The application of the large particles method of numerical modeling of the process of carbonic nanostructures synthesis in plasma

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Abstract. The article deals with the numerical solution of the mathematical model of the particles motion and interaction in multicomponent plasma by the example of electric arc synthesis of carbon nanostructures. The high order of the particles and the number of their interactions requires a significant input of machine resources and time for calculations. Application of the large particles method makes it possible to reduce the amount of computation and the requirements for hardware resources without affecting the accuracy of numerical calculations.

The use of technology of GPGPU parallel computing using the Nvidia CUDA technology allows organizing all General purpose computation on the basis of the graphical processor graphics card. The comparative analysis of different approaches to parallelization of computations to speed up calculations with the choice of the algorithm in which to calculate the accuracy of the solution shared memory is used. Numerical study of the influence of particles density in the macro particle on the motion parameters and the total number of particle collisions in the plasma for different modes of synthesis has been carried out. The rational range of the coherence coefficient of particle in the macro particle is computed.

1. Introduction

The study of synthesis processes characteristics of carbon nanostructures (CNS) which have unique mechanical and electrical properties is one of the modern science development promising directions. Having a set of unique physicochemical properties CNS (fullerenes, nanotubes, nanofibers) are considered a promising reinforcing material for polymer composites. Uniform introduction of CNS in the resin matrix only in the amount of 0.01 ÷ 5% by mass makes possible to have a promising composite materials with enhanced or improved set of properties [1]. Endowed with unique electrical, mechanical, barrier and other properties these nanostructural formatted materials are of great interest for various industries. However their industrial growth is constrained by low efficiency and high cost of existing technologies of the filler synthesis. Insufficient knowledge of the mechanism of nucleation and growth of carbon clusters forming the bulk of the nanostructure prevents the increase of the productivity and the quality of the synthesized product and reduction of its cost.

Thus the solution of modeling the process of carbon with various communication types clusters formation problem is an urgent task in terms of development and improvement modern technologies of new materials obtaining. Knowledge of the mechanism of the CNS formation will enable researchers to purposefully create and vary the methods and conditions for obtaining various types of carbon...
nanostructures and their derivatives which will significantly improve the efficiency and performance of existing synthesis technologies.

Mainly used in industry the technologies of CNS synthesis involve the application of various methods of thermal evaporation of atomic graphite by energy flux (laser, plasma, electron ion beam, etc.) or decomposition of carbon containing gases with subsequent deposition of the formed structures on the cooling surface. In all technologies there is a thermal destruction of the raw material structure with the subsequent formation and growth of polyatomic carbon clusters with different types of bonds which form the bulk of CNS.

The application of various forms of catalysts in the synthesis allows to increase significantly the output and to modify the characteristics of the finished product, but results in additional defects i.e. heterogeneity, contamination by the catalyst nanomaterial that requires further purification which significantly affects the yield, quality and cost of the finished product.

One of the most common methods for the CNS synthesis is the method of graphite thermal evaporation by plasma of arc discharge in the buffer gas environment. It allows to involve in the technological process large amounts of raw materials, to synthesize under different conditions the various types of CNS (single layer, multilayer nanotubes, nanofibers, fullerenes) and is characterized by the possibility of obtaining high-quality material.

The synthesis proceeds under the influence of low-temperature plasma (temperature of about 4500 ÷ 5500 K) in the environment of a buffer gas (usually He, Ar) followed by the deposition of material on the cooling surface. The process is characterized by a high concentration of energy, fast operation, a large number of different effects between the particle phase and structural transformations, by the influence of the large number of factors. To obtain the necessary carbon structures with the maximum output stable optimal technological parameters of the synthesis in real-time are required.

The study and search of optimum conditions of synthesis of the CNS by experimental methods are ineffective and difficult, therefore it is more productive to use methods of mathematical modeling.

Modern approaches to simulation of processes in plasma can be divided conventionally into classical, semiclassical and quantum-mechanical. To solve this class of problems in which the registration of the collective phenomena in plasma, as well as the complexity of computational calculation are characteristic is to use kinetic description which fits the task in the best way [2].

To study the kinetics of the movement and interaction of particles in a multicomponent plasma, taking into account the moving boundaries of the electrodes and condensation of supersaturated carbon vapor on the cooled cathode as well as the influence of process parameters and starting material on the formation process of the CNS a comprehensive mathematical model has been developed [3].

The Boltzmann equations (1) describing each species of particles in the plasma (electrons, carbon ions, buffer gas) and supplemented by the terms elastic and inelastic binary collisions between particles are the basis for the model describing the movement and interaction of particles in plasma [4].

$$\frac{df_\alpha}{dt} + \vec{\nabla} \cdot \frac{df_\alpha}{\vec{\nabla} \cdot \vec{v}} - \frac{q_\alpha}{m_\alpha} (\vec{E} + \frac{1}{C} (\vec{v} \times \vec{B})) \frac{df_\alpha}{\vec{v}} = \sum_{\beta=e,c,h} \int[ (f_\alpha^{f} f_\beta - f_\alpha f_\beta )] |\vec{v} - \vec{v}'| d\Omega d\vec{v}' , \alpha = e,h,c$$

where $f_\alpha, f_\alpha^{f}$ – the distribution function of the component of the plasma before and after the collision ($\alpha$: $e$ – electron, $h$ – ion-buffer gas (He), $c$ – ion carbon); $\vec{v}, \vec{v}'$ – the velocities of the particles before and after collision; $d\sigma = 4R_1 R_2 \cos \theta d\Omega$ – the differential effective scattering cross section of particles $R_1$ and $R_2$ in the solid angle $d\Omega$; $\theta$ – the angle between the velocity of the colliding particles and the line of movement; $\vec{r}$ – the coordinates of the particles; $q_\alpha, m_\alpha$ – the charge and mass of particles.

To find the parameters of the electromagnetic field the equation system (1) is supplemented by the Maxwell's equations system (2) describing the self-consistent electric field.
\[
\begin{align*}
\text{rot} \vec{H} &= \frac{4\pi j}{C} + \frac{1}{C} \frac{\partial \vec{D}}{\partial t}, \\
\text{rot} \vec{E} &= -\frac{1}{C} \frac{\partial \vec{B}}{\partial t}, \\
\text{div} \vec{B} &= 0, \\
\text{div} \vec{D} &= 4\pi \rho, \\
\rho &= \frac{q_e}{m_e} \int (f_c + f_h - f_e) d\vec{\vartheta}, \\
j &= \frac{q_e}{m_e} \int (f_c + f_h - f_e) d\vec{\vartheta},
\end{align*}
\]

where $\vec{E}, \vec{H}$ – the strength of the electric and magnetic fields; $\vec{D}, \vec{B}$ – electric and magnetic induction; $\rho$ – charge density; $j$ – the density of current; $C$ – the speed of light.

The use of distribution functions of various plasma components in the process model allows to predict on the basis of the probabilistic approach the behavior of the carbon particles in the synthesis process through the consideration of the collective phenomena of plasma: plasma oscillations, fluctuations of various characteristics, concentration and particle flows.

The presence in the right side vector of the equation (1) collision integral causes considerable difficulties in the explicit solution of this problem. Therefore using the representation of the collision integral as the Fokker-Planck equation it is possible to move from vector algebra in each point of the space to tensor analysis and to reduce the model to a dimensionless form in three-dimensional coordinate system [5].

The solution of the proposed model is possible only using a numerical method by splitting into three subsidiary problems to be solved consecutively: the formation of the initial position of the particle, the calculation of their displacement and the calculation of collisions of charged particles in plasma.

The availability of a large variety of particles present simultaneously in the plasma of the interelectrode space, make the calculations very resources demanding. Therefore to obtain physically reasonable results of numerical simulation it is necessary to use the method of large particles (MCC) [6]. This approach allows to reduce the amount of computation and accordingly the requirements for computer resources by reducing the number of similar particles in the calculation by grouping them to a reasonable level in larger (macro particles) having the same ratio of charge to mass as the original ones and the averaged speed and direction of movement. However, when combining the particles in the macro particles, it is necessary to determine the rational density of their placement, which directly determines the size of a large particles and affects the calculation accuracy.

2. Statement of the problem

The aim of this paper is to study the influence of parameters of the large particles method on the results of numerical simulation of processes in the formation of the CNS, by the method of thermal sublimation with graphite plasma and to develop efficient numerical methods for processing large volumes of data necessary for parameters calculation of these processes. It is necessary to calculate parameters such as the cell geometry of the computational domain, the number of particles forming the large particle of a certain type, the radius of macro particles and to develop the algorithms for calculation of coordinates of the centers of large particles in cells, their charge, mass, average velocity and direction of movement. The charge weighing and the current at the nodes of the computational grid should be done which are required to determine the new coordinates of the macro particles in each time step.
To perform calculations by the model in question it is necessary to develop an efficient algorithm for the numerical solution which allows to perform all calculations by a personal computer based on distributed parallel processing of large data amounts.

3. Solution method
To construct the algorithm of numerical solution of the model all the phase space computational domain is broken down into individual cubic cells the sides of which are parallel to the axes of the Cartesian coordinate system. In each cell instead of actual number of particles of each type in accordance with the distribution function by a macro particle with the total charge and mass of all particles of this sort contained in one cell is generated. To do this, the coordinates of the nodes of the computational grid and the coordinates of all particles of each species falling within the pitch range of each cell are calculated [7].

The radius and the charge of a large particle and consequently the effect of the electromagnetic field under the action of which charged particles move depends on the size of the macro particles, i.e. on the number of micro particles combined in the macro particle. The main parameter influencing the properties of large particles is the density of particles in the macro particle.

Assuming that the initial particle shape in the model is spherical the radius of the formed large particles $R_{\alpha \text{lp}}$ will be calculated by the formula:

$$R_{\alpha \text{lp}} = (\chi \cdot N_{\alpha})^{\frac{1}{3}} \cdot R_{\alpha}^{3},$$

where $R_{\alpha}$ – the radius of particles of class $\alpha$; $\chi$ – the factor bases on the assigned density of the particles in the macro particle; $N_{\alpha}$ – the number of particles in a macro particle.

The radius of the macro particles must be large enough to eliminate the interaction of particles at short range distances and to provide an approximation of self-consistent field. The coordinates of the centers of large particles in $i$ cells are calculated by finding the center of their masses.

The general algorithm for calculating the movement and interaction of particles in a multicomponent plasma is given in figure 1. It includes the consistent implementation of the 11 key tasks.

![Figure 1. Calculation scheme of the method of large particles](image-url)
After calculating the trajectory of a large particle under the action of electromagnetic field and its new position in phase space at later point of time, based on the current distribution functions is the dispersion of the particle charge over the nodes of the phase space is made and the process is repeated. To do this, we use the method of weighing the cloud in a cell for three-dimensional space [8].

The distribution of charge and current at the nodes occurs using the method of "cloud in a cell". The particle contributes only to the nodes that are vertices of the cell in which it has been inserted. Charge and therefore the current are split between them according to a linear law. Figure 2 shows the weighting for the three-dimensional case. The weighting is proportional to cell volume $V_i$.

To find the values of the potential and the forces that act on the particles in the cells of the computational grid the Poisson equation describing the electric field is solved which enables us to define subsequent coordinates of the macro particles from the equations of their motion.

Under the influence the electromagnetic field due to the collective interactions taking into account elastic and inelastic collisions with other particles each macro particle changes its speed and trajectory. The search of their collision was to verify the fact of the pairwise intersections of the particle trajectories in space. A special algorithm for the search of collisions consisting of two stages was developed. In the first phase, the information about the starting and ending position of particles in the grid cells is used as input data. Each calculated flow based on the considered data determines the number of cells where the particle had been, where the particle moved and generates a cell list in which an interaction could have taken place. In the next step according to the received list of cells to process each pair of particles to determine the coordinates of intersection of their trajectories is processed.

To develop effective methods and algorithms of calculation for the resource consuming tasks a number of additional studies were made. The main characteristic of the algorithm for the calculation that has a direct impact on the accuracy, CPU time and computational complexity is the dimension of grid of the modeled area. To obtain the necessary precision of calculations the grid of 100x100x100 dimension was specified. A further increase in dimensionality of the computational grid has practically no effect on the final results of the calculation, but significantly increases the time and resource-consuming computing. To improve computational efficiency of numerical solution of the model under consideration the analysis of the CPU time required to solve each problem indicated in figure 1 was made. The results of the time costs are shown in figure 3.
The analysis shows that the main CPU time (85.14%) in the process of numerical calculation by the model is 1, 4, 5 and 7. Moreover the longest is problem 4 – calculation of electromagnetic fields parameters by the establishment method. To reduce the overall continuous CPU time required for the calculation by the model, the first task was carried out separately by pre-generating the array of initial parameters of the particles taking into account the boundary and initial conditions of the simulation. The reduction in CPU time for the solution of other tasks was achieved through the organization of parallel calculations. As a paralleling technology GPGPU (General-purpose graphics processing units) technology was used. The technology of parallel programming allows a computer to achieve a high enough level of parallelism, while avoiding the considerable time loss in the data transfer between compute nodes and the synchronization of the computations. The GPGPU technology allows applying high-performance PC graphics card for computing which greatly increases the efficiency of processing large volumes of data without using supercomputers or large computing clusters. All calculations were performed on hardware-software complex CUDA (Compute Unified Device Architecture) by technology Nvidia CUDA which makes possible programming of the GPU [9].

A characteristic feature of the CUDA architecture is block-grid organization, implying that all threads are grouped in blocks and the hardware independently allocates resources of the computing device between them. All threads executing a particular area are grouped together in blocks, and the blocks in the grid. To identify the threads a two-dimensional indexes were used.

Using the GPGPU technology one part of the computing threads run in parallel at instant will finish the process execution not at the same time. Consequently we solved the problem of synchronization of parallel sections calculations. For each instant when the calculations of all variables were made by graphical accelerator the control was transmitted to the CPU where the results were processed, and only after that the transition passed to the next iteration of the algorithm.

The efficiency of parallel computing based on Nvidia CUDA technology besides the CPU cores performance depends on startup configuration. Therefore with the goal of minimizing the CPU time different versions of the organization of the parallelization algorithms were considered. Table 1 shows the comparative analysis of the application of various versions of parallel calculations organization with the sequential execution of iterations (sequential algorithm). All calculations have been performed for finding the parameters of the electric field by the establishment method (task 4) with the use of computational grids of $25 \times 25$ and $50 \times 50$ dimensions on a personal computer equipped with a Intel® Core™2 QuadQ 8200 2.3 GHz processor and the Nvidia GeForce GTX 660 Ti graphics card.

| Version of the algorithm | Grid $25 \times 25$ | Grid $50 \times 50$ |
|--------------------------|-------------------|-------------------|
| Consequent               | 5594.49           | 55927.15          |
| Algorithm 1              | 420.48            | 1956.72           |
| Algorithm 2              | 150.51            | 1140.28           |
| Algorithm 3              | 26.08             | 158.31            |

In algorithm 1 the error calculation only in serial mode was used. Solution of initializing the source data representing the grid in the previous and current time step is executed in single-threaded mode, and the calculation of the potential at the grid points and the accuracy of the solution in parallel mode. In algorithm 2, each block of parallel threads has been synchronized and calculates the accuracy of their nodes and obtaining the total value of the accuracy is performed in single-threaded mode. In algorithm 3 shared memory was used to calculate the precision of the solution. This implementation of the algorithm appeared to be the most time-efficient calculation and was later used in the calculations of the model. A distinctive feature of the use of shared memory is that it is addressed in same way
for all tasks within a single block, so it can be used to exchange data between the threads of that block. This memory has a high access speed which helps to maximize the number of operations performed in parallel mode, i.e. before the synchronization process, and to minimize the number of cycles within the thread, thereby to reduce the computational complexity of thread.

4. Results and discussion
The adequacy of the constructed model is confirmed by a number of experimental studies of various CNS production by the device of electric arc synthesis with AISU [10].

The research by the model to determine the effect of the coherence coefficient $\chi$ on the results of numerical calculation was performed for the two main modes of synthesis: obtaining the cathode deposit with the maximum output of multi-walled nanotubes ("Nanotubes", the power of the arc current is 150 A) and the mode with maximum input range of fullerenes $C_{60} \div C_{70}$ deposited on the chamber walls ("Fullerenes", current 350 A). The rest calculation parameters: interelectrode distance of 1 mm, the diameter of graphite electrodes of 12 mm, the voltage between the electrodes of 25 V, the pressure of the buffer gas (He) in the cell synthesis chamber of 400 Torr.

In figures 4a, 4b the influence of coefficient $\chi$ on the average speed change of carbon macro particles movement in plasma of the interelectrode space without considering collisions.

The Analysis of calculation results shows that the size of the macro particles in different modes of synthesis for $\chi = 1\div10$ affect its acceleration by electromagnetic field in the plasma.

The influence of the cohesion coefficient on the total number of collisions of particles of carbon in the plasma for the considered modes of synthesis is shown in figures 5a, 5b. The calculation time is 360 ns, with a time step of 10 ns.

The number of interactions of carbon particles depends on the size of macro particles. When increasing the cohesion coefficient the number of collisions increases respectively.

In different modes of electric arc synthesis of CNS the interaction of carbon particles is different. This is because the speed of carbon ions and their interaction energy depends on the magnitude of the current in the discharge. With the increase in the current of 150 A to 350 A the plasma temperature, magnetic field intensity increases, the average velocity of the particles without regard to collisions increases as well.
Figure 5. The change in the total number of collisions of carbon particles in the plasma along the length of the inter-electrode distance for various cohesion coefficients: (a) -mode «Nanotubes», (b) - mode «Buckyballs»

The presence of peaks in collisions in figures 5a, 5b can be explained by the fact that in the initial moment of time the particles are generated in the model at random with regard to the profile of the evaporation of the anode on the basis of the Maxwell distribution. At the initial stage there is the largest number of particles with a relatively low speed. A large number of particles gives a large number of collisions, some of which result in the formation of linkages and agglomeration of particles. The number of particles is reduced, decreasing their concentration, which leads to a decrease in the total number of collisions and collisions with formation of bonds. Further, the larger particles are accelerated by electromagnetic field that leads to an increase in the total number of collisions in the cathode region, and, consequently, the number of generated links.

The presence of intermediate extrema in the «Buckyballs» mode is due to a more rapid increase in the speed of the particles, which formerly leads to an increase in collisions, then the number of particles decreases and the number of collisions reduces. This results in intermediate maximum point on the plot.

The increase of mass of deposit sediment on the cathode containing carbon tubes, in time for different of cohesion in comparison with experimental values is shown in figure 6.

Figure 6. The change of mass deposit sediment on the cathode in time (mode «Nanotubes»)
The analysis of the numerical calculation results presented in figure 6 considering the received data for the other modes of synthesis has led to the conclusion that to correspond the proposed model to the physical process of CNS coherence coefficient synthesis of particles in the large particle method for different conditions of synthesis must be in the range $\chi = 3 ÷ 5$.

5. Conclusion

In this article we propose numerical solution of complex resource-consuming tasks of modeling of CNS synthesis based on the method of large particles which enables one to reduce the volume and the total CPU time computation with the given accuracy. This solutions based on the analysis of possible algorithms of calculation and the use of technology of parallel computing and GPGPU with application Nvidia CUDA technology are offered. A method which allows to weigh a charge and current at the nodes of the computational grid required to calculate the new coordinates of the macro particles in each time step is also offered. Dependences for definition of radius, coordinates of the centers of masses, charges, velocities and directions of motion of large particles of a certain type in the cells are given. Based on numerical studies by the model the range of the cohesion coefficient between particles ($\chi = 3 ÷ 5$) is made, which allows to describe adequately the real physical process for the synthesis of CNS.

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