

Vacuum nanoscale carbon coatings

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ABSTRACT

This article illustrates the problem ensuring homogeneity and uniformity of nanoscale coatings obtained in vacuum by carbon vapor deposition. Carbon vapors are obtained by heating in a vacuum with one or more electron beams from a water-cooled crucible, which is covered with a molten layer of refractory metal. Due to the peculiarities of the trajectory of the movement of carbon vapors from the crucible to the substrate, a situation may arise with the formation of a "visor" type defect on the coating, which prevents the uniformity of the coating

Keywords: carbon coating, uniformity, electron beam technologies, defect formation, diffusion, sublimation

1. INTRODUCTION

The unique properties of carbon and its allotropic modifications attract constant attention to it in both theoretical and practical aspects. Graphite, graphene, fullerenes, diamond, nanofibers, nanotubes are far from a complete list of forms of carbon existence. One of the important physical and chemical characteristics of this element is its practical absence in the liquid state, which causes a number of consequences. The absence of a liquid state of carbon makes it impossible to implement traditional technologies of coating it for various purposes, which use melting and spraying processes. The technology of applying coatings by methods of deposition from the gaseous phase, which is obtained mainly by evaporation or sublimation of graphite and other natural or artificial sources of carbon^{1,2,3,4}, is relevant. The problem of this process is the high temperature of evaporation, sublimation and reactivity of vapors.

The high vaporization temperature of carbon requires the use of heat sources with high energy density per unit volume. An effective variant of the graphite evaporation process is the use of electron beam technologies in a special vacuum chamber^{6,7,8,9}. It is equipped with one or more electron beam guns and process control systems. It should be taken into account that very rapid heating of graphite or the entire sample under the surface, which is characteristic of electron beam heating, can cause violent vaporization and vapor microexplosion. The vapors will spread the solid parts of the graphite around the working area, which will not allow obtaining the required high-quality nanocoating. Therefore, special measures are needed to prevent such a course of the process. A fairly simple way is to use graphite crucibles, which are water-cooled and covered with a tungsten washer. An electron beam or several beams first melt the tungsten washer, and then raise the temperature of the graphite and vaporize it^{10,11}. The atomic diameter of carbon is small, which contributes to its rapid dissolution in liquid tungsten, the formation and disintegration of tungsten carbides, the overcoming of the melt layer and the release of ions and atoms from its surface if they have a certain kinetic energy. The complexity of the process of transition of carbon into the gas phase imposes certain conditions for the implementation of the technology of applying carbon nanocoatings¹². The process of condensation of carbon vapor on a solid substrate practically takes place without the formation of a liquid phase, nucleation and spreading of droplets. Coating and substrate adhesion processes have their own specifics¹³. And if a cavity (pore) is formed on the surface of the substrate as a result of the movement of streams of carbon atoms and their deposition, then it cannot be filled with carbon (there is no liquid phase, there is no fluidity). Some processes of changing the relief of the coating are possible due to the diffusion movement of carbon atoms, which can give a noticeable effect at high temperatures.

To implement the process of applying carbon coatings, an electron-beam installation according to the scheme shown in Figure 1 was used. The electron gun melts the tungsten washer, which is covered with MG-1 graphite in the crucible.

Carbon vapors, which have the required energy from heating by an electron beam, in the form of a conical flow with an angle of 2α fall on a substrate heated to a certain temperature and condense on it.

The purpose of this work is to study the process of coating condensation and identify factors that reduce their quality. The quality indicators of the coating include its uniformity in thickness, dispersion of grain sizes, presence and configuration of inclusions of impurities. According to a number of works¹², the substrate and its temperature play an important role in the formation of carbon coatings. The surface temperature of the sprayed product is one of the most important parameters of the spraying process. It significantly affects the adhesion strength, the structure of the coating, the level of residual stresses and thus the qualitative characteristics of the coating.

2. RESEARCH METHODOLOGY AND EQUIPMENT

In this work, the temperature of the substrate samples varied in the range from 400°C to 1500°C. Control and measurement of temperature was carried out by thermocouples. The parameters of the carbon flow and the location configuration of the installation elements were calculated using the Lambert-Knudsen laws. The distance from the crucible to the substrate on which the carbon was deposited was about 300 mm. The pressure of residual gases in the working chamber was maintained at about 0.05 Pa. The power of the electron beam varied around 21 kW.

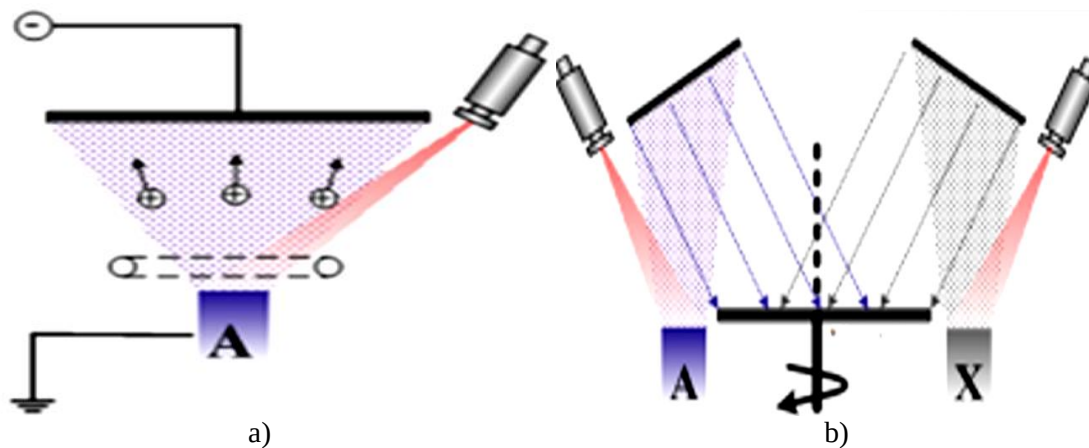


Figure 1. Drawings of installations for applying carbon coatings: a) – with one electronic gun; b) - with two electronic guns.

The research complex shown in Figure 2 was used for complex studies of the parameters of the obtained carbon coatings.



Figure 2. Auger-microprobe JAMP-9500F (JEOL, Japan): high-resolution field emission electron gun scanning electron microscope (1); Auger electron spectrometer with high resolution (2); Ar-ion gun (3); energy dispersive X-ray spectrometer INCA PentaFETx3 (4); microfocus X-ray tube with capillary (5).

Fig. 3 shows an electron microscope image of the coating surface, which was formed by the method of carbon vapor deposition obtained by evaporating graphite with an electron beam in a vacuum from a water-cooled copper crucible.

3. PRACTICAL ASPECTS OF CARBON COATING APPLICATION

The coating is deposited on a graphite substrate prepared using a special technology. It can be seen from the photos that a dense coating without pores and gaps was formed on the shown area. The surfaces of the structural components of the carbon coating are very similar in shape, but different in size. A computer program was used to determine the geometric parameters of the structural components. The smallest and largest structural components of the carbon coating are in a ratio of 1:4.5. Attention is drawn to the scattered white formations on the surface of the coating of an irregular shape. The chemical composition of these impurities (Table 1) shows the presence in them of tungsten oxides and other chemical elements contained in the residual atmosphere of the installation chamber and the evaporated carbon source. This analysis indicates the need to clean the raw materials and vapors from unnecessary chemical elements.

Table 1. The composition of impurities on the surface of the coating, which was detected by spectral analysis

Spectrum	C	O	Na	Mg	Al	Si	S	K	Ca	Fe	W	Total
S01	62,0	27,7	0,1	1,6	1,3	3,5	1,9	0,2	0,2	1,1	0,4	100,0
S02	92,9	6,3									0,8	100,0

It is obvious that the deposition of impurities occurred later than that of the carbon coating. This can be explained by the higher temperature of carbon condensation compared to other components and it settles first. An important role is played by the processes of dissolving carbon and impurities in carbon. Spectral analysis shows that at points S01 and S02, the white deposits on the surface of the carbon coating are mainly tungsten oxides, which is a consequence of the used carbon evaporation technology through the tungsten melt.

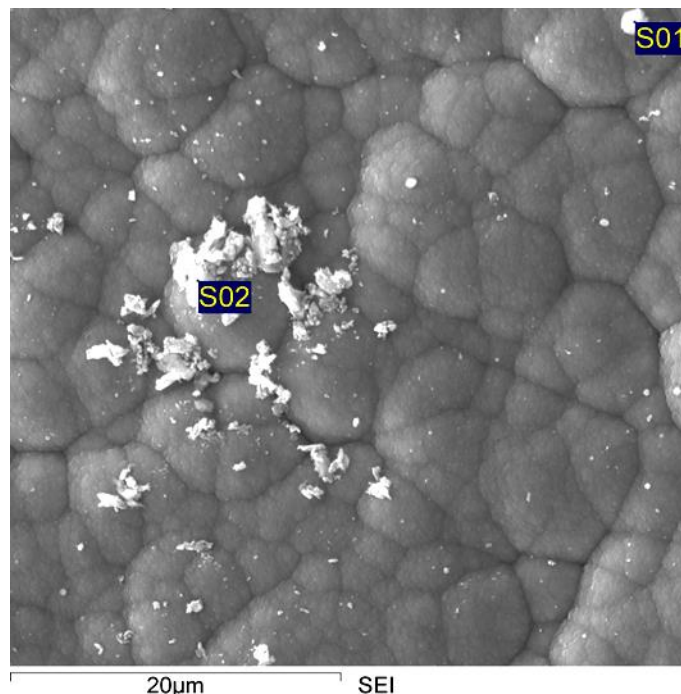


Figure 3. Carbon coating obtained on a substrate with a temperature of 570°C.

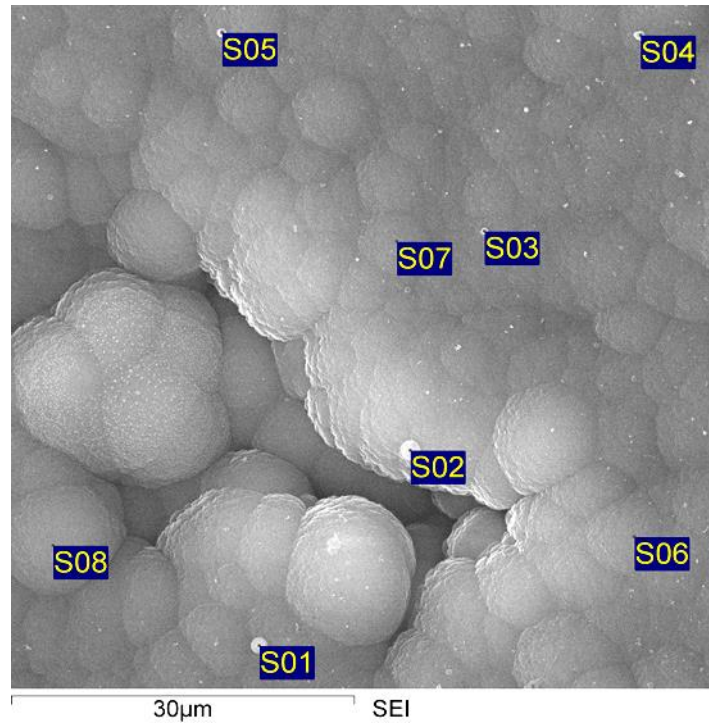


Figure 4. Mechanism of defect formation in carbon coating.

Fig. 4 shows another location of the surface of the carbon coating with a formed defect in the form of a micropore. There can be several reasons for the formation of the detected defect. First of all, the processes of formation and formation of carbon vapor flows should be carefully analyzed, taking into account the laws of Lambert-Knudsen. In addition, the streams can be direct from the evaporation source and reflected from the equipment in the vacuum chamber. An important factor in the formation of defects of this shape and size is the absence of a liquid phase in the process of forming the coating. We do not observe liquid phase flow processes that could fill such surface defects.

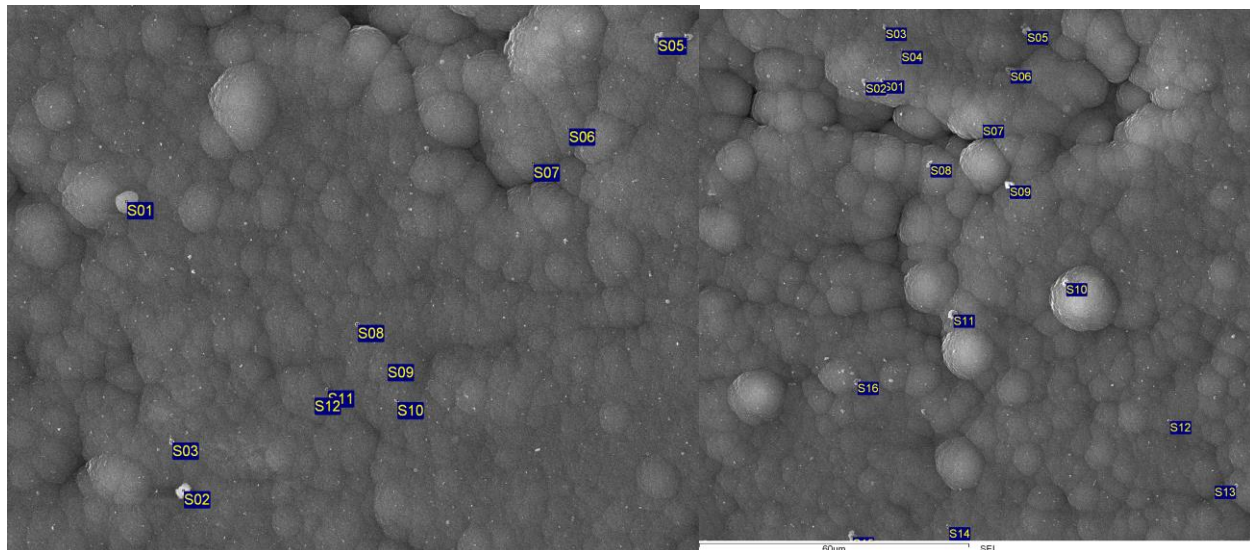


Figure 5. Photos of carbon coating with surface defects.

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4. CONCLUSIONS

Electron beam evaporation of graphite allows forming carbon coatings on various metallic and non-metallic substrates. There are no traces of the presence of a liquid carbon phase on the surface of the formed coatings. During the design of the technology and the electron beam installation, it is necessary to calculate and correct the trajectories of the movement of ions and carbon atoms in detail. For this, a system of reflectors and other similar devices should be used. It is possible to ensure the high quality of coatings by using various vapor flow separation systems.

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