Modelling of the plasma parameters of an arc discharge with sputtered composite metal-graphite anode

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Abstract. A global integral model of an arc discharge in helium with sputtered composite metal-graphite anode is presented. The arcing time was measured experimentally for different elements and mass fractions of the metal additions to the graphite anode. The obtained calculated results for pure graphite anode show a good agreement with the experimental and calculated data of other authors. In particular, a good correspondence between the absolute values of electron density and temperature, the discharge voltage and the anode ablation rate as a function of the discharge current was shown. The obtained in the work experimental and calculated data have qualitative agreement, i.e. the anode erosion velocity increases with the addition of Zr, and decreases with the addition of Al.

1. Introduction
Arc discharges are usually used for the synthesis of different nano-materials [1,2]. In particular, fullerenes were discovered in the arc discharge by Kratschmer, in 1990 [3], and carbon nanotubes (CNT) were first discovered with the deposition of carbon in the arc discharge by Iijima in 1991 [4]. There are a lot of works devoted to the modeling of the arc discharges for the synthesis of carbon nano-materials (see review [5]). Models with cathode sputtering [6] or models for discharge gap plasma [7] were developed. The experimental efforts in anodic arc discharges were directed toward studying mechanisms associated with the anode sputtering [8], current-voltage characteristics of the discharges [9], and deposition of the material at the cathode [10]. It was shown that anode erosion rate increases with decreasing anode radius, current-voltage characteristics are V-shaped, and the radius of the deposited material at the cathode increases with the increase of the discharge current.

Several one-dimensional models of an arc discharge with evaporating graphite anode were presented e.g. in [11-13]. The thermodynamics of the formation of droplets of a carbon melt in a metallic catalyst was considered in [14]. Recently, a self-consistent integral model of an arc discharge with a sputtered anode was presented in [15]. The model takes into account the relationship between discharge plasma parameters and electrodes, the continuity of current at the electrodes, the thermal regime of the electrodes, and the anode erosion. Two-dimensional model of an anodic arc discharge with the ablation of composite anode materials consisting of carbon and metal particles was presented in [16]. Based on the above-mentioned arc discharge models, the following numerical model of the arc discharge was developed to describe the main processes occurring in the synthesis of composite nano-materials.
2. Model
The stationary arc burning mode with the graphite cathode of radius \( R_c = 10 \text{ mm} \) and the graphite anode of radius \( R_a = 3.5 \text{ mm} \) is considered. A concentric core with radius \( R_a = 2.25 \text{ mm} \) is drilled out in the anode (see Figure 1a). The core is filled with the mixture of the graphite powder and catalytic metal powder (Al, Zn, etc.). During the burning mode, the anode material is constantly evaporated due to excessive heating, which is determined by the surface temperature of the anode \( T_a \). In turn, the surface temperature of the anode is related to the saturated pressure of the ablated particles from the anode and is determined by the energy flux from the discharge gap.

\[
J_{\text{gap}} = Q_e + Q_a + Q_{\text{gapi}} + Q_{\text{gap,n}} + Q_{\text{gap,rad}}.
\] 

(1)

For the inter-electrode gap, the following energy balance equation was considered [15,16]:

During the arcing, the ablation of the anode material occurs, and the length of the anode decreases from \( L_a = 65 \text{ mm} \) to 30 mm. The anode is mechanically moved towards the cathode, so that the distance between the electrodes \( L_{\text{gap}} = 1-15 \text{ mm} \), and, hence, all other discharge parameters, remain constant. Experimental observations show that erosion of the cathode does not occur in the process of discharge burning, and a slight redeposition of the anode material onto the cathode may take place. The evaporated from the anode surface flux of carbon and metal particles propagates into the discharge gap and interact with the buffer gas (helium), whose pressure is kept constant \( p_{\text{He}} = 24 \text{ Torr} \). During the discharge arcing, the discharge voltage and the discharge current are specially maintained to be constants, \( U_d = 22 \text{ V}, I_d = 100 \text{ A} \). The radius of the discharge plasma \( R_{\text{arc}} \) is considered here to be equal to the radius of the anode \( R_{\text{arc}} = R_a \) (see Figure 1).

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\] 

(1)

It was assumed that the Joule heat, \( J_{\text{gap}} = I_d U_d \), released in the discharge gap goes to heating the cathode \( Q_e \), to heating the anode \( Q_a \), to the ionization in the discharge gap \( Q_{\text{gapi}} \), to heating of the neutral particles by the electrons \( Q_{\text{gapp}} = 3(m_e/m_i)(T_e/T_{\text{arc}})n_i\nu_i\sigma\pi R_{\text{arc}}^2 L_{\text{gap}} \) and to the radiation \( Q_{\text{gap,rad}} = 2\pi R_{\text{arc}} L_{\text{gap}} \sigma_{\text{rad}} T_{\text{arc}}^4 \). Here, the total discharge current (arc current) \( I_a \) is equal to the sum of the electron current \( I_e \) and the ion current \( I_i \) at the cathode, \( I_a = I_e + I_i \). \( T_e \) is the electron temperature in the discharge gap, \( n_i \) is the electron density, and \( \nu_i \) is the total collision frequency of electrons with neutral atoms and ions. Ionization of the plasma occurs proportional to the molar fractions of atoms ablated from the composite anode, \( Q_{\text{gapi}} = I_{\text{gapi}}(\xi_{\text{C}} U_{i,\text{C}} + \xi_{\text{M}} U_{i,\text{M}}) \), where \( U_{i,\text{C}} \) and \( U_{i,\text{M}} \) are the ionization potentials of carbon and metal particle of kind \( i = \text{C}, \text{M} \) and \( \xi_{\text{C}} \) and \( \xi_{\text{M}} \) are the molar fractions of carbon and metal. Helium is assumed to be not ionized due to its very high ionization potential. Heavy particles (ions and neutrals) are in equilibrium in bulk plasma and have the same temperatures, \( T_i = T_n = T_{\text{arc}} \). The material ablated from the anode surface having temperature \( T_a \) cools down rapidly expanding into the discharge.
chamber. It is assumed in the paper that heavy particles have the temperature equal to the anode surface temperature, $T_{arc} = T_a$. However, it should be noted that the temperature of the bulk plasma $T_{arc}$ can exceed the cathode $T_c$ and the anode $T_a$ temperatures.

The energy balance at the cathode surface is determined by the heat flux from the discharge gap $Q_c$, brought by the ion flux to the cathode, and the loss of heat by the radiation $Q_{c,rad} = \pi R_c^2 \sigma_{rad} T_c^4$, the thermal electrode conductivity $Q_{c,cond} = \lambda_{c,cond} \pi R_c^2 (T_c - T_0)/L_c$, and the thermal emission of electrons from the cathode $Q_{c,emission} = \pi R_c^2 j_{c,e} \phi_{WC}$ [17]:

$$Q_c = Q_{c,rad} + Q_{c,cond} + Q_{c,emission}. \tag{2}$$

The voltage drop in the cathode layer $U_c$ depends on the work function for carbon $\phi_{WC}$ and the temperature of the cathode surface $T_c$. $T_0$ is the chamber wall temperature ($\approx 300$ K), $L_c$ is length of the cathode electrode (2 cm), $j_{c,i}$ and $j_{c,e}$ are the ion and the electron flux densities at the cathode. The total discharge current at the cathode consists of the ion and the electron components, $I_d = I_{c,i} + I_{c,e} = \pi R_c^2 (j_{c,i} + j_{c,e})$. The electron flux density from the heated cathode is determined by thermal emission:

$$j_{c,e} = AT_c^2 \exp\left(-\frac{e\phi_{WC}}{kT_c}\right), \tag{3}$$

where $A$ is a constant determined by the cathode material. The motion of ions in the cathode layer can be considered to be collisionless, and, consequently, the Bohm criterion for the ion flux density at the cathode can be used:

$$j_{c,i} = 0.64en_c \sqrt{\frac{eT_c}{m_i}}. \tag{4}$$

It should be noted that the parameter $n_c$ (electron density) connects two regions of the solution of the problem (two sub-models), i.e. the cathode layer model and the entire discharge gap model. The discharge current $I_d$ is determined by the voltage drop over the length of the discharge gap and its electric conductivity $\sigma_{gap}$.

It is assumed that the discharge plasma reaches a local thermodynamic equilibrium, and the plasma composition and the ionizing components can be calculated using the Saha equation:

$$\frac{n_{i,l}}{n_{0,l}} = \left(\frac{2\pi m_i kT_c}{\hbar^2}\right)^{3/2} \exp\left(-\frac{U_{i,l}}{kT_c}\right), \tag{5}$$

where $n_{i,l}$ and $n_{0,l}$ are the densities of ions and neutrals of particles of type $l$ ($l = Me, C$), and $\hbar$ is the Planck constant. In the discharge gap, it is assumed that the condition of electrical neutrality is fulfilled:

$$n_e + n_{i,Me} + n_{i,C} \approx 0, \tag{6}$$

where $n_{i,Me}$ is the ion density of metal particles and $n_{i,C}$ is the carbon ion density.

The anode layer of the discharge is produced in such a way as to ensure continuity of the current at the anode. As will be shown later, the voltage at the anode is negative, so that the electron flux to the anode decreases. The voltage drop at the anode $U_a$ is determined as follows [15]:

$$U_a = -T_e \ln(I_{th}/I_d), \tag{7}$$

where $I_{th} = \pi R_a^2 n_{a,thr}$ ($v_{re}$ is the thermal velocity of electrons at the anode). High flux of the electrons to the anode leads to a significant heating of the anode surface. Coming energy to the anode $Q_a$ spends on the anode material ablation $Q_{abl}$, anode radiation $Q_{a,rad} = \pi R_a^2 \sigma_{rad} T_a^4$ and heat conduction through the electrode $Q_{a,cond} = \lambda_{a,cond} \pi R_a^2 (T_a - T_0)/L_a$:

$$Q_a = Q_{abl} + Q_{a,rad} + Q_{a,cond}, \tag{8}$$

where the heat flux $q_a$ coming from the plasma per unit surface of the anode per unit time:

$$q_a = Q_a/(\pi R_a^2) = I_d (2T_e + U_a + \phi_{WC})/(\pi R_a^2) \tag{9}$$

is consumed to heat the sublimated material from the unit surface of the anode per unit time from the initial temperature $T_0$ to the melting point equal to the surface temperature of the anode $T_a$.  

$$q_a = Q_a/(\pi R_a^2) = I_d (2T_e + U_a + \phi_{WC})/(\pi R_a^2) \tag{9}$$
and subsequent vaporization of the molten material:
\[ q_{vap} = \Gamma H_{evap}. \]  
(11)

Here \( \Gamma \) is the erosion rate of the anode surface (ablation flux) in units [kg/(m²s)], \( c_p \) is the effective specific heat of the heated material of the anode taking into account the mass fractions of atoms ablated from the composite anode, i.e. mass fraction of carbon \( M_C \) and mass fraction of catalyst \( M_l \). It should be noted that in the stationary process of the evaporation of the anode material, both fluxes (10) and (11) are proportional to the rate of erosion of the anode material \( \Gamma \). In calculation of the latent heat of vaporization, the mass fractions of the components of the composite anode are also taken into account, \( H_{evap} = M_C h_C + M_l h_l \).

The Langmuir evaporation model [16] was used for the sublimation process:
\[ \Gamma = p_{sat}(T_a)(2\pi RT_a/M)^{-1/2}, \]
(12)

where \( p_{sat}(T_a) = C p_{sat,C}(T_a) + l p_{sat,l}(T_a) \) is the saturated vapour pressure of the composite ablated anode material, \( R \) is the gas constant, \( M \) is the atomic molecular weight.

3. Results

Initially, the parameters of an arc discharge in a helium medium with a sputtered pure graphite anode were calculated to verify the constructed global integral model. The calculation were made for the discharge conditions and parameters realized experimentally in [18] and simulated in [11]. The parameters of the arc discharge were as follows: both graphite electrodes 6 mm in diameter, inter-electrode gap 6 mm, helium pressure 100 Torr, arc current 50-150 A, discharge voltage \( \sim 20 \) V. With the help of the developed model, the integral characteristics of the plasma parameters (temperature \( T_e \) and density \( n_e \) of electrons, voltage on the discharge gap \( U_d \)) were calculated as a function of the discharge current \( I_d = 50-100 \) A. The calculated results are in good agreement with their absolute values obtained in [11,18], i.e. the electron temperature \( T_e \sim 0.6-0.8 \) eV, electron density \( n_e \sim 10^{15}-10^{16} \) cm⁻³, \( U_d \sim 15 \) V.

Figure 2. Electron density \( n_e \) (left) and electron temperature \( T_e \) (right) current dependencies. \( p_{He} = 100 \) Torr, \( L_g = 6 \) mm.

Within the framework of the constructed model, calculations were made for the parameters of the arc discharge plasma during the evaporation of the composite anode with the addition of different metal powders into the core of the anode, i.e. aluminium and zirconium. The calculations were made for the discharge conditions and parameters realized experimentally in a standard experimental setup described in [19,20] with usual discharge geometry (cathode and anode radius) and discharge
parameters (see Figure 1). The experimental measurements of the erosion rates of the composite anode with the addition of aluminium and zirconium were also carried out. The measurements were made in the regime when the steady-state burning mode (constant current $I_d$ and discharge voltage $U_{d}$, buffer gas pressure $p_{He}$) was achieved. It should be noted that even at small (<1% mass fraction) addition of metal, all discharge parameters vary significantly. This is primarily due to a substantial difference of the following metal parameters from carbon: a) the pressure $p_{sat}(T_a)$ of saturated vapor ablated from the surface of the anode (boiling point at a given pressure), b) the work function of the material, c) the latent heat of vaporization, d) the ionization threshold, etc.

Figure 3. Saturation pressure $p_{sat}$ of the ablated material above the surface of the anode (left figure) and ablation velocity $v_{abl}$ (right figure) depending on the mass fraction of the metal additive $P_{Al}$ or $P_{Zr}$. Solid lines are the calculated results for Al, dashed lines for Zr. Triangles denote the experimental measurements for Al, squares for Zr. $p_{He} = 24$ Torr, $U_{d} = 22$ V, $I_d = 100$ A.

The dependences of different discharge parameters on the relative mass addition $P_i$ of the metal to the core of the anode are presented in Figure 3. The $P_i$ values ($i = Al, Zr$) vary from 0, that corresponds to pure graphite anode with the absence of metal atoms, to 1, which means the same mass content of the metal and graphite in the core material. It should be noted that the entire mass of the graphite electrode material is much larger than the mass of the core, i.e. $P_i < 1$. The numerical simulations showed that the electron density increases with the addition of metal, which can be explained by the lower metal ionization threshold ($U_{i,Al} = 5.98$ eV, $U_{i,Zr} = 6.84$ eV) compared to carbon ($U_{i,C} = 11.25$ eV) (see Saha equation (5)). It should be noted that the saturated pressure (at a given temperature) of aluminium $p_{sat,Al}$ significantly exceeds the saturated vapour pressure $p_{sat,C}$ of carbon, which in turn exceeds the saturated vapour pressure of zirconium $p_{sat,Zr}$. As a result, even with a small addition of metal (except zirconium), the saturated vapour pressure above the anode sharply increases, which leads to a decrease in the surface temperature of the anode, $T_a$. In turn, the rate of erosion of the anode decreases with the addition of aluminium to the anode in accordance with the model of Langmuir evaporation (12).

4. Conclusions
A global integral model of an arc discharge in a helium medium with a sputtered carbon anode containing catalyst particles (Al, Zr, etc.) was constructed. The main features of the model are the simultaneous consideration and connection between the plasma of the discharge gap, the cathode and anode layers, the current transfer, the thermal regime of the electrodes, and the ablation of the anode. The model permits to calculate the heat balance in the entire discharge gap (radiation losses, heating of materials), the temperature of the electrodes surfaces, the concentrations of the electrons and ions of
different species in the discharge gap, the electron temperature, the voltage drops in the anode and cathode layers, the ratio of ion and electron currents at the cathode, the ablation rate of the anode material for different kind and mass of metal catalyst additives.

The results of the model were compared with the data obtained experimentally in [18] and simulated in work [11] for different discharge parameters (discharge voltage and current, helium pressure). The results of the simulation with the help of the presented model showed good agreement with the experimental and calculated data of these studies, in particular, a good correspondence between the absolute values of electron density and temperature, the discharge voltage and the ablation rate of the anode as a function of the discharge current.

The calculated results have qualitative agreement with the obtained in the work experimental data on arcing times \( T(P_a) \) and \( T(P_o) \), namely, the increase in the erosion velocity with the addition of Zr, and the decrease in the erosion velocity with the addition of Al. The model can be used to describe discharges of other geometry (electrodes diameters and inter-electrode gap) and discharge parameters (current, voltage, sort of the background gas and pressure), including calculations for additives of other metals.

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