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**Formation of nanostructured carbon coatings by laser dispersion
of the target based on a polymer and metal formates**

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Abstract:

The study considers a complex technique for developing nanostructured carbon coatings, which consists in the deposition of a sublayer based on polymer and metal formates, subsequent heat treatment, and further deposition of carbon layers from the plasma of a pulsed cathode-arc discharge.

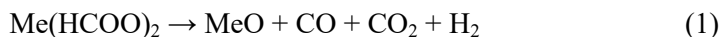
Carbon coatings are characterized by chemical inertness, high mechanical properties, high breakdown voltage, electrical resistance and thermal conductivity, transparency in the infrared region, high wear resistance, corrosion resistance, low friction coefficient and biocompatibility. The main disadvantages of carbon coatings are a high level of internal stresses and low thermal stability ($< 350\text{ }^{\circ}\text{C}$) [1]. At the same time, carbon nanostructures, in particular, nanofibers, nanotubes, fullerenes, graphene, are known to exhibit unique mechanical and thermophysical properties due to the following factors: high strength of carbon-carbon bonds, record high atomic packing density, absence or low density of structure defects [2]. However, carbon nanostructures, because of their properties and characteristics, cannot be used independently in modern technological processes for hardening the surface of parts and tools; they must be mixed or pressed with a base or introduced into a matrix in any other manner [3]. In our opinion, of great relevance are the studies aimed at developing combined technologies for the formation of planar-structured carbon coatings on microheterogeneous sublayers containing, for example, nanosized components with different plasticity and catalytic activity with regard to carbon. The deposition on such layers of a carbon coating creates conditions for the formation of surface structures with different phase compositions and, accordingly, mechanical properties. Plastic areas of the sublayers initiate the processes of internal stresses relaxation, which ultimately leads to the creation of a certain texture of the carbon coating.

We have proposed a complex three-stage procedure for the formation of carbon-based nanostructured coatings.

The molecular composition of the coatings was determined using the infrared (IR) Fourier spectrophotometer Vertex-70 (Bruker): scanning range was 4000–300 cm^{-1} , resolution was 4 cm^{-1} . The spectra of hydrocarbon coatings along the δ (C–H) band at 1465 cm^{-1} served as an internal standard.

The topography and morphological features of the resulting coatings were studied by atomic force microscopy (AFM) using Solver Pro (NT-MDT, Moscow, Russia) in the semi-contact mode; the scanning area was $4 \times 4 \mu\text{m}$. The data analysis was carried out with the specialized Gwyddion software package, which makes it possible to calculate the arithmetic mean deviation of all roughness profile points from the mean line on the evaluation length (Ra); the surface relief evaluation parameter (Rms), defined as the square root of the mean square of the distance of profile roughness vertices to its mean line; number, mean height, diameter and size distribution of individual structural formations (grains).

The first stage of forming nanostructured coatings with the laser dispersion of a composite target, which is a mechanical mixture of a polymer and lead or copper formate. The L-2137U+HG-5 laser with a wavelength of 532 nm, a pulse duration of 6 ns, and a pulse energy of 450 mJ was used for dispersion. Polytetrafluoroethylene was used as a polymeric precursor. Laser radiation causes the destruction of fluorocarbon bonds, promotes the occurrence of carbonized structures, and initiates partial decomposition of formates according to the following scheme:



The second stage is the heat treatment of the resulting layers in air at 250 °C. This temperature is sufficient for further decomposition of formates, but not sufficient to start melting polytetrafluoroethylene.

It should be noted that heat treatment allows reducing the roughness of the layers formed by laser dispersion of the composite based on polytetrafluoroethylene and formates by 2–5 times (depending on the nature of the formate). The roughness of layers containing copper formate is higher than that of layers containing lead formate. In general, these layers have a more developed morphology than the layers formed from polytetrafluoroethylene without formate.

Via the IR spectroscopy, it was found that composite layers based on polytetrafluoroethylene and lead formate intensively absorb moisture. This is indi-

cated by the presence of a broad absorption band in the region of 3600–3000 cm^{-1} (stretching vibrations of OH groups) in the IR spectra of the coatings.

The highest optical density values are typical for absorption bands at 1590 and 1370 cm^{-1} . These bands indicate the presence of ionized carboxyl groups (COO^-) in the molecular structure of the composite layer [4]. The absorption in the range of wave numbers (3000–2770 cm^{-1}) is due to the stretching vibrations of C–H bonds. All of the above is a consequence of the presence of undecomposed salt in the coating composition. The absorption bands at 1210 and 1150 cm^{-1} are due to stretching and deformation vibrations of CF_2 , CC bonds [5].

To quantitatively analyze the ratio of salt and fluorine-containing component, the composite band with a maximum at 1210 cm^{-1} was decomposed into component absorption bands. This is because the absorption bands of CH₃ groups are present in the range of wave numbers 1250–1200 cm^{-1} , in addition to the bands characteristic of fluorocarbon. The D_{1590}/D_{1210} ratio is 11.0, 3.0, and 3.1 for the coatings with initial ratios of polytetrafluoroethylene (PTFE) and lead formate of 1:2, 1:1, and 2:1, respectively. An increase in the fluoroplast fraction in the initial target is not accompanied by a predictable decrease in the value of this ratio. It is worth mentioning that the band at 1210 cm^{-1} in the IR spectrum of PTFE is due to the stretching vibrations of C–C and C–F (CF_2) bonds [5]. Laser action promotes the destruction of C–F bonds, which increases the fraction of carbon structures (carbonized) in the composition of the deposited layer. Thus, when the fraction of the fluoroplastic component in the target increases, the processes of fluorocarbon component carbonization are realized to the greatest extent in the laser radiation zone.

The third stage realizes the deposition of carbon layers from the plasma of a pulsed cathode-arc discharge at a pulse repetition frequency of 3 Hz (at higher repetition frequencies, the thermal load on the substrate increases).

The results of atomic force microscopy suggest that the carbon coatings, formed on carbonized layers containing metal oxides, are characterized by a higher degree of dispersion and a more developed morphology compared to the coatings without such a sublayer. It is established that with an increase in the content of formates in the initial target, the subroughness of the coatings increases as well. Apparently, the metal oxides formed during laser action and heat treatment are nucleation centers and contribute to the structuring the surface of carbon coatings. In addition, metals and nanoparticles based on metal oxides are known to contribute to the formation of carbon nanostructures due to their high catalytic activity [3].

The subsequent heat treatment of carbon coatings, formed on a sublayer of polytetrafluoroethylene and lead formate, promotes an increase in the content of sp^2 -clusters. However, the annealing temperature is not sufficient for thermal activation of intense graphitization processes. Based on the above, it follows that lead oxide, which is a product of the lead formate decomposition during heat treatment and as a result of laser action on the target, can contribute to the formation sp^2 clusters at the deposition stage of carbon layers and initiate phase transformations during annealing, lowering the graphitization temperature. Moreover, the polymer carbonization during laser dispersion of the initial target can enhance the high content of sp^2 hybridized bonds in carbon coatings.

Thus, the use of carbonized sublayers containing metal oxides is an effective tool for controlling the size and distribution of carbon nanostructures over the thickness of the deposited carbon layers. Such coatings are potentially promising for improving the sorption activity of the surface, and can be used, for instance, as active elements of gas sensors.

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