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## Features of nucleation in welding fumes from gas metal arc welding

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## ABSTRACT

Ionization balance and nucleation in the plasma, which is formed in welding fumes from gas metal arc welding, are studied. It is demonstrated, that large number of nuclei causes the replace of volume thermal ionization by ionization via nucleus surface. The equation for change in Gibbs free energy during nucleation should be also replaced. Absence of the easy-ionizable additional agent forces the iron atoms to execute both functions: a source of ionization and a source of nucleation. As a result nucleation occurs during short time, because condensable material promptly ends.

## 1. Introduction

Welding fumes are formed via heterogeneous ion-induced nucleation, which occurs in the mixture of welding materials' vapors from arc zone and shielding gas, if the gas metal arc welding (GMAW) is used. The condensation centers are single charged positive ions, which appear via the vapor atoms impact ionization by collisions with free electrons (thermal ionization) and by interaction with arc UV-radiation (photoionization). When first nuclei are formed, the additional ionization of vapor atoms by their collisions with condensed nuclei (surface ionization) appears. Thus, there are at least three channels of ionization, which are necessary for considering while describing the ionization balance in the welding fume plasma. It should be taken into account that different ionization-recombination channels influence each other, because each of them changes the number of electrons and ions in the system that leads to change in every channel recombination intensity.

During nuclei formation in the plasma, the nucleus-gas interaction results in the charging of nuclei, as well as in changes of plasma ionization degree (Vishnyakov, 2006). The nucleus-plasma electron exchange influence on the homogeneous nucleation is demonstrated by Doroshenko, Poletaev, and Vishnyakov (2009); Vishnyakov (2008). The same processes are observed during heterogeneous nucleation in an ionized gas containing dust component, but equilibrium nuclei formation on ions is added (Vishnyakov, Kiro, & Ennan, 2011). Nucleation in the plasma is accompanied by interphase interaction and charging of nuclei; and the equilibrium nucleus is formed when both processes (nucleation and charging) are established. Thus, ionization processes and interphase interaction influences nucleation in the plasma.

The presence of dust in the plasma causes the ionization balance displacement, which was observed by Calcote (1948); Sugden and Thrush (1951); Shuler and Weber (1954). The firsts theoretical studying were based on the modification of Saha equation (Einbinder, 1957; Arshinov & Musin, 1958a, b; Zhukhovitskii, Khrapak, & Yakubov, 1984; Sodha & Mishra, 2011) and numerical modeling of ionization balance with thermionic emission (Gibson, 1966). Special attention was given to studying of the particle charging mechanisms (Fortov, Khrapak, Khrapak, Molotkov, & Petrov, 2004; Goree, 1994; Semenov & Sokolik, 1970; Shukla & Mamun, 2002; Sicha, 1979; Sodha & Kaw, 1968).

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However, ionization balance in the dusty plasma was studied insufficiently; and the systems, in which it is possible to neglect free electrons, were not considered at all. Such a system appears in the nucleation zone of welding fumes from GMAW, where absence of alkali metals with low ionization potential causes the large number of nuclei which collect the free electrons (the presence of alkali metals leads to nucleus number density decrease (Vishnyakov, Kiro, Oprya, Shvetz, & Ennan, 2017a)), and as a result the volume impact ionization is replaced by ionization via nucleus surface (Vishnyakov, Kozytzkyi, & Ennan, 2019).

The present paper is devoted to studying of the nucleation and ionization balance in the plasma of welding fumes from GMAW. Consideration is focused on the interphase interaction, i.e. interaction of the nucleus surface with the plasma gas phase, and effect of this interaction on the ionization balance and change in Gibbs free energy at the heterogeneous ion-induced nucleation.

## 2. Nucleation in the plasma with intensive surface ionization

The classical homogeneous nucleation is described by the change in Gibbs free energy of casual nucleus formation (Cacciuto, Auer, & Frenkel, 2003; Landau & Lifshitz, 1976; Vehkamaki, 2006)

$$\Delta G_0 = 4\pi r_n^2 \gamma - \frac{4}{3}\pi r_n^3 \frac{\rho}{m_M} k_B T \ln S, \quad (1)$$

where  $r_n$  is the nucleus radius;  $\gamma$  is the surface free energy per unit area, or surface tension;  $\rho$  is the density of nucleus substance;  $m_M$  is the molecule mass;  $T$  is the Kelvin temperature;  $k_B$  is the Boltzmann constant;  $S$  is the vapor supersaturation, equal to the ratio of the pressure of condensed substance vapor  $P$  to the pressure of saturated vapor,  $S = P/P_{sat}$ ;  $P_{sat} = A \exp(-B/T)$ ,  $A$  and  $B$  are the Antoine constants.

The change in Gibbs free energy at the heterogeneous ion-induced nucleation depends on the electrostatic energy (Green & Lane, 1964; Reist, 1984)

$$\Delta G = \Delta G_0 + \frac{e^2}{2} \left( \frac{1}{\varepsilon} - 1 \right) \left( \frac{1}{r_i} - \frac{1}{r_n} \right), \quad (2)$$

where  $\varepsilon$  is the nucleus dielectric constant;  $r_i$  is the single-charged ion radius.

The nucleation regime at the expense of fluctuations is still valid at the heterogeneous nucleation, i.e. the droplets with the critical radius  $r_{cr}$ , to which the maximum of  $\Delta G(r)$  corresponds, appears. Moreover, smaller equilibrium nuclei with the radius  $r_n$  are formed on the ions. The minimum of  $\Delta G(r)$  corresponds to this nucleus. The equilibrium nucleus cannot grow at small values of supersaturation  $S$ , as their growth results in an increase of Gibbs free energy. There is a necessity for some activation energy  $E_{act} = \Delta G(r_{cr}) - \Delta G(r_n)$  for nucleus growth. The activation energy decreases monotonously as the vapor supersaturation increases (Kuni, Shchekin, & Grinin, 2001).

Classical theory of the heterogeneous ion-induced nucleation, which is based on equations (1) and (2), has been modernized for system saturated by electrons, such as plasma (Vishnyakov et al., 2011, 2013). It was proposed to determine the change in Gibbs free energy in the following form:

$$\Delta G = \Delta G_0 + E_\gamma + E_q + E_{ex}, \quad (3)$$

where  $E_\gamma$  is the change in surface free energy as a result of the electrical double layer on the nucleus surface formation:

$$E_\gamma = -\frac{r_n V_b^2}{2e^2}, \quad (4)$$

$V_b$  is the potential barrier at the nucleus surface;  $E_q$  is the change in Gibbs free energy as a result of the nucleus charging, and for conductor it has following form:

$$E_q = \frac{e^2}{2} \left( \frac{1 + Z_n^2}{r_n} - \frac{1}{r_i} \right), \quad (5)$$

$Z_n$  is the nucleus charge number;  $E_{ex}$  is the change in Gibbs free energy as a result of the interphase energy exchange:

$$E_{ex} = -Z_n \left( W_n + \frac{3}{2} k_B T \right). \quad (6)$$

$W_n$  is the electron work function for nucleus, which differs from work function for flat surface (Smirnov, 1997):  $W_n = W + 0.39e^2/r_n$ .

The last equation assumes the balance between transition of electrons from nucleus into the gas and backflow. However, when the basic ionization mechanism is the surface ionization, it is necessary to consider electron transitions between the nucleus and adsorbed atom, i.e. transitions between Fermi level in nucleus and valence electron level in atom. Thus, equation (6) should be replaced by following equation for plasma with intensive surface ionization:

$$E_{ex} = -Z_n (W_n - I). \quad (7)$$

where  $I$  is the potential of atom ionization, and in the system under consideration the predominant component is iron with ionization potential  $I = 7.9$  eV.

### 3. Ionization balance

The vapor-gas mixture contains condensable atoms of welding materials, which also are the ionizable atoms, because alkali metals are absent if GMAW is used. Iron is the predominant component and its total atom number density, without taking into account ionization and condensation, determines by following equation (Vishnyakov, Kiro, Oprya, & Ennan, 2017b):

$$n_{AT} = \frac{P}{k_B T} g_{Fe}, \quad g_{Fe} = \frac{g_{0Fe}}{\mu_{Fe}} \left[ \sum_j \frac{g_{0j}}{\mu_j} + \frac{1}{\mu_{sg}} \frac{T_{vap} - T}{T - T_{sg}} \right]^{-1}, \quad (8)$$

where  $P$  is the atmospheric pressure;  $g_{0Fe}$  is the initial iron mass fraction in vapors;  $g_{0j}$  is the  $j$ th initial component mass fraction;  $\mu_{Fe}$  is the iron molecular mass;  $\mu_j$  is the  $j$ th component molecular mass;  $\mu_{sg}$  is the shielding gas molecular mass;  $T_{vap} = 3000$  K is the initial vapors temperature;  $T_{sg} = 300$  K is the shielding gas temperature; and the temperature time dependence is described by following equation

$$T = T_{sg} + (T_{vap} - T_{sg}) \exp \frac{-t}{\tau_{mix}}, \quad (9)$$

where  $\tau_{mix}$  is the mixing time scale, which is defined experimentally. In the system under consideration  $\tau_{mix} = 1.7$  ms, that has been defined by coincidence of the calculated and measured particles' chemical composition (Vishnyakov, Kiro, Oprya, Chursina, & Ennan, 2018a, Vishnyakov, Kiro, Oprya, and Ennan, 2018b).

The disappearance of iron atoms should be taken into account while nucleation and nucleus growth occurs. The liquid particle of nucleus contains  $N_{an} = 4\pi\rho r_n^3 g_{Fe} / 3m_a$  atoms,  $\rho$  is the nucleus density;  $r_n$  is the average nucleus radius;  $m_a$  is the iron atomic mass. Thus, it is necessary to subtract  $n_n N_{an}$  from the total number density  $n_{AT}$  for determination of the available for ionization atom number density:

$$n_a = g_{Fe} \left( \frac{P}{k_B T} - \frac{4\pi\rho r_n^3 n_n}{3m_a} \right), \quad (10)$$

where  $n_n$  is the nucleus number density.

Ionization equilibrium in the thermal plasma is determined by the atoms' impact ionization and electron-ion recombination, and is described by well-known Saha equation (Mitchner & Kruger, 1973):

$$\frac{n_e n_i}{n_a} = \frac{\sum_i \nu_e}{\sum_a} \nu_e \exp \frac{-I}{k_B T} \equiv K_S, \quad (11)$$

where  $n_e$ ,  $n_i$  and  $n_a$  are the average for local thermodynamic equilibrium (LTE) region number densities of electrons, ions and ionizable atoms, respectively;  $n_a = n_A - n_i$ ,  $n_A$  is the available for ionization atom number density (10);  $\sum_i$  and  $\sum_a$  are the ion and atom statistical weights;  $\nu_e = 2(m_e k_B T / 2\pi\hbar^2)^{3/2}$  is the effective density of the electron states;  $m_e$  is the electron mass;  $\hbar$  is the Planck constant;  $K_S$  is the Saha constant.

The welding fume plasma is affected by UV-radiation from electric arc and photoionization should be considered. However in paper by Vishnyakov et al. (2019) it was demonstrated, that the influence of ionization by UV-radiation from arc can be neglected at the plasma temperature  $T > 2000$  K. The photon flux from arc with energy higher than atom ionization potential ( $h\nu \geq 7.9$  eV for iron) is  $j_{ph} \sim 10^{16} \text{cm}^{-2} \text{s}^{-1}$  and it provides the photoionization time constant  $\sim 0.1$  s. The volume collision ionization time constant is  $\sim 0.5 \mu\text{s}$  at the temperature 3000 K. Nucleation occurs at the temperature  $T \sim 2750$  K. Thus, ionization balance in the mixing zone (before nucleation, at the temperature range 2700 – 3000 K) is well described by Saha equation (11) with neglected photoionization. The neutrality equation in this case is  $n_e = n_i = n_0$ , where  $n_0$  is the unperturbed number density.

When nucleation starts, equilibrium nucleus number density is determined by following equation (Vishnyakov, Kiro, & Ennan, 2013)

$$n_n = \frac{n_{AT} - n_i}{N_{an} + N_{an}^{-3/2} \exp \frac{\Delta G(r_n)}{k_B T}}, \quad (12)$$

where  $\Delta G(r_n)$  is the change in Gibbs free energy under formation of equilibrium nucleus with radius  $r_n$ .

In the welding fume from GMAW equilibrium nucleus number density  $n_n \sim 10^{16} \text{cm}^{-3}$  (radius of equilibrium nucleus  $r_n \sim 0.3$  nm), that is much greater equilibrium (Saha) electron and ion number densities, which are  $\sim 10^{13} \text{cm}^{-3}$  at the temperature of 2750 K. Because ions are the centers of ion-induced nucleation, they disappear from gas phase under nucleation and electron-ion recombination is replaced by the neutralization of nuclei, which have initial positive charge. As a result, the balance between ionization and recombination is broken in favor of ionization, and new electrons and ions appear in the plasma via impact atom ionization, until electrons are being captured by nuclei. Therefore, achievement of equilibrium nucleus number is the time-phased process, which includes additional atom ionization and formation of additional nuclei until equilibrium will be reached. Neutrality equation is

$$n_e - n_i = Z_n n_n, \quad (13)$$

where  $Z_n$  is the average nucleus charge number.

The appearance of nuclei creates a new ionization-recombination channel. Atom ionization and ion recombination occurs via interaction with nucleus surface. Surface atom ionization degree is described by well-known Saha-Langmuir equation (Dressler, 1968)

$$\alpha_s = \frac{n_{is}}{n_{as}} = \frac{\sum_i W_i - I}{\sum_a} \exp \frac{W_n - I}{T}, \quad (14)$$

where  $n_{is}$  is the ion number density on the nucleus surface;  $n_{as}$  is the atom number density as a result of ionization on the nucleus surface.

The rate of atom surface ionization is determined by collisions between ionizable atoms and nuclei and the ion desorption from nucleus surface (Vishnyakov, 2007):

$$Q_s^{ion} = n_n n_a v_{Ta} \pi r_n^2 \frac{\alpha_s}{1 + \alpha_s} \exp \frac{V_b}{k_B T}, \quad (15)$$

where  $v_{Ta} = \sqrt{8k_B T / \pi m_a}$  is the atom thermal velocity. Here it is taken into account that ion should overcome potential barrier  $V_b$  for desorption, and in Coulomb approach  $V_b = eZ_n / r_n$ .

The rate of ion surface recombination is determined by collisions between ions and nuclei:

$$Q_s^{rec} = n_n n_i v_{Ti} \sigma_{in} \frac{1}{1 + \alpha_s}, \quad (16)$$

where  $v_{Ti} \cong v_{Ta}$  is the ion thermal velocity;  $\sigma_{in}$  is the ion-nucleus collision cross section:  $\sigma_{in} = \pi r_n^2 (1 - V_b / k_B T)$  (Fortov et al., 2004). Here collisionless approach is used, because ion mean free path is greater than screening length and nucleus size.

The nucleus surface also provides the electron emission and electron adsorption. Thermionic emission is determined by Richardson equation

$$j_e^T = \frac{4\pi m_e (k_B T)^2}{(2\pi\hbar)^3} \exp \frac{-W_n}{k_B T},$$

and thermionic emission rate is

$$Q_e^T = \pi r_n^2 n_n v_{Te} \exp \frac{-W_n}{k_B T}, \quad (17)$$

where  $v_{Te} = \sqrt{8k_B T / \pi m_e}$  is the electron thermal velocity.

The electron photoemission rate is

$$Q_e^{ph} = \pi r_n^2 n_n j_{ph} Y_n, \quad (18)$$

where  $j_{ph} \sim 10^{16} \text{cm}^{-2} \text{s}^{-1}$  is the flux of photons with energy  $h\nu > 7.9 \text{eV}$  (Vishnyakov et al., 2019);  $Y_n$  is the quantum yield, which usually is  $Y_n \sim 0.1$ .

The rate of electron adsorption by nuclei via sporadic collisions is

$$Q_e^{ads} = n_n n_e v_{Te} \sigma_{en}, \quad (19)$$

where  $\sigma_{en}$  is the electron-nucleus collision cross section:  $\sigma_{en} = \pi r_n^2 \exp(V_b / k_B T)$  (Fortov et al., 2004).

The volume collision ionization rate is

$$Q_V^{ion} = n_e n_a k_{ion}, \quad (20)$$

where  $k_{ion} = \pi r_a^2 v_{Te}$  is the ionization rate constant (Mitchner & Kruger, 1973),  $r_a$  is the atom radius.

Electron-ion collision recombination usually occurs as a three-body interaction, when two electrons collide near ion, and one of them loses the kinetic energy and is captured by ion. Three-body recombination rate is described as

$$Q_V^{rec} = n_e^2 n_i k_{rec}, \quad (21)$$

where  $k_{rec} = k_{ion} / K_S$  is the recombination rate constant.

The calculated values of the ionization/recombination rates and number densities are presented in Table 1 for thermal plasma at the initial vapor temperature 3000 K without dust component, which exists in the mixing zone, and for dusty plasma in the nucleation zone for temperature of nucleation beginning and for temperature of nucleation termination, when nucleus growth is started. The theoretical model, proposed by Vishnyakov et al. (2018a,b), was used for calculation.

The surface ionization/recombination rates are much greater than others, therefore, average ion number density can be calculated from the balance  $Q_s^{ion} = Q_s^{rec}$ :

$$n_i = \frac{n_a \alpha_s}{\left(1 - \frac{V_b}{k_B T}\right) \exp \frac{-V_b}{k_B T} + \alpha_s}, \quad (22)$$

and if  $V_b = 0$ ,  $n_i = n_{is}$ .

Balance of the others rates

$$Q_e^T + Q_e^{ph} + Q_V^{ion} = Q_e^{ads} + Q_V^{rec}$$

allows to calculate the average electron number density:

**Table 1**  
Ionization/recombination rates.

	Mixing start	Nucleation start	Nucleation end
$T$ (K)	3000	2760	2680
$Q_s^{ion}$ (cm <sup>-3</sup> s <sup>-1</sup> )	–	$3.9 \times 10^{23}$	$3.3 \times 10^{22}$
$Q_s^{rec}$ (cm <sup>-3</sup> s <sup>-1</sup> )	–	$3.9 \times 10^{23}$	$3.3 \times 10^{22}$
$Q_e^T$ (cm <sup>-3</sup> s <sup>-1</sup> )	–	$2.8 \times 10^{19}$	$6.8 \times 10^{19}$
$Q_e^{ph}$ (cm <sup>-3</sup> s <sup>-1</sup> )	–	$2.2 \times 10^{18}$	$1.6 \times 10^{18}$
$Q_e^{ads}$ (cm <sup>-3</sup> s <sup>-1</sup> )	–	$1.4 \times 10^{19}$	$2.9 \times 10^{19}$
$Q_i^{ion}$ (cm <sup>-3</sup> s <sup>-1</sup> )	$1.1 \times 10^{24}$	$3.0 \times 10^{17}$	$7.1 \times 10^{15}$
$Q_i^{rec}$ (cm <sup>-3</sup> s <sup>-1</sup> )	$1.1 \times 10^{24}$	$1.7 \times 10^{19}$	$4.1 \times 10^{19}$
$n_n$ (cm <sup>-3</sup> )	–	$3.4 \times 10^{17}$	$1.4 \times 10^{17}$
$n_A$ (cm <sup>-3</sup> )	$2.4 \times 10^{18}$	$1.2 \times 10^{16}$	$1.1 \times 10^{14}$
$n_e$ (cm <sup>-3</sup> )	$1.4 \times 10^{13}$	$8.4 \times 10^8$	$2.0 \times 10^9$
$n_i$ (cm <sup>-3</sup> )	$1.4 \times 10^{13}$	$4.3 \times 10^{15}$	$1.0 \times 10^{14}$
$r_n$ (nm)	–	0.25	0.33

$$n_e = \frac{K_S n_a r_a^2 - n_n r_n^2 \exp \frac{V_b}{k_B T}}{2 n_i r_a^2} \left[ 1 \pm \sqrt{1 + \frac{4 n_n r_n^2 n_i r_a^2 \left( \nu_e \exp \frac{-W}{k_B T} + \frac{J_{ph} \nu_n}{v_{Te}} \right)}{K_S \left( n_a r_a^2 - n_n r_n^2 \exp \frac{V_b}{k_B T} \right)^2}} \right], \quad (23)$$

where the minus sign should be used for the large number of nuclei, when the most part of atoms has transferred into liquid phase and  $n_a r_a^2 < n_n r_n^2$ .

Equations (22) and (23) are closed by neutrality equation (13). Calculation is based on the numerical modeling of the primary particles formation (Vishnyakov et al., 2018a,b). The subject of modeling is a single gas parcel of vapor-gas mixture, evolution of which under cooling based on initial temperature and vapor chemical composition is calculated.

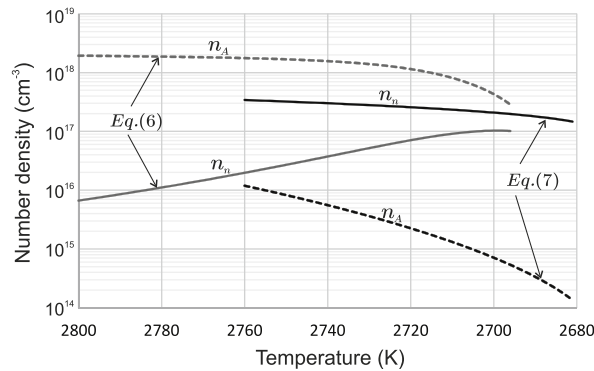
#### 4. Discussion

Calculations demonstrate, that for the initial vapor temperature  $T_{vap} = 3000$  K and content of iron in vapors  $g_{0Fe} = 0.97$ , nucleation is started at the temperature  $T = 2760$  K. The equilibrium nucleus radius corresponds to the minimum of the function  $\Delta G(r)$  (3) and is equal  $r_n = 0.25$  nm, nucleus number density (12)  $n_n = 3.4 \times 10^{17}$  cm<sup>-3</sup>, ion number density (22)  $n_i = 4.3 \times 10^{15}$  cm<sup>-3</sup>, electron number density (23)  $n_e = 8.4 \times 10^8$  cm<sup>-3</sup> and Saha unperturbed number density  $n_0 = 3.2 \times 10^{12}$  cm<sup>-3</sup>.

Investigation of Poisson-Boltzmann equation (Vishnyakov, Dragan, & Evtuhov, 2007) demonstrates that unperturbed number density can be determined as  $n_0^* = \sqrt{n_e n_i}$ , which is equal to Saha value  $n_0$  in the plasma without dust. In the system under consideration  $n_0^* = 1.9 \times 10^{12}$  cm<sup>-3</sup>  $< n_0$ , that testifies about change of ionization mechanism.

Main feature of the welding fume plasma in GMAW is the fact that same atoms are both a source of ionization and a source of nucleation. Therefore, nucleation leads to decrease of the ionizable atoms' number (10) and ionization causes decrease of the condensable atoms' number ( $n_A - n_i$ ). Both processes cause essential decrease of the iron atom number density in the gas phase, which, in turn, leads to decrease of the nucleus number density in the cooling vapor-gas mixture.

The dependencies of nucleus number density on the temperature are presented in Fig. 1 for two variants of calculation: (i) when equation (6) for electron exchange between nucleus and gas is used in  $\Delta G(r_n)$ , which is incorrect in the system under consideration (it



**Fig. 1.** Dependencies on the temperature of nucleus number density  $n_n$  (solid) and ionizable atom number density  $n_A$  (dotted) under using in Gibbs free energy Eq. (6) (grey) and Eq. (7) (black).

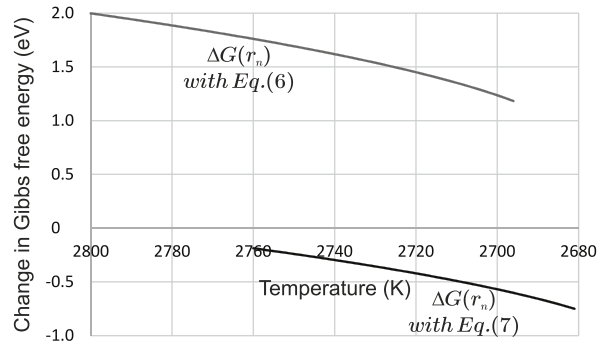


Fig. 2. Dependencies of change in Gibbs free energy on the temperature under using Eq. (6) (grey) and Eq. (7) (black).

is correct only for the first nuclei appearance, when Saha equation determines the ionization), and (ii) when equation (7) is used in Gibbs free energy.

In the first case nucleation begins at the temperature 2800 K and nucleus number density grows when the vapor-gas mixture cools. Simultaneous increase of nucleus radius leads to strong increase of iron content in the liquid phase. As a result, iron content in the gas phase is decreased and growth of nucleus number density is stopped at the temperature 2710 K. Nucleation termination occurs at the temperature 2695 K. Duration of this process  $\Delta t = 80 \mu\text{s}$  under mixing time scale  $\tau_{\text{mix}} = 1.7 \text{ ms}$ .

In the second case nucleation begins at the temperature 2760 K and already first nuclei consume large number of iron atoms. Therefore, iron content in the gas phase is decreased already at the nucleation start. The further cooling of system leads to decreasing both the number of atoms and the number of nuclei. Duration of nucleation in this case  $\Delta t = 56 \mu\text{s}$ .

The tendencies of  $\Delta G(r_n)$  under mixture cooling is identical in both cases, as it follows from Fig. 2. Such tendencies should lead to growth of nucleus number density, as it follows from equation (12). However, initial low value of  $\Delta G(r_n)$  in the second case (when (7) is used) leads to so large number of nuclei, that content of iron atoms in the gas phase is slumped and tendency  $\Delta G(r_n)$  is changed.

A simplified model has been considered above. In the real systems large nucleus number density causes their intensive collisions due to Brownian motion and coalescence, as they occur in the liquid state (Vishnyakov, Kiro, & Ennan, 2014). The system thermodynamics requires the presence of the nuclei with equilibrium number density (10). When two nuclei collide and form a new particle, the new nuclei should appear via nucleation. Thus, the nucleation is the pump for transfer of the condensable atoms from the gas phase into coagulated particles. Therefore, condensable material decreases even more promptly in the real systems. Duration of nucleation in this case  $\sim 20 \mu\text{s}$ .

## 5. Conclusion

Formation of the welding fume in GMAW is characterized by the burst of nucleation, because absence of the easy-ionizable additional agent forces the iron atoms to execute both functions: a source of ionization and a source of nucleation. As a result, the condensable material promptly comes to an end. Duration of nucleation, without taking into account nucleus coagulation, is  $\sim 60 \mu\text{s}$ . Consideration of the nucleus coagulation (Vishnyakov et al., 2014) reduces duration of nucleation down to  $20 \mu\text{s}$ , because appearance of the coagulated droplets causes the intensifying of nucleation as it the system thermodynamics requires.

When the first nuclei are formed, their large number causes the capturing of electrons and leads to change of ionization mechanism. Initial thermal ionization is replaced by ionization via nuclei surface. Accordingly, the energy exchange term in Gibbs free energy is also replaced: the electron transition between nucleus Fermi level and valence electron level of the adsorbed atom should be used instead of transition between nucleus and gas.

Surface atom ionization and ion recombination provide increase of ion number density, though average number density of charge carriers is decreased, because  $\sqrt{n_e n_i} < n_0$ . Thus, welding fume plasma in GMAW consist mainly of positive ions and nuclei with average negative charge.

The addition of alkali metal in the shielding gas leads to decrease of the fume formation rate (Vishnyakov et al., 2017a), because ionization mechanism remains without change. This fact is important for decrease in toxically hazard, when GMAW is used.

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