Applications and synthesis of nanostructured carbon in the food industry

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Abstract. Nanostructurable carbon is of considerable interest for use in the processes of the modern food industry. Equipment for its production, using the method of plasma sublimation of graphite raw materials due to the complexity of the process, due to the large number of parameters affecting the yield and quality of the resulting product. The purpose of this study is to develop a methodology for the design and calculation of plasma fusion conditions, allowing to increase the efficiency and productivity of existing technologies and equipment based on mathematical modeling of processes. This paper presents a kinetic model that allows us to study the formation of various carbon nanostructures in electric arc discharge plasma using a catalyst. The results of numerical and experimental studies of the deposited sludge mass dynamics using Ni catalyst are presented, which confirm the feasibility of using catalysts. The developed mathematical model and its elements can be used to design control systems and installations for plasma synthesis of fullerenes and nanotubes.

1 Introduction

The production of inorganic nanostructured carbon compounds (fullerenes, nanotubes) with unique mechanical, physical and chemical properties is of great interest for use in the modern food industry [1]. Hydrated fullerene C_{60} solution can act as an initiator of diverse reactions and processes, regulating the formation and neutralisation of reactive oxygen species, enabling it to be used in media for growing microorganisms, in media for cultivating and storing cell cultures, creating products with special, highly ordered structural features etc. [2 - 4]. Carbon nanotubes have unique sorption characteristics [5], enabling them to be used for finishing various food liquids from difficult to remove by-products [6].

There are a large number of industrial technologies for the synthesis of carbon nanostructures (CNS), varying in terms of the equipment used, process conditions, yield and quality of the final product, and controllability. All synthesis methods can be divided into processes using sublimation-desublimation of graphite raw materials and pyrolysis of carbon-containing gases [7]. The most widely used method is plasma sublimation of graphite in a buffer medium, which allows the synthesis of various allotropic forms of carbon: C_{52} - C_{90} fullerenes, nanotubes. The end product obtained by this method is characterised by high quality (uniformity, few defects).

The use of certain metals as catalysts can increase the yield of the material [8, 9]. Use of mixed catalysts (Ni/Co(Fe), Ni/Y(Ca,Ce) и Rh/Pt(Pd) et al.) gives even greater yield and efficiency to the synthesis process. This is due to a change in the activation energy of CNS growth, increased carbon-carbon adsorption and the formation of a surface that has more protrusions [10].

The quality of the carbon product obtained in the synthesis process also directly depends on the raw materials used, the set parameters, stability and accuracy of their maintenance in the used technological equipment. Therefore, solving the problem of determining the required synthesis parameters and managing the entire process is an urgent task in terms of development and improvement of equipment [11]. The use of an automated control system makes it possible to improve the quality of fusion control, and thus increase the economic efficiency of the equipment used.

The use of a mathematical model of the object allows for the design and purposeful creation of control systems for such complex processes, defining the necessary synthesis conditions to obtain CNS with the maximum output and quality [12].

The purpose of this work is to develop, based on mathematical modelling of processes in plasma formation of CNS, the calculation of synthesis conditions that would improve the efficiency and productivity of existing technologies and equipment.

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The results of mathematical and computer modelling will make it possible to define rational technological conditions for the catalytic synthesis of CNS and to develop recommendations for the management of this process.

2 Materials and methods

In the most common process scheme for plasma synthesis of CNS (Figure 1), an electric arc is maintained in a buffer medium between graphite electrodes at a density of $1{,}33 \cdot 10^6 \div 3{,}17 \cdot 10^6$ A/m^2 in the interelectrode gap 1 ÷ 4 mm. Graphite electrodes of a specific diameter are mounted vertically or horizontally in the cooled working chamber of the reactor [13].

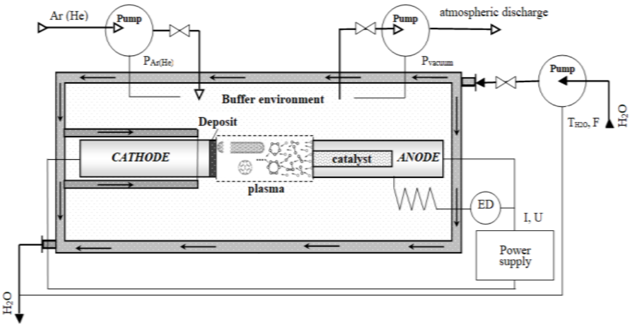

Fig. 1. Reactor plasma fusion CNS.

The yield and structure of the synthesised material is influenced by many different factors: type and pressure of the buffer medium, electrode voltage, current density, plasma temperature, electrode geometry and cooling rate, raw material structure and purity, etc. [14]. At electrode voltage *U* = 25 V and low current density ($j = 1{,}33 \cdot 10^6$ A/m^2) mainly cathode deposit with the highest content of carbon nanotubes is formed, and at high currents ($j = 3{,}17 \cdot 10^6$ A/m^2) soot with the highest content of fullerenes of series is deposited on the chamber walls $C_{60} \div C_{70}$ [15]. The stability of plasma density and current directly determines the formation of homogeneous structures.

The use of a catalyst in the synthesis process also affects the morphology of the product. The quality and diameter of the nanotubes produced is proportional to the size of the catalyst particles used. The use of a catalyst increases the efficiency of carbon feedstock breakdown and promotes the formation and deposition of ordered carbon [16].

Therefore, a study based on mathematical modelling of the effect of different catalysts on the conditions of formation and growth of CNS in plasma is an urgent problem for further improvement of synthesis technologies and industrial equipment.

For mathematical modeling of processes of CNS synthesis in low-temperature plasma, different approaches are used: single-particle approximation, molecular dynamics method, magnetohydrodynamic description, kinetic description, Monte-Carlo method, Schrodinger models. However, the existing body of papers on the kinetics of formation of carbon structures in plasma is characterized by the lack of a system model that allows us to trace the influence of the catalyst on the formation and growth of cluster carbon groups forming bulk structures, taking into account the influence of synthesis parameters and changes in the configuration of the working zone [17, 18].

The method of thermal evaporation of graphite with arc discharge plasma in a buffer gas environment under consideration has the following features: high plasma temperature (4200÷5500 K), the high rate of reactions and phase transformations, the nanosized nature of the product, the small size of the synthesis region, which make it difficult to carry out natural experimental studies. Therefore, numerical investigation of the formation of carbon nanostructures in electric arc discharge plasma is of great interest for understanding the mechanism of the process, determining technological conditions, designing control systems for it and increasing the synthesis efficiency. On the basis of modeling of kinetics of interaction of multicomponent plasma particles in a buffer medium using a catalyst, it is possible to investigate the areas of formation, rates, conditions and mechanisms of formation of the final product in plasma [19, 20].

3. Results

The proposed kinetic model of CNS synthesis by the electric arc method, describing the dynamics of charged particles in plasma with Coulomb interaction, is based on the system of Boltzmann equations written for each type of considered particles of multicomponent plasma and catalyst, augmented by the system of Maxwell equations describing the self-consistent electromagnetic field [21].

$$\frac{\partial f_\alpha}{\partial t} + \vec{\vartheta}\frac{\partial f_\alpha}{\partial \vec{r}} - \frac{q_\alpha}{m_\alpha}\left(\vec{E} + \frac{1}{c}[\vec{\vartheta}, \vec{B}]\right)\frac{\partial f_\alpha}{\partial \vec{\vartheta}} = \\ = \sum_{k=e,c,h,s} \iint_V (f'_\alpha f'_k - f_\alpha f_k) / \vec{\vartheta} - \vec{\vartheta}' / d\sigma\sigma\, \vec{\vartheta}' \quad \alpha = e,c,h,s \tag{1}$$

$$\begin{aligned} rot\,\vec{H} &= \frac{4\pi\vec{j}}{C} + \frac{1}{C}\frac{\partial \vec{D}}{\partial t}, \\ rot\,\vec{E} &= -\frac{1}{C}\frac{\partial \vec{B}}{\partial t}, \\ div\,\vec{B} &= 0, \\ div\,\vec{D} &= 4\pi\rho, \end{aligned} \tag{2}$$

Accepted designations: f_α - plasma component distribution functions (*e* - electron, *c* - carbon ion, *h* - buffer gas ion, *s* - catalyst ion); $\vec{E}, \vec{H}$ - electric and magnetic field strength; $\vec{D}, \vec{B}$ - electric and magnetic induction; q_α, m_α - charge and mass of the particle; ρ - charge density; $\vec{j}$ - current density; *C* - speed of light; $\vec{\vartheta}$ - particle velocity field; $\vec{r}$ - particle coordinates; *V* – volume of the calculated plasma area.

Initial conditions at $t = 0$:

$$f_\alpha(\vec{r},\vec{\vartheta},0)=f_\alpha^0,\quad \alpha=e,c,h,s.$$
$$E(\vec{r},0)=E^0, B(\vec{r},0)=B^0. \tag{3}$$

Boundary conditions at the anode (A):

$$\vec{r}\in\big|_A:\ f_e(\vec{r},\vec{\vartheta},t)\Big|_{\vec{r}\in|_A}=f_e^0, \tag{4}$$
$$f_c(\vec{r},\vec{\vartheta},t)\Big|_{\vec{r}\in|_A}=f_c^0,$$
$$f_h(\vec{r},\vec{\vartheta},t)\Big|_{\vec{r}\in|_A}=f_h^0,$$
$$f_h(\vec{r},\vec{\vartheta},t)\Big|_{\vec{r}\in|_A}=f_s^0,$$
$$f_\alpha^0=f_\alpha^{maksv}.$$

The resulting system of nonlinear differential equations (1 - 2) with initial (3) and boundary conditions (4) is a mathematical model that describes, based on the probabilistic approach, the motion and interaction of particles in a multicomponent plasma and allows one to predict a variety of plasma processes at given synthesis parameters. The solution to this system of equations determines the densities of the particle distribution functions in the plasma – f_e, f_c, f_h, f_s.

Plasma is seen as a collection of a large number of collectively interacting particles. Direct calculation of even the trajectories of particles using the laws of mechanics is not possible, since the real number of particles in the plasma is enormous. Therefore, to obtain a numerical solution of the problem in question, the method of large particles was used, which allows to significantly reduce the volume of calculations and reduce the requirements for computational resources [22].

The structural diagram of the interconnection of the processes considered in plasma synthesis of CNS is shown in the Figure 2.

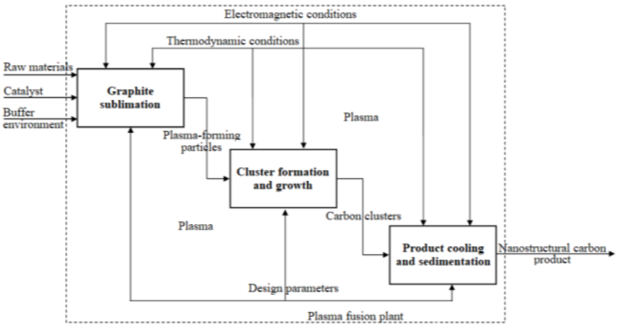

Fig. 2. Interconnection of synthesis processes CNS.

The use of a catalyst in the proposed model radically changes the picture of motion and interaction of particles in plasma in comparison with non-catalytic consideration of processes. The number of particles and interactions in the interelectrode space is increased, the requirements to computational resources and methods of computational experiment are increased.

The developed model describes motions and interactions of charged particles in a low-temperature plasma, taking into account pair elastic and inelastic collisions, which allows to calculate energy conditions and zones of probable formation of various carbon cluster groups in plasma forming finite CNS, as well as growth of deposited sludge and carbon black in the working chamber.

To confirm the developed model to the physical process, experimental studies were conducted using Ni as a catalyst, the results of which are presented in Figure 3.

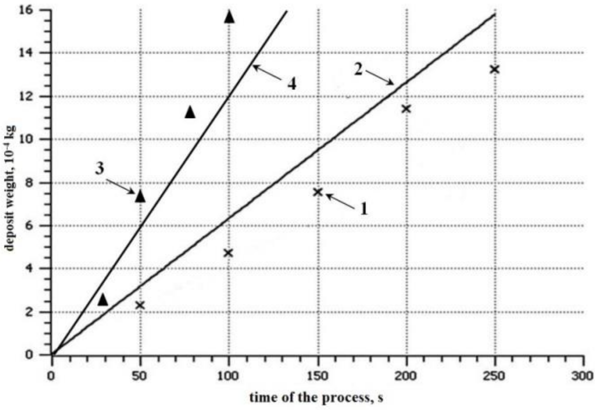

Fig. 3. Dynamics of deposit weight change: without catalyst: 1 – experimental data; 2 – modelled with catalyst (Ni): 3 – experimental data; 4 – modelled.

The analysis showed that the relative reduced error between the experimental and numerical calculations of deposit sludge growth mass using the catalyst does not exceed 21% respectively, which allows us to say that the developed model corresponds to the real process.

One of the variable parameters is the size of the area occupied by the catalyst, as well as the type and structure of the catalyst.

Figure 4 shows the distribution of total number of paired collisions of carbon ions in plasma along the length of interelectrode space with and without catalyst. Analysis of the results showed that the presence of a catalyst increases the total number of particle interactions, which in turn has the greatest influence on the formation and growth of cluster groups forming bulk CNS.

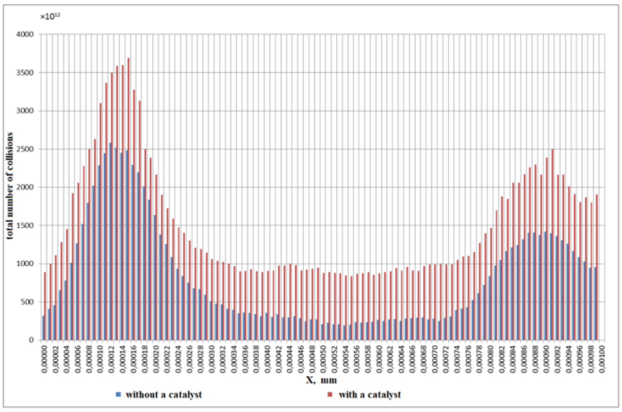

Fig. 4. Total number of paired interactions of carbon ions in the plasma (with a catalyst and without).

4 Conclusion

Thus, research in this area is quite promising and possible to implement for the design and improvement of modern equipment and control systems for plasma processes for obtaining a nanostructured carbon product, which is of interest both in the food industry and in many other areas.

The application of the proposed mathematical model of a complex control object allows for purposeful creation and variation of control methods for complex fast-flowing processes, determination of necessary synthesis conditions for producing various types of carbon nanostructures and their derivatives, which will significantly increase efficiency and productivity of existing synthesis technologies and equipment.

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