

Deposition of Nanostructured Carbon Coatings on Metal Surfaces with the Electric-Discharge Method in a Hydrocarbon Medium

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Abstract—An experimental setup for depositing nanostructured carbon coatings on structural materials is described; it exploits the principle of the electric-discharge destruction of gaseous hydrocarbons to deposit the carbon nanoparticles onto a metal surface. The results of optical metallography, atomic force microscopy, and X-ray diffraction analysis suggest that a nanostructured amorphous carbon layer with a grain size of 50–80 nm and an arithmetic average roughness of 35–40 nm and that is capable of absorbing X-rays is present on the sample surface. The coating thickness can achieve 20–40 μm. The characteristics and growth mechanisms of the coatings depend on the ability of the substrate material to interact with carbon.

Keywords: high-frequency electric-discharge method, hydrocarbon gas, destruction, nanostructured coating, absorption

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INTRODUCTION

The possible uses of nanostructured carbon coatings are fairly promising. Nanocarbon is included in coatings composition to increase the strength of materials, improve their anticorrosion properties, impart antifriction properties to them, and protect them against radiation. The ever-increasing power of radiating devices and the rapid development of equipment that should be protected against various kinds of interference lead to the fact that the development of methods for the production of reliable shielding nanomaterials and nanostructured coatings is a priority for modern science.

Solid amorphous carbon coatings (films) are ideal wear-resistant coatings on parts in friction pairs because of their combination of a low coefficient of friction and a high hardness. In the literature, these coatings are commonly referred to as diamond-like coatings because they are partially or completely composed of sp^3 -hybridized carbon atoms and do not contain large crystallites [1]. In addition, carbon-containing composite fillers have been used to develop absorbent coatings containing graphite, carbon fibers, or carbon nanotubes, which are used in the aerospace [2, 3] and machine-building industries [4], as well as in instrument engineering [5]. In particular, carbon nanotubes are used to manufacture radiation-resistant sensors, liquid and gas filters for the life-support systems of space crews, and basic components in nanotransistors and nanodiodes. The electrical conductiv-

ity of carbon fibers makes them suitable for producing protection for rocket products against the effects of static electricity. Recently, a coating capable of absorbing 99.965% of incident radiation in the optical range has been prepared using carbon nanotubes [6].

At present, nanocarbon coatings are deposited on surfaces using standard approaches that are adapted to varying degrees to particular tasks, such as chemical and physical vapor deposition, gas–plasma deposition, ion plasma sputtering, cathode sputtering, electric-arc deposition, reactive magnetron sputtering, detonation sputtering, and laser cladding [7, 8]. However, not all of these methods can be implemented on an industrial scale due to the poor quality of the resulting coatings, low productivity, or high cost.

At the Institute of Pulse Processes and Technologies of the National Academy of Sciences of Ukraine, radar-absorbent carbon nanomaterials are synthesized using electric-discharge treatment of liquid and gaseous hydrocarbons [9]. The onion-structure nanotubes and nanocarbons synthesized by these methods contain ferromagnetic nanoparticles, exhibit high electrical conductivity, and effectively absorb electromagnetic radiation in a frequency range of 25–38 GHz. We believe that, for the deposition of nanocarbon directly onto a metal surface, the high-frequency electric-discharge method, based on the formation of a nonequilibrium plasma in a carbon-containing gas, should be developed; this method will make it possible to simultaneously solve two problems in a single cycle, namely,

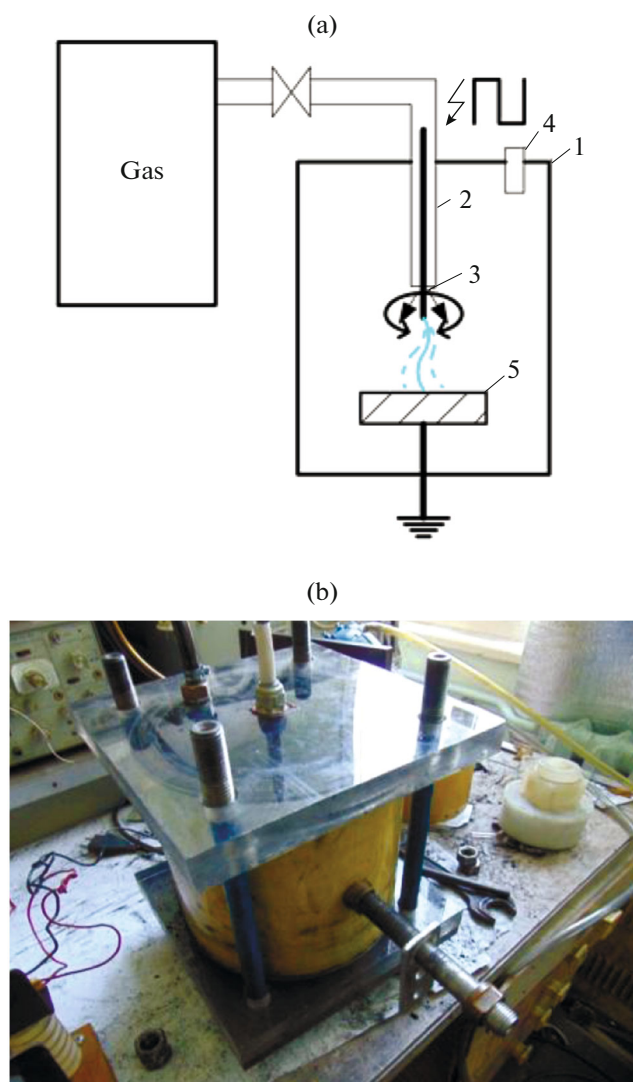


Fig. 1. (a) Diagram of the setup and (b) the outside appearance of the reaction chamber.

to synthesize carbon nanoparticles and form a nanostructured coating based on these particles. The simplicity of the implementation of this method can be attributed to the possibility of using cheap, available organic gases under normal atmospheric pressure. Preliminary studies [10] have shown that a high-frequency electric-discharge treatment of gases is characterized by high productivity: it provides the synthesis of up to 20 g/h of nanocarbon particles, most of which have an onion structure. The chemical purity of the resulting nanocarbon exceeds 99%, and the distribution of the particle sizes lies in a fairly narrow range of 10–40 nm. This nanocarbon is a high-quality material for the formation of functional surfaces of products.

This study investigated the applicability of the high-frequency electric-discharge treatment of organic gases for the deposition of nanostructured

carbon coatings on the surface of various structural materials.

EXPERIMENTAL

A diagram of the setup for synthesizing nanocarbon and depositing a nanostructured carbon coating in a single technological cycle and of the outside appearance of the reactor is shown in Fig. 1. The experimental setup includes a reaction chamber, a high-voltage equipment, and a gas container. In the upper portion of reaction chamber 1, high-voltage bushing insulator 2 with electrode 3 placed inside is mounted. The chamber is equipped with channel 4 to provide the removal of the unused working and associated gases. The working gas is fed into the chamber through the bushing insulator under normal atmospheric pressure. Any gas from the homologous series of alkanes can be used. Carbon nanoparticles are synthesized owing to the destruction of a gaseous hydrocarbon by an electric-discharge plasma generated between electrode 3 and the metal surface of substrate 5, which is used as a grounded counter electrode. The synthesis of nanoparticles and their deposition on the substrate occur simultaneously. Discharge pulses are produced by a generator of rectangular or sinusoidal voltage pulses at a voltage level of a few kilovolts to a few tens of kilovolts and a frequency of 1–100 kHz. The upper movable electrode is moved relative to the substrate along a predetermined trajectory. The interelectrode spacing can also be varied. The duration of one run of a continuous electric-discharge treatment is 5 min. According to the preliminary experiment results, during this time, an adhesively strong coating is formed and no sticking of particles deactivating the substrate surface is observed. After 5 min, the layer of stuck nanocarbon was removed from the sample; to increase the coating thickness, the process was run again (a vibratory system is currently being developed to provide a continuous shaking of the substrate). The discharge current of 0.13 A and the frequency of 56 kHz did not vary during the experiment.

Materials that had a structural surface for deposition of the coating were selected, taking into account the functional purpose and adhesive properties of the coating, the ability of the base material to interact with carbon (dissolve, form carbides, and be chemically inert), and the catalytic properties of the material with respect to the synthesis of various modifications of nanocarbon. Aluminum, titanium, and their alloys are suitable for depositing absorbing coatings for use in aerospace engineering, while steel, nickel, and copper are suitable for coatings for other fields. A satisfactory adhesion to the base material is observed in the case of sputtering carbon coatings onto carbide-forming metals (iron, titanium); therefore, iron-based alloys, particularly various steels, have a greater potential for use

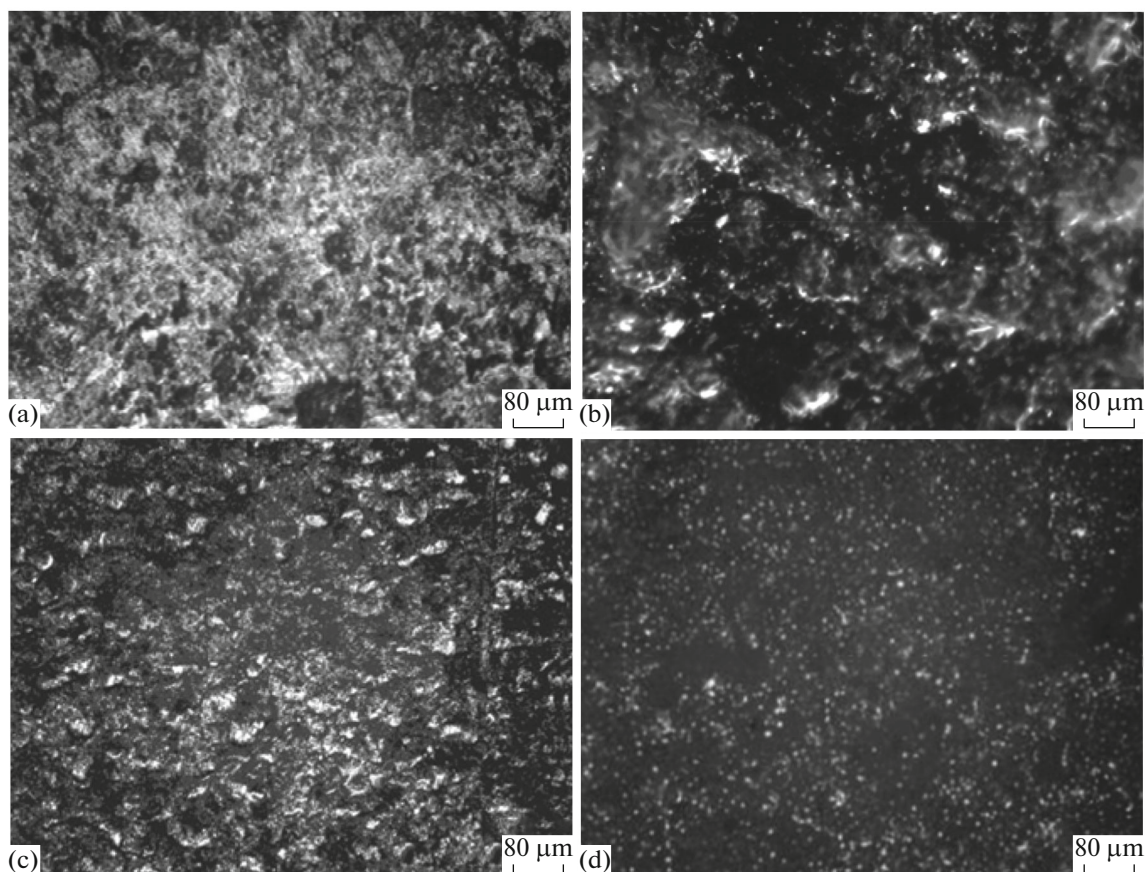


Fig. 2. Carbon coatings on the surface of (a) aluminum, (b) the nickel alloy, (c) copper, and (d) steel.

as a substrate because they contain high amounts of iron and carbon. The probability of forming nanocarbon coatings on a material is also high if the material is a catalyst for the formation of the required allotropic modifications of nanocarbon, such as iron or nickel. Taking all this into account, nanocarbon coatings were deposited using substrates made of stainless corrosion-resistant heat-resistant steel 08Kh18N10, aluminum A5, copper M1, and heat-resistant nickel-based alloy KhN75MBTYu; the substrates had diameters of 10–20 mm and heights of up to 10 mm. Before into the reaction chamber, the substrates were ground, polished, and cleaned in an alcohol bath.

The coating microstructure was studied using a Neophot-32 optical metallographic microscope. Visualization of the studied surfaces was performed on a Solver P47H atomic force microscope. To conduct an X-ray diffraction analysis and determine the ability to absorb X-rays, a DRON-4-07 diffractometer with a copper tube (wavelength of $\lambda = 1.54 \text{ \AA}$) was used.

COATING STRUCTURE AND PROPERTIES

Figure 2 shows optical images of the coatings deposited by ten runs of the electric-discharge treat-

ment. Analysis of the structure and morphological features of the coatings on the different surfaces reveals a gradual and uneven process of the coating formation, which is confirmed by the alternation of optically brighter and darker surface areas and the presence of pores. For identical coating deposition times, the structural features of the coatings are primarily determined by the substrate material, because the densest and least porous coatings are obtained on steel, in which intermediate diffusion and carbide layers, which increase the adhesion, can be formed. The average thickness of the coating on steel achieves 20–40 μm (Fig. 3); the coating is characterized by a 10% porosity and uniformly distributed pores with a size of up to 10 μm . On the substrate of the nickel alloy, the chemical composition of which is characterized by the presence of 0.1% C and about 3% Fe, the coatings with a thickness of 2–4 μm contain larger pores. The least thin coatings, the thickness of which is not determined by the optical method, are characteristic of the aluminum and copper substrates.

The presence of regions with a significant difference in thickness absolutely on all metals can be attributed to the specific features of the interaction of the surface with an electric arc and, accordingly, an

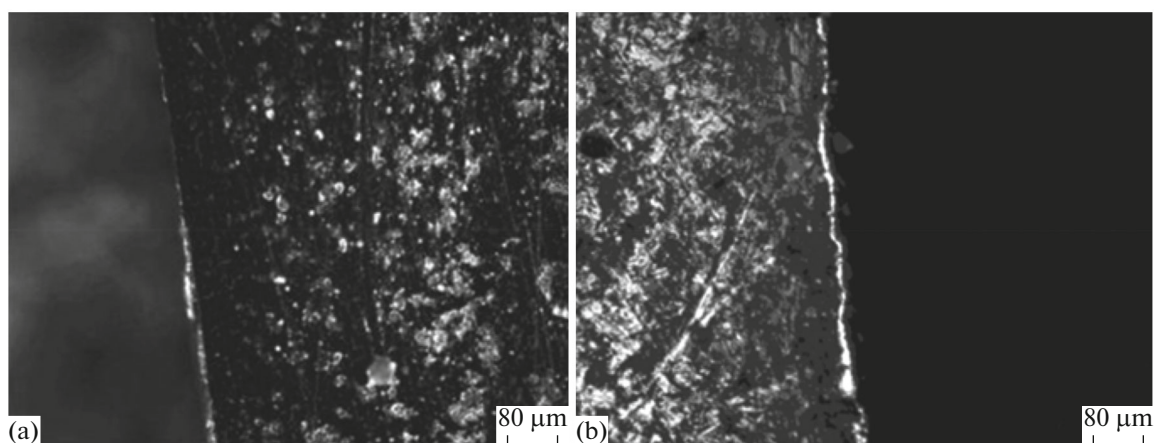


Fig. 3. Transverse sections of (a) the nickel-alloy and (b) steel samples.

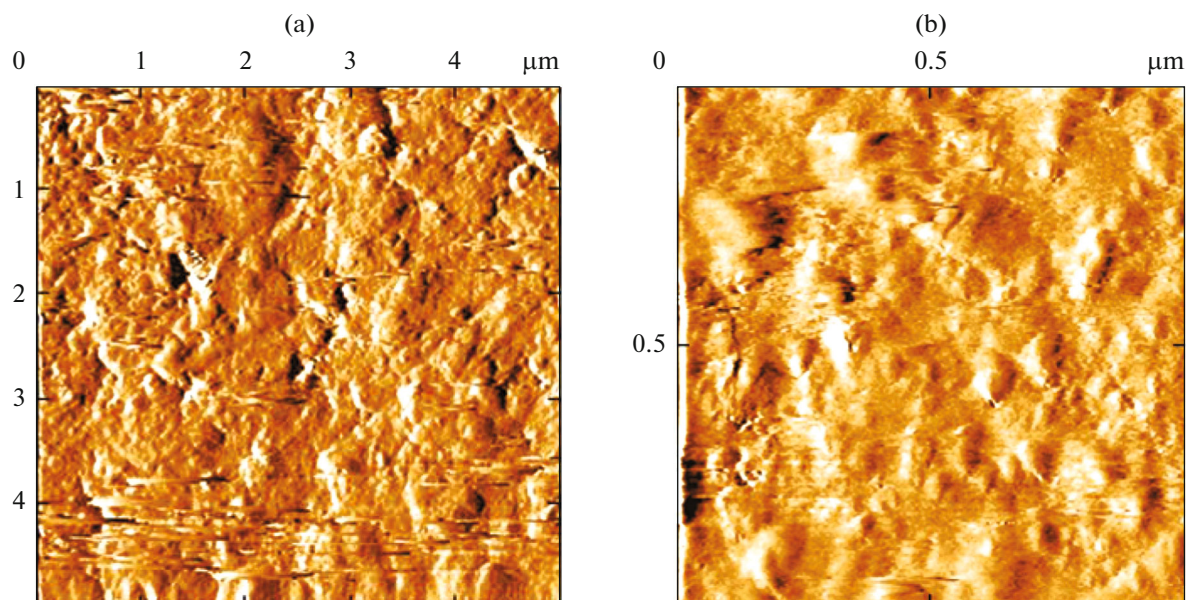


Fig. 4. Surface relief of carbon coatings on (a) aluminum and (b) copper.

uneven heating of the surface during the deposition. The surface regions to which the arc was closed were heated to higher temperatures; therefore, carbon particles were mostly deposited on these regions.

The fact that the resulting coatings are nanostructured, at least on metals characterized by weak physical and chemical interactions with carbon, is provided by atomic force microscopy data (Fig. 4). The structure of the coating on aluminum has a complex grain structure with grain sizes of 70–80 μm, which, in turn, also form a pronounced coarse-grained structure with grain sizes of 0.3–1.1 μm at the micro level. The coating deposited on copper does not have an internal structure at the micron level; the structuring becomes apparent only at the nanoscale level; it is represented

by grains with a size of 50–60 nm. The two coatings—on aluminum and copper—have almost the same arithmetic average surface roughness of $S_a = 35\text{--}40$ nm, which is determined from the baseline of 5 μm.

The actual practice of depositing metal coatings showed that the coating growth can occur either through the formation of three-dimensional nuclei at suitable surface sites with subsequent development in lateral directions and in thickness or through the initial formation of a continuous film without an island growth stage. The first path is characteristic of materials that have poor adhesion to the substrate; the second path is implemented if the elements contained in the coating exhibit a fairly high solubility in the base material or if they are capable of forming new phases

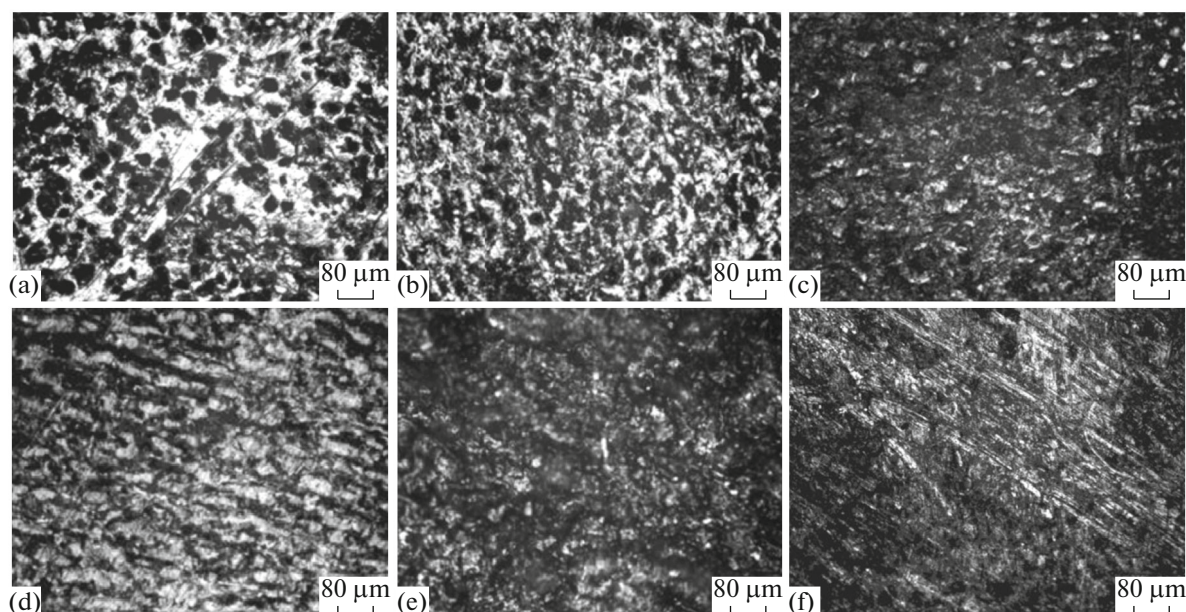


Fig. 5. Growth mechanisms of carbon coatings on (a, b, c) copper and (d, e, f) nickel; the deposition time is (a, d) 5, (b, e) 10, and (c, f) 15 min.

with the base, which are continuously distributed along the phase boundary (e.g., carbides).

Carbon is highly soluble in iron and nickel; however, it hardly interacts with copper and aluminum [11]. At the melting point, the solubility of carbon in solid copper is as low as 0.03 at %; the well-known Cu_2C_2 and CuC_2 carbides were obtained only by chemical methods. A significant solubility in aluminum (0.007 at %) is acquired by carbon only at a temperature of 1200°C ; a much higher temperature is required for the formation of the Al_4C_3 carbide. Thus, owing to the insolubility of carbon in copper and aluminum, the interfacial interaction between them will be extremely weak. However, it is known that the basic (0002) planes of graphite have a low surface energy (0.07 J/m^2); therefore, it is reasonable to expect that carbon will be deposited facing the surface with the basic planes oriented parallel to the metal surface, regardless of the crystallographic orientation of carbon, to form a continuous graphene layer. These assumptions can be supported by the results of [12, 13], where the authors, using the ion-implantation method, obtained coatings on copper and silver, which does not interact with carbon either; the coatings were composed of a graphite-like layer with onion spheres with a size of 30–200 nm that were uniformly distributed over the surface.

Figure 5 shows images that represent the coating growth mechanisms similar to those described above, namely, the island growth on copper and the film growth on the nickel alloy. It is evident that, at the initial stages, uniformly distributed growth islands are

formed on the copper substrate, which is not prone to interacting with carbon; the islands are not associated with the morphological features of the surface and increase over time. In addition, from the final bumpy morphology of the coating, it is obvious that the height growth rate significantly exceeds the rate of the lateral development of the carbon nuclei. The initial coating on the nickel alloy is a thin film that inherits the surface and reproduces the texture of the grinding grooves; the relatively uniform growth of the film ultimately forms a surface relief that is smoothed compared with that of copper.

Figure 6 shows data of X-ray diffraction analysis of the aluminum samples with and without a carbon coating. The diffraction patterns exhibiting peaks only of the matrix metal suggest that other intermediate phases are not formed in the system (carbon solutions in the substrate material, aluminum carbides) and the X-ray amorphous structure of the resulting carbon coating. Comparison of the intensity of the main diffraction peaks (see Table 1) for the uncoated and coated aluminum samples shows a considerable weakening of the intensity of X-rays reflected by most of the crystallographic planes, except for one weak diffraction peak (220). The average decrease in the X-ray intensity is 6.3%, which is reasonably high for a coating of a micrometer thickness. However, the issue of the absorbing ability of the coating remains controversial and requires a more detailed study using samples of various metals with various surface shapes.

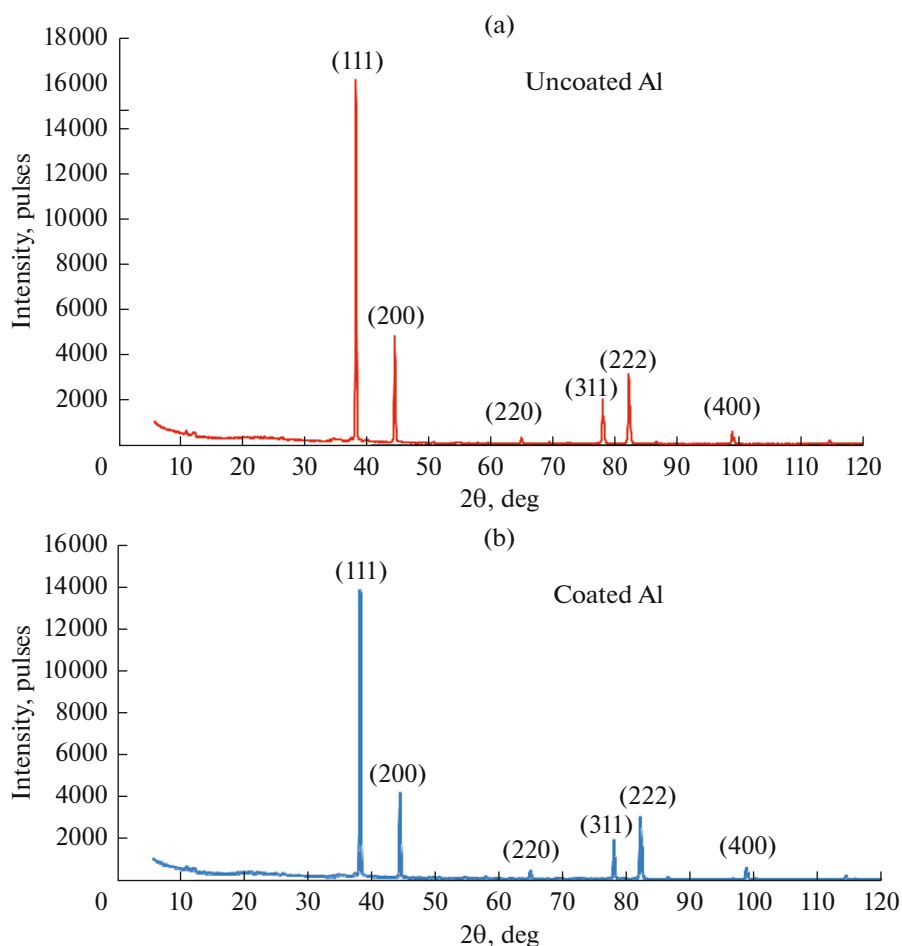


Fig. 6. Diffraction patterns of the aluminum samples.

CONCLUSIONS

The studies confirm that the high-frequency electric-discharge method of destruction of hydrocarbon gases, which was originally developed to synthesize carbon nanoparticles, can be used to deposit nano-

structured carbon coatings on surfaces of any metals, particularly copper, which does not form solid solutions with carbon and carbides.

For fixed technological parameters of deposition, the growth mechanisms, thickness, morphological

Table 1. Data of X-ray diffraction analysis of the aluminum samples

Aluminum	Diffraction pattern lines	2θ angle, deg	Intensity, pulses	Intensity variation, %
Uncoated	(111)	38.4	19243	-9.5
Coated	(111)	38.4	17407	
Uncoated	(200)	44.7	5888	-12.7
Coated	(200)	44.7	5140	
Uncoated	(311)	78.2	2623	-6.3
Coated	(311)	78.2	2457	
Uncoated	(222)	82.4	4045	-2
Coated	(222)	82.4	3964	
Uncoated	(400)	99.0	721	-1
Coated	(400)	99.0	712	
Uncoated	(220)	65.1	351	+35
Coated	(220)	65.1	537	

features, and porosity of the coatings are determined by the substrate material, namely, the ability of the metal to undergo physicochemical interactions with carbon. The highest-quality coatings, with a thickness of up to 40 μm , are obtained on steel.

The resulting coatings are composed of structured fragments of a nanoscale range, which form a surface with an arithmetic average roughness of 35–40 μm ; they are X-ray amorphous (crystal lattice is not detected) and capable of absorbing X-rays.

The electric-discharge method, which provides the simultaneous occurrence of the destruction of hydrocarbon gases, the synthesis of nanocarbon particles, and their deposition on a metal surface, does not require the generation of a vacuum and an additional heating of the substrate. However, it is necessary to eliminate the problem of coating heterogeneity, which is associated with the selective action of the arc on the substrate surface.

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