The use of quantum-kinetic models in system design synthesis of carbon nanostructures

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Abstract. In the process of designing a carbon nanostructure (CNS) synthesis system, the main task is to determine the technological and functional parameters of synthesis. We offered a mathematical model of the process for the purpose of studying the synthesis processes using the graphite thermal evaporation, based on the Boltzmann kinetic equation, which takes into account elastic and non-elastic particle interactions. We offer a numerical solving method using the parallel computing technologies. We conducted the study of the effect of the main synthesis parameters on the carbon cluster formation and the amount of obtained material containing CNS.

1. Introduction

An intense interest in the study of obtaining methods, structure and properties of nano-scale systems is due to the diversity and uniqueness of variants of their practical use. Small sizes of the structural components, which are under 100 nm, are the reason why the properties of the obtained nanomaterials differ from those of bulky analogues. For example, the application of carbon nanostructures (CNS) as polymer fillers allows creating composite systems with new and often unique performance features as compared with traditional materials. This allows using such materials, in the long view, in various fields of modern industry such as: automotive and aircraft engineering, electronics, powder-based metallurgy, paint and coating production [1].

The wide use of CNS (fullerenes, nanotubes, nanofibers) in new high-technology solutions is hindered by their high cost and low performance of the existing synthesis methods [2]. First of all, this is due to the lack of fundamental study of the CNS formation processes.

The known CNS synthesis technologies mainly imply the use of various methods of thermal evaporation of atomic carbon, or disintegration of carbon-containing gases with farther sedimentation of the formed structures on a cooled surface. One of the most spread methods in this group of synthesis methods is the graphite thermal sublimation of highly purified graphite with an arc discharge plasma in the buffer gas media (usually He or Ar) [3]. The method is distinguished by the fact that in
various technological conditions of synthesis one can get multi-layer, one-layer nanotubes (with the use of catalyzer) or fullerenes of the C_{50}-C_{92} series with various outputs and quality [4-5].

The study of the processes that take place at the graphite thermal evaporation synthesis method is a complicated issue. The process goes fast; it is performed in plasma in quite a small amount. Therefore, a mathematical model is used for the purpose of studying the general regularities and features of the process. However, building an adequate nanostructure synthesis model even for the trivial case is a non-trivial task. Multiple mutually interacting phenomena taking place in nanostructures at phase and structural transformations, which must be taken into account, significantly complicate the designing process [6]. The use of more accurate models of nanosystems results in complicated solving algorithms and extensive computational costs. The use of simple models can result in non-efficient, narrow-bound and even incorrect design solutions.

2. Problem setting
For the study of the carbon nanostructure synthesis technology based on graphite thermal sputtering, a mathematical model of the process that takes into account its specific character is needed. It must enable accounting for the whole complicated mechanism of spatial CNS formation in low-temperature plasma, with multiple influencing factors such as:

- temperature fields in reaction chamber;
- moving boundaries of electrodes that form the flows of carbon ions evaporated from the anode, and electron emission from the cathode;
- parameters of the buffer environment and electromagnetic field that influence the distribution and travel of charged particles in the multicomponent plasma with account for their interactions;
- energetical and spatial conditions required for forming stable covalent bonds in carbon.

The model must also allow the study of the process with various degrees of detalization (both at the level of particle flow, and the interactions of separate particles with each other).

3. Development of a mathematical model
The models with various levels of hierarchical detalization can be used for mathematical modelling: classical, semi-classical and quantum-mechanical ones, which differ from each other by the level of accuracy of the object description, possibility to take into account the specific features of the process and the complexity of numerical solution. Classical models (molecular dynamics method, classical potential method, and single-particle approximation) allow nanosystem modelling with low computational costs; however, they show low accuracy of the modelling results and do not let describe the processes of nanostructures interactions and formation [7]. The use of semi-classical models (hydrodynamic, diffusion-drifting, and Monte Carlo models) secure acceptable compromise between the computational costs and accuracy of the physical phenomena descriptions from the point of view of the application for the practical engineering; however, they do not allow a full-scale study of the processes of nanostructures formation, growth and interactions [8]. The models based on the quantum-mechanical approaches (Schrodinger, and quantum-kinetic approaches) have been hardly used in the practical engineering up to the present, though they provide high accuracy of the applied tool for describing physical processes [9]. This is due to extensive computational costs when the models of this hierarchical level are used. In the case of the large-dimension nanosystem modelling, the physical limits of a classical computer are the factor that hinders the wide use of such models. Basing on the quantum-kinetic models (Boltzmann kinetic equation, and the quantum-mechanical version of the Liouville equation), one can obtain more simple models, as compared with the Schrodinger ones, for describing nanostructures in a wide range of linear dimensions with account for various interactions. The use of the algorithms of parallel and distributed calculations organization allows the extension of the above stated problem.

This paper considers the quantum-kinetic approach to the CNS synthesis process modelling using the graphite thermal sublimation with account for elastic and non-elastic collisions in the arc discharge plasma. We used the system of Boltzmann equations (1) for each plasma component complemented
with the system of Maxwell equations (2) that describes electromagnetic field, to describe the processes of the CNS arc discharge synthesis in the multicomponent plasma with account for the particle collisions [10-11]:

\[
\frac{\partial f_\alpha}{\partial t} + \mathbf{j} \cdot \nabla f_\alpha - \frac{q_\alpha}{m_\alpha} (\mathbf{E} + \nabla \phi) f_\alpha = \frac{\partial f_\alpha}{\partial t} |_{CT}, \quad \alpha = e, h, c
\]

(1)

\[
\text{rot } \mathbf{H} = \frac{4 \pi \mathbf{j}}{C} + \frac{1}{C} \frac{\partial \mathbf{D}}{\partial t},
\]

\[
\text{rot } \mathbf{E} = -\frac{1}{C} \frac{\partial \mathbf{B}}{\partial t},
\]

\[
div \mathbf{B} = 0,
\]

\[
div \mathbf{D} = 4 \pi \rho,
\]

Symbols used: \( f_\alpha \) – function of plasma distribution component (\( e \) – electron, \( h \) – buffer gas ion, \( c \) – carbon ion); \( \mathbf{E}, \mathbf{H} \) – electric and magnetic field intensities; \( \mathbf{D}, \mathbf{B} \) – electric and magnetic induction; \( q_\alpha, m_\alpha \) – particle charge and mass; \( \rho \) – charge density; \( \mathbf{j} \) – current density; \( C \) – light speed; \( \mathbf{\hat{\sigma}} \) – particle velocity field; \( \mathbf{r} \) – particle coordinates.

With the admission that all interactions in plasma are between electrons, buffer gas ions and carbon particles within the whole interelectrode space, we can write the pair-wise collision integrals as follows [12]:

\[
\left. \frac{\partial f_\alpha}{\partial t} \right|_{CT} = \sum_{\beta=e,c,h} \int (f_\alpha f^\prime_\beta - f_\alpha f_\beta) \mathbf{\hat{\sigma}} \cdot \mathbf{\hat{\sigma}} |d\mathbf{\sigma}d\mathbf{\sigma^\prime}|, \alpha = e, c, h,
\]

(3)

where \( f_\alpha f_\beta \) is the function of particles \( \alpha \) and \( \beta \) distribution prior to collision; \( f^\prime_\alpha f^\prime_\beta \) is the function of particles \( \alpha \) and \( \beta \) distribution after collision; \( \mathbf{\hat{\sigma}}, \mathbf{\hat{\sigma}^\prime} \) are the velocity vectors prior and after particles collision (m/s); \( d\mathbf{\sigma} \) is the differential effective cross-section.

The mathematical heat transfer model with moving boundaries was used for forming the initial boundary conditions and accounting the change of the boundary conditions in the course of the synthesis. The Maxwell distribution was used as the function describing the velocity-wise distribution of the particles in plasma.

The presence of the collision integral (3) in the Boltzmann equations (1) significantly complicates the solution of the offered model that can be carried out with a numerical method only. For this purpose, the system of input Boltzmann-Maxwell equations (1-2) is split basing on the splitting method modification [13] into three auxiliary problems which are solved in sequence. The scheme of decomposition is shown in Fig. 1.

The first problem, basing on the heat transfer model with account for the changes in the operating area configuration, forms the energetic and spatial particle parameters at the initial moments of time in the cells of the computational grid [14]. The second problem is a system of dimensionless Vlasov-Poisson equations, the solution of which is modelled by the particle motion through the boundaries of the cells and gives the initial condition for the third problem. The solution of the third problem that takes into account the particles collisions allows the determination of the coefficients in the collisions integral and obtaining the particle distribution functions for the considered moments of time. The found particle distribution functions allow determining the areas that meet the spatial and energy conditions of the probable formation of carbon cluster groups with various bonds, the growth of which forms linear carbon chains that are closed into monocyclic rings (pentagons and hexagons) and form convex carbon structures (fullerenes, nanotubes) both in plasma and on the cathode.
The presence of a large amount of various particles that at the same time participate in the numerical calculation requires significant computational resources and time. Therefore, to obtain physically justified modelling results we used the large-particle method (particle-in-cell method, or PIC) [15]. PIC allows decreasing the scope of calculation and, thus, the requirements to the computational resources without compromising the calculation accuracy due to grouping one-type particles into larger ones (macro-particles), with the same ratio of the charge to the mass, as for the input ones, and the averaged velocity and direction.

The parallelization technology GPGPU (General-purpose graphics processing units) [16] was used to decrease the time and monetary expenditures for the problem numerical solution. This parallel programming technology allows reaching a rather high parallelization level on one computer and avoiding significant time losses for data transmission between computation nodes and synchronization of the calculation results. The GPGPU technology allows using general purpose graphical processors on one PC for calculations, which significantly improves the efficiency of large data processing without using a supercomputer or computational clusters. All calculations were performed on the hardware-software complex CUDA (Compute Unified Device Architecture) with the use of the nVidia CUDA technology, which enables graphical processor programming [17].

One of the special features of GPGPU is that not all similar data flows started at one moment finish calculation simultaneously. Therefore, an algorithm allowing solving the problem of parallel calculation segments synchronization was developed. For each moment of time, after the calculation of all variables on the graphical accelerator, the process control was transmitted to the central processor where the results were processed, and after that the calculation proceeded with the next algorithm iteration.

4. Results and Discussions
A number of experiments on obtaining various CNS with electric arc method in the inert gas medium (He) were performed on the laboratory facility with AICS (Automated Informational Control System) [18] to prove the adequacy of the developed complex model. The use of AICS allows the stabilization of required synthesis parameters in the real-time mode. The investigations were conducted for two regimes of synthesis without using the catalyzer: obtaining fullerences with the maximum output C60÷C70 and multiwall carbon nanotubes (MCNT). Plasma discharged was automatically maintained within the space of 1 mm between high-purity graphite electrodes (ash content < 0.05 %), with a diameter of 12 mm. The buffer gas pressure in the work chamber was set at the level of 400 Tor, the...
voltage on the electrodes was 25 V. At a constant current of 120÷170 A, deposit sediment containing MCNT is formed on the cathode, and at currents of 350÷400 A, when the cathode deposit is utterly not formed, ash with a high content of fullerenes is sedimented on the walls of the reaction chamber. The output and the quality of the final product strongly depend on the set technological parameters and their stability.

The model adequacy was assessed over the results of the experimental study. The change in the cathode deposit mass depending on the process time (Fig. 2) and the change in the anode sublimation profile (Fig. 3) were assessed. The results suggest a rather good agreement of the experimental and calculated data.

**Fig. 2.** Cathode deposit mass change in the mode of the MCNT synthesis vs. synthesis time: 1 – calculation with the model 2 – experimental data. Current – 150 A.

The model allows the study of the formation and the growth rate of the cathode deposit containing MCNT depending on the current intensity, buffer gas type and pressure in the synthesis chamber (Fig. 4, 5). The growth rate of the cathode deposit in the He environment significantly differs from that in Ar. The use of Ar as a buffer medium increases the growth rate of the deposit at similar synthesis parameters as compared with He. The analysis of numerical calculations proves that the synthesis process at high currents goes without leaving deposit sedimentations.

The absence of a buffer environment in the work area at a discharge less than 70 Torr does not result in the MCNT formation, but leads to the cathode breakdown at high currents and sedimentation of ash on the chamber walls with the admixture of modified graphite.

**Fig. 3.** Experimental and calculated data of the anode profile change in the regime of the fullerene synthesis within the synthesis period 100 s. Current – 350 A.
The model allows the study of the cluster groups formation in plasma. The cluster groups with connections C=C–C (C3) are the basis for building pentagons and hexagons that form the spatial structures of fullerenes and nanotubes. The amount of their formations in the arc discharge plasma determines the output of the final synthesized product.

Fig. 6 shows the calculated dependences of the qualitative characteristics of stable carbon C3 cluster formation in plasma along the inter-electrode space for the MCNT synthesis regime (nanotubes regime) and fullerenes (fullerenes regime). The time interval of the numerical calculation of the total amount of the interactions shown in Fig. 6 is ∆t = 360 ns.

The analysis suggests that the C3 cluster formation in the considered synthesis regimes goes on in different ways. This can be explained by different parameters of the electromagnetic fields that accelerate particles, plasma temperature and different initial particle velocities. The amounts of C3 formations on the whole interval are different, but their greatest number is found in the vicinity of the electrodes in the inter-electrode space. The amount of collisions is determined by the concentrations, velocities and sizes of the particles. At the initial stage, the greatest amount of particles with the
relatively low velocity is present, and this gives a large amount of collisions, some of which result in the formation of bonds and enlargement of particles. When particles move from anode to cathode, their amount decreases due to the formation of groups, and the particle concentration decreases, which results in the decrease in the total amount of collisions and bond-forming collisions. Then larger particles are accelerated by the electromagnetic field, which results in the growth of the total amount of collisions in the near-cathode area and, hence, the amount of forming bonds.

5. Conclusions
This paper presents a mathematical model based on the use of the quantum-kinetic approach based on the Boltzmann kinetic equation with account for the pair-wise particles collisions for designing the MCNT using the thermal sublimation method. The use in the model of the functions of various plasma components distribution allows the calculation of the carbon particle behaviour during the synthesis basing on the probabilistic approach due to the consideration of collective plasma phenomena: plasma oscillations, fluctuations of various characteristics, concentration and particle fluxes.

The presented technique and the algorithm of numerical solving in the considered multidimensional nonlinear problem with the application of the nVidia CUDA technology combined with the parallelization technology GPGPU allows obtaining a resource-saving solution on one calculation module. Numerical studies using the model often allow determining the effect of the main synthesis process parameters (current intensity, voltage, pressure and buffer gas) on the final product output, determine the probability areas with the maximum amount of the C-C=C clusters formation in plasma in various synthesis regimes. In the nanotube synthesis regime, the greatest amount of stable bonds is formed at the initial and final phases, which depends on the initial particle distribution and particle acceleration with electromagnetic field and necessity of their sedimentation on the cathode to form nanotubes. In the fullerenes regime, the formation of bonds goes on more even in the whole range of the space, which allows obtaining fullerenes and blowing them out of the inter-electrode space without sedimenting on the cathode.

The obtained results suggest that the developed mathematical model allows adequate description of the processes that take place in plasma during the synthesis of carbon nanostructures, taking into account temperature fields, moving electrode boundaries, buffer medium and electromagnetic field parameters, energy and spatial conditions required for the forming of stable covalent carbon bonds. The obtained results also agree well with the experimental results of other researchers. The developed mathematical model and its elements can be used at the designing of the carbon nanostructure synthesis facilities using the graphing evaporation method.

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