coatings the relative maintenance of N– Csp^3 bonds is 3.5–3.7 times higher than in the carbon coatings formed in the presence of molecular nitrogen or in the treating conditions by nitrogen ions of the growing carbon layer. This result can be explained by the modification of activation conditions at the impact of nitrogen ions on the surface, the smaller content of Csp^2 -clusters in the initial coating.

Table 4 introduces the measurement results of microhardness of H_k , value of volume coefficient of counterbody wear j of carbon coatings before and after their ionic nitriding.

It is obvious that the subsequent ionic nitriding leads to the increase in microhardness for all carbon coatings. This effect is a consequence of the modifications of a phase and chemical composition of coverings when nitriding. At the same time

Table 3 The results of XPS of carbon coatings subjected to nitriding by different methods

Alloying means	$Csp^2/C1s$ (%)	N–C sp^3 /N–C sp^2
No alloying	33.98	–
Ion nitriding	50.51	0.68
Deposition in N2 environment	56.00	0.18
Ion assisting	59.00	0.19

Table 4 The influence of ionic nitriding on the hardness of Hk and wear coefficient of counterbody j

Coating	Hk (GPa)		j ($\times 10^{-18}$ m ³ /(N m))	
	Before	After	Before	After
a-C	10.74 ± 0.22	11.21 ± 0.15	419.3 ± 4.6	345.6 ± 2.9
a-C:Cr	12.45 ± 0.23	12.81 ± 0.18	138.1 ± 2.7	172.5 ± 3.3
a-C:Cu	10.23 ± 0.26	10.79 ± 0.21	120.1 ± 4.2	165.2 ± 3.8
a-C:Ti	11.91 ± 0.25	12.62 ± 0.14	128.9 ± 5.0	191.0 ± 4.2

considering that the hardness increase is observed also when nitriding single component carbon coatings, apparently, the greatest contribution to the hardness increase is produced by formation processes of CN_x bonds.

The decrease in volume coefficient of wear of a counterbody at nitriding of non-alloyed carbon coatings (Table 4) is explained by the significant increase in content of a graphite sp^2 -phase (by 1.5 times) which being on surfaces produces a lubricant effect at contact interaction. At friction subjected to nitriding of the carbon coatings alloyed by metal the value of wear volume coefficient of a counterbody increases that is caused by the formation in a surface layer of firm heat-resistant bonds (nitrides, carbonitrides), capable to abrasive destruction of the contacting surface.

4 Conclusion

The main modification laws of properties and phase structure of the single component and Cr, Ti, Cu alloyed carbon coatings subjected to ionic nitriding are defined. The increase in a sp^2 -phase content, concentration decrease in near-surface layers of Me_yC_x bonds, formation of Me_yN_x and CN_x bonds with the prevailing $N-Csp^2$ content of bonds are established. After ionic nitriding of single component and composite coatings the increase in microhardness is observed at 0.5–0.7 GPa and in 1.2–1.5 wear volume coefficients of a steel counterbody at friction with a coating.

It is defined that at ionic nitriding of single component carbon coatings the relative content of $N-Csp^3$ bonds is 3.5–3.7 times higher in comparison with carbon coatings, formed in the molecular nitrogen presence or in the conditions of simultaneous deposition and treatment of the surface by nitrogen ions.

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