Homogeneous nucleation in thermal dust-electron plasmas

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The homogeneous nucleation in the dust-electron plasma, which is formed in the zone of metal powder combustion products in the premixed laminar two-phase flame, has been studied. The classical nucleation theory has been used to determine the free energy and the critical radius of the nucleus. The influence of nucleus charging as a result of interaction between the nucleus and the electronic component of the plasma on the free energy has been determined. The dependence of the nucleus' critical radius on the plasma temperature and number density of the plasma's dust component has been determined. The proposed theoretical model shows that nucleation in the thermal dust-electron plasma is a self-consistent process, which is opposed to changing of the plasma's disperse structure.

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I. INTRODUCTION

The study of nucleation and nucleus growth is of interest in terms of both the fundamental science and technological applications. The important problem of modern technology is the production of new materials, for example, high-quality ceramics, including flexible ceramics, which can be used to make crucibles for melting metals, gas turbines, liners for jet and rocket motor tubes, resistance furnaces, and ultra-high-frequency furnaces [1]. The raw materials for such ceramic are nanosized particles, in particular the particles of metal oxides of sizes about 10 nm. New materials are not the only issue, as refining, preservation of materials, and new processes are also targeted; the particles are used in various forms such as powders, composite materials, suspensions, and films [2]. Another direction of application of such materials is the manufacturing of fuel cells [3]. Solid oxide fuel cells differ from other fuel cell technologies because they are composed of all-solid-state materials, and as a result, the cells can operate at temperatures significantly higher than any other category of fuel cell.

The promising method of obtaining high-purity thin powders of metal oxides and nitrides is the method of gas-dispersion synthesis, which is based on combustion of metal powder in an oxygen medium. The premixed laminar two-phase flame is formed to provide for finely divided particles of metal oxide. In this case, the gas suspension of the metal powder agitates with the oxygen and this mixture moves into the combustion zone. Such a flame is characterized by the presence of a developed combustion zone, which expands through the gas mixture at a certain rate. The mechanism of the flame expansion is related to the heat produced as a result of chemical reaction, and its subsequent transmission into the warm-up zone. In such mode of burning, the metal oxide particles are formed as a result of vapor-phase condensation, and the condensation occurs in the thermal dust-electron plasma, formed in the zone of combustion products. This plasma consists of a gas of atmospheric pressure and the solid or liquid particles of metal oxide, which emit electrons. The absolute temperature of such a plasma is usually about 1500–3500 K ($T\sim 0.1-0.3$ eV), and the system is considered isothermal.

In such a dust-electron plasma, the condensation of new particles, i.e., the process of formation of a nucleus and nucleus growth, occurs in the background of collective interaction of particles, which have been condensed earlier. Both homogeneous and heterogeneous nucleation are studied well enough [4–11], but nucleation in the heterogeneous medium in the background of interaction of charged particles is not studied sufficiently—one should note, for example, Ref. [12]. Nevertheless, such study is necessary to be able to control the gas-dispersion synthesis, i.e., to obtain the particles of the required size and structure.

In this paper, the formation of a nucleus in the thermal dust-electron plasma is considered taking into account the influence of the collective interaction of a dust component on this process. Actually, we consider the homogeneous nucleation in electronic gas. Thus there exist only two parameters that exert additional influence on the nucleation—namely the number density and the temperature of electrons. If the temperature is determined by the mode of the burning of the flame, the electron number density is determined by the interaction of the dust component, which is taken into account in terms of the theory of neutralizing charges [13].

It is necessary to note that we do not consider the mechanism of the nucleus' charging. These mechanisms are reviewed in detail in Refs. [13,14]. We consider only change of the free energy of the nucleus. Nevertheless, a small review of the theory of the neutralizing charges is presented in the following section.

II. DUST-ELECTRON PLASMA

The theory of neutralizing charges suggests that the basic part of electrons in the plasma volume is distributed uniformly with some unperturbed number density of n_0. Only in the thin layer near the surface of the dust particles the electron number density differs from the unperturbed value. The dust particles are charged positively as a result of the thermionic emission. The surface electron number density n_{es} is constant because it represents the saturated steam of electrons above the surface of the dust particle, as described by the Richardson formula

$$n_{es} = \nu_e \exp\left(\frac{-W}{T}\right),$$

where $\nu_e = 2(m_e T/2\pi\hbar^2)^{3/2}$ is the effective density of the electron states; m_e is the electronic mass; $\hbar$ is the Planck constant; and W is the electronic work function.

Some part of the particles charge $Z_0 = n_0/n_d$ (n_d is the total number density of the dust particles) and the electronic gas, with the number density n_0, create a uniform background of neutralizing charges. The ratio of the surface electron number density n_{es} to the unperturbed number density determines the height of the potential barrier V_b at the boundary between the electronic gas and the dust particle,

$$V_b = T \ln \frac{n_{es}}{n_0} = T \ln \frac{\nu_e}{n_0} - W, \tag{1}$$

which provides for the equality between the flux of thermionic emission and the backflow, caused by the thermal motion of electrons.

The dust-electron plasma in the two-phase flame has the polydisperse distribution of the particles sizes [15], and the neutrality of charge is described by the following equation:

$$\sum_j Z_j n_j = \bar{n}_e \cong 5n_0, \tag{2}$$

where Z_j is the charge number of particles of the kind j, with the number density of n_j; $\bar{n}_e$ is the average electron number density, which is connected with the unperturbed number density as $\bar{n}_e = n_0 \exp(3/2) \cong 5n_0$. The charge number of the dust particles is defined by the following expression:

$$Z_j = Z_0 + \frac{\sqrt{2}T(\lambda_D + a_j)a_j}{\mathrm{sgn}(V_{bj})e^2\lambda_D}\sqrt{\exp\frac{V_{bj}}{T} - \frac{V_{bj}}{T} - 1}, \tag{3}$$

where a_j is the radius of the particles of the kind j; $\lambda_D = \sqrt{T/4\pi e^2 n_0}$ is the screening length.

Equations (1)–(3) fully describe the dust-electron plasma. As follows from Eq. (3), the interaction of the dust particles in this case is determined not by the absolute charge number Z, but by the relative ("visible") charge number $\tilde{Z} = Z - Z_0$. In the event that the charge of some particle is equal to Z_0, the potential barrier on the boundary of phases is absent.

Thus the influence of a set of dust particles on the nucleation is reduced to the change of the background in which the nucleation occurs, i.e., to the change of the unperturbed electron number density n_0, which defines the height of the potential barrier at the surface of the nucleus and the nucleus charge. The unperturbed number density depends on the temperature of the plasma and the parameters of the dust particles.

Let us consider the monodisperse system of dust particles of small radius $a \ll \lambda_D$ in dust-electron plasma. In this case the combined Eqs. (1)–(3) are reduced to the equation

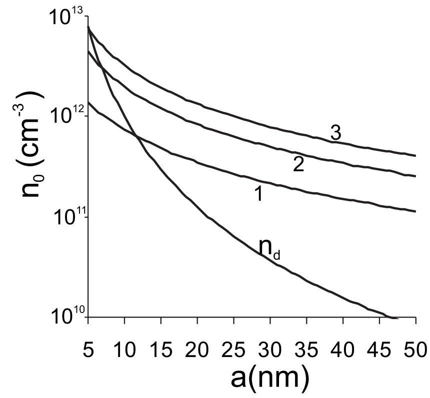

FIG. 1. Typical dependencies of the unperturbed number density n_0 on the radius of particles in the thermal dust-electron plasma of zirconia for various temperatures: (1) 2700; (2) 3000 K; and (3) 3200.

$$n_0 = n_d \frac{\sqrt{2}Ta}{4e^2}\sqrt{\exp\frac{V_{bj}}{T} - \frac{V_{bj}}{T} - 1}, \tag{4}$$

from which it follows that the unperturbed number density linearly depends on the number density of dust particles and their size.

The formation of the laminar two-phase flame depends on the density of metal powder in the gas mixture. Thus there is very little range of density, which allows carrying out a self-supported mode of burning of the powder-gas mixture, not requiring an additional source of inflaming. Therefore at all varieties of the condensed dust particles in the combustion products, the bulk material remains approximately constant, i.e., at the monodisperse distribution of the particles, the part of the total volume captured by the dust particles $a^3 n_d \sim \mathrm{const}$. This quantity is different for different metals, but usually stays within the limits of $a^3 n_d \sim 10^{-6} - 10^{-5}$. Thus the dependence n_0 on the radius of the dust particles becomes $n_0 \sim 1/a^2$, and the dependence on the number density becomes $n_0 \sim n_d^{2/3}$.

In Fig. 1 the dependencies of the unperturbed number density on the radius of dust particles for different temperatures of the thermal dust-electron plasmas of zirconium oxide (zirconia), taking into account the maintenance of the bulk material $a^3 n_d = 10^{-6}$, are presented. We can see that the decreasing of the radius of the dust particles leads to the increasing of the unperturbed number density. These dependencies will be required to define the influence of the dust component on the nucleation.

III. INFLUENCE OF CHARGE ON THE NUCLEATION

The product of combustion of the metal particles in an oxidizing medium is the gas consisting of oxides molecules, when the burning is homogeneous. This gas in the condensation zone is similar to supercooled vapor, in which the droplets of liquid are formed. The formation of the liquid droplet is accompanied by the occurrence of the phase boundary, which required the expenditure of energy. Therefore there should be a balance between the volume of the

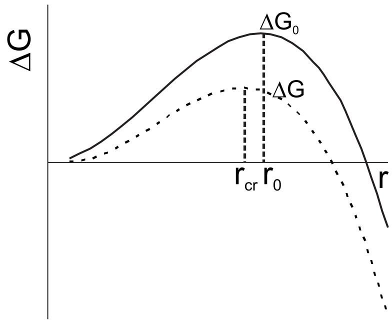

FIG. 2. Dependence of the free energy on the radius of nucleus: ΔG_0 is the CNT; ΔG is charge influence.

droplet and its surface so that formation of a droplet was energetically favorable. If the liquid droplet has sufficient size to compensate the energy spent for occurrence of the phase boundary, it is steady and continues to grow. Therefore there is some critical radius of the droplet r_0, which defines the metastable state of the nucleus. If the radius of the droplet is less than r_0, it eventually breaks up. If the radius of the droplet is more than r_0, it represents a steady nucleus of the condensed phase.

Let us consider the formation of a nucleus in the isotropic medium [16,17]. At the lack of exterior action, according to the classical nucleation theory (CNT), the Gibbs free energy of nucleation is

$$\Delta G = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 \frac{|\Delta\mu|}{V_l}, \tag{5}$$

where r is the radius of the nucleus; V_l is the molecular volume of the nucleus; γ is the surface free energy per unit area, or surface tension; and $\Delta\mu = \mu_l - \mu_g$ is the difference in chemical potential between the liquid and gas phases.

Equation (5) describes a potential barrier, which is necessary to overcome to form a steady nucleus (Fig. 2), and has a maximum at the value of critical radius

$$r_0 = \frac{2\gamma V_l}{|\Delta\mu|}. \tag{6}$$

If the nucleus gets some charge the free energy [Eq. (5)] changes. First of all, it should be noted that acquisition by the nucleus of charge eZ_n is accompanied by the exchange of energy between phases, therefore in Eq. (5) it is necessary to add the corresponding term $\Delta G(Z_n)$: $\Delta G = \Delta G_0 + \Delta G(Z_n)$. The change of chemical potentials is insignificant, therefore we neglect it.

This question has been studied in Refs. [17–21]. However, it is necessary to point out that the influence of the nucleus charging on the change of free energy ΔG cannot be considered as electrostatic energy of the Coulomb [19] or Debye [20] interactions as both phases take part in this interaction, while the change of the free energy $\Delta G(Z_n)$ concerns only the nucleus.

As a result of the thermionic emission, the electrons transfer charge and energy to the gas, decreasing the free energy ΔG. Thus there is a backflow of electrons on the surface of the nucleus, which increases the free energy ΔG. The balance of these streams determines the displacement of ΔG and, accordingly, the change of critical radius Eq. (6). One electron, leaving the particle as a result of thermionic emission, transfers energy to the gas

$$E_{l\to g} = W_n + \frac{p_e^2}{2m_e},$$

where W_n is the work function from the nucleus; p_e is the impulse of the electron; and m_e is the electronic mass.

The backflow of electrons transfers average energy of the electron motion $3T/2$ to the nucleus. Further, the electron absorbed by the nucleus should give it the potential energy, which is equal to the electronic work function as the potential energy of the electron in the nucleus differs from the potential energy of the free electron on this quantity. Thus, on average, the absorbed electron transfers to the nucleus the energy [22]

$$\langle E_{g\to l}\rangle = W_n + \tfrac{3}{2}T.$$

The transfer of the charge and energy through the nucleus surface, which is in equilibrium, is equal to zero. It is reached by the alignment of streams via the charging of the nucleus, which provides a field adjusting the backflow of electrons. Therefore, the average energies, transferable by one electron through the nucleus surface, must be equal between themselves:

$$\langle E_{l\to g}\rangle = \langle E_{g\to l}\rangle = W_n + \tfrac{3}{2}T.$$

The change of the free energy $\Delta G(Z_n)$ is determined by the nucleus charge. If the nucleus has positive charge, then for support of the equilibrium between streams, it transfers the energy $Z_n(W_n + 3T/2)$ to the gas, and ΔG decreases on this value. If the nucleus has negative charge, then the free energy ΔG increases by $|Z_n|(W_n + 3T/2)$. Therefore, to calculate the exchange of electrons between the charged nucleus and gas, instead of Eq. (5) it is necessary to use the expression

$$\Delta G = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 \frac{|\Delta\mu|}{V_l} - Z_n\left(W_n + \frac{3}{2}T\right). \tag{7}$$

The particles interaction in the dust-electron plasma is determined by a "visible" charge $\tilde{Z}$, but the change of the nucleus free energy in Eq. (7) is determined by the absolute value of charge, in order to provide for the surface electron number density of $n_{es} = n_0$, the nucleus should emit electrons and get the positive absolute charge.

Further, it is necessary to consider that the nucleus charge leads to the formation of the electrical double layer on its surface and, accordingly, to change of the surface tension γ. This change can be considered, using the Lippmann equation [23]

$$\frac{d\gamma}{dV_{bn}} = -\frac{Z_n}{4\pi r^2},$$

where V_{bn} is the potential barrier on the plasma-nucleus boundary.

From here, taking into account Eq. (3), it follows that $\gamma = \gamma_0 - \delta\gamma$, where γ_0 is the surface tension of the neutral nucleus and

$$\delta\gamma = \frac{Z_0 V_{bn}}{4\pi r^2} + \frac{\sqrt{2}T^2}{4\pi e^2 r}\int_0^{V_{bn}/T} \sqrt{\exp(x) - x - 1}\,dx, \quad (8)$$

and, accordingly,

$$\Delta G = \Delta G_0 - 4\pi r^2 \delta\gamma - Z_n\left(W_n + \tfrac{3}{2}T\right), \quad (9)$$

where ΔG_0 is the free energy of a neutral nucleus [Eq. (5)]. Equation (9) considers the change of the free energy of the nucleus as a result of exchange of electrons and changes of the surface tension.

IV. INFLUENCE OF PLASMA TEMPERATURE ON THE NUCLEATION

The control of condensation when the gas-metal mixture burns is reduced only to change (in small limits) the number density of the dust component and to change the temperature of the plasma, which is determined by the content of oxygen in the submitted mixture. Therefore we shall determine the influence of the temperature of dust-electron plasmas in the combustion products on the nucleus' critical radius.

Let us consider the thermal dust-electron plasma consisting of the monodisperse dust particles of small radius ($a \ll \lambda_D$), the electrons emitted by these particles, and the buffer gas containing the vapor of a condensable substance.

Then formation of the nucleus is described by Eq. (9) together with the equation defining the unperturbed number density [taking into account Eqs. (1) and (4)]

$$n_0 = n_d \frac{\sqrt{2}Ta}{4e^2}\sqrt{\frac{\nu_e}{n_0}\exp\frac{-W_d}{T} - \ln\frac{\nu_e}{n_0} + \frac{W_d}{T} - 1}, \quad (10)$$

and the equation defining the nucleus charge

$$Z_n = Z_0 + \frac{\sqrt{2}Tr}{\mathrm{sgn}(V_{bn})e^2}\sqrt{\exp\frac{V_{bn}}{T} - \frac{V_{bn}}{T} - 1}, \quad (11)$$

where the subscript "d" concerns the dust particles, and the subscript "n" concerns the nucleus; and we remind one that $Z_0 = n_0/n_d$.

The dust particles that have been condensed earlier are charged positively rather than Z_0, as they determine the neutralized background. The value of the nucleus charge is unknown; therefore we have left the signum function in Eq. (11).

The critical radius of the charged nucleus is defined from the equation $\partial\Delta G/\partial r = 0$, from which it follows that the ratio of the critical radius of the charged nucleus r_{cr} to the critical radius of the neutral nucleus Eq. (6) is described by the equation

$$\frac{r_{cr}}{r_0} = \frac{1}{2} + \frac{1}{2}\left\{1 - \frac{\sqrt{2}T}{2\pi\gamma_0 r_0 e^2}\left[T\int_0^{V_{bn}/T}\sqrt{\exp(x) - x - 1}\,dx + \mathrm{sgn}(V_{bn})\left(W_n + \frac{3}{2}T\right)\sqrt{\exp\frac{V_{bn}}{T} - \frac{V_{bn}}{T} - 1}\right]\right\}^{1/2}. \quad (12)$$

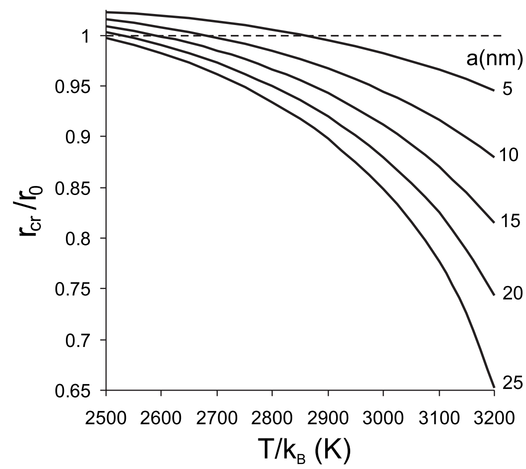

FIG. 3. Dependences of the ratio of critical radii [Eq. (12)] on the temperature of plasma for various sizes of dust particles of zirconia (ZrO_2).

Let us note that the change of the critical radius as a result of nucleus charging Eq. (12) depends on the value of the potential barrier, i.e., on the "visible" charge $\tilde{Z}_n = Z_n - Z_0$, but not on the absolute charge of the nucleus. If the nucleus charge is equal to Z_0, the potential barrier is absent and the critical radius of the nucleus is equal to r_0. In Eq. (9) Z_0 changes a free energy ΔG but does not change the standing of maximum in Fig. 2. If the nucleus charge is also positive, but is less than Z_0, the critical radius increases, and if $Z_n > Z_0$, the critical radius decreases.

In order to construct the dependence of the critical radius on the temperature of the plasma we shall use the following parameters that are typical for the combustion of the gas-powder mixture of particles of zirconium: the electronic work function for zirconia W_d=4.5 eV [24], the parameter $a^3 n_d = 10^{-6}$, and the surface tension $\gamma_0 = 100$ erg/cm^2. The electronic work function for the nucleus differs from W_d—according to Ref. [18]

$$W_n \cong W_d + \frac{0.39e^2}{r},$$

and in our case the allowance to the work function makes $\sim$(0.2–0.3) eV.

The results of the calculation, taking into account the maintenance of the bulk material of the combustion products, are presented in Fig. 3. The increase of the temperature of plasma leads to a decrease of the nucleus' critical radius. The absolute temperature of the flame in the condensation zone, when the zirconium powder-gas mixture burns, is usually about 2700–3200 K ($T \sim 0.23$–0.28 eV). The decrease of the temperature of the flame leads to the increase of the nucleus' critical radius ($r_{cr} > r_0$). It is determined by the change of the sign of the potential barrier—at low temperatures $V_{bn} < 0$, accordingly $Z_n < Z_0$.

Let us pay attention to the dependence of critical radius on the size of dust particles that form the dust-electron plasma. The increase of their size leads to the decrease of the critical radius. It means that if the large particles are formed

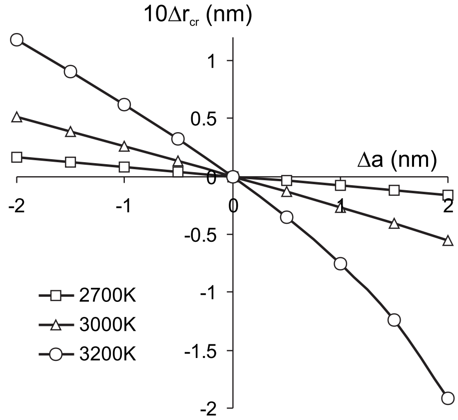

FIG. 4. Dependence of deviation of the nucleus' critical radius on the deviation of the average radius of dust particles.

during the nucleus growth, the nucleus' critical radius decreases, leading to the emergence of finer particles, i.e., the dust-electron plasma is a self-consistent system from the point of view of nucleation. This self-consistence causes the diminution of the dispersion of the sizes of particles: at constant mass of the condensed substance the decrease of the size of dust particles leads to the increase of the critical radius and, after the nucleus growth, to the increase of the sizes of particles; and the increase of the sizes of dust particles—on the contrary—to the decrease of their sizes.

Let us suppose the sizes of particles is incremented ten times, during the nucleus growth, and the average radius of the dust particles is 10 nm. Then, the deviation of the average radius to this or that side will cause the change of the nucleus' critical radius, which is shown in Fig. 4. It is visible that at the absolute temperature of 3200 K the change of the critical radius almost fully compensates for the change of the average size of the dust particles.

Thus the increase of the temperature of the thermal dust-electron plasma causes the decrease of the nucleus' critical radius and the decrease of dispersion of the sizes of condensed dust particles.

V. CONCLUSION

The most fine particles are formed in the combustion products of metal powders in the premixed laminar two-phase flame at homogeneous nucleation from the gas phase. In the condensation zone of such a flame the forming of the thermal dust-electron plasma consisting of condensed dust particles and the electrons emitted by them takes place. The collective processes in the plasma influence the nucleation, changing the charge of the nucleus. The interaction of the nucleus and the electronic component of the plasma causes dependence of the nucleus' critical radius on the temperature and the disperse structure of the plasma.

The increase of temperature of the flame, which can be carried out via the increase of the content of oxygen in the bearing gas, leads to a decrease of the nucleus' critical radius, and this decrease is more, the more the average size of the dust particles forming the plasma is. As a result, the increase of temperature of the flame causes the decrease of the dispersion of the sizes of dust particles.

Thus it is possible to draw a conclusion that the formation of the condensed phase as a result of homogeneous nucleation in the thermal dust-electron plasma, formed in the premixed laminar two-phase flame, is the process with the negative feedback, whose role is played by the nucleus' critical radius, and the coefficient of the feedback is proportional to the temperature of the plasma.

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