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TRANSFER PROCESSES IN LOW-TEMPERATURE PLASMA ON THE FORMATION OF CARBON NANOSTRUCTURES ON THE STEEL SURFACE OF A REACTOR AS A RESULT OF THE DECOMPOSITION OF HYDROCARBONS IN THE LOW-TEMPERATURE PLASMA.

2. MODERNIZATION OF THE EXPERIMENTAL SETUP, SEARCH FOR OPTIMUM OPERATING CONDITIONS, DETERMINATION OF ADDITIONAL CONTROLLING FACTORS OF THE PROCESS

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Results of experimental investigations on the formation of carbon nanostructures in a reactor as a result of the decomposition of hydrocarbons in a low-temperature plasma are presented. Data on the production rate of the process and the content of structured carbon in the material obtained before and after the modernization of the setup were compared. Different schemes of supply of the working mixture to the plasma flow are proposed.

Keywords: *carbon nanomaterials, nanotubes, nanofibres, plasma, electric discharge, decomposition of hydrocarbons, carbide-cycle mechanism.*

Introduction. Among the main results of the investigation carried out in [1] is the formation of carbon nanostructures under the conditions of the process being considered on the steel surface of a reactor and not in its volume, as was expected before. The formation of these structures on the reactor surface is determined by many factors, the most important of which are the composition and the temperature of the surrounding gas medium and the temperature of the steel surface. It is also essential that a temperature gradient be realized between the surface and the gas phase, more exactly, in the near-surface layer of the metal, which by and large conforms with the mechanism of formation of the carbon structure framework on metal catalysts by the "carbide cycle" [2, 3]. Moreover, the earlier investigations have shown that the structured-carbon fraction in the deposit obtained decreases with time and this material consists mainly of amorphous and graphitized carbon. This is explained by the carbonization of the steel surface serving as a catalyst. In accordance with the mechanisms revealed, we modernized the experimental setup for the purpose of increasing the production rate and efficiency of the process.

The present work is a continuation of the investigations on the formation of carbon nanostructures on the steel surface of a reactor, the optimization of the operating conditions of the reactor, and the determination of additional factors influencing the process being investigated.

Experimental Setup. The experimental setup used in the present work (Fig. 1) is similar in design to the setup described in [1]. It consists of the following main units: a plasma-chemical reactor, a plasma generator of power 30 kW, a cooling system, a system for supply of the working mixture and the plasma-forming gas (air), a system for control and diagnostics, and a system for gathering of the deposit.

The modernized setup does not include a hardening-scrubber system and a recycling system because, as the previous investigations [1] have shown, the volume processes play an insignificant role in the formation of structured carbon forms. The new setup contains a system for gathering of the deposit, including a cleaning apparatus and a chamber for collection of the carbon nanomaterials, which made it possible to scrape off the deposit from the walls of the plasmachemical reactor in the process of an experiment. The geometric parameters of the plasmachemical reactor and the cathode-anode system, the ranges of the flow rates of the plasma-forming gas and the working mixture, the

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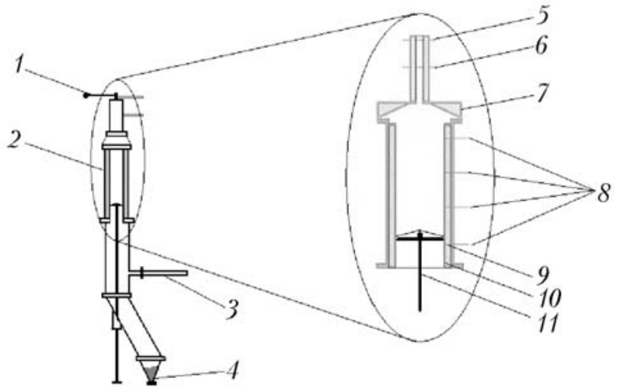


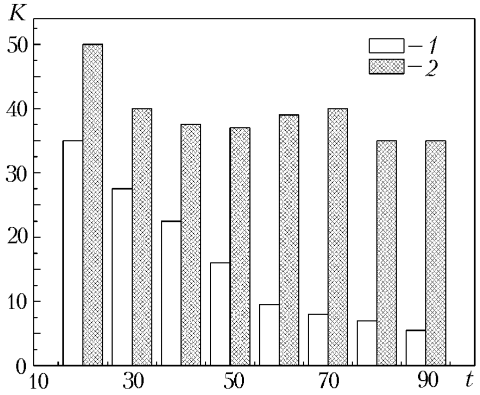


Fig. 1. Scheme of a setup for production of carbon nanomaterials in a low-temperature plasma in a reactor: 1) power-supply system; 2) plasma-chemical reactor; 3) pipeline for removal of the secondary products of the process; 4) chamber for gathering of carbon nanomaterials; 5) pipeline for supply of the plasma-forming gas (air); 6) pipeline for supply of the working mixture (air + gaseous carbon); 7) cooled cover of the reactor; 8) thermocouples; 9) heat-insulating layer; 10) surface of carbon-nanomaterial formation; 11) cleaning apparatus.

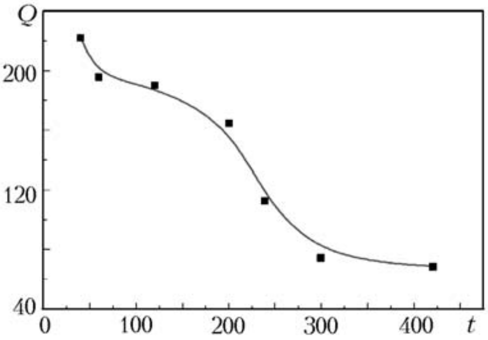
Fig. 2. Change in the content of structured carbon with time: 1) prior to the reconstruction; 2) after the reconstruction. K, %; t, min.

electrical parameters of the power-supply system, and the other operating parameters were identical to those used in the previous investigation.

A mixture of a gaseous hydrocarbon material and air (hereafter, the working mixture) was supplied to the flow of an air plasma immediately at the output of the anode. As the raw material, a propane-butane mixture was used. The composition of the working mixture was somewhat richer than that required for the finishing of the partial-oxidation reaction. After the partial-oxidation reaction ended, as a result of the interaction of the working mixture with the hot plasma flow, a mixture consisting of nitrogen, hydrogen, carbon oxide, and the undecomposed hydrocarbons was formed. This part of hydrocarbons interacted with the metal of the insert of the plasma-chemical reactor and formed carbon nanostructures. The deposit formed on the metal surface was removed from the reactor at certain time intervals (5–20 min) with the use of the cleaning apparatus and was dumped into the collection chamber. The temperature of the growth surface was varied from 650 to 950°C depending on the experimental conditions and the distance between the flow to the reactor and its input.

Results and Discussion. The experimental setup was modernized for the purpose of increasing the production rate of the process of formation of carbon nanomaterials and the degree of their structurization. As was noted in [1], the reason for the decrease in the rate of production of these materials with increasing time of operation of the plasma-chemical reactor is the carbonization of its surface, which leads to a decrease in the number of the active metal particles capable of causing a growth of the carbon nanostructures. We proposed to solve this problem with the use of a cleaning apparatus positioned in the zone of the plasma-chemical reactor; this apparatus executed a translatory motion along the walls of the reactor and, in doing so, scraped off the deposit formed on them. Periodic cleaning of the walls of the reactor allowed the undecomposed hydrocarbons and the reaction products to interact with the reactor metal surface and form carbon nanostructures on it.

Figure 2 reflects the general tendency for the change in the degree of structurization of the carbon nanomaterials with increasing the time of operation of the reactor. It is seen that in experiments of duration of up to 90 min, the content of the structured carbon decreased significantly only in the case where the old-design setup was used. However, as was established in the subsequent experiments, the production rate of the modernized setup decreases too with increase in the time of operation (Fig. 3); in this case, the degree of structurization of the material obtained decreases. For example, the average content of structured carbon in the material obtained did not exceed 35% in experi-



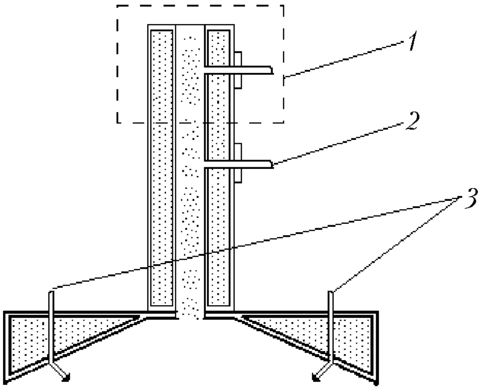


Fig. 3. Change in the average production rate of the process for experiments of different durations. *Q*, g/h; *t*, min; the points correspond to the experimental data.

Fig. 4. Variants of supply of the working mixture: 1) plasma generator; 2) supply directly to the plasma flow; 3) supply to the high-temperature zone of the plasma-chemical reactor downstream of the plasma flow.

ments of duration longer than 120 min, was equal to 25–30% in experiments of duration longer than 200 min, and hardly reached 20% in experiments of longer than 300–350 min.

The decrease in the production rate of the process and in the degree of carbon structurization can be explained by the following reasons.

1. *The imperfection of the cleaning apparatus.* It represented an "umbrella" with four "blades" of stainless steel that opened in the process of movement of the "umbrella" downwards along the surface of the plasma-chemical reactor and scraped off the deposit formed. In the process of operation of the reactor, the thermal expansions can prevent the blades of the apparatus from forming a complete contact with the insert of the reactor and, therefore, a certain amount of carbon can be retained and can obstruct the access of the undecomposed hydrocarbons to the metal surface.

2. *The decrease in the near-surface temperature gradient.* Actually, when stationary operating conditions were established (within 150–200 min after the beginning of the experiment), the temperature gradient between the flow and the surface decreased, and the temperature fields inside the metal became most homogeneous.

3. *The modification of the surface of the plasma-chemical reactor.* As the temperature of the metal surface of the reactor increases, its structure can change as a result of the restructurization and the transformations α–Fe $\Rightarrow$ β–Fe $\Rightarrow$ γ–Fe caused by the changes in the crystal lattice, which can influence the catalytic properties of the metal.

The investigations on determination of the role of each of these factors in the process being considered will be continued.

For the purpose of optimization of the process of formation of carbon nanomaterials, different schemes of blowing of the working mixture were tested (Fig. 4). We investigated the blowing directly into the plasma flow, the blowing into the high-temperature zone of the plasma-chemical reactor downstream of the plasma flow, and the combined blowing providing the supply of the working mixture in different ratios into both the plasma flow and the high-temperature part of the plasma-chemical reactor.

In Fig. 5, comparative diagrams on the rate of production of the deposit and its quality, constructed for different schemes of blowing of the working mixture, are presented. These data show that the average production rate of the process is lower in the case where the working mixture is supplied into the plasma flow than in the case where the working mixture is supplied into the plasma-chemical reactor; however, the degree of structurization of the product obtained in the first case is higher. This is probably due to the large difference between the temperatures of these zones. The temperature of the flow in the upper part of the plasma-chemical reactor is insufficiently high for the complete decomposition of hydrocarbons, which is favorable for the formation of soot clusters that are deposited on the surface of the reactor and prevent the structurization of carbon due to both the carbonization of the metal surface and the formation of massive accumulations of amorphous carbon on the carbon nanostructures. The average value of γ of

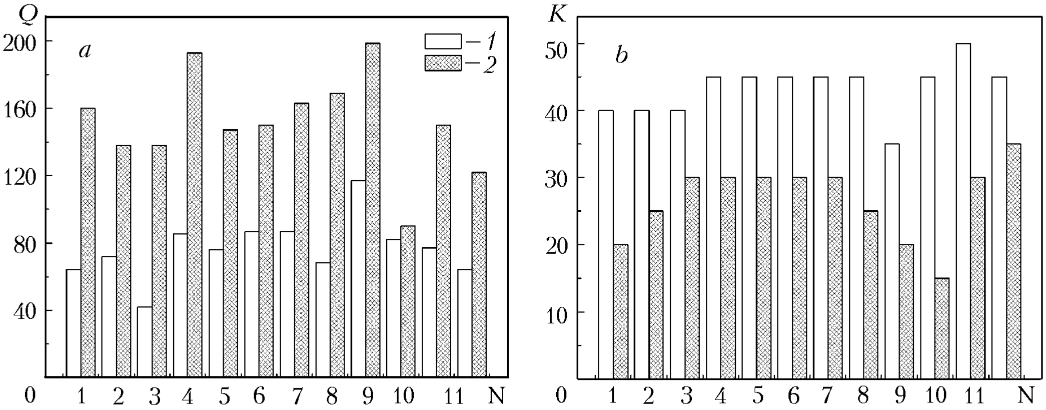


Fig. 5. Production rate of the process (a) and the quality of the material obtained (b) in the case where the working mixture is supplied to the plasma flow (1) and to the upper zone of the plasma-chemical reactor (2). *N*, number of experiment. *Q*, g/h; *K*, %.

the working mixture was 3.7–4.0. Thus, it may be concluded that the increase in the production rate of the process being considered in the case where the working mixture is supplied to the upper part of the plasma-chemical reactor downstream of the plasma flow is due mainly to the increase in the mass fraction of the amorphous carbon in the product obtained (the TEM photographs support this conclusion).

The combined blowing of the working mixture was performed in the following way: a part of the working mixture with a ratio of components required for a partial oxidation ($\gamma = 3.3$) was supplied into the plasma flow, and the other part with a γ of up to 4.5 was supplied to the plasma-chemical reactor downstream of the plasma flow. Thus, a part of the carbon was subjected to oxidation with formation of CO, and the remaining carbon entered the high-temperature zone and could participate in the formation of carbon nanostructures. However, the results of our experiments indicate that the efficiency of the process of formation of carbon nanomaterials did not increase substantially under these conditions; in this case, the average production rate did not exceed 150 g/h and the degree of structurization of the material obtained reached approximately 30–40%.

Conclusions. Our experimental investigations have shown that periodic cleaning of the surface of a plasma-chemical reactor from the deposit formed on it influences positively the process of formation of carbon nanomaterials because it prevents the carbonization of the metal particles playing the role of a catalyst. However, the efficiency of the process of formation of carbon nanomaterials in this reactor decreases substantially with increase in the time of its operation, which is due to the change in certain factors of growth of carbon structures. It was also established that, in the case where the working mixture is supplied to the high-temperature zone of the plasma-chemical reactor downstream of the plasma flow, the production rate of the process increases substantially; however, the quality of the product obtained decreases in this case. On the other hand, when the working mixture is supplied to the plasma flow, the degree of structurization of the material increases, but the production rate of the process decreases.

Thus, the production rate of the setup proposed, operating under optimum conditions, reached 150 g/h, and the degree of structurization of the material obtained was 50%.

NOTATION

K, content of structured carbon (quality of the deposit), %; *Q*, production rate of the process, g/h; *t*, experimental time, min; γ, equivalence factor (stoichiometric ratio).

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