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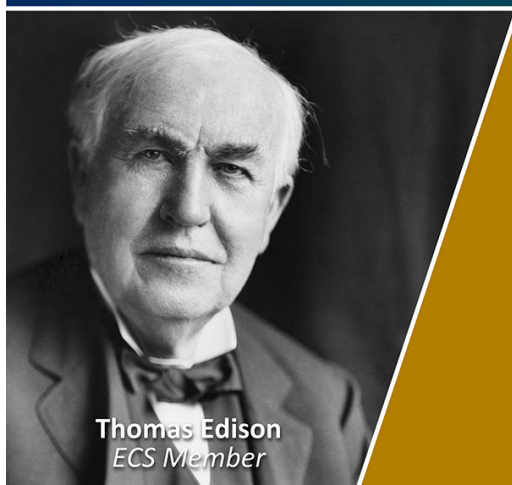
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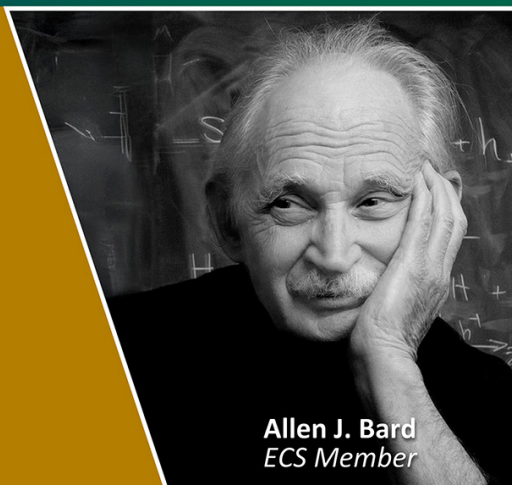


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The influence of the ion plasma flow on the phase composition and microhardness of carbon coatings doped with metals

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Abstract. The Raman spectroscopy method established that subsequent treatment with ion ions leads to a change in the microstructure of coatings based on carbon and metals. It is established that the structure change is determined by the changes occurring at the interface and depends on the $sp^3 \rightarrow sp^2$ phase transition due to the appearance of local thermal peaks at the end of tracks of nitrogen ions implanted in the coating volume. It is shown that the microhardness of metal-carbon coatings (α -C: Cu, α -C: Ti, α -C:Al) increases after ion-plasma treatment, which is determined by the formation of solid interstitial phases based on CN_x and metal carbonitrides.

1. Introduction

Amorphous carbon coatings (α -C), produced by various methods, have a unique combination of electrical, optical, thermal and mechanical properties. At the same time, they are characterized by a number of defects, including low temperature stability, high internal stresses, and low adhesion to dielectric substrates [1]. The most effective method of enhancing the properties of α -C is their doping with nitrogen and various metals, which have different chemical activity with respect to carbon [2–4]. For the production and usage of such coatings it is very important to control the properties of the produced nanocomposite systems, in which the chemical interaction processes can lead to the formation of carbide and nitride phases in the carbon matrix. The choice of individual components and their concentration in the coating layer, as well as the effect of the ion-plasma treatment method and regimes on the carbon structure, largely determine its basic performance characteristics. At ionic processing of composite carbon coatings, selective etching of a certain coating component occurs, the concentration and character of distribution in the volume of alloying elements change. With such treatment, the processes of chemical interaction during heating, radiation modification of components become more complex [1, 2]. An increase in the operational properties of metal-carbon coatings is



possible with a directed change in the structure of the layer due to a change in the modes and parameters of doping or ion treatment during their formation [1–4].

The matter of topical interest is to select the composition of the individual components of the coating and develop technological recommendations for directed changes in the structure and mechanical properties of metal-carbon coatings formed under the conditions of ions assisting of different nature and energies with subsequent technological ion treatment.

The effect of the subsequent technological ion-plasma treatment on the structure and microhardness of composite metal-carbon coatings formed by simultaneous deposition of carbon from a pulsed cathode plasma and ions / metal atoms (Cu, Ti, Al) generated by magnetron sputtering is under study.

2. Models and research methods of production and properties

Carbon coatings were formed on a silicon substrate by simultaneously depositing carbon from the plasma source of a pulsed cathode-arc discharge with a graphite cathode and metal from the flow of the generated magnetron sputtering system. As alloying elements, metals possessing different chemical activity with respect to carbon and nitrogen (Cu, Ti, Al) were used. Subsequent processing of the produced coatings with nitrogen ions (ion energy up to 1.5 keV) promotes phase transitions $sp^3 \rightarrow sp^2$ and the formation of metal nitrides and chemical compounds of nitrogen and carbon CN_x in the near-surface layers. The thickness of the coatings was 270–300 nm, the metal concentration was of 2.5 at. %, the microhardness varied from 10 to 12 GPa, depending on the nature of the alloying metal.

The phase composition of the carbon coatings was determined by analyzing the Raman spectra obtained with a Senterra spectrometer with an excitation wavelength of 532 nm and power of 10 mW. The obtained spectra were decomposed into two Gaussians (D- and G-peaks).

Raman spectroscopy is one of the most widely used methods of non-destructive quality control of diamond [1], graphite, carbon nanotubes and carbon-based coatings [2, 4–6].

There are three main reasons for the change in the Raman spectra of α -C coatings [7]:

- conjugated π -bonds increase the polarizability range;
- G and D modes are conjugated;
- the phenomenon of double resonance for the D mode [8].

A large range of polarizability substantially increases the intensity of the G and D modes. Particularly, the intensity of the D mode increases, which is caused by the respiratory mode. In the graphite layer there is an amplifying interference of the eigenvectors of each six-atom ring and weakening interference for rings of other orders.

All three factors increase the intensity of respiratory modes and suppress the modes of other symmetries. In [9] it is noted that the ratio I_D/I_G is inversely proportional to the size of graphite L_a grains:

$$I_D/I_G = c(\lambda)/L_a, \quad (1)$$

where I_D and I_G are the intensities of the corresponding peaks, $c(\lambda)$ is the proportionality coefficient that depends on the wavelength of exciting radiation, and L_a is the grain size of graphite (nm). This means that the ratio I_D/I_G is proportional to the number of rings at the grain boundary. Obviously, this L_a can not tend to zero. For ta-C coatings, it was found that for L_a is less than 2 nm, the ratio decreases according to the expression (2) [10]:

$$I_D/I_G = c(\lambda) \cdot L_a^{-2} \quad (2)$$

Since the G-peak of the mode exists due to sp^2 -hybridized atoms, and the D-peak is only due to the rings, I_D/I_G decreases with a decrease in the number of carbon rings and an increase in the proportion of carbon chains.

Figure 1 shows the causes of the displacement of the G and D peaks, as well as the changes in their relative intensities.

In [6, 11], a three-stage model for increasing the degree of disorder in carbon is presented:

- ideal graphite passes into a nanocrystalline;

- nanocrystalline graphite passes into a-C form;
- sp^2 a-C goes to sp^3 ta-C.

Stage 1 corresponds to a decrease in the grain size of an ordered graphite layer, but with the preservation of aromatic rings. The G-peak shifts to 1600 cm^{-1} . Mode D is banned for an ideal layer of graphite, but the disorder of bonds and the reduction in grain size leads to an increase in its intensity. It is worth noting that the width of the D- and G-peaks is a characteristic of the disorder degree.

Stage 2 corresponds to the topological disorder of graphite, the decrease of aromatic bonds, but with the preservation of the perfect sp^2 matrix. The G-peak shifts to 1520 cm^{-1} .

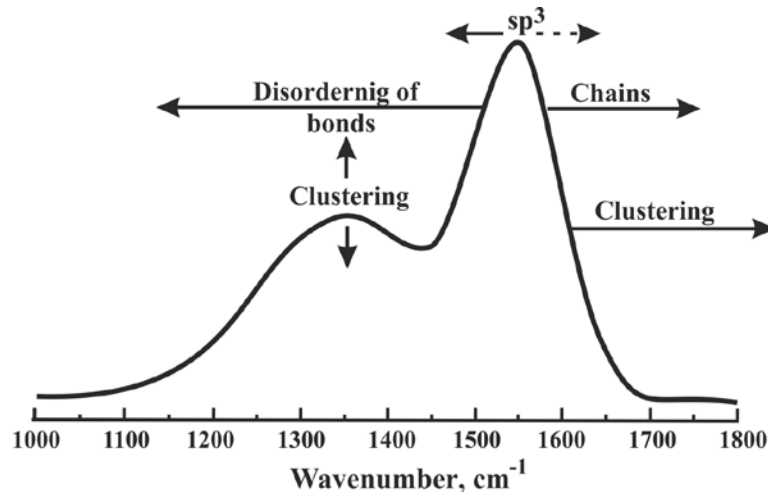


Figure 1. The schematic diagram of the change in the Raman spectra of carbon coatings [7].

At stage 3, the content of sp^3 increases to 100 %. This fact changes the sp^2 -configuration from rings to short chains [6]. The length of bonds of chains (olefins) is shorter than that of carbon rings, since their oscillation frequencies are higher. The G-peak shifts to $1580\text{--}1600\text{ cm}^{-1}$, its intensity increases, and the D-peak intensity tends to zero.

An increase in the I_D/I_G ratio indicates a decrease in the size of sp^2 clusters, narrowing of the width of the G peak indicates an increase in the order degree, its shift to the region of large wavenumbers can be explained by an increase in the level of internal stresses, and a shift to the region of smaller wave numbers by a decrease in the content and disordering of sp^3 -bonds.

To measure the microhardness according to Knupp, the microfirms *AFFRI DM-8* were used during experiments. The evaluation of microhardness is based on measuring the length of the diagonal of the reprint produced by indenting a diamond pyramid with a certain load into the material under study. When measuring the microhardness according to Knupp, a pyramid with a square base is used, in which the angle between the opposite lateral faces was $172^\circ 30'$.

The sizes of prints were determined with the help of an optical microscope with interchangeable lenses providing an increase in $400\times$ and $100\times$. The load value F is 245 mN; the duration of indentation of the pyramid during measurements by both methods was the same – 10 s. Since the thickness of the coatings analyzed in the research does not exceed 200 nm, the measured microhardness of the samples is a superposition of the hardness of the "coating-substrate" system and was determined according to the expression (1):

$$H_k = 14,23 \cdot F/L^2, \quad (3)$$

where L is the diagonal length and F is the load.

3. The results and their analysis

Figure 2a–e shows the results of statistical treatment of the data of Raman spectroscopy of metal-carbon coatings (α -C: Cu, α -C: Ti, α -C: Al) after ion-plasma treatment.

The analysis of Raman spectroscopy shows that the subsequent ion-plasma treatment of metal-carbon coatings leads to an increase in the I_D/I_G ratio, which indicates a decrease in the size of sp^2 clusters. In addition, a decrease in the width of the G peak is observed, which is explained by an increase in the degree of ordering of the sp^2 clusters.

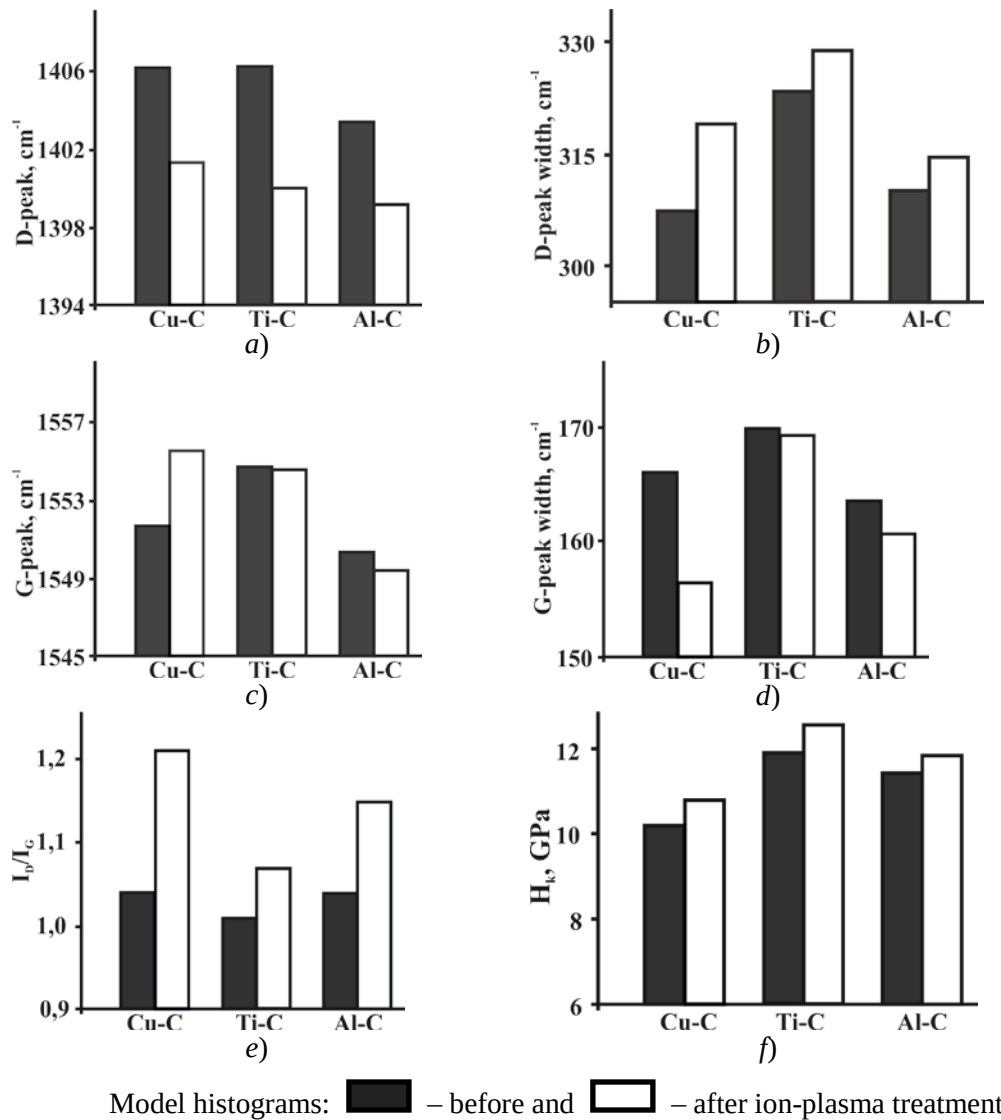


Figure 2. Histograms of values of position (a, c), width (b, d), intensity of absorption peaks (e) of Raman spectra and microhardness (f) of produced metal-carbon coatings (α-C: Cu, α-C: Ti, α-C: Al) after their subsequent technological ion-plasma treatment.

The position of the G peak, in the case of α-C: Al and α-C: Ti coatings, practically does not change. Its shift to the region of large wave peaks after ion-plasma treatment of copper-doped coatings can be caused by an increase in the level of internal stresses due to the formation of a larger number of crystalline inclusions of N-Csp², in contrast to titanium and aluminum. Since Co-C coatings initially, even before ion-plasma treatment, are characterized by a high content of sp^2 phase, while sp^2 -hybridized carbon atoms in α-C: Al and α-C: Ti coatings are bound in the form of metal carbides. In addition, the level of internal stresses after ion-plasma treatment in α-C: Cu coatings can increase as a result of the formation of Cu₃N, however, the formation of such compounds by vacuum methods is

unlikely.

The increase in the width of the D-peak and its shift to the region of lower wave numbers may indicate disordering and a decrease in the number of sp^3 -clusters. Such changes can be caused by the destruction of the grain boundaries and $sp^3 \rightarrow sp^2$ phase transition, due to the formation of local thermal peaks at the end of tracks of nitrogen ions implanted in the coating volume during ion-plasma treatment.

The results of measuring the microhardness of samples of metal-carbon coatings before and after ion-plasma treatment are introduced in Figure 2f, where it is shown that the microhardness of metal-carbon coatings (α -C: Cu, α -C: Ti, α -C: Al) increases after ion-plasma treatment. It can be assumed that this increase in microhardness is mainly due to the formation of solid interstitial phases based on CN_x and metal nitrides. It should be noted that the formation of Cu_3N as a result of ion-plasma treatment is less likely than AlN and TiN.

The previously established fact of decreasing the size of sp^2 clusters due because of ion-plasma treatment also makes it possible to explain the change in microhardness from the point of view of the Hall-Petch law. The relatively small (0.5–0.7 GPa) increase in microhardness can be explained by the formation of CN_x phases in near-surface layers, the thickness of which is much smaller than the depth of penetration of the indenter.

4. Conclusion

Raman spectroscopy showed that the subsequent ion-plasma treatment of metal-carbon coatings leads to the increase in the ratio of the I_D/I_G absorption peaks of their Raman spectra, which indicates the decrease in the size of sp^2 clusters. At the same time, the increase in the width of the D-peak and its shift to the region of lower wave numbers may indicate disordering and the decrease in the number of sp^3 -clusters. Such changes can be caused by the destruction of the grain boundaries and the $sp^3 \rightarrow sp^2$ phase transition due to the formation of local thermal peaks at the end of tracks of nitrogen ions implanted in the coating volume during ion-plasma treatment. It is shown that the microhardness of metal-carbon coatings (α -C:Cu, α -C:Ti, α -C:Al) increases after ion-plasma treatment, which is possible due to the formation of solid interstitial phases based on CN_x and metal nitrides.

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