COAGULATION AND DYNAMICS NANOPARTICLES IN LOW PRESSURE PLASMA JETS

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One of the most promising methods for creating nanostructured films is the use of plasma jets of low pressure with nanoparticles. In this case, it is important to control the size of the nanoparticles, their temperature and energy to optimize the properties of the films. In this paper, using computer simulations, a study is conducted on coagulation of nanoparticles in a plasma jet that expands into rarefied gas. In our model, we use a hydrodynamic model for describing the dynamics of a plasma with a multidisperse phase, as well as a sectional method for describing the coagulation of nanoparticles. At the entrance to the plasma torch, the plasma parameters were stationary, and the dust particles were considered the same size. Calculations were made at various concentrations of dust particles in the plasma jet. The simulation results show that nanoparticles of various sizes appear in the plasma stream as a result of coagulation. With increasing distance from the inlet, the average modulus charge and the dispersion of the charge of nanoparticles decreases due to the decrease in the temperature of the ions and, consequently, the ion current on the dust particles.

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INTRODUCTION

Plasma-assisted technologies represent important tools for deposition of nanostructured films on substrates. The growth of thin and ultra-thin films may be achieved using a large variety of techniques such as chemical vapour deposition, RF sputtering, pulsed laser deposition or plasma enhanced chemical vapour deposition [1-3]. Recently, a new process, which uses a plasma torch operating at low pressure has been developed with the aim of depositing uniform thin layers on large surfaces [4, 5]. In this plasma spraying process plasma jets are used as a heat sources to melt and accelerate the injected nanoparticles which subsequently impinge and solidify on a substrate. Modelling the nanoparticles, which create and assemble the film it is possible to enhance the physical properties of thin films. As is known, nanoparticles have the ability to coagulate, resulting in a change in their size. This process can be significant in plasma and it must be taken into account when transporting nanoparticles to a substrate in a plasma jet. It is important to be able to control the size of the nanoparticles, their kinetic energy, the temperature and the magnitude of the flow on the substrate.

The aim of this work is to simulate the dynamics and coagulation of nanoparticles in a plasma jet expanding through a round hole into a dilute gas.

1. MODEL AND SIMULATION METHOD

In this paper, the expansion of an axially symmetric plasma jet with nanoparticles into a rarefied neutral gas is studied. A hydrodynamic model is used to describe a problem that takes into account the processes of coagulation of dust particles. At the initial moment of time, it is assumed that the plasma flows through a circular hole into a space filled with neutral gas. The plasma consists of neutral argon atoms, single charge ions, electrons and dust particles. It was believed that at the initial moment of time dust particles were of the same radius $r_d = 4\,nm$. The plasma flow velocity at the inlet was v_0=*40 m/s,* plasma pressures were in the range of 4 to 80 mbar.

To describe the problem, a hydrodynamic model is used, which is described in [6]. This model includes continuity equations for ions, atoms and dust particles

$$\frac{\partial n}{\partial t} + div\left(n\vec{w}\right) = 0,$$

$$\frac{\partial n_i}{\partial t} + div\left(n_i\vec{w}\right) = -I_i n_d / e,$$

$$\frac{\partial n_d}{\partial t} + div\left(n_d\vec{w}_d\right) = 0\,,$$

momentum equations for heavy plasma particles (ions and atoms) and dust particles

$$\frac{\partial\left(nu\right)}{\partial t} + div\left(nu\vec{w}\right) = -\frac{1}{m_i}\frac{\partial P}{\partial r} - \frac{n_d f_r}{m_i} + \frac{e}{m_i} n_i E_r\,,$$

$$\frac{\partial\left(nv\right)}{\partial t} + div\left(nv\vec{w}\right) = -\frac{1}{m_i}\frac{\partial P}{\partial z} - \frac{n_d f_z}{m_i} + \frac{e}{m_i} n_i E_z\,,$$

$$\frac{\partial\left(n_d u_d\right)}{\partial t} + div\left(n_d u_d\vec{w}_d\right) = -\frac{\alpha_d}{m_d}\frac{\partial P}{\partial r} + \frac{n_d f_r}{m_d} + \frac{q_d}{m_d} n_d E_r\,,$$

$$\frac{\partial\left(n_d v_d\right)}{\partial t} + div\left(n_d v_d\vec{w}_d\right) = -\frac{\alpha_d}{m_d}\frac{\partial P}{\partial z} + \frac{n_d f_z}{m_d} + \frac{q_d}{m_d} n_d E_z\,,$$

equations for internal energies ions and atoms ε, electrons ε_e and dust particles ε_d

$$\frac{\partial\left(\rho\varepsilon\right)}{\partial t} + div\left(\rho\varepsilon\vec{w}\right) + P\,div\,\vec{w} = Q_{ei} + Q_{en} - n_d Q,$$

$$\frac{\partial\left(\rho\varepsilon_e\right)}{\partial t} + div\left(\rho\varepsilon_e\vec{w}\right) + P_e\,div\,\vec{w} + div\,q_e =$$
$$-Q_{ei} - Q_{en} - n_d Q_{ed}\,,$$

$$\frac{\partial\left(\rho_d\varepsilon_d\right)}{\partial t} + div\left(\rho_d\varepsilon_d\vec{w}_d\right) = n_d Q + n_d Q_{ed} + Q_{id}\,.$$

Here n, n_d, n_i are the sum of ion and neutral atom concentrations, dust particles and ion concentrations respectively; $\overrightarrow{w = \left(u, v\right)}$ and $\vec{w}_d = \left(u_d, v_d\right)$ are drift velocities of plasma and dust component; P, P_e are partial pressures of the heavy plasma component and electrons. In these equations Q, Q_{ed}, Q_{id} are the energy exchanges between a dust particle and neutral atoms, electrons and ions; Q_{ei} is the energy exchange between electrons and ions; Q_{en} is the energy exchange between electrons and neutrals [6].

In this model, we believe that all dust particles have a single hydrodynamic velocity, since they effectively exchange impulse in collisions. This velocity differs from the hydrodynamic velocity of the plasma component. We also note that due to the low plasma pressure we allow for a difference between the temperature of the electrons and the temperature of the heavy plasma particles (ions and neutrals), as well as the surface temperature of dust particles.

The system of hydrodynamic equations is solved numerically by the method of large particles [7].

To determine the distribution of nanoparticles by charge, we use the model proposed in [8, 9]. This model takes into account the stochastic nature of the charging of dust particles associated with the chaos of the thermal motion of electrons and ions. As a result, dust particles with different charges are present in each elemental volume of plasma. Nanoparticles in the plasma are charged because of collisions with electrons and ions. The electron and ion currents collected by a dust particle in the nanometer regime can be described by the orbital-motion-limited (OML) probe theory [10]. A particle with radius r_d which carries a charge $Z_k = k \cdot e$ (with e the elementary charge and k an integer) is charged to a surface potential of $\Phi_k = Z_k / 4\pi\varepsilon_0 r_d$, with ε_0 the vacuum dielectric constant. Using OML theory, expressions for the frequency with which a particle with charge Z_k is hit by electrons and ions, respectively, can be derived

$$\nu_{e,i}^k = n_{e,i} S v_{e,i} \exp\left(-\frac{q_{e,i}\Phi_k}{k_B T_{e,i}}\right), \quad q_{e,i}\Phi_k \ge 0$$

$$\nu_{e,i}^k = n_{e,i} S v_{e,i} \left(1 - \frac{q_{e,i}\Phi_k}{k_B T_{e,i}}\right), \quad q_{e,i}\Phi_k < 0.$$

Here $S = 4\pi r_d^2$ is the particle surface area, $v_{e,i} = \left(k_B T_{e,i} / 2\pi m_{e,i}\right)^{1/2}$ is the electron (ion) thermal velocity; $n_{e,i}$ stands for the electron and ion densities, $m_{e,i}$ and $T_{e,i}$ are the mass and temperature of electrons and ions, respectively, and $q_{e,i} = \mp e$ is the respective charge, k_B is Boltzmann constant.

The charge distribution of particles of a given radius r_d is described by the fraction of particles F_k carrying a charge $k \cdot e$. It is normalized by $\sum_k F_k = 1$. The rate equation for a charge state k can then be written as

$$\frac{dF_k}{dt} = \nu_e^{k+1} F_{k+1} - \nu_e^k F_k - \nu_i^k F_k + \nu_i^{k-1} F_{k-1}.$$

It is assumed that the charging of particles is much faster than coagulation so the charge distribution can be considered in steady state [9]. This assumption enables the use of recursive relations for the charge distribution

$$F_{k+1} = \frac{\nu_i^k}{\nu_e^{k+1}} F_k \; .$$

In addition, in the presented model, coagulation of dust particles is considered, which is described by the model proposed in [11,12]. The volume distribution function of dust particles $n(v)$ is described by the general dynamic equation

$$\frac{\partial n(v)}{\partial t} = \frac{1}{2}\int_0^v \beta(v', v - v') n(v') n(v - v') dv' - \int_0^\infty \beta(v, v') n(v) n(v') dv',$$

where v is the volume of the dust particle, $n(v)\,\mathrm{dv}$ denotes the particle number density in a volume range $[v, v + dv]$. Coefficient $\beta(v, v')$ is the frequency for coagulation between two particles with a volume v and v'. According to [11], $\beta(v, v')$ is given

$$\beta(v, v') = \alpha(v, v') \left(\frac{3}{4\pi}\right)^{1/6} \left(\frac{6 k_B T}{\rho_p}\right)^{1/2} \left(\frac{1}{v} + \frac{1}{v'}\right)^{1/2} \times \left(v^{1/3} + v'^{1/3}\right)^2,$$

where v and v' are the volumes of the particles interacting, ρ_p is the density of the particles, and T is the temperature of the particles. $\alpha(\mathrm{v}, \mathrm{v}')$ is a coefficient which describes that the effective cross section for coagulation depends on the charge of both particles

$$\alpha(v, v') = \sum_{k=-\infty}^{\infty} \sum_{k'=-\infty}^{\infty} F_k(v) F_{k'}(\mathrm{v}') \mathrm{Q}(\mathrm{k}, \mathrm{k}', \mathrm{v}, \mathrm{v}')$$

with

$$Q(k, k', v, v') = \exp\left(-\frac{kk'e^2}{4\pi\varepsilon_0 R_s k_B T}\right), \quad kk' > 0$$

$$= 1 - \frac{kk'e^2}{4\pi\varepsilon_0 R_s k_B T}, \quad kk' \le 0,$$

and $R_s = \left(\frac{3}{4\pi}\right)^{1/3} \left(v^{1/3} + v'^{1/3}\right)$.

2. RESULTS AND DISCUSSION

Fig. 1 shows distributions on the charge of nanoparticles of a radius $r_d = 4\,nm$ at different distances from the inlet. Here F is the fraction of particles with charge Ke. As can be seen from the figure, with increasing z the average charge of the nanoparticles decreases in absolute value.

The obtained results are explained by the fact that when the distance from the inlet of the plasma jet increases, the temperature of the ions decreases rapidly, and the electrons temperature remains practically unchanged due to their high thermal conductivity. This leads to an increase in the flow of ions on the surface of the dust particles and, consequently, to a decrease in its negative charge.

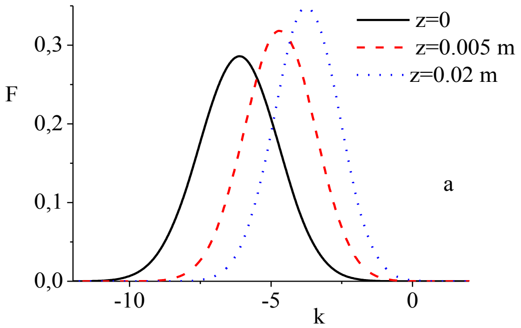

Fig. 1. Distributions by charge of nanoparticles at different distances from the inlet of plasma jet

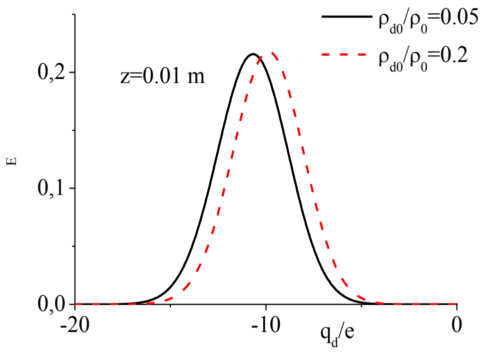

Fig. 2. Distributions by charge of nanoparticles at z = 0.001 m from the inlet of plasma jet for different dust densities

Consider now how the concentration of nanoparticles in the plasma jet affects their charge distributions. In Fig. 2 depicts the charge distributions of nanoparticles with a radius r_d = *4 nm* for two modes: at ρ_{d0}/ρ_0=*0.05* and ρ_{d0}/ρ_0=*0.2*. Here ρ_{d0} is a dust density, ρ_0 is a plasma density at the inlet of the plasma torch. The plasma density in these modes was ρ_0=*0.122 kg/m*^{3}. As can be seen, the decrease in the density of dust particles leads to a shift of the charge distribution of dust particles in the region of negative charges. This result is because when the concentration of negatively charged dust particles increases, the concentration of electrons decreases (due to the quasi-neutrality of the plasma). This leads to a decrease in the electron current to the dust particles.

Consider now the coagulation of nanoparticles in a plasma jet. Fig. 3 shows axial profiles along the jet axis of the dust particles densities on a semi-logarithmic scale for different their radii. In this mode of calculation, the concentration of nanoparticles at the inlet was $n_d = 5{\cdot}10^{-9}$m^{-3}, and their radius was $r_d = 4{\cdot}10^{-9}$m. We can see that nanoparticles with r_d >*4 nm* appear in the plasma jet, the maxima of densities which are at a certain distance from the inlet. This can be explained by the coagulation of dust particles in the plasma jet. As a result of this process, the concentration of nanoparticles with a radius $r_d = 4.7\ nm$ exceeds the concentration of particles which are injected through the inlet (with a radius $r_d = 4\ nm$) at $z \geq 0.025\ m$.

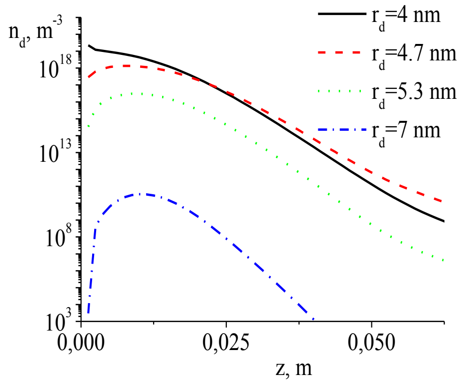

Fig. 3. Axial profiles on jet axis of the dust densities for different their radii

Fig. 4 shows the distributions of nanoparticles by their radius at different distances from the inlet. These results correspond to the calculation mode presented in Fig. 3. As can be seen, because of the coagulation, at a distance from the inlet *z = 0.001 m* in the plasma appear particles of different radii. When increasing the distance to the inlet, the number of particles of larger radii first increases and then decreases. Decrease in concentrations of dust particles is due to the expansion of the plasma jet.

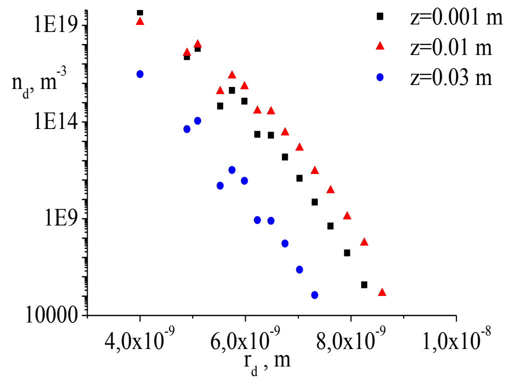

Fig. 4. Distributions of dust particles by their radius at different distances from the inlet of plasma jet

CONCLUSIONS

In this work, a sectional model that is selfconsistently coupled to a plasma fluid model was used to conduct numerical simulations of a low-pressure plasma jet in which nanoparticles grow due to coagulation. The simulation was carried out at different plasma pressures, and the concentration of dust particles at the inlet of the plasma torch. As a result of the calculations, the spatial distributions of the plasma parameters, size and charge distributions of nanoparticles in the different points of space have been obtained. Influence of nanoparticle coagulation on the parameters of a plasma jet and the dynamics of nanoparticles is studied. It is shown that due to coagulation in the jet appear dust particles of larger radii. The maximum concentrations of these particles are at some distance from the inlet. We found that with the increase of the distance from the inlet due to the decrease of the ion temperature, the average charge of dust particles per module and the width of their distribution by charge decreases. When the density of dust particles in the jet increases, their average charge decreases modulo due to a decrease of the electron density in the plasma, which leads to an increase of the coagulation rate of nanoparticles.

REFERENCES

1. P. Roca i Cabarrocas, N. Chaabane, A.V Kharchenko, S. Tchakarov. Polymorphous silicon thin films produced in dusty plasmas: application to solar cells // *Plasma Phys. Controlled Fusion*. 2004, v. 46, p. 235.
2. N.M. Hwang, D.K. Lee. Charged nanoparticles in thin film and nanostructure growth by chemical vapour deposition // *J. Phys*. 2010, D 43:483001.
3. N. Chaabane, V. Suendo, H. Vach, P. Roca i Cabarrocas. Soft landing of silicon nanocrystals in plasma enhanced chemical vapor deposition // *Appl. Phys. Lett.* 2006, v. 88, p. 2031111.
4. I. Biganzoli, F. Fumagalli, F. Di Fonzo, R. Barni, C. Riccardi. A Supersonic Plasma Jet Source for Controlled and Efficient Thin Film Deposition // *J. Mod. Phys*. 2012, v. 3, p. 1626-1638.
5. V. Trifiletti., R. Ruffo, C. Turrini, D. Tassetti, R. Brescia, F. Di Fonzo, C. Riccardi, A. Abbotto // *J. Mater. Chem.* 2013, v. A 1, p. 11665.
6. O.Yu. Kravchenko, I.S. Maruschak. Dynamics of dust particles in a plasma jet // *Problems of Atomic Science and Technology. Ser. "Plasma Physics"*. 2017, № 1, p. 159-162.
7. O.M. Belozerkovskiy, Yu.M. Davydov. *Metod krupnyh chastiz v gasovoj dinamike*. M.: "Nauka", 1982, 392 p. (in Russian).
8. M.S. Sodha, S.K. Mishra, S. Misra, S. Srivastava. Fluctuation of charge on dust particles in a complex plasma // *Physics of Plasmas*. 2010, v. 17, p. 073705-7.
9. Themis Matsoukas, Marc Russell, and Matthew Smith. Stochastic charge fluctuations in dusty plasmas // *J. Vac. Sci. Technol.* 1996, v. A 14, p. 624-630.
10. P.K. Shukla, A.A. Mamun. *Introduction to Dusty Plasma Physics.* Bristol and Philadelphia: "IoP Publishing Ltd", 2002.
11. P. Agarwal, S.L. Girshick. Sectional modeling of nanoparticle size and charge distributions in dusty plasmas // *Plasma Sources Sci. Technol*. 2012, v. 21, p. 055023-12.
12. U. Kortshagen, U. Bhandarkar. Modeling of particulate coagulation in low pressure plasmas // *Physical Review*. 1999, v. 60, p. 887-898.

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КОАГУЛЯЦИЯ И ДИНАМИКА НАНОЧАСТИЦ В ПЛАЗМЕННЫХ СТРУЯХ НИЗКОГО ДАВЛЕНИЯ

А.Ю. Кравченко, И.С. Марущак

Одним из наиболее перспективных методов создания наноструктурированных пленок является использование плазменных струй низкого давления с наночастицами. При этом для оптимизации свойств пленок важным является контроль за размером наночастиц, их температурой и энергией. В работе с помощью компьютерного моделирования проводится исследование коагуляции наночастиц в плазменной струе, которая расширяется в разреженный газ. В нашей модели используются гидродинамическая модель для описания динамики плазмы с мультидисперсною фазой, а также секционный метод для описания коагуляции наночастиц. На входном отверстии плазменного факела параметры плазмы задавались стационарными, а пылевые частицы считались одного размера. Расчеты проводились при различных концентрациях пылевых частиц в плазменной струе. Результаты моделирования показывают, что в потоке плазмы вследствие коагуляции появляются наночастицы различных размеров. С увеличением расстояния от входного отверстия уменьшаются средний заряд по модулю и дисперсия заряда наночастиц, что связано с уменьшением температуры ионов и, соответственно, ионного тока на пылевую частицу.

КОАГУЛЯЦІЯ І ДИНАМІКА НАНОЧАСТИНОК У ПЛАЗМОВИХ СТРУМЕНЯХ НИЗЬКОГО ТИСКУ

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Одним з найбільш перспективних методів створення наноструктурованих плівок є використання плазмових струменів низького тиску з наночастинками. При цьому для оптимізації властивостей плівок важливим є контроль за розміром наночастинок, їх температурою та енергією. У цій роботі за допомогою комп'ютерного моделювання проводиться дослідження коагуляції наночастинок у плазмовому струмені, який розширюється в розріджений газ. У нашій моделі використовуються гідродинамічна модель для описання динаміки плазми з мультидисперсною фазою, а також секційний метод для описання коагуляції наночастинок. На вхідному отворі плазмового факела параметри плазми задавалися стаціонарними, а пилові частинки вважалися одного розміру. Розрахунки проводилися при різних концентраціях пилових частинок у плазмовому струмені. Результати моделювання показують, що в потоці плазми внаслідок коагуляції з'являються наночастинки різних розмірів. Зі збільшенням відстані від вхідного отвору зменшуються середній заряд по модулю та дисперсія заряду наночастинок, що пов'язано із зменшенням температури іонів та, відповідно, іонного струму на пилову частинку.