Journal of Aerosol Science 58 (2013) 9-16

Contents lists available at SciVerse ScienceDirect

Journal of Aerosol Science

journal homepage: www.elsevier.com/locate/jaerosci



Formation of primary particles in welding fume

V.I. Vishnyakov*, S.A. Kiro, A.A. Ennan

Physical-Chemical Institute for Environmental and Human Protection, National Academy of Sciences of Ukraine, 3 Preobrazhenskaya, Odessa 65082, Ukraine

ARTICLE INFO

Article history: Received 31 July 2012 Received in revised form 12 December 2012 Accepted 12 December 2012 Available online 19 December 2012

Keywords: Welding fume Thermal dusty plasma Nucleation Primary particles Particles' growth

ABSTRACT

The formation of primary particles in the welding fume with regard to gas phase ionization is studied. It is shown that the classical theory is applicable only to the initial moment of condensation of the metals' vapors. The fast coagulation of nuclei leads to the formation of droplets which can unrestrictedly grow and get charged. The subsequent nucleation and growth of the primary particles take place in the charged gas environment with the intensive interphase exchange of the charges and energy. It is shown that the increase of the coagulated droplets' charge leads to the shift of the nucleation in the high-temperature range and to the increase of the primary particles sizes.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Arc welding is a widespread technological processes in modern manufacturing, but there are deficiencies such as formation of aero-disperse toxic particles of the so-called welding fume. Therefore, studying of the welding fume formation is necessary to minimize the harm superimposed by the welding process.

The source of welding fume is the vapor, formed mainly by evaporation of welding materials. A vapor phase condensation, formation of primary particles, their growth and coagulation are the result of scattering of the multicomponent vapor-gaseous mixture from the high-temperature zone of arc discharge into the environment with the lower temperature. So, the fume generation rate, size distribution and the chemical composition of the primary particles are the key processes that determine the harmful environmental impact of the welding fume (Pokhodnya et al., 2011). Many authors investigated the quantitative relationship between these processes, the welding conditions and the composition of the welding materials, for example: Voitkevich (1995), Zimmer & Biswas (2001), Jenkins & Eagar (2005), Jenkins et al. (2005), Sowards et al. (2008), Oprya et al. (2012), and Worobec et al. (2007). However, the problem is far from being solved because of the complexity of the experimental study of the welding fume (Jenkins et al., 2005). The available for study inhalable particles are the agglomerates of primary particles or the coarse fume particles (Sowards et al., 2008). The experimental study of the molecular and phase composition of the fume formed by the shielded metal arc welding demonstrated that the inhalable particles contain more than five phases (molecular groups) (Sowards et al., 2008; Voitkevich, 1995). Meanwhile the primary particles with the size less than 50 nm cannot contain several phases because they are formed during fast condensation. If agglomerates contain more than one phase, it means the presence of different



^{*} corresponding author. Tel.: +38 487237528; fax: +38 487231116.

E-mail addresses: drvishnyakov@mail.ru, eksvar@ukr.net (V.I. Vishnyakov).

kinds of primary particles. Thus, there can be varies between the chemical composition of the primary particles depending on their sizes, but they are not registered by experiment because of the averaging of many particles in the agglomerate (Oprya et al., 2012). Besides, the primary particles and their agglomerates can have very different physicochemical properties and biological influence than their macroscopic analogues. For example, the increase of the chemical potential at the interphase boundary of high curvature changes the miscibility, sorption capacity, reactionary and catalytic abilities of the particles (Holsapple et al., 2005). As the primary particles determine the resultant fume, investigations allowing the study the primary particles formation have a large applied importance.

It is necessary to consider that the primary particles are formed in the thermal dusty plasma, i.e. there is interphase exchange of the energy and charges. In papers by Vishnyakov (2008), Vishnyakov et al. (2011) was proposed a theoretical model of the nucleation in the dusty plasma, and in presented paper this theory develops by considering the nuclei growth in the ionized environment and taking into account the interaction of the welding fume with the ultra-violet radiation of the arc.

2. Nucleation environment

The welding fume forming zone, where the nucleation occurs, is the ionized vapor–gas mixture and the interphase interaction strongly influences the nuclei sizes. Therefore, before describing nucleation, it is necessary to determine the parameters of the environment which influence this process. The formation of a new phase strongly depends on the emission and absorption of electrons by the nucleus, i.e. it charging (Vishnyakov et al., 2011). In order to describe this process we will use the results of Vishnyakov (2012), in which it is necessary to take into account the external photoelectric effect.

The electron number density in the dusty plasma should satisfy to the neutrality equation

$$n_e = Zn_p + n_i,\tag{1}$$

where *Z* is the average charge number (the particle charge in the elementary charges); n_e and n_i are the average electron and ion number densities, respectively; n_p is the average particle number density in the nucleation zone. In the nucleation zone there is feeble dilution of metal vapors by air, therefore the gas temperature usually not lower than 2000 K, the vapor supersaturation $S = P/P_{sat} \sim 1-10$ (*P* is the vapor pressure, P_{sat} is the pressure of the saturated vapor).

The particles charging in the complex plasma (containing particles, electrons and ions) is described by Vishnyakov (2012) as the development of the theory of the neutralized charges, which has been created for the dust-electron plasma, i.e. a system consisting of the charged particles and the electrons emitted by these particles only (Vishnyakov & Dragon, 2006). According to this theory most of the electrons in the plasma volume are distributed uniformly with some unperturbed number density n_{e0} . The displacement of the electron number density from the unperturbed value is observed only in the thin layer near the particles surface. The unperturbed electrons and some part of the particle charges $Z_0 = n_{e0}/n_p$ neutralize each other and create the neutralized background which determines the bulk plasma potential φ_0 . Thus, the charge of any particle is composed of two parts $Z_j = \tilde{Z}_j + Z_0$, and only the relative part of the total charge \tilde{Z}_j determines the interaction between the particles and forms the potential barrier U_b on the plasma-particle boundary with respect to the level of the neutralized background $e\varphi_0$.

In the complex plasma, the unperturbed ion number density n_{i0} has been entered along with the unperturbed electron density. In that case, the charge of the neutralized background is $Z_0 = (n_{e0} - n_{i0})/n_p$. The particles charge influences the ionization balance in gas, therefore the nonequilibrium ions and electrons appear near the surface of the particles (Vishnyakov, 2005, 2006). The nonequilibrium ionization around the charged particles leads to the uniform spatial distribution of ions, i.e. the ion unperturbed density is equal to the average value $n_{i0} = n_i$. Therefore, in the complex plasma,

$$Z_0 = \frac{n_{e0} - n_i}{n_p},$$
 (2)

and as follows from Eqs. (1) and (2), the average value of the relative charge determines by the difference between the average and the unperturbed electron number density

$$\tilde{Z} = \frac{n_e - n_{e0}}{n_p}.$$
(3)

The particle charge depends on the balance of electron fluxes on its surface. There are the flux of thermionic emission by Richardson–Dushman with the density

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

the flux of photoemission

$$I_e^{pn} = -\pi r_p^2 e Y j_{ph},$$

and the backflow of electrons absorbed by the particle's surface at the expense of their sporadic collisions, with the density

$$j_e^{abs} = \frac{1}{4}en_{es}v_{Te},$$

where *W* is the electronic work function; *T* is the temperature in kelvin; *e* is the elementary charge; m_e is the electronic mass; k_B is the Boltzmann constant; \hbar is the Plank constant; r_p is the particle's radius; *Y* is the quantum yield; j_{ph} is the flux of photons (the power of UV-radiation is $20-25 \text{ W/cm}^2$ at the wave length $\sim 250 \text{ nm}$, which corresponds to $j_{ph} \sim 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ with the photon energy 5 eV); n_{es} is the electron number density near the particle surface; $v_{Te} = \sqrt{8k_BT/\pi m_e}$ is the thermal velocity of electrons.

The equilibrium between the plasma and the particle exists if the sum of the fluxes is equal to zero: $4\pi r_p^2 j_e^T + I_e^{ph} + 4\pi r_p^2 j_e^{abs} = 0$. Consequently, the surface electron number density is

$$n_{es} = v_e \exp \frac{-W}{k_B T} + \frac{Y j_{ph}}{v_{Te}}$$

where $v_e = 2(m_e k_B T/2\pi\hbar^2)^{3/2}$ is the effective density of the electron states.

The ratio of the surface electron number density to the unperturbed electron number density determines the potential barrier on the plasma-particle boundary

$$U_b = k_B T \ln \frac{n_{es}}{n_{e0}} = k_B T \ln \frac{n_{es}}{Z_0 n_p + n_i},$$
(4)

which is linked with the relative charge by the following equation:

$$\tilde{Z} = \frac{\sqrt{2}k_B T r_p}{e^2 sgn(U_b)} \sqrt{\exp\frac{U_b}{k_B T} - \frac{U_b}{k_B T} - 1.}$$
(5)

The relative charge as a function of Z_0 could be defined from Eqs. (4) and (5) as

$$\tilde{Z}(Z_0) = \frac{\sqrt{2}k_B Tr_p}{e^2 \, sgn(U_b)} \sqrt{\frac{n_{es}}{Z_0 n_p + n_i}} - \ln \frac{n_{es}}{Z_0 n_p + n_i} - 1.$$
(6)

The bulk plasma potential (the potential of the background) is a correction factor to the chemical potential of electrons; therefore the average electron number density is linked to the unperturbed value by the following equation (Vishnyakov, 2012):

$$n_e = n_{e0} \exp \frac{e\varphi_0}{k_B T}$$

then, from Eq. (3) its follows that average value of the particle relative charge in the fume is

$$\tilde{Z} = \frac{n_{e0}}{n_p} \left(\exp \frac{e\varphi_0}{k_B T} - 1 \right).$$
(7)

The bulk plasma potential is defined by the neutralized charge (Vishnyakov, 2012)

$$\varphi_0 = \frac{3e}{2n_p} (Z_0^2 n_p^{4/3} - n_e^{4/3} + n_i^{4/3}),$$

therefore, the relative charge is defined as a function of Z_0 from Eqs. (2) and (7) in the following form:

$$\tilde{Z}(Z_0) = \frac{Z_0 n_p + n_i}{n_p} \left\{ \exp\left[\frac{3e^2}{2k_B T n_p} (Z_0^2 n_p^{4/3} - (Z_0 n_p + n_i)^{4/3} + n_i^{4/3})\right] - 1 \right\}.$$
(8)

Having calculate Z_0 by Eqs. (6) and (8) it is easy to define other parameters of the environment, such as the electron number density, the particles charge, the bulk plasma potential and the surface potential barrier.

The ion number density in the thermal plasma is defined by the Saha equation (Landau & Lifshitz, 1976):

$$\frac{n_e n_i}{n_a} = \frac{\sum_i}{\sum_a} v_e \exp \frac{-I}{k_B T} = K_S,$$

where $n_a = n_A - n_i$ is the atom number density as a result of ionization; n_A is the initial atom number density; Σ_i and Σ_a are the statistical weights of the ions and atoms, respectively; I is the potential of atom ionization; K_S is the Saha constant.

The existence of UV-ionization (the photon energy of 5 eV is sufficient for ionization of the alkali metal atoms) can be taken into account by the continuity equation in the following form:

$$\frac{\partial n_{e(i)}}{\partial t} + di\nu \,\mathbf{j}_{e(i)} = \pi r_a^2 n_a j_{ph} + k_{ion} n_e n_a - \beta_{ei} n_e n_i = 0,$$

where r_a is the atom radius; k_{ion} is the factor of thermal ionization; $\beta_{ei} \sim 10^{-6}$ cm³/s is the factor of electron-ion recombination (Pal' et al., 2001).

In absence of UV-radiation, $j_{ph} = 0$ and $k_{ion}n_e/\beta_{ei} = K_S$. From here follows:

$$\frac{n_e n_i}{n_a} = K_S + \frac{\pi r_a^2 j_{ph}}{\beta_{ei}}.$$
(9)

For potassium and sodium, contained in the vapor–gas mixtures, it is necessary to solve Eq. (9) separately, and then summarize the calculated number densities.

The interaction of the welding fume with the UV-radiation leads to the formation of the additional electrons, and UV-radiation influence the ionization of alkali atoms more than the photoemission from the particles' surface. As the result, the flux of additional electrons to the particle exceeds the photoemission flux from the particle. In the dust-electron plasma, the particles are charged positively, therefore $Z_0 > 0$. However, the high ionization degree of the alkali atoms, whose number density usually reaches $n_A \sim 10^{16} - 10^{17}$ cm⁻³ in the vapor–gas mixtures, can change the situation at the expense of increased electron backflow to the particle. The potential barrier should accept the negative value for the neutralization of this backflow. Thus, $Z_0 \rightarrow 0$, $\tilde{Z} < 0$, i.e. the particles can carry the negative charge and $n_e < n_{e0}$, because some part of electrons are absorbed by negative charged particles.

3. Nucleation

The welding fume formation is the result of heterogeneous ion-induced nucleation in the environment reached by the electrons. Thus, there is an exchange of energy and charges between the nucleus and the environment. Therefore, the classical nucleation theory (Green & Lane, 1964; Reist, 1984; Vehkamaki, 2006) requires update. The modernization of classical theory by Vishnyakov et al. (2011) defined the change in Gibbs free energy as a result of nucleation in the following form:

$$\Delta G = 4\pi r_n^2 \gamma - \frac{4}{3}\pi r_n^3 \frac{\rho k_B T \ln(S)}{m_{ca}} + E_{\gamma} + E_{ex} + E_q, \tag{10}$$

where r_n is the nucleus radius; $\gamma = \gamma_0 r_n/(r_n + 2\delta)$ is the surface free energy of the nucleus; γ_0 is the surface free energy of the flat; δ is the Tolmen length (Bahadur & Russel, 2008); m_{ca} is the mass of the condensable atoms; ρ is the nucleus density; S is the supersaturation of the condensable vapor.

In Eq. (10) the first two terms describes the change in Gibbs free energy defined by the classical nucleation theory (Reist, 1984). The term E_{γ} is the change in surface free energy as a result of formation of the double layer on the nucleus surface

$$E_{\gamma} = -Z_0 U_b - \frac{2\sqrt{2}(k_B T)^2 r_n}{3e^2} \left(\exp \frac{U_b}{k_B T} - \frac{U_b}{k_B T} - 1 \right)^{3/2},\tag{11}$$

 E_{ex} is the change in Gibbs free energy as a result of the interphase energy exchange

$$E_{ex} = -Z_n \left(W_n + \frac{3}{2} k_B T \right), \tag{12}$$

 E_q is the change in Gibbs free energy as a result of the nucleus charging; it has a different definition for the conductor and dielectric:

$$E_{qm} = \frac{e^2}{2} \left[\frac{Z_n^2}{r_n} + \frac{1}{r_n} - \frac{1}{r_i} \right] \quad -\text{for conductor,} \tag{13}$$

$$E_{qd} = \frac{e^2(\varepsilon - 1)}{2\varepsilon} \left[\frac{6}{5} \frac{Z_n^2}{(\varepsilon - 1)r_n} + \frac{1}{r_n} - \frac{1}{r_i} \right] \quad -\text{for dielectric,}$$
(14)

where ε is the dielectric constant; r_i is the radius of the single-charged positive ion, which induces the nucleation.

The two kinds of nuclei are formed by the heterogeneous ion-induced nucleation: the equilibrium nuclei with radius r_{eq} , which are in the equilibrium state with the environment; and the nonequilibrium critical nuclei with radius $r_{cr} > r_{eq}$, which appear as the result of the fluctuations. The radius of the equilibrium nucleus is defined as a minimum of the function $\Delta G(r_n)$

$$\left(\frac{\partial \Delta G}{\partial r_n}\right)_{eq} = 0 \quad \left(\frac{\partial^2 \Delta G}{\partial r_n^2}\right)_{eq} > 0,\tag{15}$$

the radius of the critical nucleus is defined as the maximum of the function $\Delta G(r_n)$

$$\left(\frac{\partial \Delta G}{\partial r_n}\right)_{cr} = 0 \quad \left(\frac{\partial^2 \Delta G}{\partial r_n^2}\right)_{cr} < 0.$$
(16)

The equilibrium nucleus is in the stable state and some activation energy is necessary for the nucleus growth $U_{act} = \Delta G(r_{cr}) - \Delta G(r_{eq})$. This activation energy decreases down to zero ($U_{act} \rightarrow 0$) with the cooling of the gas–vapor mixture, thus the equilibrium and the critical radii tend to equal values ($r_{cr} \rightarrow r_{eq}$). After that, the unrestricted growth of nuclei begins, while the condensable material does not deplete.

The number density of the equilibrium nuclei is defined by the thermodynamics balance between the subsystem of the condensable atoms and the subsystem of the nuclei that are equal

$$\mu_n = \mu_{ca},\tag{17}$$

where $\mu_n = G_n/N_n$ is the chemical potential of the nuclei subsystem; G_n is the Gibbs free energy of this subsystem; N_n is the number of nuclei; $\mu_{ca} = G_{ca}/N_{ca}$ is the chemical potential of the condensable atoms subsystem; G_{ca} is the Gibbs free energy of this subsystem; N_{ca} is the number of condensable atoms.

The Gibbs free energy of the subsystem of condensable atoms within the limits of ideal-gas approximation is Kittel (1969)

$$G_{ca} = N_{ca}k_BT \ln \frac{N_{ca}V_q}{V} = N_{ca}k_BT \ln \frac{n_{ca}}{v_{ca}},$$
(18)

where n_{ca} is the atom number density; $V_q = (2\pi\hbar^2/m_{ca}k_BT)^{3/2}$ is their quantum volume; $v_{ca} = 1/V_q$ is their effective density of states; *V* is the system volume.

Accordingly, the Gibbs free energy of the nuclei subsystem is

$$G_n = N_n k_B T \ln \frac{n_n}{v_n} + N_n \,\Delta G(r_{eq}),\tag{19}$$

where n_n is the nuclei number density; $v_n = (m_n k_B T/2\pi\hbar^2)^{3/2}$ is their effective density of states; ΔG is the change in Gibbs free energy for formation a nucleus Eq. (10). It is obvious, that the nucleus mass is defined by mass of contained atoms $m_n = N_{an}m_{ca}$, hence, $v_n = N_{an}^{3/2}v_{ca}$, where $N_{an} = 4\pi\rho r_n^3/3m_{ca}$ is the number of atoms in one nucleus.

Prior to the nucleation start all the condensable material was in the gaseous state with the atom number density n_{a0} . At nucleation, some part of atoms pass into the nuclei; therefore, the atom number density decreases $n_{ca} = n_{a0} - N_{an}n_n$. Then, from Eqs. (17)–(19) follows:

$$n_n = \frac{n_{a0}}{N_{an} + N_{an}^{-3/2} \exp \frac{\Delta G(r_{eq})}{k_B T}},$$
(20)

but the number of nuclei is restricted by the number of inducing ions.

4. Formation of primary particles

The nucleation will be considered in the example of welding fume formed by the shielded metal arc welding using the standard mild steel electrode with rutile coating (Oprya et al., 2012). Besides the manganese and silicon vapors, the vaporgas mixture contains the alkali metals and iron with the portions: $g_K = 0.06$, $g_{Na} = 0.03$, $g_{Fe} = 0.36$. When the vapors stream from the arc zone mixes with the air, the partial pressures of the condensable vapors P_i in the vapor-gas mixture and their supersaturations $S_i = P_i/P_{i,sat}$ can be calculated from the temperature and the vapor composition

$$P_i = \frac{\delta m_i/\mu_i}{\delta m_0/\mu_0 + \delta m_{air}/\mu_{air}} P,$$
(21)

where $\delta m_i = g_i \delta m_0$ is the flow rate of the *i*th component; $\delta m_0 = 10^{-2}$ g/s is the mass flow rate of the vapors stream from the arc zone; μ_i is the atom mass of the *i*th component; μ_0 is the effective atom mass of the vapors stream:

$$\mu_0 = \left(\sum_i \frac{g_i}{\mu_i}\right)^{-1} = 26 \text{ g/mol,}$$

 μ_{air} is the air molecular mass; $P = 1.01 \times 10^5$ Pa is the atmospheric pressure; δm_{air} is the mass rate of entrainment of the air by the vapor stream, which is defined by the current temperature of the vapor–gas mixture *T*, the temperature of environment $T_{\infty} \sim 300$ K and the temperature of the vapors stream from the arc zone $T_0 \sim 3000$ K

$$\delta m_{air} = \frac{T_0 - T}{T - T_\infty} \delta m_0. \tag{22}$$

At the initial moment of nucleation the environment contains only the particles of disintegration of the welding materials that are neglected. The neutralized charge $Z_0 = 0$, the average relative nuclei charge $\tilde{Z} \sim -0.1$ (disregarding the ion charge), i.e. only one nucleus out of ten has the charge 1*e*; and the whole system can be considered neutral. Such a situation well describes by the classical theory.

4.1. Neutral environment

The results of calculations of the nucleation of iron (the basic component of welding fume) in such environment with taking into account the typical temperature range rate $dT/dt \sim 1 \text{ K/}\mu\text{s}$ are shown in Fig. 1.

The equilibrium nuclei formation begins at the temperature of vapor–gas mixture of T = 2340 K (t = 0) and at the temperature of 2135 K ($t = 205 \mu$ s) the activation energy of growth tend to zero and the unrestricted growth of nuclei begins.



Fig. 1. Time dependencies of the supersaturation *S*, the equilibrium nuclei radius r_{eq} , the primary particles radius r_p and the number density of condensable atoms n_{ca} at the nucleation and growth of particles in the neutral environment.

The growth of nuclei, already the primary particles, is defined by the increment of the mass at the account of the difference of the absorption and transpiration fluxes (Fuchs, 1964)

$$\frac{dm_p}{dt} = \pi r_p^2 \alpha_c \nu_{Ta} m_{ca} (n_{ca} - n_{cs})$$

where α_c is the condensation factor; $v_{Tc} = \sqrt{8k_BT/\pi m_{ca}}$ is the thermal velocity of the condensable atoms; m_{ca} is their mass; n_{cs} is the number density of the condensable atoms near the particle surface $n_{cs} = n_{ca}S_R/S$; *S* is the current supersaturation; $S_R = P_{sat}(r_p)/P_{sat}(\infty)$ is the change in vapor partial pressure at the account of the surface curvature and exchange interaction as defined by the modernized Kelvin equation with taking into account Eqs. (10)–(13)

$$\ln(S_R) = \frac{m_{ca}}{4\pi\rho k_B T} \left[8\pi\gamma_0 \frac{r_p + 3\delta}{(r_p + 2\delta)^2} - \frac{e^4\tilde{Z}^3}{3k_B T r_p^5} - \frac{\tilde{Z}(W_p + 3k_B T/2)}{r_p^3} - \frac{e^2(1 + Z_0^2 - \tilde{Z}^2)}{2r_p^4} \right].$$
(23)

The change in the primary particle radius as a result of growth is

$$\frac{dr_p}{dt} = \frac{1}{4\pi r_p^2 \rho} \frac{dm_p}{dt} = \frac{\alpha_c \nu_{Ta} m_{ca}}{4\rho} n_{ca} \left(1 - \frac{S_R}{S}\right). \tag{24}$$

The results of calculations of the growth of the primary particles under condition that their charge is determined only by the positive charge of the initiation ion ($\tilde{Z} = Z_0 = 0$), are shown in Fig. 1. The calculation is limited by the melting point of iron (1800 K). Thus, in the terminating point of calculation, the number of iron atoms is much less than the number of primary particles $n_{ca}/n_p \sim 0.1$; i.e. it is possible to consider that all the iron has transitioned to the condensed phase.

4.2. Charged environment

The major nuclei number density ($\sim 10^{15}$ cm⁻³) causes the intensive Brownian coagulation already at the initial moment of nucleation. Suppose that coagulation occurs only as a result of the pair collisions. Then this process can be described by the Smoluchowski equation (Heilmann, 1992)

$$\frac{\partial n_k}{\partial t} = \frac{1}{2} \sum_{i=1}^{k-i} \beta_{i,k} n_i n_{k-i} - n_k \sum_{i=1}^{\infty} \beta_{i,k} n_i,$$
(25)

where n_k is the number density of the agglomerates containing k primary particles; the kernel of coagulation in the free molecular regime is

$$\beta_{i,k} = \pi (r_i + r_k)^2 \left(\frac{8k_B T}{\pi} \frac{m_i + m_k}{m_i m_k} \right)^{1/2}.$$

The number of fractions limits by the presence of 1 agglomerate in the fraction. Then the calculation produces $n_p^{ag} \sim 10^{12} \text{ cm}^{-3}$ agglomerates with the radius larger than the critical radius ($r_p^{ag} > r_{cr} = 0.6 \text{ nm}$) are formed per 1 µs at the temperature of 2340 K.

It should be noted that the particles are in the liquid phase, therefore the coagulation process leads to the formation of the new droplets that can unrestrictedly grow, having the radius larger than the critical radius. Besides, the agglomerates get charges, accordingly the gas environment also gets a charge as the whole system remains neutral. Thus, further nucleation and growth of the particles occur in the charged environment, and the charge of the neutralized background can change in the range $1 \le Z_0 \le 2$.



Fig. 2. Time dependencies of the particles' average radius at the nucleation and growth in the environments with different neutralized charges.



Fig. 3. Time dependencies of the particles' average relative charge at the nucleation and growth in the environments with different neutralized charges.

The time dependencies of the particles' average radius and their average relative charge \tilde{Z} are shown in Figs. 2 and 3, respectively, for the environments with different charges of the neutralized background. The dependencies correspond to the cooling of the vapor–gas mixture from the temperature of 2650 K down to the iron melting temperature of 1800 K.

The exchange processes causes the increase of the nuclei equilibrium radius; and the growth start earlier than in the neutral environment. Such behavior is caused by the change in Gibbs free energy. As it follows from Eqs. (10) and (12) the change in ΔG by the interphase energy exchange $E_{ex} \sim -Z_0$, that decrease it on a par with supersaturation *S*. The radius of the primary particles is increased when the neutralized charge increases; the absolute value of \tilde{Z} is increased too, because it linearly connected with the particle radius Eq. (5). Such behavior is caused by the decrease of $\ln(S_R) \sim -Z_0^2$ (Eq. (23)) with increasing of the neutralized charge.

5. Conclusion

So, the classical nucleation theory is applicable only at the initial moment of the welding fume formation. Further, the dispersion environment of agglomerates of the equilibrium nuclei is formed, and new environment changes the process of the vapor condensation. This change leads to the increase of the charge of the neutralized background and, accordingly, to initiation of the nucleation under the conditions of small saturation of vapor–gas mixture by iron vapor, i.e. at higher temperature than in the neutral environment.

Thus, the processes of interphase exchange of energy and charges contribute to the nucleation and growth of the primary particles of the welding fume, and influence the displacement of the area of fume formation to the boundary of the inferior zone of arc where the oxidizing of the multi-component vapor–gas mixture can be neglected.

The UV-radiation of arc in the welding fume leads to the decrease of the positive charge of particles or to the increase of the negative charge. Such influence decreases the charge of the neutralized background and, accordingly, decreases the condensed particles radius.

It should be noted also that in such statement of a problem the theory allows to describe the distribution of the primary particles in the sizes at any moment of their nucleation and growth with regard for the interphase exchange processes.

References

Bahadur, R., & Ressell, L.V. (2008). Effect of surface tension from MD simulations on size-dependent deliquescence of NaCl nanoparticles. *Aerosol Science* and Technology, 42, 369–376.

Fuchs, N.A. (1964). Mechanics of Aerosols. Pergamon Press: New York.

Green, H., & Lane, W. (1964). Particulate Clouds: Dusts, Smokes and Mists 2nd ed.). Van Nostrand: New York.

Heilmann, O.J. (1992). Analytical solutions of Smoluchowski's coagulation equation. Journal of Physics A: Mathematical and General, 25, 3763–3771.

Holsapple, M.P., Farland, W.H., Landry, T.D., Monteiro-Riviere, N.A., Carter, J.M., Walker, N.J., & Thomas, K.V. (2005). Research strategies for safety evaluation of nanomaterials, part II: Toxicological and safety evaluation of nanomaterials, current challenges and data needs. *Toxicological Sciences*, 88, 12–17.

Jenkins, N.T., & Eagar, T.W. (2005). Chemical analysis of welding fume particles. Welding Journal, 84 87-s-93-s.

Jenkins, N.T., Pierce, W.M.-G., & Eagar, T.W. (2005). Particle size distribution of gas metal and flux cored arc welding fumes. *Welding Journal*, 84 156-s–163-s. Kittel, Ch. (1969). *Thermal Physics*. Wiley: New York.

Landau, L.D., & Lifshitz, E.M. (1976). Statisticheskaya Fizika Statistical Physics, vol. 1. Nauka: Moscow Translated into English 1980. Pergamon: Oxford. Oprya, M., Kiro, S., Worobiec, A., Horemans, B., Darchuk, L., Novakovic, V., Ennan, A., & Van Grieken, R. (2012). Size distribution and chemical properties of

welding fumes of inhalable particles. Journal of Aerosol Science, 45, 50–57.

Pal', A.F., Starostin, A.N., & Filippov, A.V. (2001). Charging of dust grains in a nuclear-induced plasma at high pressures. *Plasma Physics Reports*, 27(2), 143–152.

Pokhodnya, I.K., Yavdoshchin, I.R., & Gubenya, I.P. (2011). Welding fume—Factors of influence, physical properties. *The Paton Welding Journal*, *6*, 33–35. Reist, P.C. (1984). *Introduction to Aerosol Science*. Macmillan Publishing: New York.

Sowards, J.W., Lippold, J.C., Dickinson, D.W., & Ramirez, A.J. (2008). Characterization of welding fume from SMAW electrodes—Part 1. Welding Journal, 87 106-s-112-s.

Vehkamaki, H. (2006). Classical Nucleation Theory in Multicomponent Systems. Springer: Berlin.

Vishnyakov, V.I. (2005). Interaction of dust grains in strongly collision plasmas: Diffusion pressure of nonequilibrium charge carriers. *Physics of Plasmas*, 12, 103502(1)–103502(6).

Vishnyakov, V.I. (2006). Electron and ion number densities in the space charge layer in thermal plasmas. *Physics of Plasmas*, 13, 033507(1)–033507(4). Vishnyakov, V.I. (2008). Homogeneous nucleation in thermal dust-electron plasmas. *Physical Review E*, 78, 056406(1)–056406(5).

Vishnyakov, V.I. (2012). Charging of dust in thermal collisional plasmas. *Physical Review E*, 85, 026402(1)–026402(6).

Vishnyakov, V.I., & Dragan, G.S. (2006). Thermo-emission (dust-electron) plasmas: Theory of neutralizing charges. *Physical Review E*, 74, 036404(1)-036404(4).

Vishnyakov, V.I., Kiro, S.A., & Ennan, A.A. (2011). Heterogeneous ion-induced nucleation in thermal dusty plasmas. *Journal of Physics D: Applied Physics*, 44, 215201(1)–215201(7).

Voitkevich, V.G. (1995). Welding Fumes Formation, Properties and Biological Effects. Abington Publishing: Cambridge. Worobec, A., Stefaniak, E., Kiro, S., Oprya, M., Bekshaev, A., Spolnik, Z., Potgieter-Vermaak, S.S., Ennan, A., & Van Grieken, R. (2007). Comprehensive

microanalytical study of welding aerosols with X-ray and Raman based method. X-Ray Spectrometry, 36, 328–335.

Zimmer, A.T., & Biswas, P. (2001). Characterization of the aerosols resulting from arc welding processes. Journal of Aerosol Science, 32, 993–1008.