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CLUSTER GENERATION FROM FLOWING PLASMA

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The method of generation of cluster beams is analyzed in the regime when large clusters grow in a flow of a dense afterglow plasma, and clusters are formed in a narrow region near the axis of this flow. This method gives a high intensity of the cluster beam in comparison with standard methods of cluster generation. Numerical parameters are evaluated for processes involving iridium clusters in an argon plasma.

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The method of generation of clusters from a plasma [1] deals with growing of clusters in a dense plasma. This method is profitable for metals of a not low boiling temperature when the standard method of transformation of a vapor into clusters [2–6] is useless because of low pressures of metallic vapors, and the laser method of cluster generation [7–10] gives a low intensity and small cluster sizes. The afterglow plasma in which clusters grow consists of a dense buffer gas and a small admixture of a metal which is inserted in the plasma in the form of a gaseous compound and exists in this form in a cold plasma region. In a hot region this compound is decomposed into an atomic vapor, and metallic clusters grow in the plasma. These clusters reach large sizes because of a large time of the cluster growth process. Since clusters are charged, they can be separated from a plasma, and this method provides intense cluster beams. The analysis of these processes is made recently [1]. Now we focus on the regime of plasma evolution when clusters are formed near the center of the plasma flow and analyze the processes during evolution of this cluster plasma.

Gasdynamics and heat processes in plasma flow. A generator of cluster beams under consideration consists of three basic elements. The first one is a plasma generator of a low power (below 1 kW), and in the second part of this generator a narrow beam of molecules containing metallic atoms is inserted near the axis of the flowing afterglow plasma. Molecules are decomposed in this region, and forming metallic atoms join in clusters or attach to clusters. As a result, all the metal is collected near the flow axis in the form of clusters. After this stage, the central flow part is directed in a vacuum through a nozzle where atoms of a buffer gas are removed by pumping, and a beam of charged clusters is governed by external electric fields.

When a gaseous compound of a heat-resistant metal is inserted in a flow of a buffer gas, molecules of the compound are mixed with a gas and are decomposed in atoms in hot regions which temperatures exceed the boundary temperature T_1 of their decay. An atomic vapor of a heat-resistant metal may be transformed in a gas of clusters in regions which temperatures are below the boundary temperature T_2 of existence of these clusters. In the second part of the cluster generator, where clusters are formed, the flow temperature at the center varies from T_2 up to T_1. For definiteness, below we will

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guided by the compound IrF_6 inserted with concentration of 10^{-3} in argon at pressure of 100 Torr, so that forming iridium clusters can be used for fabrication of rhodium-iridium thermocouples. In this case we have $T_1 = 1300\,\mathrm{K}$, $T_2 = 3200\,\mathrm{K}$ with the accuracy 100–200 K.

Because of a small concentration, the metallic compound does not influence on gasdynamical and thermal properties of a plasma flow. We take a simple parabolic temperature distribution over the flow cross section. Introducing an effective temperature T_{ef} of the flow, we have for the flow rate

$$Q = \int N_a u_z 2\pi\rho d\rho = N_a(T_{ef}) u_z \cdot \pi r_o^2, \tag{1}$$

where ρ is the distance from the tube center, r_o is the tube radius. Under the argon pressure of $p = 100\,\mathrm{Torr}$, the center flow temperature $T_o = 3000\,\mathrm{K}$, the tube radius $r_o = 1\,\mathrm{cm}$, and the average flow speed $u_z = 6 \cdot 10^3\,\mathrm{cm/s}$, we have for the effective flow temperature $T_{ef} = 1800\,\mathrm{K}$, and the flow rate is $Q = 1 \cdot 10^{22}\,\mathrm{s}^{-1} = 0.7\,\mathrm{g/s}$. Then the Reynolds number is $\mathrm{Re} = u_z r_o m_a N_a(T_{ef})/\eta(T_{ef}) \sim 300$, where m_a is the atom mass, $\eta(T_{ef})$ is a typical gas viscosity, and the gas flow is laminar. Next, from the Navier-Stokes equation it follows for the pressure gradient $dp/dz = 2 \cdot 10^{-3}\,\mathrm{Torr/cm}$ under the above parameters. This means that we have $p = \mathrm{const}$ along the flow.

Cooling of this plasma is determined in part by heat transport to the walls due to the gas thermal conductivity, and the heat balance equation for the afterglow plasma has the form

$$u_z H = 2\pi r_o \kappa \frac{dT}{d\rho}(r_o) = 4\pi\kappa(T_w)\Delta T. \tag{2}$$

Here $H = \int c_p T(\rho) \cdot N_a 2\pi\rho d\rho \approx c_p Q(T_{ef} - T_w)/u_z$ is the enthalpy per unit length of the flow, c_p is the specific heat capacity per atom of a buffer gas, and $\kappa(T_w)$ is the thermal conductivity coefficient of a buffer gas near walls. In particular, under the above flow conditions we have $u_z H = 400\,\mathrm{W}$, $4\pi\kappa\Delta T = 7\,\mathrm{W/cm}$. At laboratory tube lengths $l \approx 30 - 40\,\mathrm{cm}$ the flow cooling from T_2 up to T_1 can be attained additionally by a tube expansion.

The basic condition for the flow parameters is such that, on the one hand, decay of molecules at the flow center proceeds fast, and, on the other hand, nucleation of a forming metallic vapor is possible there. The rate constant of detachment of halogen atoms in collisions of a molecule with argon atoms can be represented in the form $k_{det} = k_g \exp(-\varepsilon_{ch}/T)$, where in the iridium case at $T = 3000\,\mathrm{K}$ the gas-kinetic rate constant is $k_g = 2 \cdot 10^{-10}\,\mathrm{cm}^3/\mathrm{s}$, and ε_{ch} is the binding energy of halogen atoms in the molecule ($\varepsilon_{ch} \approx 2.5\,\mathrm{eV}$ for the IrF_6 molecule). Under conditions considered the decay of molecules proceeds during a time $\tau_{ch} \sim 10^{-4}\,\mathrm{s}$ at $T = 3000\,\mathrm{K}$. This process leads to cooling of the buffer gas, and at the concentration 10^{-3} of the IrF_6 molecules the temperature decrease is $\delta T = 60 - 70\,\mathrm{K}$ in average. In reality, the cooling is stronger because decay of molecules proceeds fast and heat is taken from a restricted central region of the flow. This effect is compensated particularly by heat release resulting from formation of metallic clusters. The optimal temperature at the center can be operated by the initial plasma temperature.

Nucleation and charging processes in afterglow plasma. The character of the nucleation process in this plasma is similar to that in the case when an atomic vapor is transformed in a gas of clusters in a buffer gas [11]. Indeed, the first stage of the nucleation process is formation of diatomic metallic molecules in three-body collisions of metallic atoms and atoms of a buffer gas, and then diatomic molecules are nuclei of

condensation for cluster growth. Therefore clusters are large in the end of the growth process, and a typical time τ of transformation of metallic atoms in clusters and the average cluster size n (the number of cluster atoms) are given by [11]

$$\tau \sim \frac{1}{k_o N}\left(\frac{k_o}{K_3 N_a}\right)^{1/4}, \quad n \sim (k_o N \tau)^3 \sim \left(\frac{k_o}{K_3 N_a}\right)^{3/4}. \tag{3}$$

Here k_o is the specific rate constant of atom attachment to a cluster ($k_o = 3 \cdot 10^{-11}\,\mathrm{cm}^3/\mathrm{s}$ for iridium at $T = 3000\,\mathrm{K}$), $K_3 \sim 10^{-33}\,\mathrm{cm}^6/\mathrm{s}$ is the three-body rate constant of formation of diatomic molecules in three-body collisions, N_a is the number density of atoms of a buffer gas, N is the number density of free and bound metallic atoms. In particular, in the iridium case under consideration, the transformation time is $\tau \sim 10^{-4}\,\mathrm{s}$ and the mean cluster size is $n \approx 7 \cdot 10^3$.

The nucleation process proceeds in a narrow region near the axis. In particular, the way Δx which atoms pass in a buffer gas during the transformation process, is $\Delta x \sim$ $\sim \sqrt{D\tau} \sim 0.1\,\mathrm{cm}$, where $D \approx 50\,\mathrm{cm}^2/\mathrm{s}$ is the diffusion coefficient of metallic atoms in a buffer gas at the tube axis. As a result of the nucleation and diffusion processes, the effective radius of the region occupied by clusters is $\rho_o = 0.2\,\mathrm{cm}$ in the iridium case and is smaller than the tube radius. Thus, formed clusters are located in a narrow region near the axis and do not change their positions during the flight time because of a large mass. The subsequent cluster growth results from coagulation of clusters, but during the flight time at the axis $\tau_{fl} \sim 3 \cdot 10^{-3}\,\mathrm{s}$ this process does not change practically the mean cluster size in this case.

Charging of clusters proceeds simultaneously with cluster growth. When clusters are forming, the charging process results from the equilibrium

$$e + M_n^{-Z} \longleftrightarrow M_n^{-Z-1}, \quad A^+ + M_n^{-Z} \longleftrightarrow A + M_n^{-Z+1}, \tag{4}$$

where e, M, A are an electron, a metallic atoms and a buffer gas atom correspondingly, and the cluster charge Z for iridium clusters in argon is equal in electron charges to

$$Z/n^{1/3} = 0.08(T/1000), \tag{5}$$

where the temperature T is expressed in K, and we assume Ar^+ to be the basic ion in argon. Similar values of the charge correspond to other metals. In particular, averaging over 18 heat-resistant metals gives for the numerical coefficient in formula (5) $0.080 \pm$ $\pm\, 0.005$, if clusters are located in argon.

Processes (4) determine also the rate of recombination of this plasma. The rate of attachment of electrons and ions to clusters is

$$1/\tau_{at} = k_1 N_b / n^{1/3}. \tag{6}$$

The rate constant is $k_1 \sim 10^{-10}\,\mathrm{cm}^3/\mathrm{s}$, N_b is the number density of bound atoms in clusters, and in the iridium case we have $1/\tau_{at} \sim 10^5\,\mathrm{s}^{-1}$. As a result of processes (4), the number density of electrons and ions drops fast in the region occupied by clusters. One can neglect the thermoemission of electrons from the cluster surface, if the criterion is valid

$$1/\tau_{rel} \ll (dT/dt)(W/T^2), \tag{7}$$

where τ_{rel} is a typical time of a decrease of the plasma density, and W is the metal work function which is the ionization potential of a large cluster. In the iridium case the right-hand side of this relation is equal to $\sim 4 \cdot 10^3\,\mathrm{s}^{-1}$, so that on the first stage of cluster

evolution the criterion (7) is not fulfilled. Hence, through a time $\sim \tau_{at}$, when the plasma number density drops significantly, thermoemission of electrons becomes responsible for the charge equilibrium of clusters. Table lists the temperatures T_* at which the cluster charge is zero at a given number density N_e of electrons and the rates $\nu_{em}(T_*)$ of thermoemission of electrons for iridium clusters. If the thermoemission process is dominant in cluster charging and released electrons remain in the cluster region, the positive charge of clusters is close to zero because of a high number density of clusters.

N_e, cm^{-3}	10^8	10^{10}	10^{12}	10^{14}
$T_*, 10^3\,\mathrm{K}$	1.85	2.19	2.69	3.47
$\nu_{em}/n^{2/3}$, s^{-1}	1.2	170	$2.6 \cdot 10^4$	$4.2 \cdot 10^6$

At low temperatures the cluster charge is determined by transport of electrons and ions to the cluster region from regions where clusters are absent. We have the following balance equation for the plasma density

$$\rho_o^2 \frac{N_e'}{\tau_a} \sim D_a N_e. \tag{8}$$

Here ρ_o the radius of a region contained clusters, N_e' is the electron number density in this region, N_e is the electron number density in neighboring regions where clusters are absent, and D_a is the coefficient of ambipolar diffusion of the plasma. In particular, in the iridium case at the flow exit ($T = 1500\,\mathrm{K}$ near the axis) we have $N_e = 3 \cdot 10^{12}\,\mathrm{cm}^{-3}$, and $N_e' \sim 1 \cdot 10^{10}\,\mathrm{cm}^{-3}$. A typical relaxation time due to transport of electrons and ions to walls is $\tau_{rel} \sim 0.1\,\mathrm{s}$. Hence, the criterion (7) holds true now, and clusters get a negative charge which is lower than that according to formula (5) because of a large time of establishment of the equilibrium (4). As a result, clusters are charged negatively, and the equilibrium (4) may be restored partially at low temperatures.

Processes in expanding afterglow plasma. On the last stage of plasma evolution, the central part of a plasma flow which contains clusters passes through a nozzle in a vacuum. Then atoms of a buffer gas are extracted by pumping, and the beam of clusters is crossed by an electron beam, so that clusters obtain a negative charge. This cluster beam can be governed by external transverse and longitudinal electric fields when the buffer gas pressure becomes small. In particular, the mobility of charged iridium clusters reduced to the normal density of argon atoms under the equilibrium (4) is $K = K_o n^{-1/3}$, where $K_o = 0.47\,\mathrm{cm}^2/(\mathrm{V} \cdot \mathrm{s})$ at $T = 1000\,\mathrm{K}$. From this it follows that transport of charged clusters in an external field is negligible in a plasma flow and can be remarkable in a vacuum camera, when the gas pressure becomes small. Then the cluster beam can be focused and accelerated.

When the afterglow plasma with clusters flows after a nozzle and expands in a vacuum, atomic particles are scattered and pumped from the plasma flow, while collisions of clusters with atoms of a buffer gas do not create a remarkable transverse momentum of an individual cluster because of a large cluster mass. Pumping allows one to remove the scattered atoms which move towards the walls. As a result, after a while the plasma flow is transformed into a beam of clusters. Collection of clusters near the center of the plasma flow allows us to use only the central flow part for generation of a cluster beam.

Above we neglect the presence of halogen atoms in the plasma flow. Indeed, at high temperatures $T > T_1$ the halogen atoms do not react with clusters, and at low temperatures these atoms are pumped out. Nevertheless, halogen atoms can partake in some processes, in particular, attachment of electrons to halogen atoms can change plasma

properties and the character of cluster charging. In addition, the presence of halogen atoms in a buffer gas requires a certain material of walls and a special purification of a pumped buffer gas. Hence, this problem demands an additional analysis.

Thus, generation of a cluster beam from a plasma is determined by competition of some processes and is possible in a certain range of plasma parameters. In particular, on the first stage of the process, on the one hand, a fast decomposition of molecules is required with formation of metallic atoms at the flow axis and, on the other hand, a fast nucleation of metallic atoms must proceed in this region. Though due to competition of various processes this method requires a special analysis for each certain case, it can be used for generation of cluster beams of various heat-resistant metals.

As it follows from the above analysis, generation of a cluster beam from a plasma includes a variety of competing processes and provides a high intensity of the output cluster beam. In particular, the maximum specific intensity of clusters is $80\,\mu g/(cm^2 s)$ [12] for the standard method and silver clusters. In the iridium case under consideration we have for this value $20\,mg/(cm^2 s)$ and $3\,mg/s$ for the total rate of clusters. Note the importance of chemical regeneration [13] in this method which provides a high number density of metallic atoms. If metallic atoms result from metal vaporization, the number density of atoms can not exceed that at the saturated vapor pressure. In particular, for iridium this value at the melting point is $3 \cdot 10^{13} cm^{-3}$, while using of decomposition of IrF_6 molecules allows one to increase this value by two-three orders of magnitude. In addition, collection of clusters near the flow axis simplifies extraction of clusters from the plasma flow and increases the specific intensity of the beam of metallic clusters. Because all the metal is transformed in clusters, this method of generation of cluster beams can provide the same rate of metal deposition on targets as that in the case of beams of atoms or atomic ions. But intense beams of charged clusters are governed better than intense beams of atomic ions. Therefore the cluster technology of deposition of films of heat-resistant metals has advantages with respect to usage of atomic beams and atomic ion beams.

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