RAPID COMMUNICATION A new model for the floating potential of fine particles in plasma

Chen Yunming and Li Ming

Laboratory for Mechanics of Materials Processing, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, China

Received 26 January 1993

Abstract. In the plasma processing of ultrafine particles of material, the heat transfer and force are considerably affected by particle charging. In this communication a new model, including thermal electron emission and incorporating the effect of electric field near the particle surface, is developed for metallic spherical particles under the condition of a thin plasma sheath. Based on this model, the particle floating potential, and thus the heat transfer and force, can be detemined more accurately and more realistically than previously.

In plasma processing of fine particles of material (metal or non-metal), the plasma-particle interaction becomes very complicated due to gas ionization and the presence of negative electrons and positive ions. The difference in average thermal velocities of electrons and ions leads to negative charge accumulation on the particle surface, and this continues until the charge flux incident on and emitting from the particle surface balance each other. Because the charging process is very rapid compared with thermal and hydrodynamic processes, the plasma-particle charging interaction can be treated quasi-steadily with an equilibrium (floating) potential of the particle $\varphi_p = \varphi_f$ [1-4]. In recent years, the momentum and energy transport properties of charged particles in plasma have been studied in many works [1-8], Chen and He [3] analysed the floating potential and heat transfer properties under conditions of rarefied plasma (Knudsen number $Kn \gg 1$) and thin sheath (the Debye length λ_D or the thickness of the plasma sheath around the sphere is much less than the particle radius $R_0, \lambda_{\rm D} \ll R_0$, Uglove and Gnedovets [4] gave the correction for a thick sheath $\lambda_D \ge R_0$. However, the effects of thermal electron emission on the floating potential, heat transfer and momentum are neglected in the literature. In fact, at high surface temperatures for some metal materials, for example tungsten and molybdenum, the thermoemitting effect is very important and is not negligible, as proved by some results published recently [9, 10]. In these analyses, the original Richardson formula without any correction is used to describe the thermal electron emission-a method too simple and worth further discussion. Generally, the floating potential of the particle is of the order of several volts [3, 4, 8], according to the thin sheath theory;

determined by $\psi_{j(\theta)} = \int_{v_{zj}}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} v_z f_j^{-} \mathrm{d} v_x \, \mathrm{d} v_y \, \mathrm{d} v_z$

j = a, e, i.

The velocity distribution function of the jth gas particle in the non-disturbed region of plasma can be written as [3, 4, 8-10]

$$f_j^- = \frac{n_j}{(2\pi k_{\rm B} T_j / m_j)^{3/2}}$$

the corresponding static electric field intensity near the particle surface can reach 10^7-10^8 V m⁻¹ and such a high electric field intensity will greatly enhance the thermal electron emission intensity and further increase the incident electron flux through changes in the particle floating potential. The interaction between the floating potential and thermal electron emission incorporating the effect of the electric field is treated in this paper, and a new model is developed to study the particle charging in plasma under the condition of a thin sheath.

Electron and ion fluxes incident on the particle surface

For gas fluxes incident on the particle surface, the usual assumptions and method similar to that described previously [3] are adopted-namely, a spherical particle is considered as located in the rarefied plasma and $\lambda_{\rm D} \ll R_0$, the particle radiation and particle evaporation are neglected.

The coordinate system as shown in figure 1 is adopted in this study. The local flux of the *j*th gas particle incident on the sphere surface at point A is

(1)

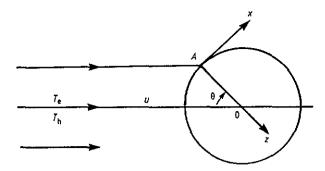


Figure 1. Coordinate system.

$$\times \exp\left(-\frac{(v_x - u\sin\theta) + v_y^2 + (v_z - u\cos\theta)^2}{2k_{\rm B}T_j/m_j}\right)$$
(2)

where *n* is the number density, $k_{\rm B}$ is Boltzmann's constant, *T* and *m* are the temperature and mass respectively, subscript *j* means the *j*th gas particle, *u* is the incoming gas velocity, while the low integration limit v_{zj} for dv_z is selected as 0 for j = a, i and $\sqrt{2e\phi_t/m_e}$ for j = e. For electrons and ions, from formula (1), ψ_j is

$$\begin{cases} \psi_{i} = \frac{1}{4}n_{i}\bar{v}_{i}\{\exp(-S_{i}^{2}\cos^{2}\theta) \\ +\sqrt{\pi}S_{i}\cos\theta[1 + \operatorname{erf}(S_{i}\cos\theta)]\} \\ \psi_{e} = \frac{1}{4}n_{e}\bar{v}_{e}\{\exp[-(S_{e}\cos\theta - \sqrt{e\phi_{f}/k_{B}T_{e}})^{2}] \\ +\sqrt{\pi}S_{e}\cos\theta[1 + \operatorname{erf}(S_{e}\cos\theta - \sqrt{e\phi_{f}/k_{B}T_{e}})]\} \end{cases}$$

where \bar{v}_j (j = i, e) are the average thermal velocities $\sqrt{8k_BT_j/\pi m_j}$ and $S_j = u/\sqrt{2k_BT_j/m_j}$ are the speed ratios for gas particles. The whole metallic sphere surface is at equal potential, so the value of ϕ_j is determined by the total fluxes of electron and ions. We then define the average fluxes over the whole sphere surface as

$$\bar{\psi}_j = \frac{1}{4\pi R_0^2} \int_0^{\pi} \psi_j \left[\int_0^{2\pi} R_0 \sin \theta \, \mathrm{d}\psi \right] R_0 d\theta$$
$$= \frac{1}{2} \int_0^{\pi} \psi_j \sin \theta \, \mathrm{d}\theta. \tag{4}$$

On the other hand, to deduce the relation between the thermal electron emission and floating potential we can select the simplest case of zero relative velocity $(S_i = S_e = 0)$, then

$$\tilde{\psi}_{i} = \frac{1}{4}n_{i}\tilde{v}_{i} \qquad \tilde{\psi}_{e} = \frac{1}{4}n_{e}\tilde{v}_{e}\exp(-e\phi_{f}/k_{B}T_{e}).$$
(5)

Thermal electron emission

The thermal electron emission flux described by the Richardson formula has beeen adopted by Gnedovets and Uglov [9] and Chen and Chen [10] to study the floating potential and heat transfer properties of particles

$$\psi_{\rm em} = \frac{A_{\rm R}T_{\rm s}^2}{e} \exp{-\frac{\chi}{k_{\rm B}T_{\rm s}}} \tag{6}$$

where ψ_{em} is the emitting electron flux, T_s is the particle surface temperature and $k_B T_s$ is in eV, A_R is the Richardson constant, e is the elementary charge and χ is the work function of material.

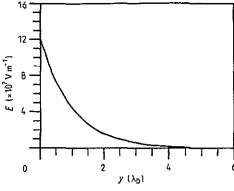


Figure 2. Electric field distribution around the particle surface.

It is well known, under the condition of a thin sheath, that the potential distribution near the charged particle with floating potential ϕ_f is $\phi = \phi_f \exp(-\sqrt{2}y/\lambda_D)$ (y is the distance from the particle surface). The corresponding static lectric field E can then be obtained by $-d\phi/dy = (\sqrt{2}\phi_f/\lambda_D) \exp(-\sqrt{2}y/\lambda_D)$. For example, the floating potential of a metallic spherical particle in a local thermal equilibrium (LTE) Ar plasma with $T_e = 10^4$ K and $S_i = S_e = 0$ is about 4.83 V, the corresponding lectric field, as shown in figure 2, is very strong near the particle surface. For the negative charged metallic particle, the decreasing work function due to the effect of the outer electric field can be determined as [11]

$$\Delta \chi = 3.8 \times 10^{-5} \sqrt{E} \text{ (eV)} \tag{7}$$

where E takes the value at the particle surface. Then the Richardson formula should be corrected as

$$\psi_{\rm em} = \frac{A_{\rm R}T_{\rm s}^2}{e} \exp{-\frac{\chi}{k_{\rm B}T_{\rm s}}} \exp{\frac{\Delta\chi}{k_{\rm B}T_{\rm s}}}.$$
 (8)

The floating potential can be obtained by balancing the total electron flux and the ion flux

$$\bar{\psi}_{\rm e} - \psi_{\rm em} = \bar{\psi}_{\rm i}.\tag{9}$$

Substituting equations (5) and (6) into equation (9), we can obtain the floating potential of a metallic spherical particle. When ψ_{em} is neglected,

$$\phi_{\mathrm{f}} = \phi_{\mathrm{f}}(T_{\mathrm{e}}, T_{\mathrm{e}}/T_{\mathrm{i}}) = rac{k_{\mathrm{B}}T_{\mathrm{e}}}{e} \ln \sqrt{rac{m_{\mathrm{i}}T_{\mathrm{e}}}{m_{\mathrm{e}}T_{\mathrm{i}}}}$$

is an explicit function of T_e and T_e/T_i ; when ψ_{em} without the effect of electric field is considered,

$$\phi_{\rm f} = \phi_{\rm f}(T_{\rm e}, T_{\rm e}/T_{\rm i}, n_{\rm e}, \chi, T_{\rm s})$$

= $-\frac{k_{\rm B}T_{\rm e}}{e} \ln \left[\left(\frac{m_{\rm e}T_{\rm i}}{m_{\rm i}T_{\rm e}} \right)^{1/2} + \frac{4A_{\rm R}T_{\rm s}^2}{en_{\rm e}\tilde{v}_{\rm e}} \exp - \frac{\chi}{k_{\rm B}T_{\rm s}} \right]$

which is also an explicit function of $T_e, T_e/T_i, n_e, \chi$ and T_s ; only when the effect of the electric field is considered, is ϕ_f an implicit function and can be obtained by the numerical method; the coupling between particle

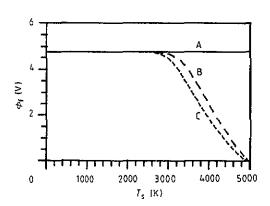


Figure 3. Floating potential against particle temperature. A, without thermal electron emission; B, with thermal electron emission without E effect; C, with both thermal electron emission and E effect.

charging and E effect is thus described by the present model.

A typical example is selected for atmospheric Ar plasma in LTE with $T_e = 10^4$ K and zero relative velocity, the electron number density n_e can be determined by the Saha equation

$$n_{e} = n_{a}^{1/2} \left(\frac{2G_{1}}{G_{0}}\right)^{1/2} \left(\frac{2\pi k_{\rm B} m_{\rm e}}{h^{2}}\right)^{3/4} T_{e}^{3/4} \exp{-\frac{E_{\rm i}}{2k_{\rm B} T_{e}}}$$
(10)

where G_1 and G_0 are statistical weights, h is the Planck constant, T_e is electron temperature and $k_B T_e$ in eV, n_a (the number density of netural atoms) is determined by $p = n_a k_B T_i$. E_i is the first ionization energy. For atmospheric Ar plasma with $T_i = T_e = 10^4$ K, n_e is about 1.5×10^{22} m⁻³, the corresponding Debye length $\lambda_D = 69\sqrt{T_e/n_e} \approx 5.63 \times 10^{-8}$ m, the Knudsen number for submicron particles is of the order of ten.

For tungsten, $A_{\rm R} = 0.6 \times 10^6 \text{ A} \text{ m}^{-2} \text{ K}^{-2}$, $\chi =$ 4.52 eV. The floating potential of tungsten corresponding to the surface temperature is shown in figure 3. When $\psi_{\rm em}$ is neglected, $\phi_{\rm f} = 4.83$ V is independent of the surface temperature, but when thermal electron emission is considered, $\phi_{\rm f}$ decreases rapidly as the temperature of the particle increases due to the exponential dependence of the thermoemitting intensity on $T_{\rm s}$. At the same time it can be seen that the floating potential decreases more rapidly when the effect of E on its thermoemitting is considered, because the electric field enhances the particle thermal electron emission by reducing the work function. Figure 4 shows the ratio of floating potentials with and without the electric field effect considered, which are represented by $\phi_{\rm f}^E$ and $\phi_{\rm f}$ respectively. It can be seen that at low temperature the effect of E is negligible but at high temperatures it is important and must be considered. For example, the floating potential difference is less than 10 per cent when T_s < 3150 K but more than 30% when $T_{\rm s} \ge 4300$ K. Therefore, in the plasma processing of refractory metallic material the influence of the thermal electron emission and the $\psi_{em}-E$ interaction on the particle floating potential must be considered.

Figure 5 shows the ratio of total electron fluxes incident on the particle surface with and without the

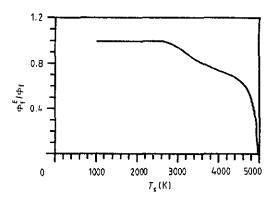


Figure 4. Ratio of floating potentials with and without E effect.

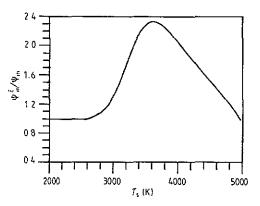


Figure 5. Ratio of electron fluxes incident on the particle surface with and without *E* effect.

E effect taken into account, which are represented by ψ_{in}^E and ψ_{in} respectively. Obviously, in the most interesting temperature region, ψ^E_{in} is greatly larger than $\psi_{\rm in}$, and $\psi_{\rm in}^E/\psi_{\rm in}$ reaches a maximum at $T_{\rm s}=3600$ K, as does the difference between the floating potentials with and without the E effect because $\psi_{in}^E/\psi_{in} =$ $\exp e/k_{\rm B}T_{\rm s}(\phi_{\rm f}-\phi_{\rm f}^E)$. The ratio of thermal electron fluxes emitted from the particle surface with and without the E effect is shown in figure 6. When the particle surface temperature increases, this ratio decreases due to the decrease in floating potential (shown in figure 3) and electric field intensity. But the E effect is very important and is not negligible over the whole temperature region of 2000-5000 K because of the high ψ_{em}^E/ψ_{em} value. It can therefore be expected that the effect of electric field on particle heat transfer through the additional increase in incident electron flux and thermoemitting electron flux is very important; the details will be given in another paper.

In calculation, the floating potential of particle may become positive, i.e. positive particle charging, when the thermal electron emission increases with T_s further increasing. In this case the present model is invalid and a new model is needed.

The main conclusions are as follows.

(1) A new model is developed to describe the interaction of $\phi_{\rm f} - \psi_{\rm em} - E$ for rarefied, thin plasma sheath plasma-particle systems.

(2) In the plasma processing of refractory metal-

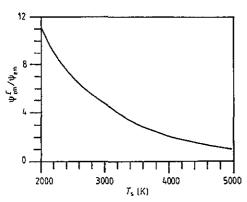


Figure 6. Ratio of thermo-emitting electron fluxes with and without E effect.

lic material, for negative particle charging, the thermal electron emission and the coupling effects of $\phi_{\rm f}$ - $\psi_{\rm em}$ -E make the particle floating potential decrease greatly as the particle surface temperature increases. The effect of static electric field around the particle is very important and not negligible.

(3) Due to the effects of E, the electron flux incident on the particle surface and the thermoemitting electron flux from the particle is greatly enhanced, resulting in a great change in the floating potential. The present model provides a basis for a rigorous analysis of particle heat transfer.

This work has been supported by the National Natural Science Foundation of China.

References

- [1] Godard R and Chang J S 1980 J. Phys. D: Appl. Phys. 13 2005
- [2] Lee Y C, Chyou Y P and Pfender E 1985 Plasma Chem. Plasma Process 5 391
- [3] Chen Xi and He P 1986 Plasma Chem. Plasma Process 6 313
- [4] Uglov A A and Gnedovets A 1991 Plasma Chem. Plasma Process 11 251
- [5] Boxman R L and Goldsmith S 1981 J. Appl. Phys. 52 151
- [6] Chen Xi and Chen Xiaoming 1989 Plasma Chem. Plasma Process 9 387
- [7] Chang C H and Pfender E 1990 IEEE Trans. Plasma Sci. 18 958
- [8] Gnedovets A G and Uglov A A 1992 Plasma Chem. Plasma Process 12 383
- [9] Gnedovets A G and Uglov A A 1992 Plasma Chem. Plasma Process 12 371
- [10] Chen Xi and Chen Ji 1992 Transport Phenomena Science and Technology ed B X Wang (Beijing: Higher Education Press) p 228
- [11] Dobretsev 1952 Electron and Ion Emission, GETTL (in Russian)