The mathematical model for synthesis process management of the carbon nanostructures

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Abstract. In this article, key difficulties of management process for carbon nanostructure synthesis are described. Tasks of optimum control of the carbon nanostructure synthesis process and management in case of emergency situations are formulated. The mathematical model of carbon nanostructure synthesis is offered. The equations for calculation of quantitative, qualitative indexes, indicators of safety and operability of engineering procedure are provided. The necessity of mathematical model use for carbon nanostructure synthesis is caused by improvement of the quality, the quantity, a decrease in the cost value of carbon nanostructures and an increase in safety of the engineering procedure of their obtaining. Testing and approbation of the mathematical model for carbon nanostructure synthesis are executed on a fullerene industrial production line. Suitability of the mathematical model of carbon nanostructure synthesis for production control in the mode of optimum control and management in case of emergency situations is confirmed. The obtained solution is recommended for implementation on the enterprises of a similar purpose.

1. Introduction
At the end of the 20th century, on the bases of the innovative centers, scientific research institutes, there was determined uniqueness of physical and chemical properties of the carbon nanostructures, such as fullerenes, nanotubes allowing the creation of new types of products with the improved properties. Developers of the ultraprecise military radio equipment are interested in C₆₀ fullerenes with purity >99.9%. Lubricating oil and lubricant production companies use the carbon nanostructures having antifriction properties. Consumers of carbon nanomaterials are producers of medicinal antibacterial and anticarcinogenic means. Fullerene, having the disinfecting properties, acts as a very perspective modifying additive for the sorbent furnace charge which is capable of competing with the silver applied nowadays [1, 2].

The numerous researches described in the works of Krechmer [3], Zuev V.V., Charykov N.A. [4], Yelets A.V. [5], Churilov G.N. [6], Sysun V.I. [7], etc., have proved that it is most productive to receive fullerene soot in plasma of an electric arc, based on burning graphite electrodes in the environment of helium of low pressure.

The technological scheme of receiving carbon nanostructures in the plasma of the electric arc is provided in figure 1.

Designations accepted in figure 1 are the following: E – dc power; CW – Wilson's camera; CC – a cathode cover; M – the step engine; P – the pump; He – a cylinder with inert gas; SC – a soot
container; F – a filter; \( \nu_a \) – an anode feed rate in the camera of burning, m/s; \( L_e \) – an interelectrode distance, m; \( U_a \) – an electric arc voltage, V; \( I_a \) – electric arc current, A; \( T_a \) – electric arc temperature, K; \( G_c \) – consumption of coolant, m\(^3\)/s; \( P_c \) – pressure of coolant, Pa; \( T^e_c \) – reference temperature of coolant, K; \( T_f \) – final temperature of coolant, K; \( T_w \) – reactor wall temperature, K; \( G_{gw} \) – consumption of inert gas via the Wilson’s camera, m\(^3\)/s; \( G_{gc} \) – consumption of inert gas via the Reactor, m\(^3\)/s; \( G_g \) – consumption of inert gas via the gas blower, m\(^3\)/s; \( P_g \) – pressure of inert gas, Pa.

Figure 1. The technological scheme of synthesis of carbon nanostructures in the plasma of an electric arc.

The process of synthesis of carbon nanostructures in the plasma of an electric arc takes place with a low pressure of inert gas equal to \((10-20) \times 10^3\) Pa and a high temperature of \((3,8-4,2) \times 10^3\) K in the field of production of carbon clusters. Besides, this process is characterized by the increased risk of loss of highly cost raw materials – graphite of high degree of purity and helium for ionization of a working environment of the reactor. Any wrong action from the side of the managerial personnel can entail development of an emergency and a breakdown of the functioning equipment.

Difficult interactions between plasma elements – ionization, recombination, chemical reactions, mechanical interactions – are characteristic of the process of synthesis of carbon nanostructures [7]. Plasma is thermodynamically unstable. The arc can be broken or transferred to the reactor case owing to the installation of the wrong operating mode that attracts a number of emergency situations – a break of a graphite electrode, burn of the reactor of the electric arc, depressurization of the working camera etc. As a result of combustion of a graphite electrode in an electric arc in the atmosphere of helium, the fullerene soot containing fullerenes, mainly \( C_{60} \) and \( C_{70} \), is formed.

The increase in safety of the course of the process of synthesis of carbon nanostructures and the reduction in the cost of target products prove the need for development of the mathematical model and creation on its basis the automated workplace of the managerial factory personnel of a production line of carbon compounds synthesis. The use of the offered mathematical model of synthesis of carbon nanostructures promotes an increase in the degree of readiness of the managerial factory personnel for the optimum conduction of the chemical engineering procedure and elimination of possible emergency situations on the production line.

2. Tasks of management
The problem definition of optimum control of the synthesis process of carbon nanostructures is the following. For the set vector of input parameters \( X \), by varying control actions \( U \) in procedural ranges
\[
L_e < L_{ec}, \quad U_{a}^{\min} \leq U_{a} \leq U_{a}^{\max}, \quad G_{c}^{\min} \leq G_{c} \leq G_{c}^{\max}, \quad G_{g}^{\min} \leq G_{g} \leq G_{g}^{\max}, \quad \tau_{\min} \leq \tau \leq \tau_{\max},
\]
let us find such vector of optimum control actions \( U_{opt} = \{ L_e, U_{a}, G_{c}, G_{g}, \tau \} \) which provides the maximum content of a target product of \( C_n \) in fullerene soot on condition of accomplishment of the following criteria restrictions: \( m_{C_n} \geq m; \quad T_{a} \leq T_{w}^{\max}; \quad T_{c} < T_{c}^{b}; \quad P_{g}^{\min} \leq P_{g} \leq P_{g}^{\max} \). Here, \( L_{ec} \) – the critical interelectrode distance corresponding to a gap of an electric arc, m; \( U_{a}^{\min}, U_{a}^{\max} \) – minimum and maximum voltages on electrodes, V; \( G_{c} \) – consumption of coolant, \( m^3/s; \quad G_{g}^{\min}, G_{g}^{\max} \) – minimum and maximum consumption of coolant, \( m^3/s; \quad P_{g}^{\min}, P_{g}^{\max} \) – minimum and maximum pressure of inert gas in the reactor, Pa.

The managerial factory personnel in case of an emergency situation works relying on messages from the expert system. The expert system uses the knowledge base with the description of emergency situations and procedural restrictions on safety and operability indicators of the equipment.

Problem definition of the management of the carbon nanostructure synthesis process in case of emergency situations is the following: when the input parameters of X are set taking into account the messages, received from the expert system on emergence of an emergency situation, it is necessary to correct the operating actions of U for its fastest elimination.

3. The mathematical model of the carbon nanostructures process

For calculation of criteria indicators of Y, depending on the operating influences of U, characteristics of reactor K, properties of raw materials S, the mathematical model of synthesis of carbon nanostructures is offered: \( Y = F (X, U, A) \), where \( A = \{ a_1, a_2, a_3, b_1, b_2, b_3, c_1, c_2, d_1, d_2, d_3, e_1, e_2, f_1, f_2, f_3, g_1, g_2, g_3, h_1, h_2, h_3, i_1, i_2, i_3 \} \) – a vector of empirical coefficients of the model, where \( e \) – a degree of blackness of the radiating body; \( a_1 \) – a heat emission coefficient from inert gas to a wall of the reactor, \( W/(m^2\cdot K) \); \( a_2 \) – a heat emission coefficient from a reactor wall to coolant, \( W/(m^2\cdot K) \).

Works [3, 4, 5, 6, 7] in the field of synthesis and carbon nanostructure research were analyzed during the mathematical model synthesis. The works in the field of mathematical model creation of carbon nanostructure synthesis were also analyzed [8].

In Krechmer’s reactor of fullerene soot, the mass-exchanged processes are proceeding as a result of formation of fullerene soot from the graphite anode evaporated by the electric arc, heat-exchange processes proceed owing to transfer of warmth from the burning arc to inert gas, from inert gas to a reactor wall, from a reactor wall to coolant.

In case of development of the mathematical model, the following assumptions are accepted:
- resistance of the graphite anode does not depend on the arc temperature since when heating the anode from 3800 K to 5000 K its resistance changes slightly;
- the core is made of graphite, which is uniform in physical and chemical parameters, since requirements to the purity of graphite for production of cores are \( r_a = 99,9999\% \);
- the core has the cylinder form with the \( L_a \) length, as ultra precise lathe machines allowing one to make details of the correct cylindrical form are used for production of the cores;
- losses of warmth through the external wall of the reactor to the environment are not considered since the working temperature of the external wall of the reactor is 290-340 K, and the temperature in the reactor hall lies in the range of 300-305 K;
- the thermal processes happening in Krechmer’s reactor are stationary as the time of full warming up of the reactor after arc ignition, not exceeding 2 min, is scornfully not enough in comparison with the time of fullerene soot synthesis \( \tau > 4 \) h [9].
The offered mathematical model of synthesis of carbon nanostructures includes the following equations:

- the equation for calculation of percentage of fullerene depending on the temperature of the arc and the pressure of inert gas is:

\[
F_{C_n} = b_0 + \sum_{i=1}^{5} b_i \cdot T_a^i + b_6 \cdot \ln(P_g),
\]

where

\[
T_a = a_0 + \sum_{i=1}^{3} a_i \cdot U_a^i + \sum_{i=1}^{3} c_i \cdot Z^{i} + Z \cdot U_a \cdot (\chi_1 + \chi_2 \cdot Z + \chi_3 \cdot U_a),
\]

\[
I_a = p_1 \cdot e^{p_2 \cdot L_e} \cdot \left( \frac{U_a}{R_a} \right)^{p_3};
\]

- the equation for calculation of mass of \( C_n \) fullerene depending on the lump of the synthesized soot and contents of \( C_n \) fullerene in it is:

\[
m_{C_n} = m_s \cdot \frac{F_{C_n}}{100},
\]

where

\[
m_s = \nu_d \cdot \tau - m_{gr},
\]

\[
\nu_d = d_1 \cdot e^{d_2 \cdot I_a};
\]

- the equations of thermal balance describing the heat exchange between the electric arc, inert gas and coolant and temperatures of the wall of reactor \( T_w \), necessary for calculation, and the final temperature of coolant \( T_c \) are:

\[
\rho_g \cdot G_g \cdot c_g \cdot T_g^3 - \rho_g \cdot G_g \cdot c_g \cdot T_g^3 + e \cdot \sigma_0 \cdot S_a \cdot T_a^4 - \alpha_g \cdot S_w \cdot (T_g - T_w) = 0,
\]

\[
\alpha_g \cdot S_w \cdot (T_g - T_c) - \alpha_c \cdot S_w \cdot (T_w - T_c) = 0,
\]

\[
\rho_c \cdot G_c \cdot c_c \cdot T_c^3 - \rho_c \cdot G_c \cdot c_c \cdot T_c^3 + \alpha_c \cdot S_w \cdot (T_w - T_c) = 0.
\]

In equations (1)-(10), the following designations are used: \( Z=\ln(I_a) \); \( R_a=\rho_a \cdot L_a \); \( D_a \) – resistive resistance of the anode, Ohm; \( \rho_a \) – unit resistance of the anode, Ohm/m; \( m_a \) – mass of fullerene soot during burning of the arc, kg; \( \tau \) – speed of burning of the anode, kg/s; \( m_e=\sigma_0(m_a) \) – mass of gaseous impurity, kg; \( m_0=f_0(L_a, D_a, \rho_a) \) – mass of the anode, kg; \( \rho_g \) – density of the anode; \( \rho_f=\rho_0 \); \( \rho_g \) – density of inert gas, kg/m³; \( c_g \) – thermal capacity of inert gas, \( J \cdot kg^{-1} \cdot K^{-1} \); \( \chi_1 \) – constant Stephan–Boltzmann, W/(m²·K⁴); \( S_a \) – surface area of the radiating body, m²; \( S_w \) – area of a heat-transmitting surface of a wall of the reactor, m²; \( \rho_c \) – density of coolant, kg/m³; \( c_c \) – thermal capacity of coolant, \( J \cdot kg^{-1} \cdot K^{-1} \); \( T_g^i \) – initial temperature of inert gas, K; \( T_c \) – final temperature of inert gas, K.

Equation (1) is received by handling the results of the experiments consisting in synthesis of fullerene soot in case of an arc temperature variation (within 1500-6000 K), pressure of inert gas within (13-20)·10³ Pa and the subsequent chromatographic analysis of soot. The pressure of inert gas is determined depending on its expense: \( P_f=\rho_f(f_0) \).

With the use of the industrial pyrometer, taking temperature of the lightest part of the burning arc in the field of forming of carbon clusters in fullerenes, and a variation of \( U_a \) and \( I_a \) experimental data...
which handling allowed one to construct the equation, are obtained (2). In case of arc gap \( I_a = 0 \), soot is not synthesized. Therefore, \( T_a \) in equation (2) is not calculated.

Equations (1)-(10) describe the processes proceeding in Krechmer’s reactor and determine dependence of criteria indicators of processes of synthesis of fullerenes \( Y \) on characteristics of equipment \( K \), raw materials \( S \) and corrective actions of \( U \).

Assessment of adequacy of the mathematical model is executed for graphite of high degree of purity, helium as inert gas and water as coolant.

The results of calculation of characteristics of the process of the mathematical model and their comparison with experimental values in a graphical view are reflected in figures 2-7.

The volt-ampere characteristic (figure 2) exerts impact on the temperature of the arc. In the dependence of \( F_{C_60}(T_a) \) (figure 5), there is maximum \( F_{C_60} \) corresponding to the optimum temperature of arc \( T_{a_{\text{opt}}} \), but \( F_{C_60} \) asymptotically decreases in case of too high temperature of an arc, which means high content impurity emergence in soot.

When \( T_a \) increases (figure 7), more warmth, transferred to inert gas, a reactor wall and coolant, is formed. Therefore, \( T_a \) should be established during the reactor control, at which the requirements to safety and operability of equipment \( B \) will be fulfilled.

4. The managerial personnel interface

The program interface of the managerial factory personnel of the industrial line of synthesis of carbon nanostructures includes a dynamic symbolic circuit of the process, monitoring indicators of safety and
operability of Q and qualitative indexes of B during the course of the chemical engineering procedure in real time.

The intellectual adviser based on the current Y, X, U, Q parameters, values and speeds of change of characteristics of the process draws a conclusion about a current status of the process and development of emergency situations. Thus, it creates recommendations for the managerial factory personnel on management [10].

5. Conclusion
Testing of the mathematical model of synthesis of carbon nanostructures is executed by the example of a production line of the entity of Ltd "Innovation of Leningrad Institutes and Enterprises" (Ltd ILIP, St. Petersburg) [9]. Testing and confirmation of mathematical model adequacy testifies to its accuracy and applicability for the automated workplace of the managerial factory personnel. The application of the carbon nanostructure synthesis mathematical model promotes an increase in the degree of readiness of the managerial factory personnel for optimum and safe conduction of the process. As a result, material costs of recovery of the process and risks of origin and development of emergency situations decrease. The cost value of target products decreases and business competitiveness increases [10].

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