Method of modeling the heat exchange process in the synthesis of carbon nanostructures in arc discharge plasma

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Abstract. The method for calculating the temperature field during the synthesis of carbon nanostructures by plasma of electric arc discharge is proposed. The calculation scheme of heat exchange process is given. An algorithm for constructing a discrete model of the numerical solution of the heat transfer problem by the finite-element method in the environment of multiphysical modeling COMSOL Multiphysics is considered. The research of influence of parameters of different types of finite element grids on the convergence rate, calculations time and simulation accuracy is carried out. The rational parameters of the discretization of the computational domain of the considered system are determined. The results of correspondence of the constructed model of heat exchange process to the physical process are presented.

1. Introduction

Carbon nanostructures (CNS) with unique physicochemical properties are of significant interest for various branches of modern industry [1]. However, their widespread use is constrained by the high cost and low productivity of existing synthesis methods, which is due to the lack of study of the features of the processes of formation of the final product.

Different variations of plasma sublimation of graphite raw materials with subsequent deposition of the synthesized product on the cooled surface is one of the directions which allows to obtain high-quality nanostructured carbon material in sufficiently large volumes. The most famous variety of such technologies is the electric arc synthesis of CNS in an inert gas medium [2]. This method is different by a high passing speed, a small synthesis zone and the ability of obtaining various carbon nanostructures (fullerenes, nanotubes, nanofibers).

The processes occurring in the electric arc synthesis of CNS can be attributed to high-temperature technological processes. Plasma temperature (4500 - 5500 K), heating and cooling of graphite electrodes have a direct impact on the quality of the final product [3]. Therefore, the aim of this work is to develop a methodic of modeling the heat transfer process in the anode-plasma-cathode system in the electric arc synthesis of CNS, which allows to take into account the influence of temperature fields on the evaporation of the anode and the formation of final carbon fractions in sediment deposition and on the walls of the operating chamber. The proposed mathematical model of heat transfer is distinguished by taking into account the total heat flux power in the heat equation of the buffer medium and the mobile boundaries of the considered system.
2. Theoretical analysis

When constructing a model of the heat exchange process of the considered system, a number of the following assumptions are accepted: the thermophysical parameters of the system components are constant; the plasma of the interelectrode space is considered to be optically thin and the interaction of radiation with the plasma is not considered due to a slight effect on the process [4]; the mechanism of heat transfer in the anode, cathode, and sediment – is convective heat conductivity, in the buffer gas – thermal conductivity, in low-temperature plasma – convective heat conductivity with a volumetric heat source; electrodes in the synthesis process retain uniformity and the constancy of the density. Helium is considered as a buffer medium.

In the course synthesis, there is a change in the configuration of the working zone caused by the destruction of the initial graphite raw material and the growth of sediment, which must be taken into account in the model. Taking into account of the moving boundaries of the electrodes for the process of electric arc synthesis of CNS in a helium medium, the design scheme of heat-exchange will be of the form shown in figure 1.

![Design scheme of process of heat transfer](image)

**Figure 1.** Design scheme of process of heat transfer: $T_{\text{amb}}$, $T_{\text{cat}}$, $T_{\text{sed}}$, $T_{\text{pl}}$, $T_{\text{evap}}$, $T_{\text{amb}}$ – temperatures, respectively, of the anode, cathode, sediment, plasma, evaporation zone, and ambient; $l_{\text{cat}}$, $l_{\text{sed}}$, $l_{\text{pl}}$, $l_{\text{evap}}$, $l_{\text{an}}$ – distance from the beginning of coordinate to the right border of the cathode, sediment, plasma, evaporation, anode, respectively; $R$ – radius of the electrodes; $R_{\text{hel}}$ – helium border.

A mathematical model of the heat transfer process, taking into account the accept assumptions in the cylindrical coordinate system has the form:
where \( k_{an} \), \( k_{cat} \), \( k_{sed} \), \( k_{pl} \) – the thermal conductivity of the anode, the cathode, the sediment and plasma, 
\( \rho_{hel} \), \( \rho_{an} \), \( \rho_{cat} \), \( \rho_{sed} \), \( \rho_{pl} \) – density of helium, anode, cathode, sediment and plasma, \( C_{hel} \), \( C_{an} \), \( C_{cat} \), \( C_{sed} \), \( C_{pl} \) – specific heat of helium, anode, cathode, sediment and plasma; \( u \) – the velocity field; \( V_{hel} \), \( V_{pl} \) – is the volume of plasma and helium in the synthesis chamber; \( Q \) – the power of the heat source, \( Q_{\Sigma} \) – the power of the heat flux in helium.

The total capacity of the heat flow in helium:

\[
Q_{\Sigma} = Q_{cat} + Q_{catb} + Q_{sedb} + Q_{plb} + Q_{anh} + Q_{ant} - Q_{loss},
\]

The boundary and initial conditions for the elements of the developed model have the form:

\[
\rho \frac{\partial u}{\partial t} = \nabla \cdot (\mu \nabla u - \lambda \nabla \cdot u) + \nabla T + \rho \nabla \cdot \mathbf{f},
\]

where \( \alpha_{ht} \) – coefficient of heat transfer to the environment; \( Q \) – power of the loss; \( S_{cham} \) – surface area of the operating chamber.

The boundary and initial conditions for the elements of the developed model have the form:
The functions obtained by approximating of experimental data are used as expressions which describes the moving boundaries of electrodes. For the boundary of the evaporation anode - plasma:

\[ l_{\text{evap}}(t) = l_{\text{init}}^{\text{evap}} + (a_1 \cdot T^2 + a_2 \cdot T + a_3) \cdot t, \] (4)

where \(a_1, a_2, a_3\) – proportionality coefficients, are determined on the basis of experimental data. For the boundary plasma - sediment on the cathode:

\[ l_{\text{sed}}(t) = l_{\text{init}}^{\text{sed}} + \frac{\rho_{\text{sed}}}{\rho_{\text{an}}} \cdot u_{\text{evap}} \cdot t. \] (5)

At the initial moment \(t = 0\):

\[ T_{\text{cat}}(0) = T_{\text{sed}}(0) = T_{\text{pl}}(0) = T_{\text{an}}(0) = T_{\text{amb}} = T_{\text{init}}^{\text{amb}} = \text{const.} \] (6)

The constructed mathematical model of heat-exchange (1-3) for the system under consideration differs by taking into account the total heat flux power in the equation of thermal conductivity of the buffer medium and the mobile boundaries of the anode-plasma-cathode system.

The system of non-stationary differential equations (1-2) describing the heat-exchange process in the system under consideration, taking into account the boundary conditions (3) and the variable boundaries of the system (5-6), is a complex mathematical problem, the finding an accurate analytical solution of which is extremely difficult. Therefore, to obtain a solution, the finite-element method was used [5].

The use of the finite-element method involves the partition of the region in which the solution of differential equations is sought into a number of subfields (finite elements), in each of which an unknown quantity (moving and temperature of body points) has a simple analytical expression. Outside its element, this function is zero. Finite elements have common nodal points where they are related between themselves. The function values in the nodes are the solution to the task. The number of equations at use of the finite-element method is equal to the number of unknown values in the nodes on which the solution of the original system is sought, and is directly proportional to the number of elements. Each of the elements is associated with a limited number of neighbors, therefore so the system of linear algebraic equations has a sparse view, and this greatly simplifies its numerical solution.

The algorithm for constructing a discrete model when using the finite-element method of a continuous magnitude is the following:

1. The phase plane is divided into a finite number of nodal points.
2. The value of a continuous magnitude at each nodal point is considered a variable parameter, which must be found.

3. The whole area of calculation of a continuous quantity is divided by a finite number of elements, which have common nodal points and, in sum, approximates the shape of the entire region.

4. The analogue quantity is approximated on each element by a polynomial found on the basis of nodal values. Each finite element is set by form and function. These form and function determine the accuracy of the approximate solution.

To implement the developed numerical scheme for solving the heat transfer problem considered above, was used the environment of multiphysical simulation COMSOL Multiphysics [6]. The use of the Heat Transfer Module in this software environment allows you to perform the necessary numerical calculations based on the developed model, taking into account accepted assumptions and mobile boundaries of the system.

The construction a grid of finite elements is one of the most important steps in the algorithm for calculating the heat transfer model. In the modern COSMOL Multiphysics simulation environment, the thermo exchange problem is solved using an adaptive grid. The different shape of the finite elements also directly affects the convergence rates. Therefore, to obtain a stable numerical solution to the problems of the model (1-5), a study when using three- and four-node elements was carried out. The density of the grid used and the view itself of the final element clearly affect the accuracy of the calculation and the convergence. The calculation accuracy is reduced if the sizes of the neighboring elements near the stress concentrator are differ significantly. Therefore, for the most important and small construction components of the model (areas of plasma, evaporation and sediment), a fine-mesh grid was used.

Contrastive analysis when using different types of grids of finite element for the numerical calculation of heat-exchange of the considered system (figure 1) is presented in table 1.

| Criterion                                      | Grid 1       | Grid 2       | Grid 3       | Grid 4       | Grid 5       | Grid 6       |
|-----------------------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| View of finite element                        | Thre-node    | Thre-node    | Thre-node    | Thre-node    | Four-node    | Four-node    |
| Number of grid nodes                          | 302          | 442          | 815          | 1183         | 1403         | 4704         |
| Number of grid elements                       | 580          | 860          | 1603         | 2320         | 1333         | 4562         |
| Number of grid degrees of freedom             | 2581         | 3862         | 7573         | 9826         | 7209         | 24468        |
| The number of elements of the plasma          | 269          | 368          | 543          | 1076         | 1152         | 3893         |
| The number of elements of the anode           | 44           | 67           | 59           | 176          | 77           | 280          |
| The number of elements of the cathode         | 197          | 303          | 739          | 788          | 69           | 289          |
| The number of elements of the working chamber | 56           | 66           | 224          | 224          | 26           | 86           |
| Calculation time (min.)                       | 6            | 7            | 8            | 14           | 2            | 8            |

3. Results and discussion
The analysis of the results of numerical calculations showed that the data obtained for the grids 2 - 6, characterizing the temperature values at the anode end and at the plasma-anode border, differ slightly. The relative error of discrepancy of the performed numerical calculations for these grids does not exceed 0.012 %. In the figure 2 studies of the convergence rate of solutions for the meshes of the finite elements considered above are presented.
Figure 2. Convergence rate of problem-solving for different grids.

Figure 3. The influence of grid size on calculation time when using the finite-element method.

The best convergence rate of the solving the problem by the finite element method show grids 5 and 6. The analysis of influence of the elements quantity for four-node calculated grid on the total computation time when using the model is shown in figure 3. Based on the analysis of the convergence rate of the solution of the problem under consideration for different grids (figure 2), the influence of the grid size on the calculation time (figure 3), and the accuracy of the simulation results, grid 5 with the number of nodes – 1403 is the best. For the numerical solution of the developed model, it is more rational to use four-node finite elements with a height of 1/5 R and with clotting in the region with the highest temperature gradient (of plasma) to 1/10 R (figure 1).

To verify the conformity of the constructed model to the physical process, a series of experiments was performed on the installation of an electric arc synthesis CNS. The installation is equipped with an automation control system [7], which allows maintaining stable synthesis parameters. The results of comparison of the calculated and experimental data of the time variation of the butt profile of anode and the temperature at a fixed point of the cathode surface are presented in figure 4 and 5.

Figure 4. Changing of the profile of the burnup of the anode: the synthesis parameters: the time $t = 120$ s, the force of the arc current $I = 150$ A, voltage $U = 25$ V, the helium pressure in the camera $P_{He} = 53.3$ kPa.

The analysis showed that the average relative reduced error $\delta$ of the numerical calculation based on the heat-exchange model on the deviation of the anode evaporation profile is $\delta \approx 9\%$ (figure 4), and for the temperature deviation on the cathode surface (figure 5) is $\delta_{an} \approx 5.79\%$, which does not exceed the maximum permissible error value of 12% accepted for this model, allowing to describe the influence of temperature fields on the evaporation of the anode and the formation of the final carbon fractions. This gives the right to talk about the adequacy of the heat-exchange model to the real process.
4. Conclusion

Thus, a method is proposed for mathematical modeling of the heat-exchange process during the electric arc synthesis of CNS, taking into account the total heat flux power in the heat equation of the buffer medium and the mobile boundaries of the system anode – plasma – cathode, which makes it possible to calculate the dynamics of the temperature field of the system taking into account the changing configuration of working zone. The rationally view and size of the grid for numerical calculation of the model under consideration by the finite element method is determined. This makes it possible to study the influence of the technological parameters of synthesis (of the arc current, voltage, etc.) on anode volatilization and the formation of final carbon fractions in the sediment deposition and on the walls of the operating chamber.

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