Journal of Engineering Physics and Thermophysics, Vol. 81, No. 4, 2008

PROCESSES OF TRANSFER IN A LOW-TEMPERATURE PLASMA

FORMATION OF CARBON NANOSTRUCTURES IN THE DECOMPOSITION OF METHANE IN THE PLASMA OF A HIGH-VOLTAGE ATMOSPHERIC-PRESSURE DISCHARGE

S. A. Zhdanok, A. V. Krauklis, I. F. Buyakov,
V. M. Volzhankin, K. O. Borisevich, and P. P. Samtsov

UDC 541.16 678.675(088.8)

Results of experimental investigations of the conditions of formation of carbon nanomaterials in the decomposition of methane in the plasma of a high-voltage atmospheric-pressure discharge have been presented. The influence of the temperature gradient, the cathode material, and the deposition-surface material on the process of formation of carbon nanostructures has been investigated. It has been established that the processes of catalytic decomposition of methane occur, with a large degree of probability, on the metallic deposition surface in the presence of the temperature gradient between the gas flow and the surface.

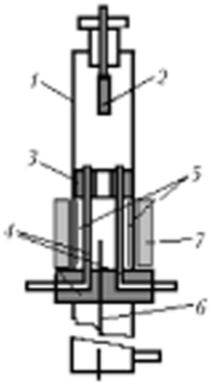
Introduction. Carbon nanomaterials have been discovered comparatively recently but they already have a wide range of fields of potential application. A great number of different methods for production of carbon nanomaterials are known today [1–3]. We have proposed the technique of producing multiwalled carbon nanotubes and nanofibers in the decomposition of hydrocarbons in a high-voltage atmospheric-pressure discharge [4]. Initially it was assumed that the formation of structurized (cross-linked) forms of carbon in this process is based on the disproportionation reaction $CO(v) + CO(w) \to CO_2 + C$, which could be realized under nonequilibrium electric-discharge conditions on excitation of high vibrational levels of carbon oxide. However, the subsequent experiments and numerical modeling of the process have shown that, under conditions realized in practice, the population of high vibrational levels of CO is unlikely because of the high concentrations of hydrogen in the working mixture.

The hypothesis for formation of carbon nanomaterials on the so-called carbide cycle [6] has received wide recognition from investigations of the processes of production of carbon nanomaterials in catalytic decomposition of hydrocarbons [5]. The mechanism proposed is based on the possibility of the hydrocarbon decomposing into highly dispersed particles of the iron subgroup followed by the diffusion of carbon atoms through a metal particle and their structurization on its back side.

Considering this mechanism as applied to our experimental conditions, we can assume the existence of two ways of forming carbon structures. The first is the process occurring in the entire volume of the working gas medium and including the reduction of carbon oxide to carbon, the evaporation of the cathode metal from cathode spots, the formation of metal clusters in the gas flow, the formation of skeleton carbon structures on the metal clusters, and the deposition of the structures formed on the reactor walls. The second possible way is the adsorption of hydrocarbon molecules on the metallic surface of the reactor wall, their catalytic decomposition to form carbon, the dissolution of carbon in the metal, the diffusion of carbon atoms within the metal, the saturation of the surface metal layer with carbon, and next the "growth" of the skeleton carbon structures from the wall. Simultaneous realization of the two ways is not improbable.

In the present work, we give experimental results enabling us to draw the unambiguous conclusion in favor of one noted way of forming carbon nanomaterials according to the technique proposed.

A. V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus, 15 P. Brovka Str., Minsk, 220072, Belarus; email: borisevich-kir@yandex.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 81, No. 4, pp. 617–620, July–August, 2008. Original article submitted November 23, 2007.



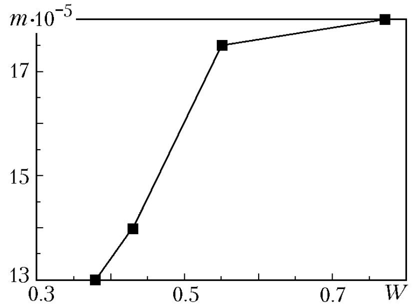


Fig. 1. Diagram of the modified reactor: 1) quartz tube; 2) cathode; 3) anode; 4) tubes for injection of the gas mixture; 5) deposition surface (foil); 6) thermocouple; 7) heat insulation.

Fig. 2. Specific quantity of the deposited carbon nanomaterial vs. discharge power. The composition of the mixture at the reactor outlet is 18% CO + 37% $H_2 + 42\% \, N_2 + 3\%$ CH_4. *m*, g/(mm^2·h); *W*, kW.

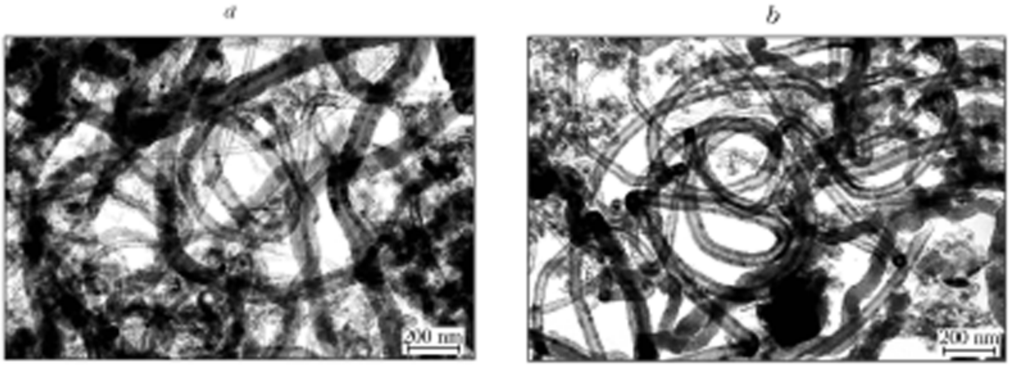


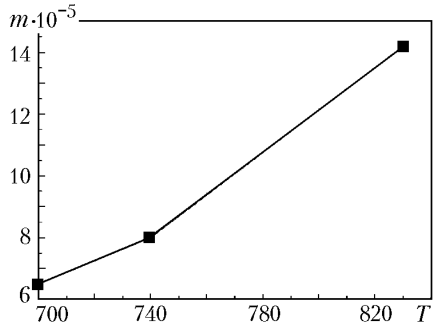
Fig. 3. TEM photographs of the carbon nanomaterial formed when the cathode made of Invar (a) and graphite (b) is used.

Results and Discussion. We carried out investigations on a setup (described in [4] in detail) with a modified reactor in which the replacement of the deposition surface of a carbon nanomaterial was allowed for (Fig. 1). To access the role of carbon oxide in the process of formation of a carbon nanomaterial we used two model mixtures in the experiments: 18% CO + 36% $H_2 + 46\% \, N_2$ and 18% CO + 37% $H_2 + 42\% \, N_2 + 3\%$ CH_4; their flow rate was 600 liters/h for each mixture.

The experiments carried out have shown that the formation of a carbon deposit containing carbon nanomaterials occurred only when the methane-containing mixture was used. Figure 2 plots the yield of the carbon nanomaterial as a function of the power of the discharge in the case of treatment of the methane-air mixture with it.

The degree of influence of the clusters arising from evaporation of the metal from the cathode surface on the process of formation of carbon nanostructures was elucidated by comparative experiments with Invar and graphite cathodes. Figure 3 gives the photographs of transmission electron microscopy (TEM) of two samples of a carbon material produced under identical conditions in the discharge system with different cathodes. In the photographs, it is seen that the carbon nanomaterial was formed in both cases, which enables us to infer that the metal clusters in the gas flow exert no pronounced influence on the formation of skeleton carbon structures.

To elucidate the influence of the surface material on the yield of a carbon nanomaterial we placed two semicylinders made of nickel and molybdenum foil into the reactor; the deposit was formed on these semicylinders. The working mixture consisted of methane (200 liters/h) and air (456 liters/h). The discharge power was 380 W; the av-



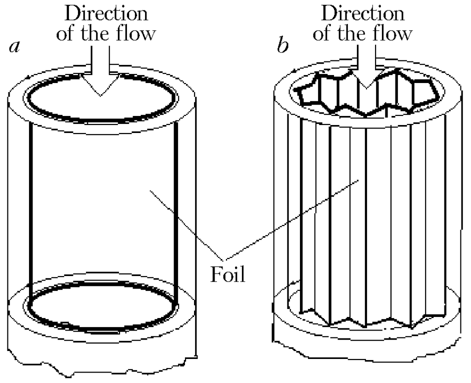


Fig. 4. Yield of the carbon nanomaterial vs. surface temperature. *m*, g/(mm^2·h); *T*, ^{o}C.

Fig. 5. Shape of the surfaces of collection of the carbon nanomaterial: a) the foil is tight against the quartz-tube wall; b) the foil is "pleated."

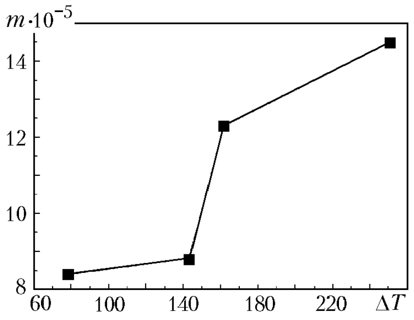


Fig. 6. Yield of the carbon nanomaterial vs. temperature gradient between the gas flow and the surface. *m*, g/(mm^2·h); Δ*T*, ^{o}C.

erage deposition-surface temperature was 780^{o}C. The specific quantity of the carbon nanomaterial collected from the nickel-foil surface was $16\cdot10^{-5}$ g/(mm^2·h); no material was detected on the molybdenum foil.

When the heterogeneous character of formation of carbon nanostructures is considered, the decomposition-surface temperature which influences the disintegration rate of hydrocarbons and the diffusion of carbon in the metal is of importance. In [7], in the case of a ferrocatalyst the formation of ordered carbon structures is of the threshold character and begins with a temperature of 680^{o}C. In our investigations, it has been established that carbon structures are formed at a surface temperature no lower than 500^{o}C; the yield of a carbon nanomaterial increases with temperature too, as is shown in Fig. 4.

The important role of the presence of the temperature gradient between the gas flow and the material-collection surface has been revealed during the work. If the surface temperature is close or equal to the flow temperature, no carbon nanomaterial is formed on it. This proposition is illustrated in Fig. 5. It is seen that the foil surface is tight against the wall of the quartz tube (Fig. 5a), whereas the foil is "pleated" (Fig. 5b). The carbon nanomaterial is formed in the first case and is not formed in the second for identical parameters of the discharge and the gas flow. Conceivably the reason might be thermodiffusion processes which determine the rate of feed of gaseous hydrocarbon to the metal surface. For the first case we plotted the specific yield of the carbon nanomaterial as a function of the temperatures difference at the center of the flow and the wall (Fig. 6). The two temperatures were measured with thermocouples during the experiment. As is shown in the figure, the specific yield of the carbon nanomaterial grows with temperature gradient between the gas flow and the wall.

Conclusions. The experimental investigations carried out show that the formation of a carbon nanomaterial in the case of treatment of the methane-air mixture with the plasma of a high-voltage atmospheric pressure discharge occurs on a metallic surface and is similar to the processes of catalytic decomposition of hydrocarbons by the mechanism of a carbide cycle. This determines the dependence of the yield of the carbon nanomaterial on the material of the deposition surface and its temperature and on the entire configuration of the temperature field in the deposition zone. The probability of disproportionation reaction exists under nonequilibrium high-voltage-discharge conditions, but the contribution of this process to the general picture is insignificant.

NOTATION

m, specific mass of the carbon nanomaterial, $\mathrm{g/(mm^2 \cdot h)}$; T, temperature, $^{\circ}$C; v and w, different vibrational molecular levels; W, discharge power. kW; ΔT, temperature gradient, $^{\circ}$C.

REFERENCES

1. P. J. F. Harris (Ed.), *Carbon Nanotubes and Related Structures*, Cambridge University Press (1999).
2. A. V. Eletskii, Carbon nanotubes, *Usp. Fiz. Nauk*, **167**, No. 9, 945–972 (1997).
3. É. G. Rakov, Methods of production of carbon nanotubes, *Usp. Khim.*, **69**, 41–59 (2000).
4. S. A. Zhdanok, I. F. Buyakov, A. V. Krauklis, A. E. Shashkov, and A. P. Solntsev, Carbon nanotubes synthesis under non-equilibrium conditions, in: *Proc. Int. Workshop on Carbon Materials for Energy Applications*, (2004), pp. 31–36.
5. E. F. Kukovitsky, S. G. L'vov, N. A. Sainov, and V. A. Shustov, CVD growth of carbon nanotube films on nickel substrates, *Appl. Surf. Sci.*, **215**, 201–208 (2003).
6. R. A. Buyanov and V. V. Chesnokov, On the processes occurring in metal particles in catalytic decomposition of hydrocarbons on them by the mechanism of carbide cycle, *Khim. Inter. Ustoich. Razv.*, No. 13, 37–40 (2005).
7. M. A. Ermakova, D. Yu. Ermakov, A. L. Chuvilin, and G. G. Kuvshinov, Decomposition of methane over iron catalysts at the range of moderate temperatures: The influence of structure of the catalytic systems and the reaction conditions on the yield of carbon and morphology of carbon filaments, *J. Catal.*, **201**, 183–197 (2001).