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Carbon nanoparticles in the radiation field of the stationary arc discharge

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The paper considers a simple theoretical model of heating the nanoparticles, depending on their size and the parameters of the radiating arc and the surrounding gas. This problem is of interest to diagnostics and modeling of the dynamics of the nanoparticles formation and their local size distribution. Heating of nanoparticles by the radiation can affect the process of synthesis. The degree of heating of the particle is determined by its geometry, which opens, apparently, additional possibilities for nonintrusive optical diagnostics. © *2015 AIP Publishing LLC*.
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INTRODUCTION

The arc discharge between the graphite electrodes burning in the atmosphere of inert gases is one of the standard methods of nanoparticle synthesis.[1–5] Typically, in theoretical models, it is assumed (see, e.g., Refs. 2, 3, and 5) that the synthesis starts in the areas where the density of carbon atoms and the catalyst is still high, and the temperature of a buffer gas is reduced down to 1000–2000 K.

The arc is a very powerful light emission source, which is close to the blackbody. This radiation is scattered and partly absorbed by the nanoparticles. In the areas where a synthesis can occur theoretically, the radiation intensity of the arc is still quite high, and therefore, one should expect that the temperature of nanoparticles that absorb radiation may considerably exceed the local ambient gas temperature. The paper considers a simple theoretical model of heating the nanoparticles, depending on their size and the parameters of the radiating arc and the surrounding gas. This problem is of interest to diagnostics and modeling of the dynamics of the nanoparticles formation and their local size distribution.

By now, the Laser Induced Incandescence (LII) has become a recognized method of study of nano- and microparticles suspended in gas became LII diagnostics.[6–11] However, LII studies were conducted mainly for the nanoparticles in weakly ionized plasma of combustion products with a very low degree of ionization or nonionized gas, when the effects associated with radiation heating of the particles are negligibly small. Applying the LII diagnostics to determine the characteristics of the nanoparticles formed in the peripheral regions of the arc needs to be justified. It seems natural to question whether it is possible to use the LII diagnostics for nanoparticles in the radiation field of the stationary arc and how much these measurements could be trusted.

A significant progress in the understanding of the physical processes inherent to small particles in plasma has been achieved in the study of dusty plasma.[12,13] It is known that the particles in the plasma are charged to the negative floating potential $\sim T_e$ when the absolute values of the electron and the ion current to the particles become equal to each other. The electron and ion currents to the particle may affect the heat balance of the particle. This question is investigated in detail in Refs. 14–16. However, for the arc burning in a high pressure buffer gas the degree of ionization is negligible ($<10^{-7}$) in the peripheral regions where synthesis becomes possible. Therefore, the role of electrons and ions in the energy balance of the particle is negligible in comparison with the processes of radiation heating and cooling by radiation and in collisions with the buffer gas particles. In general, the presence of plasma, even at a very low degree of ionization, can influence the potential of the nanoparticles and, thus, influence the thermionic emission. However, as we shall see below, the effect of thermionic emission on the overall heat balance of the nanoparticles is very small, so this paper will not consider the plasma effects in the heat balance of the nanoparticle.

MODEL AND ASSUMPTIONS

According to the numerical modeling,[2,3] the arc plasma in a buffer helium, in which the synthesis of nanoparticles takes place, has a complex composition, which contains ions of C+, Ni+, Y+, and the corresponding neutral atoms and cluster molecules. However, the concentrations of these atoms and cluster molecules are very small and, therefore, we can assume that the collisional cooling of the nanoparticles is determined mainly by the collisions with atoms of the buffer gas. For simplicity of analysis, we assume that all nanoparticles are spherical. Also, we will restrict our consideration to the conditions where the ablation and vaporization of the particles can be neglected in accordance with the results presented in Refs. 7 and 8.

For a spherical particle with a diameter $D = 2a$, the absorption cross section for coherent radiation in the Rayleigh approximation ($\lambda \gg a$)[8,17] is

$$c_{abs} = \frac{\pi^2 D^3 E(m)}{\lambda} = \frac{\pi^2 D^3 E(m)\nu}{c}, \tag{1}$$

where $\nu = c/\lambda$ is the radiation frequency; $E(m)$ is the function of the complex refractive index m, $E(m) = -\mathrm{Im}\left(\frac{m^2-1}{m^2+2}\right)$.

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We use the broadband value $E(m) \approx 0.35$, which is close to the value estimated in Refs. 7 and 10 for soot particles, $E(m) \sim 0.32 - 0.4$.

Considering the arc radiation as a blackbody radiation with a certain known emissivity $\zeta < 1$ and the Planck blackbody radiation spectral intensity

$$I(\nu) = \frac{2\pi h\nu^3}{c^2}\frac{1}{e^{h\nu/kT} - 1}, \tag{2}$$

where $I(\nu)d\nu$ is the radiant power per unit area of radiating surface in the frequency range from ν to $\nu + d\nu$, we find the total rate of absorption of the radiation energy by a spherical particle of the diameter D at a distance r from the boundary of the arc with the temperature T_{arc}

$$\begin{aligned} Q_{abs} &= \zeta \int_0^\infty c_{abs} I(\nu, r) d\nu = \zeta \frac{8}{15}\frac{\pi^7 D^3 E(m) T_{arc}^5}{h^4 c^3}\frac{r_0^2}{r^2} \\ &= \zeta \frac{4\pi^2 D^3 E(m)\sigma_{SB} k_B T_{arc}^5}{hc}\frac{r_0^2}{r^2}. \end{aligned} \tag{3}$$

$\sigma_{SB} = \frac{2}{15}\frac{\pi^5 k_B^4}{h^3 c^2} \approx 5.670373 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}}$ is the Stefan–Boltzmann constant. Formula (3) takes into account that in the experiment[2,4,5] and the computational models (e.g., Ref. 3), the interelectrode gap is small (~2–3 mm), as compared to the distance from the arc $r > 1.5$ cm, wherein the gas temperature is reduced to a level where synthesis becomes possible. Therefore, it is natural to assume that the radiation intensity of the arc decreases with distance as $\propto 1/r^2$. For a typical arc discharge used for the synthesis of carbon nanoparticles, the emissivity is $\zeta \approx 0.8$.[4,5]

The heated particle is cooled by radiation with the radiative heat losses, determined by the expression[7,8]

$$Q_{rad} = 4\pi a^2 \int_0^\infty \varepsilon_\lambda \frac{2\pi h c^2 d\lambda'}{\lambda'^5\left[\exp\left(hc/\lambda' k_B T_p\right) - 1\right]}, \tag{4}$$

where $\varepsilon_\lambda = 8\pi a E(m)/\lambda$ is the emissivity of the particle. Integrating in Eq. (4) over the entire frequency spectrum, we find a convenient formula for the power of the radiation energy losses

$$Q_{rad} = \frac{16\pi^2 D^3 E(m)\sigma_{SB} k_B T_p^5}{hc}. \tag{5}$$

Along with the radiation cooling, a particle with an absorption coefficient (1) is heated by the thermal radiation from the background gas with the temperature T_g and the emissivity $\zeta_g \ll 1$. Taking this into account, the rate of radiative losses

$$\begin{aligned} Q_{rad} &= \frac{4\pi^2 D^3 E(m)\sigma_{SB} k_B}{hc}\left(4T_p^5 - \zeta_g T_g^5\right) \\ &\approx \frac{16\pi^2 D^3 E(m)\sigma_{SB} k_B T_p^5}{hc}. \end{aligned} \tag{6}$$

The particle is also cooled in the collisions with the buffer gas atoms (conduction conductivity). The rate of heat loss in these collisions with the buffer gas atoms (conductive cooling) is Q_g,[8,17,18]

$$Q_g = \frac{2\pi a^2 \alpha_T p_g}{T_g}\sqrt{\frac{R_m T_g}{2\pi\mu}}\left(\frac{\gamma + 1}{\gamma - 1}\right)(T_p - T_g). \tag{7}$$

For helium as a buffer gas: $\mu_{He} = 4$ g/mol; $\gamma = 1.66$; $R_m = 8.314$ J/mol K. α_T is the thermal accommodation coefficient of ambient gases with the surface of a particle. The exact value of the accommodation coefficient can be determined only by comparison of the theoretical calculations with the results of measurements. In this paper, we take $\alpha_T \approx 0.1$, given in Refs. 19 and 20 for the carbon nanoparticles in helium.

The heating of the particles to high temperatures is accompanied by the thermionic emission, which reduces the intensity of heating. In plasma, where the particles are negatively charged, taking into consideration the Schottky effect, the thermionic emission current is[21]

$$I_{e,T} = 4\pi a^2 A T_p^2 \exp[-(w_a - \Delta\phi)/k_B T_p], \tag{8}$$

where $A = 120$ A/cm^2 K^2, $w_a = 4.7$ eV is the work function for the carbon nanoparticle; $\Delta\phi = \left(\frac{e|\varphi|}{4\pi\varepsilon_0 a}\right)^{1/2}$ is the reduction in the work function at the negative potential of the particle, $\varphi < 0$. However, in the non-ionized gas or, for typical conditions of weakly ionized plasma, at the distances of centimeters from the arc discharge when the electron current from the plasma on the particle is negligible as compared to the current thermionic emission, the particle loses electrons through the thermionic emission, acquiring a positive charge

$$q = \int_t I_{e,T} dt, \tag{9}$$

and the potential

$$\varphi = q/C > 0, \tag{10}$$

where $C = 4\pi\varepsilon_0 a$ is the capacity of the particle.

In this case, the positive potential suppresses the thermionic current and is equal to

$$I_{e,T} = 4\pi a^2 A T_p^2 \exp[-(w_a + \varphi)/kT_p]. \tag{11}$$

The thermionic emission results in an additional cooling of the nanoparticles, because each "evaporating" electron carries away the energy $(w_a + \varphi)$. The corresponding power of heat loss is

$$Q_{TE} = -(|I_{e,T}|/e)(w_a + \varphi)\ [\mathrm{eV/s}]. \tag{12}$$

The energy balance of the particle is determined by the equation

$$M_p c_p \frac{dT_p}{dt} = Q_{abs} - Q_{TE} - Q_g - Q_{rad}. \tag{13}$$

Here, $M_p = \frac{4}{3}\pi\rho_p a^3$ is the mass of the particle. The local quasi-stationary temperature of the particle is determined by the condition

$$Q_{abs} - Q_{TE} - Q_g - Q_{rad} = 0. \qquad (14)$$

The heat balance equation (13), together with Eqs. (3), (6), (7), (9), (10), and (12) was solved for the initial conditions at t = 0: $q = 0$, $\varphi = 0$; $T_p = T_g$.

RESULTS AND DISCUSSION

As already mentioned, we consider spherical soot particles, assuming non temperature dependent value of density and heat capacity: $\rho_p = 2660$ kg/m^3; $c_p = 1900$ J/kg/K,[6,8] for the sake of simplicity. The calculations were performed for pressure $p = 68$ kPa, as in Ref. 3, and the two values of the background gas temperature: $T_g = 1000$ and 1500 K. We assumed that the equilibrium temperature at the center of an arc with a radius of $r_0 = 5$ mm was $T_{arc} = 7000$ K, which is close to the data obtained in the calculations[3] and the experimental works.[4,5]

The results presented in Fig. 1 show that in the radiation field of the arc, the temperature of the particles becomes very different from the background temperature, and depends on their sizes. The quasi equilibrium temperature of the particle is higher, the closer this particle is to the arc. Thus, the particle temperature $T_p(r,a)$ is established for the time of the order of 10 ms. Fig. 2 shows an example of the calculation of the transitional regime for the particles of different sizes. In the presence of a convective flow of the buffer gas, the particles are not static and move with the flow. However, for the characteristic time for the establishment of a quasi-stationary temperature, the convective displacement of the particles is negligible, ~1 mm or less. Figure 3 shows some examples of the quasi-stationary temperature of the particles with the radii 25 and 50 nm, depending on the distance from the arc at the same background temperature $T_g = 1500$ K.

Under our considered conditions, the nanoparticles' temperatures are a function of their sizes, because electromagnetic energy absorption in the Rayleigh regime is volume dependent, and cooling (dominated by thermal conduction to the ambient gas) is area-dependent. Therefore, larger particles are heated to higher temperatures, than small particles.

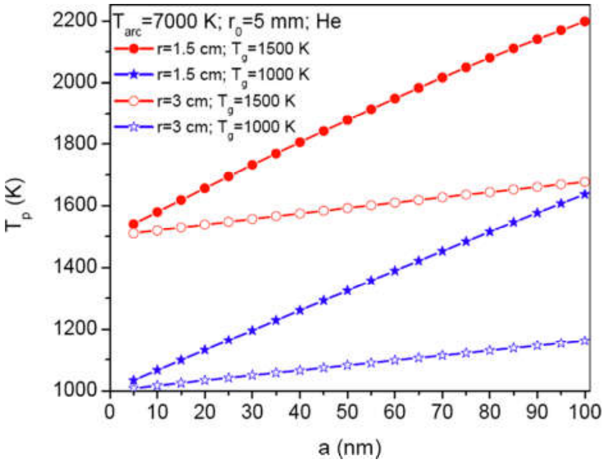

FIG. 1. Stationary temperature of particles, depending on their radius for two positions of the particles r = 1.5 and 3 cm; and for two values of the buffer gas temperature $T_g = 1000$ and 1500 K.

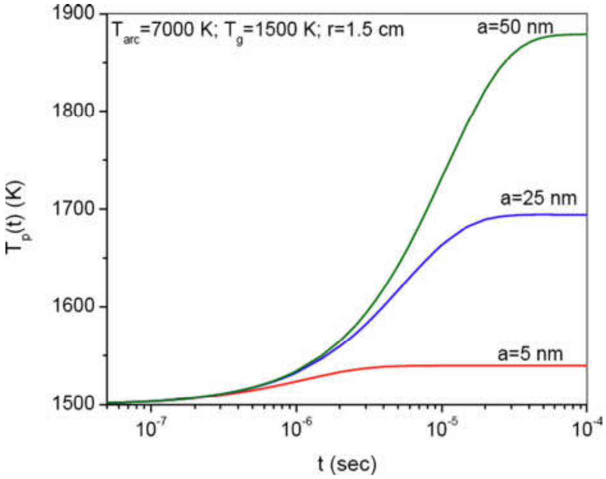

FIG. 2. Establishment of a quasi-stationary temperature for the particles of different sizes: a = 5, 25, and 50 nm, at a distance of 1.5 cm from the arc axis.

An example of the contribution of various components of the heat balance at a steady-state regime, depending on the size of the particles at the distance of 1.5 cm from the center of the arc and the assumed background temperature $T_g = 1500$ K, is shown in Fig. 4.

Although we considered the impact of arc radiation on carbon nanoparticles, our results and conclusions may be applicable to other types of nanoparticles if the radiation absorption is in the Rayleigh regime.

CONCLUSIONS

- The influence of arc discharge radiation with graphite electrodes on the synthesis of carbon nanoparticles in the helium buffer gas was analyzed.
- It is shown that the nanoparticles are heated by the blackbody radiation of the arc and their temperatures significantly exceed the local temperature of the buffer gas.
- The heating of nanoparticles by the radiation can affect the process of synthesis.

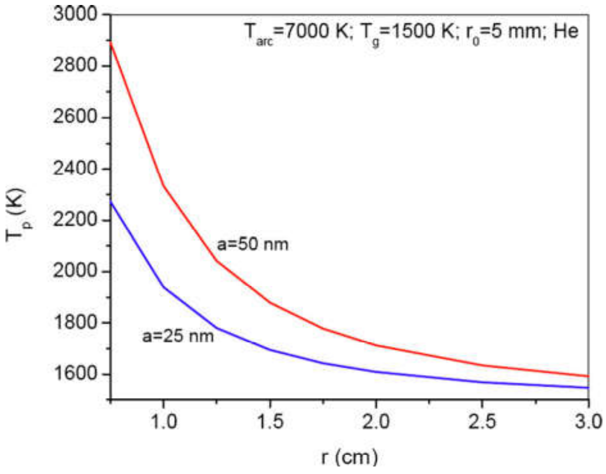

FIG. 3. Stationary temperature of particles of radius a = 25 and 50 nm, depending on distance from the center of the arc.

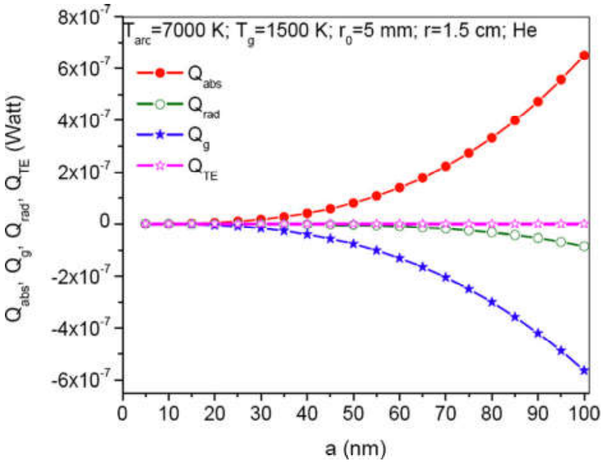

FIG. 4. Quasi-stationary sources of heating and cooling of particles, depending on their radius, at a distance $r = 1.5$ cm from the center of the arc and the background temperature $T_g = 1500$ K.

- The degree of heating of the particle is determined by the particle's geometry, and that opens additional possibilities for nonintrusive optical diagnostics.

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