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Change of internal stress of carbon superhard condensates at a process of annealing

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Abstract

Superhard carbon coatings with thickness from 5 nm up to 10 μm were obtained by vacuum-arc deposition of carbon plasma on sublayers from stainless steels, titanium and silicon under the temperature from 50 up to 150 °C. Correlation dependences between conditions of formation of carbon condensates and change of internal stresses in them at a process of annealing in a range of temperatures from 200 up to 475 °C were examined. It was shown that the character of internal stresses changing at a process of annealing of carbon condensates had proof correlation with the parameters of deposition (the temperature of sublayer, duration of a pulse of discharge) and it could be used for identification of coatings and for control of their properties. It was determined that superthin layers of carbon obtained by impulse vacuum-arc method effectively protected a surface from oxidation in an atmosphere of air up to 425 °C. Researches of surface structures of coatings by use of scanning probe microscopy (SPM) were carried out. It was classified as fractal and an explanation of mechanism of change of internal stress value in carbon coatings at a process of annealing was given.

Keywords: Amorphous carbon; Cathodic arc discharge; Thermal stability; Coatings

1. Introduction

Superhard carbon coatings formed as a result of condensation of the accelerated particles of carbon on a substrate draw special attention of researchers [1]. A characteristic property of these coatings is abnormally-high internal stress of compression which causes bending of a sublayer and it carries to its flaking at increase of thickness up to the certain value [1,2].

In 2000 the researchers of the scientific centre 'Sandia Corporation' declared successes which they had reached in a problem of decrease of internal stress in carbon films (amophous-tetrahedrally coordinated carbon films) [3]. However, it concerned only coatings obtained by the method of laser deposition by use of ekcimer laser. There are some features in annealing of carbon coatings obtained by vacuum-arc sputtering of graphite.

In this work we give the results of researches of influence of annealing in air on a value of internal stress in a carbon condensate obtained by impulse vacuum-arc sputtering of graphite cathodes and also the features of annealing of thin carbon films.

2. Theoretical discussion

Annealing of structures obtained in thermodynamic unbalanced conditions, namely at low temperatures of a sublayer and also in conditions of the ion bombardment of a growing condensate allows to determine thermal stability of the received object and besides to receive the information on influence of parameters of condensates deposition on its physic-mechanical properties.

In our case such property is a value of internal stress in a carbon coating, and parameters of a process of carbon coating formation are temperature of a sublayer and duration of a pulse of discharge determining power characteristics of plasma. Change of internal stress value in a carbon condensate as a result of annealing allows us to estimate quantitatively structural changes in it with the high accuracy inaccessible as it is paradoxical for the majority of methods of researches.

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Internal stresses in carbon coatings have a structural character and their beginning is connected to processes of generation and evolution of radiating defects in a condensate as a result of the ion bombardment bringing to its swelling, i.e. increase of volume in a process of increase of coating thickness.

The next annealing activates diffusion process in a structure of a coating, migration of point defects (partial atoms in interstitial sites and partial vacancies).

Let's carry out comparison of speeds of diffusion processes (time of diffusion for atoms in interstitial sites Δt_i and vacancies Δt_v), preliminary having calculated values of a coefficient of diffusion for temperature of a sublayer T_s in a range 100–500 °C (373–773 K).

$$D_v = D_{ov}\exp(-E_{mv}/kT_s) \quad (1)$$

$$D_i = D_{oi}\exp(-E_{mi}/kT_s) \quad (2)$$

here: D_{ov}–a preexponential multiplier for a coefficient of diffusion of vacancies; D_{oi}–a preexponential multiplier for a coefficient of diffusion of interstitial sites; E_{mv} – energy of vacancies migration, E_{mi} – energy of atoms migration in interstitial sites.

$$\Delta t_v = \frac{\delta^2}{2D_v} \quad (3)$$

$$\Delta t_i = \frac{\delta^2}{2D_i} \quad (4)$$

here: δ–thickness of a coating (approx. 1 μm).

Having taken advantage of values of parameters of the point defects given in Ref. [4] and having carried out estimated calculation, it is possible to draw a conclusion that the atoms in interstitial sites survived after processes of recombination are practically instantly absorbed on interclaster borders in pores and complexes of vacancies formed in a carbon condensate at its formation on a 'cold' sublayer which has a temperature (50–150)°C. Annealing of the formed carbon condensate at temperature (200–500)°C can result to self-diffusions of vacancies in coatings and to change of its structure, volume and value of internal stress in it. Thus, it is necessary to take into account probability of formation of complexes of vacancies, which have various values of energy of migration.

3. Experimental procedures

3.1. Preparation of films

Carbon coatings were obtained using an impulse vacuum-arc source of carbon plasma with a graphite cathode described in detail in Ref. [5]. The same source but equipped with a titanium cathode, was used for deposition of interlayers of titanium.

Capacitor the store with general capacitance 2000 μF was charged up to voltage 300 V. Duration of a pulse of discharge was adjusted by changing a value of inductance of the shaper of pulses in limits from 0.5 ms up to 0.7 ms. Repetition frequency of pulses of discharge was adjusted in limits from 0.5 Hz up to 10 Hz for maintenance of temperature of a sublayer at the given level.

Speed of coatings deposition was 0.6–0.8 nm for one pulse. The temperature of a substrate was measured by the thermocouple.

For research of influence of annealing on a value of internal stress in carbon coatings strips from stainless steel with thickness 0.09 mm, width 7 mm and length 37 mm were used on which carbon coatings with thickness 1 μm were deposited. On the same plates a carbon coating with general thickness 1 μm with titanium interlayers with thickness 200 nm was deposited.

For deposition of thin carbon condensates with thickness 5 nm and 300 nm sublayers from monocrystal silicon with titanium precoat with thickness 0.1 μm were used. Carbon films with thickness 5 nm were deposited through the mask, which closes a part of a sublayer from hit of carbon on it. For deposition of carbon condensates with thickness 10 μm a sublayer from stainless steel with thickness 3 mm, width 10 mm and length 10 mm were used.

Further, the samples were annealed in the muffle furnace MP-2UM in an interval of temperatures from 150 up to 500 °C with step of change of temperature 50 °C. The temperature was measured by the thermocouple. At each temperature the samples were withstood within 1 h.

3.2. Structure of condensate surface

Structure of a surface of carbon condensates was examined using a scanning probe microscope 'Smena-A' made in 'NT-MDT' enterprise. It was used in a contact mode by use of a silicon cantilever.

3.3. Thickness of films

Thickness of carbon films was measured using a scanning probe microscope 'Smena-A' preliminary having created 'a step' on a sample by use of the mask.

3.4. Film stress

A value of internal stress was measured in accordance with a value of deflection of the samples which was measured by an optical microscope. Internal stress was expected under the formula of Stoney [6]:

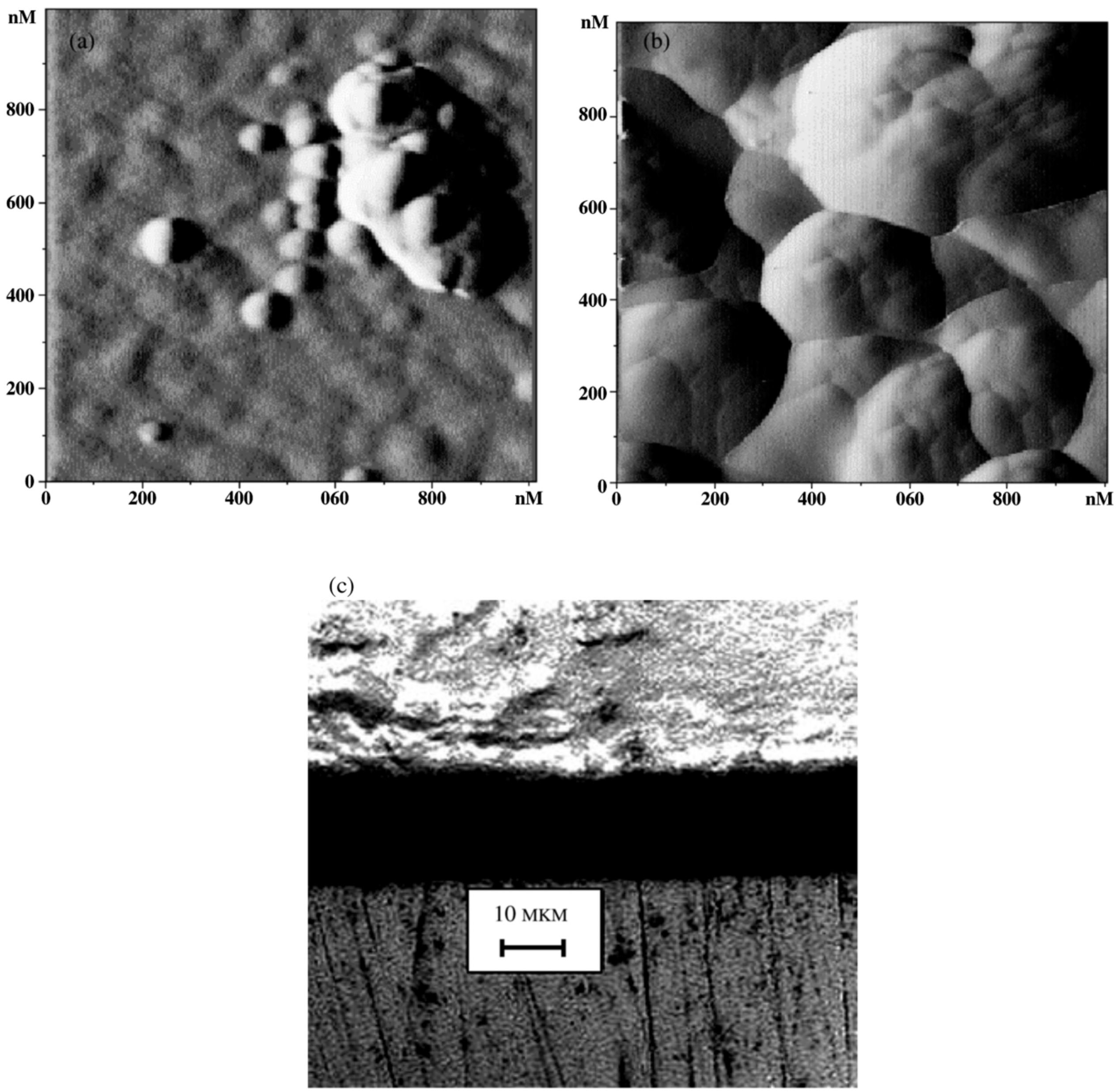

Fig. 1. Superficial structures of a carbon condensate with thickness 300 nm (a) and 10 μm (b); (c) an appearance of a superhard carbon coating with thickness 10 μm on a sublayer from silicon after cross microgrinding.

$$\sigma = \frac{E \cdot t^2}{6(1-\nu) \cdot R \cdot h} \tag{5}$$

here: E–modulus of elasticity of sublayer material; t – sublayer thickness; R – radius of curvature of the bent strip; ν–Poisson's coefficient of sublayer material; h – film thickness.

Considering that $R = \frac{l^2}{8 \cdot f}$, where l – length of the strip; f – value of deflection; ν–for steel $= 0.3$.

$$\sigma = \frac{E \cdot t^2 \cdot f}{0.525 \cdot h \cdot l^2}. \tag{6}$$

4. Results and discussion

4.1. Surface structure of coatings

In Fig. 1a,b structures of a surface of a carbon condensate with thickness 300 nm and 10 μm are shown.

In these figures it is possible to trace dynamics of formation so-called fractal structures. Mandelbrot was the first who had entered a new concept for description of complex structures consisting of parts similar whole and had named such structures as fractals [7].

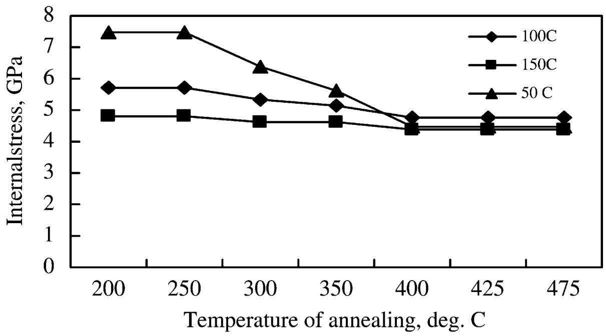

Fig. 2. Dependences of change of internal stress value on temperature of annealing in carbon condensates obtained at the temperature of a sublayer 50, 100 and 150 °C and duration of a pulse of discharge 0.5 ms.

For presentation in Fig. 1c an appearance of a superhard carbon coating with thickness 10 μm on a sublayer from silicon after cross microgrinding is shown.

Fractal structures as against crystal are characterized by presence of free volume (pores, cavities) which at a process of annealing can serve as effective drains for point defects.

It is necessary to note that up to thickness 100 nm such formations on the surface of a carbon condensate are not observed.

4.2. Dependence of internal stresses value from temperature of annealing

In Fig. 2 there is a plot with dependences of change of internal stress value from temperature of annealing in carbon condensates obtained at the temperature of sublayer 50, 100 and 150 °C and duration of a pulse of discharge 0.5 ms.

Reduction of a value of internal stress for coatings obtained at higher temperature is probably connected to partial annealing of radiation-induced defects at the process of coatings formation. At this stage energy of superficial migration for vacancies has essentially smaller values than energy of migration of vacancies in volume of a condensate.

Change of a value of internal stresses at the next annealing occurs in steps. It is connected to presence of vacancy complexes of various configurations in a condensate and, hence, described by various energy of migration.

Extremely interesting feature of these dependences is a value of change of internal stress in condensates at the process of annealing correlating with temperature of a sublayer at deposition of carbon coatings.

In a range of temperatures 400–475 °C a value of internal stress is stabilized. In a range of temperatures 475–500 °C there is a sharp reduction of a value of

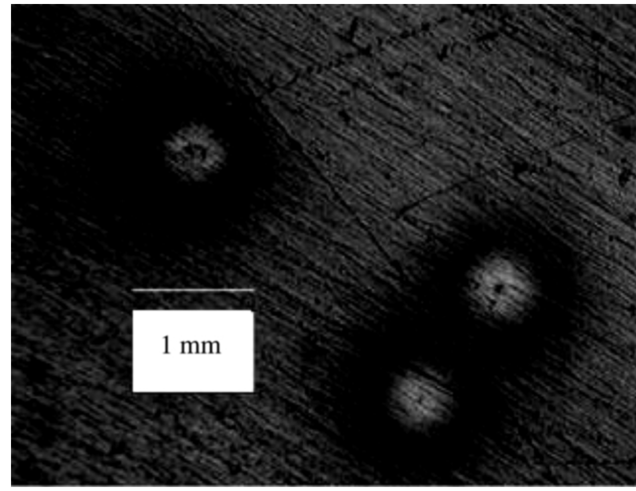

Fig. 3. Zones of change of coatings thickness caused by diffusion processes in places of defects.

internal stress. It is connected to infringement of adhesion between a substrate and coatings that is fixed as flaking of separate areas of coatings. In this range of temperatures diffusion migration of vacancies, their association in micro-pores on border with a substrate is intensified and finally it reduces to flaking of coatings from a substrate.

In a range of temperatures 450–475 °C in a process of rise in temperature zones of change of coatings thickness are observed caused by diffusion processes in places of defects that are shown in Fig. 3.

In Fig. 4 there is a plot with dependences of change of internal stress value from temperature of annealing in carbon condensates obtained at the temperature of sublayer 50 and 150 °C and duration of a pulse of discharge 0.7 ms.

Reduction of internal stress value for a carbon condensate obtained at the greater duration of a pulse and

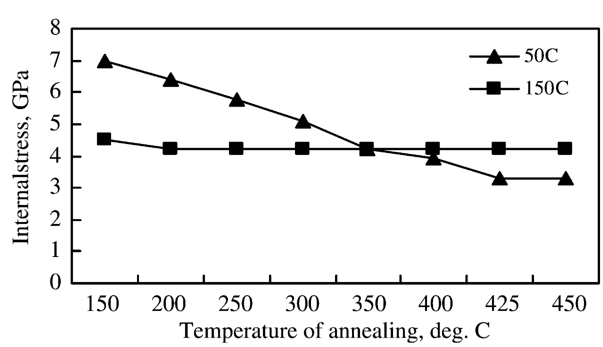

Fig. 4. Dependences of change of internal stress value on temperature of annealing in carbon condensates obtained at the temperature of a sublayer 50, 100 and 150°C and duration of a pulse of discharge 0.7 ms.

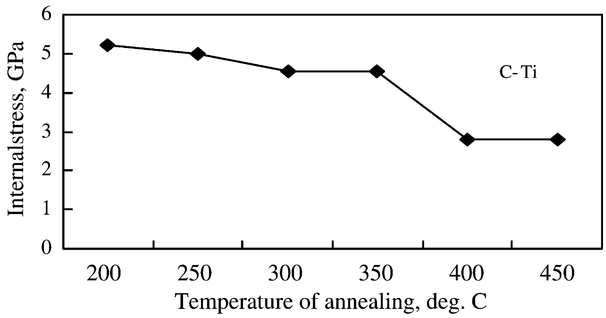

Fig. 5. Dependences of change of internal stress value on temperature of annealing in carbon condensates with general thickness 1.0 μm with interlayers of titanium with thickness 200 nm, obtained at the temperature of a sublayer 100 °C.

temperature of a substrate 50 °C was 52% from initial values of internal stress. Corresponding reduction of internal stress value for a condensate obtained at the temperature of sublayer 150 °C was 6.5%. It is a little bit less than for the condensates obtained at the same temperature but at smaller duration of a pulse of discharge. There are some prominent features of the dependences given in Fig. 4. These are lower temperature appropriated to the beginning of process of change of internal stress value in a condensate (200 °C) and an essentially big difference between temperatures of stabilization of internal stress value in coatings at annealing (200 °C for the condensates obtained at the temperature of a substrate 150 and 425 °C for carbon coatings obtained at the temperature of a sublayer 50 °C). Carbon condensates obtained at lower temperature of sublayer (50 °C) are characterized by practically linear dependence of change of internal stress value from temperature of annealing in a range 200–400 °C. It can testify to presence of defects with approximately identical energy of activation of diffusion processes in coatings.

In Fig. 5 there is a plot with dependences of change of internal stress value from temperature of annealing in carbon coatings with general thickness 1.0 μm with interlayers of titanium with thickness 200 nm obtained at the temperature of sublayer 100 °C. Their feature is clearly defined step character of dependence. It is possible to explain presence of additional drains for defects in coatings as titanic interlayers.

Reduction of values of internal stresses in carbon coatings at the process of annealing can be caused by two principal causes: these are reduction of volume of a condensate due to its consolidation or change of physic-mechanical properties of a coating owing to transition to another allotropic modification of carbon caused by annealing. In Ref. [8] there are the results of electronic-microscopic researches of annealing of an amorphous carbon condensate separated from a sublayer obtained by condensation of particles with energy 10–300 eV. In accordance with this work structural transformations in a condensate begin from 550 °C. Thus, it is possible to assume that annealing in a range 200–450 °C results in consolidation of a carbon condensate with fractal structure having superfluous free volume as a result of diffusion of point defects. Reduction of a value of internal stress testifies to it. It is necessary to note, that annealing of carbon coatings in a range of temperature 200–425 °C does not result in change such as connection between atoms of carbon. Stability of electric and optical characteristics of a condensate testifies to it and it is proved by the results of researches shown in the Ref. [9]. The same results were received in the Ref. [10].

4.3. Stability of superthin carbon films to influence of temperature in an atmosphere of air

The surprising result which has been found out at the process of annealing of superthin carbon condensates with thickness 5 nm high protective properties of these films were. They interfered with oxidation of titanium on the surface of a silicon sublayer up to the temperature 425 °C that testified about continuity of the film.

5. Conclusions

Annealing of carbon condensates obtained by impulse vacuum-arc sputtering of a graphite cathode in an atmosphere of air at the temperature 400–425 °C allows decrease a value of internal stress of compression in coatings without deterioration of other properties.

Change of a value of internal stress in carbon condensates obtained using impulse vacuum-arc discharge at their annealing depends on conditions of formation (temperature of sublayer and duration of a pulse of discharge) in the greater degree than a value of internal stress in not annealed coatings and can be used for control of their properties and also for analysis of conditions of coatings obtaining.

A carbon film with thickness 5 nm interferes with oxidation of a surface of a sublayer from titanium up to the temperature 425 °C.

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