ISSN 1995-0780, Nanotechnologies in Russia, 2017, Vol. 12, Nos. 3–4, pp. 139–146. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © G.V. Abramov, A.N. Gavrilov, I.S. Tolstova, A.L. Ivashin, 2017, published in Rossiiskie Nanotekhnologii, 2017, Vol. 12, Nos. 3–4.

Formation of Clusters of Carbon Structures in Plasma under Thermal Destruction of Graphite

G. V. Abramov[a]*, A. N. Gavrilov[b], I. S. Tolstova[b], and A. L. Ivashin[b]

[a] *Voronezh State University, Voronezh, 394006 Russia*

[b] *Voronezh State University of Engineering Technologies, Voronezh, 394000 Russia*

**e-mail: ganivrn@mail.ru*

Received September 26, 2016; in final form, December 13, 2016

Abstract—This article is devoted to the consideration of areas of formation of linear clusters of C–C, C=C, and C–C=C carbon bonds based on a numerical simulation of the plasma arc fusion method. The data on average velocities of carbon ions in plasma for different modes of synthesis of carbon nanostructures are obtained. A simplified mechanism for the formation of linear clusters of space multimolecular carbon nanostructures is proposed.

DOI: 10.1134/S1995078017020021

INTRODUCTION

The discovery of a new class of inorganic compounds of carbon [1] possessing a set of unique mechanical and electrical properties, which are prospective materials for many industrial fields, set a target of the development of effective and highly profitable technologies of synthesis of qualitative nanomaterial in an industrial scale. The growth of industrial production of carbon nanomaterials is restrained by the low productivity and high cost of existing technologies caused by the insufficient study of the carbon-nanostructure (CNS) formation process. To date, there is no common opinion on the model of carbon atom dissociation in clusters with the formation of bulk nanostructures (fullerenes, nanotubes, and nanofibers).

Mainly, the technology of CNS synthesis implies the use of different methods of thermal evaporation of pure graphite or decomposition of carbon-containing gases followed by the deposition of the obtained structures on a cooling substrate [2]. All the technologies include the thermal destruction of the initial material structure followed by the formation of new compounds of carbon.

The use of different forms of catalysts in various synthesis process makes it possible to increase the yield considerably and change the characteristics of the final product, but it leads to additional defects, inhomogeneities, and pollution of the nanomaterial by catalyst, requiring additional purification, which influences the final yield, quality, and price of the CNS [3].

A study of the mechanism of CNS formation upon the thermal evaporation of graphite in plasma is a complicated task due to a diversity of different factors influencing the process [4], and the solution to this task is impossible without the concept and detailed analysis of all phase and structural transformations taking place in synthesis process.

In this work, some of the abovementioned problems and the ways to solve them, with respect to the formation of an ensemble of carbon clusters forming different CNSs upon the thermal spraying of carbon, were considered.

In a connection with the above, the aim of this article is to investigate areas of carbon-cluster formation with different covalent bonds, which are the basis of CNS formation in low-temperature plasma based on the mathematical model and the subsequent increase of synthesis efficiency.

EXPERIMENTAL

The most well-known technology of CNS synthesis, consisting of the thermal spraying of graphite in arc discharge plasma in a medium of buffer gas (He, Ar) was chosen as an object for research [5, 6].

An investigation of phase and structural transitions occurring in multicomponent plasma is possible on the basis of different methods (single-particle approximation, molecular dynamics, Monte Carlo, magnetodynamic description, Schroedinger model, etc.), but the most favorable approach to investigate the collective phenomena in low-temperature plasma is a kinetic approach [7]. The use of the distribution function of different components of plasma in this approach makes it possible to predict the behavior of carbon particles during the synthesis on the basis of

the probabilistic approach by the consideration of collective phenomena of plasma: vibrations of plasma, fluctuations of different characteristics, concentrations, and particle flows [8].

Modeling of kinetics of the formation of different carbon cluster groups with C–C, C=C, and C–C=C covalent bonds, which is the basis of CNS using the elastic and inelastic collisions of different particles in plasma, taking into account the influence of buffer medium and change of working-zone configuration, makes it possible to investigate the phase transitions in plasma, number of interactions with the formation of stable bonds, zone of formation, and the conditions for effective formation of carbon nanostructures during synthesis process.

At the kinetic approach, the system of Boltzmann equations [9, 10] for each type of particles in plasma, supplemented by the conditions of elastic and inelastic pair interactions between particles, was taken as a basis:

$$\frac{\partial f_\alpha}{\partial t} + \vec{\vartheta}\frac{\partial f_\alpha}{\partial \vec{r}} - \frac{q_\alpha}{m_\alpha}\left(\vec{E} + \frac{1}{C}[\vec{\vartheta}, \vec{B}]\right)\frac{\partial f_\alpha}{\partial \vec{\vartheta}} = \left.\frac{\partial f_\alpha}{\partial t}\right|_{CT}, \quad (1)$$
$$\alpha = e, c, h,$$

where f_α is the function of plasma components distribution (e, electron; c, helium ion; and h, carbon ion); $\vec{E}$ is the electric field strength; $\vec{B}$ is the magnetic induction; q_α, m_α are the charge and mass of particle; $\vec{\vartheta}$ is the field of particle velocities; and $\vec{r}$ is the coordinate of particle.

To find the parameters of electromagnetic field, the initial system of equations (1) was complemented by the Maxwell system of equations [11], describing the self-consistent field.

The presence of an integral of collision in the right side of Eq. (1) complicates the numerical solution to the resulting system of equations.

Assuming that the collisions in arc discharge plasma occur between the electrons, ions of buffer gas, and carbon particles, the integrals of pair collision will be as follows:

$$\left.\frac{\partial f_\alpha}{\partial t}\right|_{CT} = \sum_{k=e,c,h}\iint_V (f_k' f_{k_1}' - f_k f_{k_1})|\vec{\vartheta}_k - \vec{\vartheta}_k'|d\sigma d\vec{\vartheta}_k', \quad (2)$$

where f_k', f_{k_1}' are the distribution function of particles before and after collision; $\vec{\vartheta}_k$, ϑ_k' are the velocities of particles before and after collision; $d\sigma = 4R_1R_2\cos\theta d\Omega$ is the differential effective scattering cross section of particles with the radius of R_1 and R_2 to a solid angle of $d\Omega$; and θ is the angle between velocity of collided particles and the line of motion.

The Maxwell distribution [12] was used as a function describing the distribution of particles by the velocities in plasma.

Carbon atoms are able to provide more than one electron from each atom for the formation of a covalent bond during their interaction, which allows them to form three types of hybridization of electron clouds with single, double, and triple bonds. These bonds are different in length, bond energy, and valence angle.

We consider that the condition of occurrence of a stable bond at the inelastic collision of two particles of carbon in plasma is their rapprochement to a distance lower than the length of the covalent bond with the total kinetic energy of interacting particles higher than the activation energy of bond E_{bond} between them [13].

For the formation of a C–C covalent bond, the distance between the interacting particles must fall in the range of 1.34 Å < ε < 1.54 Å, and the total kinetic energy must be in the range of 348 kJ/mol < E_{bond} ≤ 614 kJ/mol; to form the C=C bond, the distance must appear as the value of 1.34 Å < ε < 1.20 Å, and the energy must appear as the value of 614 kJ/mol < E_{bond} ≤ 839 kJ/mol [14]. The carbon atoms bonded with triple bond C≡C do not take part in the formation of CNS; thus, they were not considered in this article.

A cluster with the bonds of C=C–C type is the basis for the building of pentagons and hexagons forming the bulk structures of fullerenes and nanotubes.

As a result of chemical bond formation between particles, additional energy ΔE is released, which was not taken into account in calculations:

$$\Delta E = (E_1 + E_2) - (n-1)E_{bond}, \quad (3)$$

where E_1, E_2 are the kinetic energies of interaction particles; n is the number of atoms in particle.

The formation of C_n molecule is determined by the equation:

$$C + C_n \rightarrow C_{n+1} + \Delta E. \quad (4)$$

Presenting the integral of collisions (2) in the form of Fokker–Planck equation [15] and performing the transition from vector algebra to tensor analysis using the corresponding transformations, the overall system of equations describing the processes occurring in plasma was obtained.

Solving the developed model is possible only using the numerical method. The obtained system was divided into three auxiliary tasks, successively calculating their movement and collisions of charged particles in plasma. The first task is solved on the basis of heat and mass transfer process with the moving boundaries of synthesis [16, 17]. The calculation of particle movement is the system of Vlasov–Poisson dimensionless equations [18], the solution to which is functions giving the initial condition for the third task, allowing one to determine the coefficients in an integral of collisions and function of particle distribution for considered moments of time.

The presence of a huge number of particles taking part in a calculation (only by one atom of carbon for

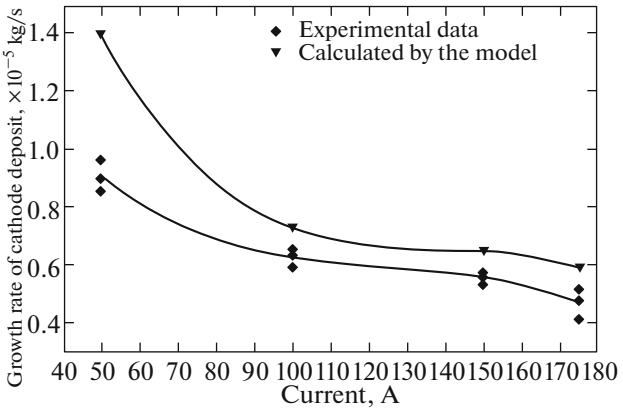

Fig. 1. Experimental and calculated values of growth rate of cathode deposit depending on current. The pressure of He in chamber was 400 Torr. Diameter of electrode was 12 mm.

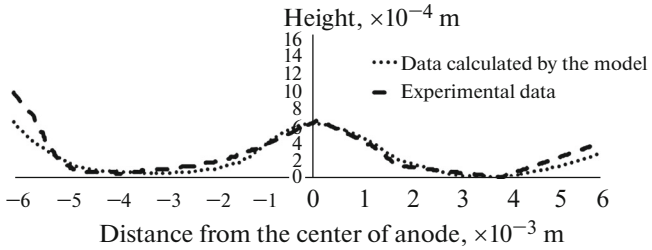

Fig. 2. Experimental and calculated values of anode burnout profile with diameter of 12 mm for the time of $t = 120$ s. Synthesis parameters: current was 150 A and He pressure was 400 Torr.

12-mm electrodes this value is ~10^{16}–10^{17}) makes it very complicated. Thus, to obtain the physically justifiable results of numerical modeling, the method of large particles (MLP) [19], allowing one to decrease the number of calculations and requirement for computer resources by the decrease in the number of particles taking part in calculation by grouping them, is used. On the basis of numerical analysis carried out of particles grouping in MLP, the optimal coefficient of particle connectivity was found to be $\chi = 3$ [16] for calculation.

To decrease the time and price of computations of a three-dimensional task, the calculations were performed using the technology of parallel computations GPGPU (graphical processor of general purpose graphic card [20] on a CUDA hardware–software complex with the use of nVidia CUDA technology [21].

RESULTS AND DISCUSSION

To confirm the adequacy of the model, a set of experimental investigations on the acquisition of various CNS by the described method on an automatic laboratory setup [22], allowing one to stabilize the technological parameters of process, was carried out.

MPG-4 graphite electrodes with a diameter of 12 mm with a distance of 1 mm maintained between them was used as a raw material. The current was automatically kept on the level of 150 A during synthesis. The voltage between electrodes was 25 V. The working pressure of buffer gas (He) in a chamber was kept constant on the level of 400 Torr. The set of experiments was carried out at high DC current values (350–400 A), when a cathode deposit is practically not formed and all the carbon black, having a high content of C_{60}, C_{70} fullerenes, is deposited on the walls of chamber.

The results of an experiment carried out and of numerical calculation on the basis of the developed model at the same synthesis parameters are shown in Figs. 1 and 2.

Graphite from anode is sublimated at a plasma temperature of 4500–5500 K and it dissociates, forming the vapor phase, consisting of separate carbon ions. The carbon ions are accelerated by an electromagnetic field. The presence of the oncoming flow of electrons and heavy molecules of buffer gas in plasma lead to different collisions and changes in the direction of particle movement. As a result, energetic and space conditions are created for stable covalent bonds between carbon particles, leading to the nucleation and further growth of clusters. This approach was confirmed and explained in [23]. The formation of clusters takes place by ion-molecular synthesis, in which

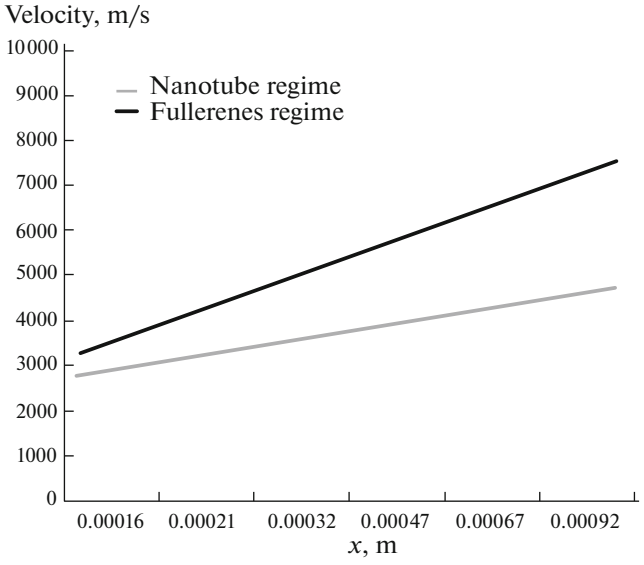

Fig. 3. Calculated values of average velocities of carbon ion motion without taking into account the collisions at the current I: 150 A corresponded to the Nanotube regime; 350 A corresponded to the Fullerene regime. The voltage was 25 V, and the He pressure in chamber was 400 Torr.

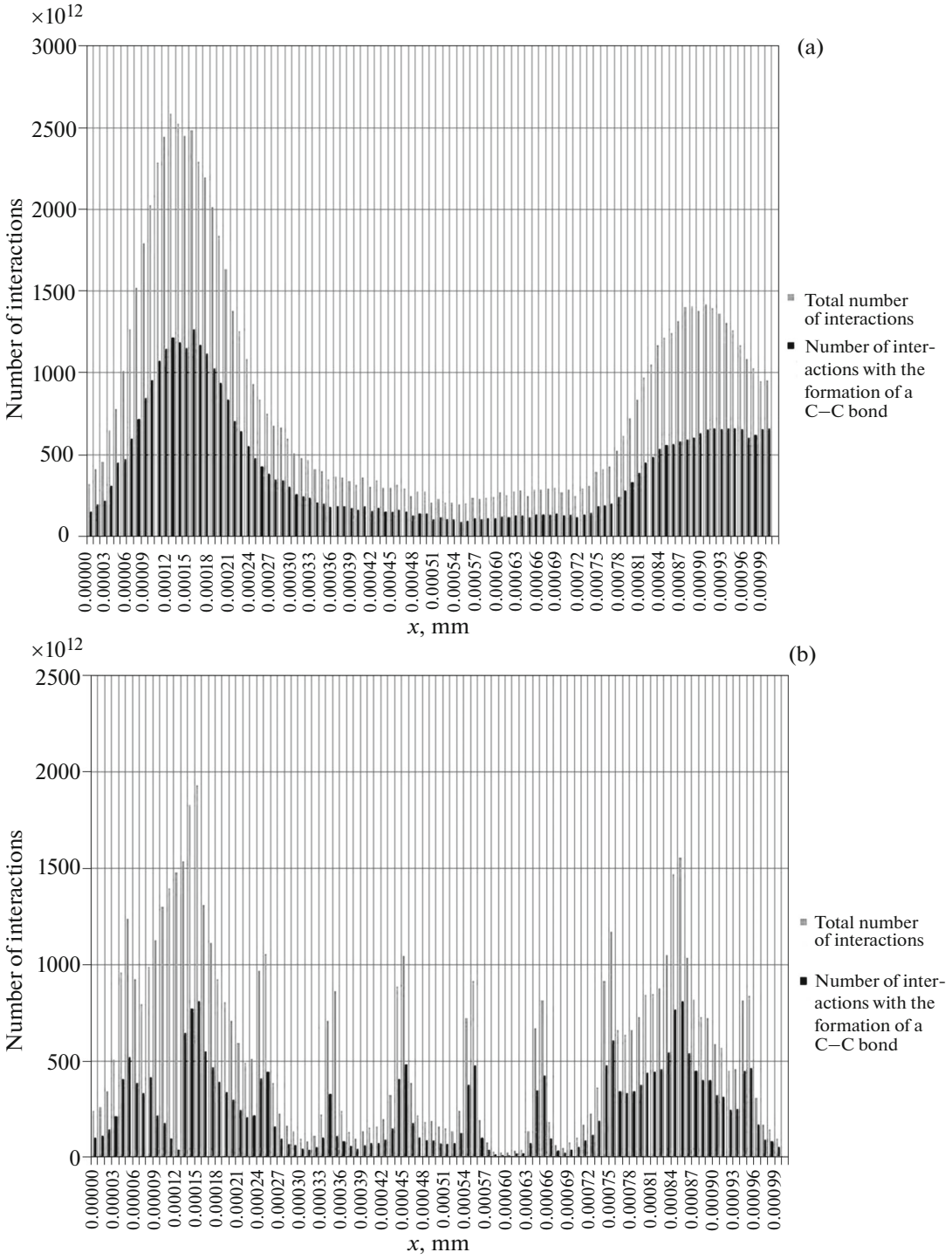

Fig. 4. Total number of pair collisions of carbon ions in plasma and the formation of a C–C bond in Nanotube (a) and Fullerene (b) synthesis regimes.

the linear carbon chains grow until the moment when they close to monocycle rings. Monocycle rings form double and triple rings exposed to condensation reactions. These rings are transformed to fullerenes and multiatom clusters, forming nanotubes on a cathode by condensation.

The velocities of carbon ion movement and, correspondingly, the energy of their interaction in plasma depend on the current maintained in arc. The change of average velocities of carbon ions at the movement from anode to cathode in the center of arc is shown in Fig. 3 without taking into account of collision in two

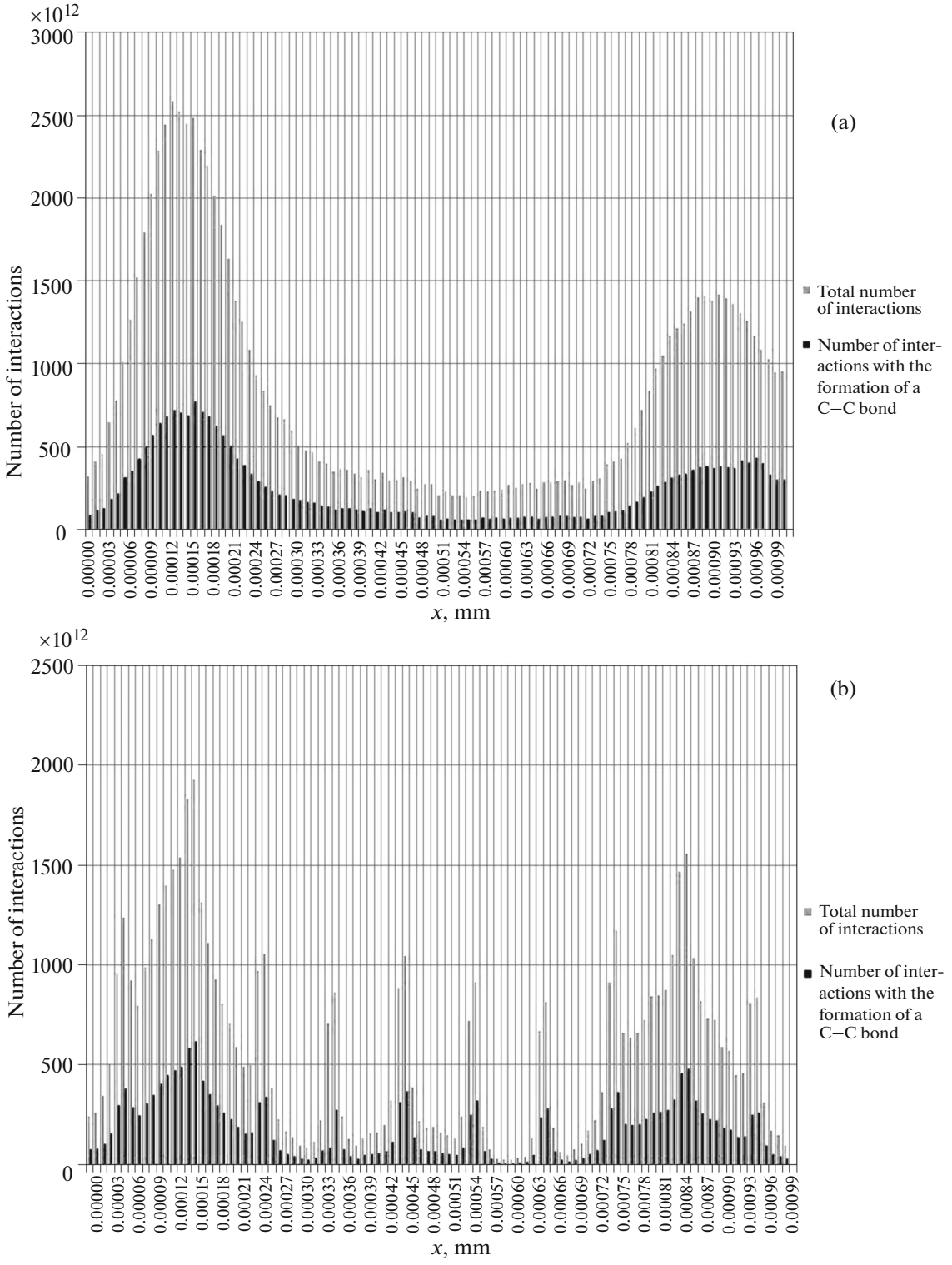

Fig. 5. Total number of pair collisions of carbon ions in plasma and formation of C=C bond in Nanotube (a) and Fullerene (b) synthesis regimes.

synthesis regimes, "Nanotubes" and "Fullerenes," differencing by the maximum yield of final product.

The analysis of calculations shows that the plasma temperature grows approximately to 20% while the current increases from 150 to 350 A. The average particle velocity increases 1.4 times of the magnitude without taking into account the collision.

The use of distribution function of carbon particles, calculated by the model, allows one to investigate the zones and conditions of the probable formation of

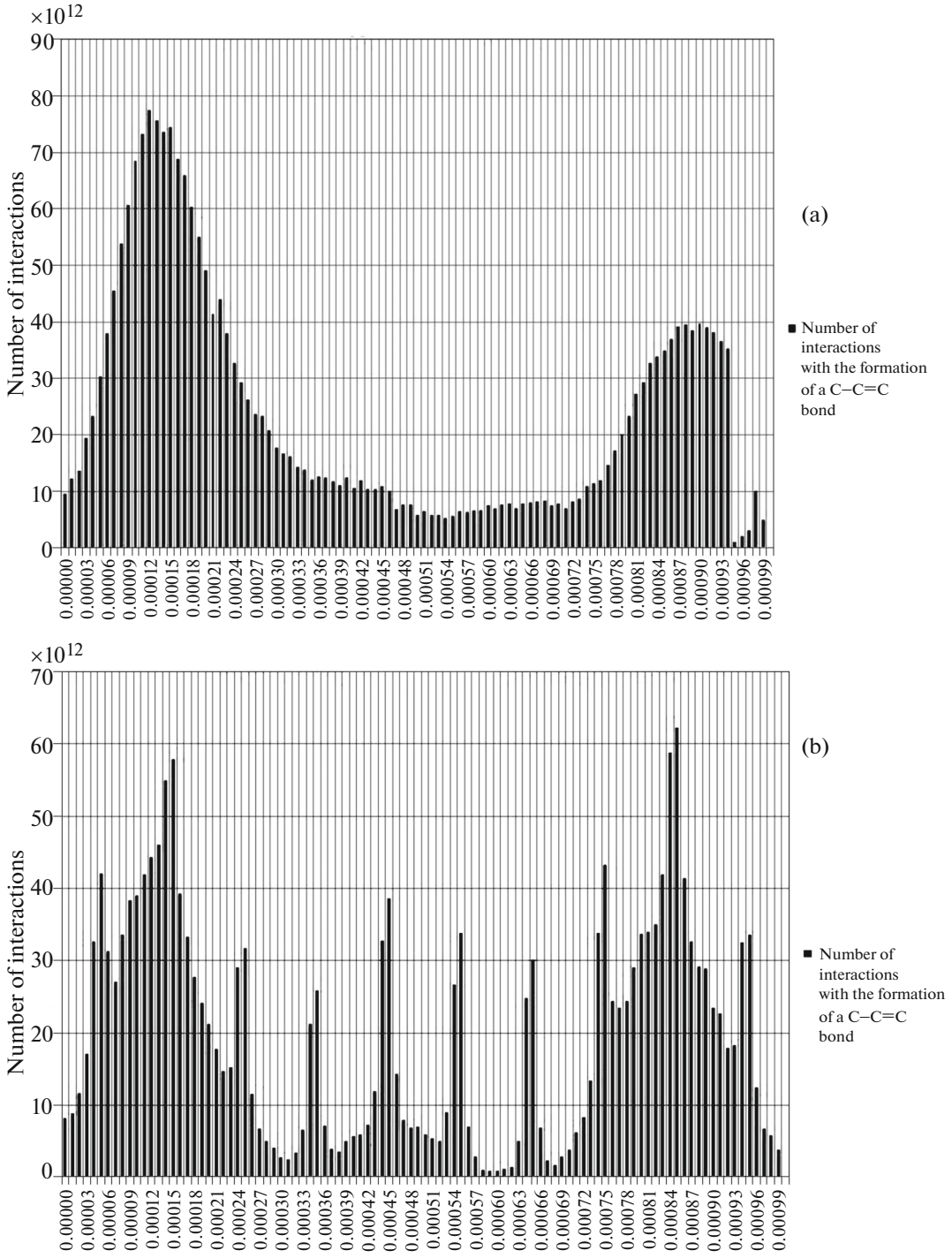

Fig. 6. Formation of C=C–C bonds in Nanotube (a) and Fullerene (b) synthesis regimes.

the highest concentrations of linear cluster groups with C–C, C=C (C2), and C=C–C (C3), bonds in plasma, which are the basis of CNS formation.

The calculated dependences of qualitative values of the total number of pair interactions of carbon ions and formation of C2 linear bonds in plasma by the length of interelectrode gap for the Nanotube regime (Figs. 4a, 5a) and Fullerenes regime (Figs. 4b, 5b) are shown. The calculated dependences of C3 linear bond formation in the interelectrode distance for considered synthesis regimes are presented separately in Fig. 6.

The time interval for a numerical calculation of the total number of different interactions for the Fullerene

regime, shown in Figs. 5 and 6, is $\Delta t = 330$ ns, and for the Nanotube regime it is equal to $\Delta t = 360$ ns.

In the Nanotube regime, the carbon particle flies the interelectrode distance for 6 calculation cycles (1 cycle is equal to 10 ns), taking into account the collisions, and it takes 3 cycles in the Fullerene the regime.

An analysis of numerical calculations shows that the formation of C2 and C3 bonds in considered synthesis regimes passes differently. This is explained by the different parameters of electromagnetic fields accelerating the particles, temperature of plasma, and the different initial velocities of particle. The number of particle interaction in plasma is different on the entire interval, but the highest number, according to numerical calculations, was detected near the electrodes of interelectrode space.

An analysis of mathematical modeling showed that the number of collisions has the most influence on the formation of cluster groups. The ratio of the number of collisions with the formation of bonds to the total number of collisions in the investigated conditions changes insignificantly. The total number of collisions is determined by the particle concentration and their velocity and size.

The initial direction of movement of carbon particles and their velocity is generated in a model randomly taking into account the profile of anode evaporation on the basis of Maxwell distribution. The particles grow in size when moving due to the formation of bonds upon collisions with other particles. These particles are accelerated under an electric field, but their total number decreases. There are highest numbers of particles with relatively low velocity on the initial stage. The high number of particles gives a high number of collisions, part of which leads to bond formation and coarsening of the particles. The number of particles decreases and the concentration of particles decreases, which leads to a decrease in total number of collisions and collisions with bond formation. Then the larger particles are accelerated by an electromagnetic field, which leads to an increase in the total number of collisions in the cathode area and to an increase in the number of bonds that formed, consequently.

The presence of intermediate extrema in the Fullerene regime can be explained by the faster growth of velocity of particles, which leads to an increase in collisions first, then the number of particles decreases and the number of collisions decreases as well. This leads to the few maxima shown in graph. The total number of formed clusters in this regime is distributed more evenly by the length, which corresponds to experimental research (the fullerenes are predominantly formed in a gap, and the nanotubes are deposited on a cathode).

CONCLUSIONS

In this work two main tasks were set: first, to investigate the mechanism of nucleation and formation of carbon clusters with C–C and C=C bonds in plasma in detail. Second, to show the probability regions of C2 clusters association in the C–C=C structure with maximum quantity, which are the basis of fullerenes and nanotube formation in the process of graphite sublimation in plasma.

Using the developed mathematical model of movement and interaction of particles with the formation of stable C2 and C3 bonds in multicomponent arc discharge plasma, the velocity characteristics were determined for two regimes of synthesis.

Fullerenes were mainly presented in carbon black deposited on the walls of chamber, and the carbon nanotubes were presented in cathode deposit. To determine the maximum quantitative yield of fullerenes, the main condition of synthesis is preventing the formation of cathode deposit; i.e., the whole evaporated amount of anode can be deposited on the walls of chamber, and for nanotubes the main product is a cathode deposit.

Boltzman equations were used for modeling the CNS synthesis process by the thermal spraying of graphite using low-temperature plasma for the first time.

Technological parameters for different regimes of synthesis were calculated and it was shown that the formation of stable C2 and C3 bonds occurs on the entire space of interelectrode space with different intensities. The highest number of stable bonds is formed in initial and final phase of nanotubes synthesis regime, which is caused by the initial distribution of particles and accelerations of particles by the electromagnetic field and the necessity of their deposition on the cathode to form nanotubes. In a regime of fullerenes formation, the formation of bonds passes more evenly in a whole space, which makes it possible to obtain fullerenes and blow them out from the interelectrode space without deposition on a cathode.

The results show that technology of thermal synthesis of carbon nanostructures gives an opportunity to increase the possibility for enhancing the process efficiency by the selecting optimal technological parameters of synthesis. Keeping stable process parameters directly influences the quality and yield of the synthesized product.

Thus, the technology of CNS synthesis by the arc discharge method, characterized by a high rate of process, allows one to include considerable volumes of raw materials in the process. The synthesis directly depends on the condition of technological process, and the capabilities of technology are far from being exhausted.

REFERENCES

1. H. W. Kroto, R. J. Heath, and S. C. O'Brien, "C60: Buckminsterfullerene," Nature **318**, 162 (1985).
2. A. N. Gavrilov, E. A. Pologno, and A. N. Ryazanov, "Analysis of methods of synthesis and industrial production of carbon nanotubes," FES: Finansy. Ekon. Strateg., No. 6, 14–19 (2010).
3. E. G. Rakov, *Nanotubes and Fullerenes* (Logos, Moscow, 2006) [in Russian].
4. Y. Ando, "Carbon nanotube: The inside story," J. Nanosci. Nanotechnol. **10**, 3726–3738 (2010).
5. W. Kratschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, "Solid C60: A new form of carbon," Nature **347** (6291), 354–358 (1990).
6. J. L. Hutchison, N. A. Kiselev, E. P. Krinichnaya, A. V. Krestinin, R. O. Loutfy, A. P. Morawsky, and D. N. Zakharov, "Double-walled carbon nanotubes fabricated by a hydrogen arc discharge method," Carbon **39**, 761–770 (2001).
7. B. V. Alekseev, "Physical principles of the generalized Boltzmann kinetic theory of gases," Phys. Usp. **43**, 601 (2000).
8. V. P. Silin, "Kinetics of weakly collisional plasma," Phys. Usp. **45**, 955 (2002).
9. M. N. Kogan, *Dynamics of a Rarefied Gas: Kinetic Theory* (Nauka, Moscow, 1967) [in Russian].
10. V. V. Aristov, *Direct Methods for Solving the Boltzmann Equation and Study of Nonequilibrium Flows* (Kluwer Academic, Dordrecht, Boston, London, 2001).
11. L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics,* Vol. 2: *The Classical Theory of Fields* (Nauka, Moscow, 1988; Pergamon, Oxford, 1975).
12. C. V. Heer, *Statistical Mechanics, Kinetic Theory and Stochastic Processes* (Academic, New York, 1972; Mir, Moscow, 1976).
13. G. V. Abramov, A. N. Gavrilov, and E. S. Tatarkin, "Simulation of carbon cluster formation processes in plasma of graphite thermal sputtering," Vestn. Voron. Univ., Ser.: Fiz. Mat., No. 2, 5–8 (2011).
14. J. Emsley, *The Elements* (Clarendon, Oxford, 1991).
15. M. N. Rosenbluth, W. MacDonald, and D. Judd, "Fokker-Planck equation for an inverse-square force," Phys. Rev. **107**, 1–6 (1957).
16. G. V. Abramov, A. N. Gavrilov, and E. A. Pologno, "Numerical solution of heat transfer with moving boundaries in the arc synthesis of carbon nanotubes," Vestn. Voron. Tekhnol. Akad., Ser.: Inform. Tekhnol., Model. Upravl., No. 2 (44), 9–14 (2010).
17. G. V. Abramov, A. N. Gavrilov, and I. S. Tolstova, "Formation of the initial distibution of plasma components on the phase plane of large particles method in electric arc synthesis CNS," Vestn. Voron. Univ. Inzh. Tekhnol., Ser.: Inform. Tekhnol., Model. Upravl., No. 3 (61), 67–71 (2014).
18. A. A. Vlasov, *Theory of Vibrational Properties of Electron Gas and Its Applications,* Vol. 75: *Uch. Zap. Mosk. Gos. Univ.* (Mosk. Gos. Univ., Moscow, 1945) [in Russian].
19. O. M. Belotserkovskii and Yu. M. Davydov, *Method of Large Particles in Gas Dynamics. Computation Experiment* (Nauka, Fizmatgiz, Moscow, 1982) [in Russian].
20. R. Farber, *CUDA Application Design and Development* (Morgan Kaufmann, San Francisco, CA, 2011).
21. J. Sanders and E. Kandrot, *CUDA by Example: An Introduction to General-Purpose GPU Programming* (Addison-Wesley Professional, Reading, MA, 2010; DMK Press, Moscow, 2011).
22. G. V. Abramov and A. N. Gavrilov, "Automatic control system of the carbon nanostructures synthesis in the arc discharge plasma," Avtomatiz. Sovrem. Tekhnol., No. 3, 10–14 (2016).
23. R. P. A. Bettens and E. Herbst, Ins. J. Mass. Spectrom. Ion Process. **149–150**, 321 (1995).

Translated by A. Bannov