THERMOEMISSION CHARGING OF METAL PARTICLES SURROUNDED WITH CONDENSED DISPERSE PHASE

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Experimental data on the charging of metal spherical particles at high-temperatures are presented. A model of thermoemission charging, which is based upon the application of the method of a boundary sphere with regard for the charge exchange between a heated particle and the condensed disperse phase (CDP), is proposed.

One of the parameters characterizing a particle during its interaction with the environment is its electric charge formed, in particular, as a result of the thermoemission from the particle itself and that from the CDP which surrounds it. For example, CDP is formed around a heated copper particle and consists of particles of Cu_2O which is stable when temperature $T < 2073$ K and disintegrates at higher temperatures. Under certain conditions, when the work function of an electron from a particle A_1 is more than that of an electron from particles of CDP A_2, a metallic particle can get a negative charge because the flow of negative charge from CDP to the particle exceeds the inverse one. For copper, A_1=5.5 eV, and A_2=4.9 eV for Cu_2O [1].

Such a phenomenon, in particular, takes place during the experimental research of the thermoemission charging of drops of a copper melt and other metals [2—4]. While describing the process of thermoemission charging of a spherical metallic particle, we use the well-known method of a boundary sphere [5—14]. The essence of this method is that the particle is surrounded by a concentric sphere which is positioned from its surface at a distance equal to the middle length of the free path of an ion of oxygen and an electron. The region limited by the particle surface and the boundary sphere is called a kinetic zone. The distance from the boundary sphere to the particle surface is called the width of a kinetic zone. It is supposed that, inside the kinetic zone, electrons and ions of oxygen move without mutual collisions, colliding only with the particle surface and with the boundary sphere. When the temperature of a particle is T_1, the kinetic zone width is found as $l_1 = (T_1/T_0)\, l_0$, where l_0 is the kinetic zone width at $T_0 = 273$ K. Let us examine the equation for the negative charge of a spherical metallic particle surrounded with CDP under conditions of thermoemission charging [3]

$$\frac{dQ}{dt} = \pi r^2 n_{O_2}[\upsilon_{O_2} - \Psi(Q)]e -$$

$$-4\pi r^2 F(Q)\, AT_1^2 \exp\left[-\frac{A_1 - \Delta A_1}{kT_1}\right]. \quad (1)$$

The first member on the right-hand side of (1) defines the flow of negative ions of oxygen O_2^- from CDP to the surface of a spherical particle with radius r. This flow is defined as the product of the particle surface area $S = 4\pi r^2$, the concentration n_{O_2} of O_2^-, by one fourth part of the mean velocity of O_2^-, and the charge of an electron e.

Let us denote the threshold temperature for the formation of CDP by T_2. In particular, $T_2 = 2073$ K for CDP from Cu_2O. If $T < T_2$, CDP is destroyed. Then the condition for the charge equilibrium of a particle of CDP with a volumetric negative charge becomes

$$4\pi r_k^2 AT_2^2 \exp\left(-\frac{A_2}{kT_2}\right) = \pi r_k^2 \upsilon_{O_2} n_{O_2} e, \quad (2)$$

where r_k is the radius of the particle of CDP, A is the Richardson—Deshman constant. The mean velocity of O_2^- $\upsilon_{O_2} = \left(\frac{8kT_2}{\pi \cdot m_{O_2}}\right)^{1/2}$ is defined when temperature is equal to T_2. From Eq. (2), we find

$$n_{O_2} = 4AT_2^2 \exp\left(-\frac{A_2}{kT_2}\right)/e\upsilon_{O_2}. \quad (3)$$

The function $\Psi(Q)$ takes into account the braking of the flow of O_2^- inside the kinetic zone. It was derived in [5] as

$$\Psi(Q) = \frac{el_1}{(2m_{O_2}kT_2)^{1/2}\pi^{3/2}\varepsilon_0 r}\left(Q^{1/2} - \frac{re^{1/2}}{2l_1}\right)^2, \quad (4)$$

where m_{O_2} is the mass of O_2^-, k is the Boltzmann constant, and ε_0 is the electric constant.

Work [10] shows that, inside the kinetic zone of a negatively charged particle, there exists a potential

barrier caused by the superposition of the electrostatic field of electrons pushed away and O_2^- and the field of the mirror reflection of a charge. For the negative charge of a particle, whose value satisfies the inequality $0 \le Q \le er^2/4l_1^2$, the resulting field near the particle will be the field of attraction. In this case, $\Psi(Q) = 0$.

The second term on the right-hand part of Eq. (1) defines the flow of electrons from the surface of a particle. The coefficient $F(Q)$ defines a decrease of the flow of electrons from the surface of the particle due to their elastic scattering, at which a part of electrons returns to a particle. This coefficient is a function of the negative charge of a particle. The analytical expression for $F(Q)$ is derived in [10], where it was shown that $F(Q)$ varies in the limits from its minimal value equal to 0.645 to the maximal value equal to 1. In the subsequent calculations, we take $F(Q) = F$ as a constant value accepting these extreme numerical values by turns. This will enable us to determine the extreme values of the quantities under study.

The reduction of the work function of an electron from the surface of a particle carrying a negative charge is defined by Schottky effect [15]:

$$\Delta A_1 = \frac{Q^{1/2}e^{3/2}}{4\pi\varepsilon_0 r}. \tag{5}$$

Substituting $n_{O_2} from$ (3) in Eq. (1), we get

$$\frac{dQ}{dt} = 4\pi r^2 AT_2^2[1 - \Psi(Q)/\upsilon_{O_2}] \exp\left(-\frac{A_2}{kT_2}\right) -$$

$$-4\pi r^2 FAT_1^2 \exp\left[-\frac{A_1 - \Delta A_1}{kT_1}\right]. \tag{6}$$

Let us deduce the formula for the equilibrium charge of a particle. The condition of charge balance is defined by the equality $\frac{dQ}{dt} = 0$. At first, we define the temperature of the particle T_{01}, when its equilibrium charge $Q = 0$. At such a temperature, the thermoemission current from the surface of the particle is compensated by the flow of ions from CDP to its surface. For a neutral particle, $\Psi(Q) = 0$ and $\Delta A_1 = 0$. We can easily get the equation for the definition of T_{01} from Eq. (6) as

$$FT_1^2 \exp\left(-\frac{A_1}{kT_1}\right) = T_2^2 \exp\left(-\frac{A_2}{kT_2}\right). \tag{7}$$

In particular, for a drop of fused copper which is surrounded with CDP of copper oxide, $T_{01} = 2345$ and 2310 K if, respectively, $F = 0.645$ and 1. At the temperatures of a copper drop $T_1 < T_{01}$ or $T_1 \ge T_{01}$, the drop will have, respectively, a negative or positive charge.

For the negative charge of a particle, whose value satisfies the inequality $0 \le Q \le er^2/4l_1^2$, the potential barrier inside the boundary sphere is absent, and $\Psi(Q) = 0$. For this situation, the condition of charge equilibrium looks like

$$FT_1^2 \exp\left(-\frac{A_1 - \Delta A_1}{kT_1}\right) = T_2^2 \exp\left(-\frac{A_2}{kT_2}\right). \tag{8}$$

In view of relation (5), we get the equilibrium negative charge present on a spherical metallic particle as a function of its temperature T_1:

$$Q = \left[\frac{4\pi\varepsilon_0 r}{e^{3/2}} kT_1 \ln\left(\left(\frac{T_2^2}{FT_1^2}\right) \exp\left(\frac{A_1}{kT_1} - \frac{A_2}{kT_2}\right)\right)\right]^2. \tag{9}$$

For the negative charge of a particle, whose value satisfies the inequality $Q > er^2/4l_1^2$, the condition of charge equilibrium of a particle with CDP follows from Eq. (6) as

$$T_2^2\left[1 - \frac{\Psi(Q)}{\upsilon_{O_2}}\right] \exp\left(-\frac{A_2}{kT_2}\right) =$$

$$= FT_1^2 \exp\left(-\frac{A_1 - \Delta A_1}{kT_1}\right). \tag{10}$$

Let's assume that $\Delta A_1 = 0$. Taking into account the above-presented formula for υ_{O_2} and relation (4), we get the dependence of the equilibrium negative charge on the T_1 in the form

$$\sqrt{Q} = \sqrt{\left[\frac{4\pi kT_2\varepsilon_0 r^2}{el_1}\left(1 - \frac{FT_1^2}{T_2^2}\exp\left(\frac{A_2}{kT_2} - \frac{A_1}{kT_1}\right)\right)\right]} +$$

$$+ \frac{re^{1/2}}{2l_1}. \tag{11}$$

When T_1 falls to the value of the maximal limiting temperature of the formation of CDP T_2, CDP will be formed directly at the surface of a particle. Setting $T_1 = T_2$ in this case, we get Eq. (11) as

$$\sqrt{Q} = \sqrt{\left[\frac{4\pi kT_2\varepsilon_0 r^2}{el_1}\left(1 - F\exp\left(\frac{A_2 - A_1}{kT_1}\right)\right)\right]} +$$

$$+ \frac{re^{1/2}}{2l_1}. \tag{12}$$

Under our conditions, the calculated negative charge of particles $Q \approx 10^{-13}$ C. The lowering of the work function of an electron under these conditions caused

by the Schottky effect is 0.01 eV. This value is lower than the error in the definition of the work function of an electron from a particle. So, the neglection of ΔA_1 under these conditions is fully proved.

In the case where the temperature of a particle is more than the temperature, at which the equilibrium charge is zero, $T_1 > T_{01}$, the thermoemission current from a particle surpasses the flow of ions of oxygen O_2 from CDP to the particle. Under such conditions, the particle will be charged positively. In this case, the equation of thermoelectronic charging of particles can be deduced by analogy with (6), but with the only difference that $\Psi(Q) = 0$ when the charge is positive. The work function of an electron from the surface of a particle increases to the value of the work of the Coulomb field on its positive charge $\Delta A_1 = Qe/(4\pi\varepsilon_0 r)$. By noting that $F(Q) = F = \text{const}$ [5], we get

$$\frac{dQ}{dt} = 4\pi r^2 F A T_1^2 \exp\left[-\frac{A_1}{kT_1} - \frac{Qe}{4\pi\varepsilon_0 rkT_1}\right] -$$

$$-4\pi r^2 A T_2^2 \exp\left(-\frac{A_2}{kT_2}\right). \quad (13)$$

The condition for the charge equilibrium of a particle with CDP is defined by the equality $\frac{dQ}{dt} = 0$ and looks as

$$FT_1^2 \exp\left[-\frac{A_1}{kT_1} - \frac{Qe}{4\pi\varepsilon_0 rkT_1}\right] = T_2^2 \exp\left(-\frac{A_2}{kT_2}\right). \quad (14)$$

Solving Eq. (14), we get that the charge

$$Q = \left[\frac{4\pi\varepsilon_0 r}{e} kT_1 \ln\left(\left(\frac{FT_1^2}{T_2^2}\right) \exp\left(\frac{A_2}{kT_2} - \frac{A_1}{kT_1}\right)\right)\right]. \quad (15)$$

If T_1 decreases to the value T_2, the border of the formation of CDP is at the surface of a particle. In this case, expression (15) becomes

$$Q = \left[\frac{4\pi\varepsilon_0 r}{e} kT_1 \left(\ln(F) + \frac{A_2 - A_1}{kT_1}\right)\right]. \quad (16)$$

In this work, we used the experimental method of determination of the charge of particles which is based on the deviation of particles in the electrostatic field formed by vertical metal plates. The equation of motion of a particle looks as

$$m\frac{d\vec{V}}{dt} = m\vec{g} + Q\vec{E} +$$

$$+6\pi\eta(T) r \vec{V}\left[1 + 0{,}265\left(\left|\vec{V}\right| r \Big/ \nu(T)\right)^{2/3}\right], \quad (17)$$

where m is the particle mass, $\vec{V}$ is its velocity, $\vec{E}$ is the external electrostatic field intensity, $\eta(T) = \eta_0((273 + 117)/(T + 117))(T/273)^{3/2}$ is the dynamic viscosity of air which depends on the temperature, η_0 is the dynamic viscosity of air at T_0=273 K, $\bar{T} = (T_1 + T_\infty)/2$ is the medium value between the T_1 and the temperature of the air surrounding it on the infinity T_∞=300 K, and $\nu(T) = \eta(T)/\rho$ is the kinematic viscosity of air. The density of air is defined as $\rho = \rho_0(T_0/T)$. Here, ρ_0 is the density of air at T_0=273 K.

The projection of Eq. (17) an the horizontal axis directed along the direction of $\vec{E}$ is represented in final differences and looks like

$$m\frac{x_{i+1} - 2x_i + x_{i-1}}{\Delta t^2} = Q\left|\vec{E}\right| - 6\pi\eta(T) r \frac{\Delta S_{i+1,i}}{\Delta t} \times$$

$$\times \left(1 + 0.265\left(\Delta S_{i+1,i} r \Big/ \Delta t\nu\left(\bar{T}\right)\right)^{2/3}\right)\cos(\alpha_i). \quad (18)$$

Here, Δt is the time interval of the opening of the lens of a camera by a chopper; x_{i-1}, x_i, x_{i+1} are the sequential horizontal coordinates of a particle in the time interval Δt; $\Delta S_{i+1,i}$ is corresponding region of the trajectory of a particle passed by it during the time Δt; α_i is the angle formed by the horizontal axis of coordinates and the transference of the particle along a trajectory $\Delta\vec{S}_{i+1,i}$. The temperature of the particle moving along the trajectory was defined by an electron quasimonochromatic pyrometer. Thus, the processing of experimental results allows us to define the dependence of the charge of the particle on its temperature by using Eq. (18).

Figure 1 shows the experimental (black rectangles) and calculated (solid line) dependences of the equilibrium charge on a particle of copper with the radius r=117 μm upon its temperature. Figure 2 presents similar dependences (black rectangles are the experimental values of a charge and the broken line gives the calculated values) for a particle of tantalum with the radius r =185 μm for A_1=4.13 eV [1]. According the supposition, the condensed dispersed phase consists of the most stable oxide Ta_2O_5, A_2=4.65 eV [1]. The limiting maximal temperature of the existence of CDP was determined by the value T_2=1743 K which is the fusion temperature of oxide with disintegration. In this case, the work function of an electron from the surface of a metallic particle is less than that of an electron from a particle of CDP. This promotes the accumulation of a positive charge on the particle of tantalum, and this phenomenon is confirmed experimentally.

The calculated dependence of the equilibrium positive charge found on the particle on its temperature

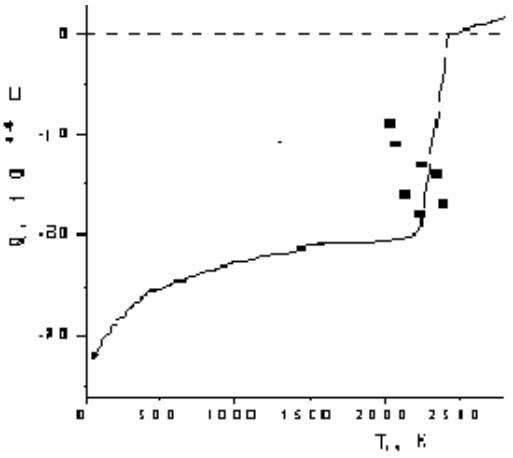

Fig.1

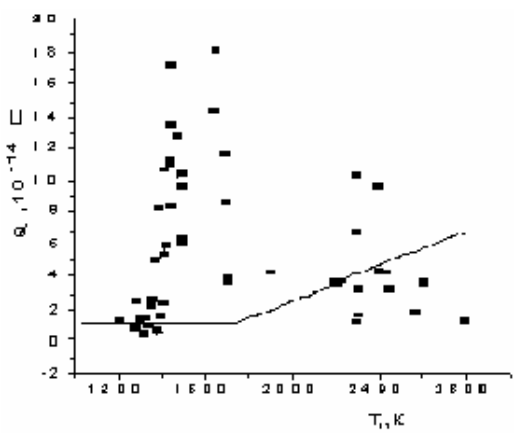

Fig.2

is given by relations (15), (16). For F=1, relation (16) becomes

$$Q = \left[\frac{4\pi\varepsilon_0 r}{e}\,(A_2 - A_1)\right]. \qquad (19)$$

The calculations which were carried out with the help of Eqs. (15), (16), and (19) show that the charge of a particle of tantalum is positive at any temperatures. For $T_1 > T_2$, the dependence of its equilibrium charge upon T_1 practically is linear. When $T_1 \leq T_2$ and F=1, the charge of a particle is not changed, and its value is defined by expression (19). The derived values of equilibrium charge of a particle at F=0.645 and F=1 are close. Therefore, the calculated dependences shown in Figs. 1 and 2 correspond to F=1.

To the reasons defining the inaccuracy of calculations, we refer the following ones. First, for the thermoemission constants of metallic particles and CDP, we took the same value $A = 1.2 \times 10^6$ A/(m^{2}K) (there are no corresponding data in reference books). Secondly, in addition to oxide Ta_2O_5, CDP of tantalum contains oxides TaO_2 and TaO, whose electron work functions are absent in the reference literature. That's why it was impossible to account their influence on the process which is researched. Thirdly, the choice of the kinetic zone width which appears in expressions (11) and (12) is conditional.

Thus, in view of the presence of many parameters in the problem under study, the agreement between the experimental and theoretical results can be considered as satisfactory.

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ТЕРМОЕМІСІЙНА ЗАРЯДКА МЕТАЛІЧНИХ ЧАСТИНОК, ОТОЧЕНИХ КОНДЕНСОВАНОЮ ДИСПЕРСНОЮ ФАЗОЮ

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Р е з ю м е

Наведено експериментальні дані з зарядки високотемпературних металічних сферичних частинок. Запропоновано модель термоемісійної зарядки, яка грунтується на використанні методу граничної сфери, що враховує обмін зарядом між частинкою і конденсованою дисперсною фазою.