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The Formation of Negatively Charged Particles in Thermoemission Plasmas

V. I. Vishnyakov*, G. S. Dragan, and A. V. Florko
Mechnikov Odessa National University, Odessa, 65082 Ukraine

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Abstract—The results of measuring the charges of the magnesium oxide particles formed near a block of metallic magnesium burning in air are presented. It has been found that, apart from positively charged magnesium oxide particles, there are negatively charged particles in the thermoemission plasma of the burning products. It has been shown that within the framework of the model of neutralizing charges, the oxide particles can acquire unlike charges in the thermoemission plasma. The calculations agree with the experimental data.

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1. INTRODUCTION

The burning of dispersed metals in an air-oxygen environment is a promising method of producing highly pure nanopowders to be used in technological processes. The flame of the burning products of a metallic particle or a gas-dispersed mixture is a low-temperature plasma with a condensed dispersed phase [1–3]. The temperature of this plasma is typically 1500–3500 K, with the system being considered isothermal. If the fuel contains no specially injected alkali metal additives, then the ion number density in the plasma is negligible compared to the number density of the electrons produced by thermoelectron emission from the particle surfaces. This plasma is called a thermoemission one and consists of charged particles and electrons [4, 5].

The condensed particles in the thermoemission plasma of burning products generally have a fairly wide size distribution and often different chemical compositions. This affects the particle charge and the properties of the plasma as a whole as well as the particle nucleation and growth. Therefore, this work is devoted to experimental and theoretical studies of the charge state of the magnesium oxide particles in the thermoemission plasma of the burning products of a metallic magnesium block.

2. THE STATUS OF THE PROBLEM

The study of thermoemission plasmas began after the discovery of an abnormally high conductivity of soot flames [6, 7]. This stimulated theoretical studies of the mechanisms of the increase in electrical conductivity in dusty flames [8–12]. In these papers, the acquisition of a charge by particles was likened to multiple ionization and an attempt was made to determine the equilibrium constant of this process.

Experimental studies of the flames of hydrocarbon liquid fuels showed an increase in electron number density in the plasma when magnesium oxide particles were injected [13]. This increase turned out to be several times larger than that predicted by the above theoretical models.

The current thermoemission plasma models use various approximations: from the system of uniformly distributed dust grains in an electronic gas [14, 15] to the Wigner–Zeitz single-particle approximation [16, 17] and even the interaction of charged planes [18]. For all of the variety of approaches to the problem, none of the above models can describe the experimental data presented in this paper, more specifically, the appearance of negatively charged particles in thermoemission plasmas. The systems consisting of electrons and homogeneous particles that can be charged positively and negatively were considered previously [1, 2, 12]. However, these studies do not explain the formation mechanism of a significant number of negatively charged particles in a thermoemission plasma that contains no other free electrons than those emitted by the particles themselves.

The possible formation of both positive and negative dust grains in thermoemission plasmas was described most clearly in the model of neutralizing charges [19]. The essence of the model of neutralizing charges is the assumption that most of the electrons in the thermoemission plasma volume are distributed uniformly with some unperturbed number density n_0. Only in a thin layer near the grain surface does the electron number density deviate from its unperturbed value. In the state of equilibrium between the dust grain and the electronic gas, the electron number density in the immediate vicinity of the grain surface is constant and defined by Richardson's formula [2]

$$n_{es} = \nu_e \exp\left(-\frac{W}{kT}\right), \quad (1)$$

where

$$\nu_e = 2\left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2}$$

is the effective electron state density and W is the electron work function from the grain surface.

The relationship between the electron surface density and the unperturbed density defines the height of the potential barrier V_b at the electronic gas–dust grain boundary,

$$V_\mathrm{b} = kT\ln\frac{n_{es}}{n_0}, \quad (2)$$

which provides an equality between the thermoelectron emission flux from the grain surface and the reverse flux due to the thermal motion of the electrons.

Generally, the condensed particles have different sizes and compositions. Therefore, the neutrality of the system's charge is described by the equation

$$\sum_j Z_j N_j = \bar{n}_e, \quad (3)$$

where Z_j is the charge number of the particles of type j with concentration N_j; $\bar{n}_e$ is the mean electron number density, which is related to the unperturbed number density by $\bar{n}_e = n_0\exp(3/2) \approx 5n_0$ [19].

Thus, the total charge of the particles determines the unperturbed number density n_0. At the same time, the surface density n_{es} is determined only by the electron work function and the temperature. Consequently, if the electron work function from the grain surface is equal to such a value of W_0 that the surface density (1) is equal to the unperturbed density n_0, then there is no potential barrier near the surface of such a particle, although its charge is nonzero. Therefore, dust grains with the electron work function W_0 and an electronic gas with the density n_0 produce a neutralizing background for other grains, just as in the model of a one-component plasma [20, 21]. Clearly, particles with the work function W_0 may be absent altogether in the plasma. This parameter is needed for the convenience of description as some reference point. If the electron work function from the surface of an actual grain W < W_0, then the potential barrier is positive, $V_\mathrm{b} > 0$. If, however, W > W_0, then the potential barrier is negative, $V_\mathrm{b} < 0$, since, in this case, the number density of the electrons uniformly distributed in space is higher than the number density required for the thermoelectron emission flux to be balanced.

Thus, the model of neutralizing charges allows for the existence of both positive and negative potential barriers near the surfaces of condensed particles and even negatively charged particles can exist at high values of the work function.

3. EXPERIMENTAL RESULTS

To experimentally study the charge state of the magnesium oxide particles in a thermoemission smoke plasma, we used the flame of a metallic magnesium block 2–3 mm in size burned in air. Magnesium was suspended on a refractory metallic needle and was ignited by an alcoholic burner. Magnesium burned in vapor-phase regime: the metallic block melts and heats up to the boiling temperature, while the metal that reacts with air oxygen at some distance from the droplet surface to produce a spherical zone of chemical reaction evaporates intensely. Magnesium oxide condenses on both sides of the reaction zone due to the temperature and density gradients. The growth and agglomeration of oxide particles also take place near the reaction zone. Thus, we can assume that at some distance from the metallic droplet surface, the chemical reactions and other nonequilibrium processes like condensation terminate and the gas-phase and particle temperatures level off. Therefore, in the absence of atoms of an easily ionized impurity in the gas phase, the plasma may be considered as an equilibrium thermoemission one.

We performed a dispersion analysis of the magnesium oxide particles by selecting a sample of the burning products on a special substrate and by analyzing its microphotograph taken with an electronic microscope. The condensed phase was found to have two fractions with mean particle sizes $a_1 = 0.05$ μm and $a_2 = 0.3$ μm.

The temperature T_d of the condensed phase in the burning zone, where it reaches its maximum, was determined by a polycolor method based on Wien's formula for the spectral luminosity Γ_λ. For this purpose, we plotted $\ln(\Gamma_\lambda\lambda^5)$ against $1/\lambda$. In the wavelength range where the plot is a straight line, the measurement source was assumed to be gray. This allowed us to determine the true temperature from the slope of the straight line, $T_d = 2650 \pm 50$ K.

A light scattering method was used to determine the number density of the condensed magnesium oxide particles. The essence of this method is that we experimentally determined the extent of the emitting zones from the radial distribution of the light fluxes expressed in absolute units and processed using Abelian transforms. The absolute values of the spectral luminosity were determined by comparing the light fluxes using a SI 10-300 ribbon tungsten lamp as the reference source.

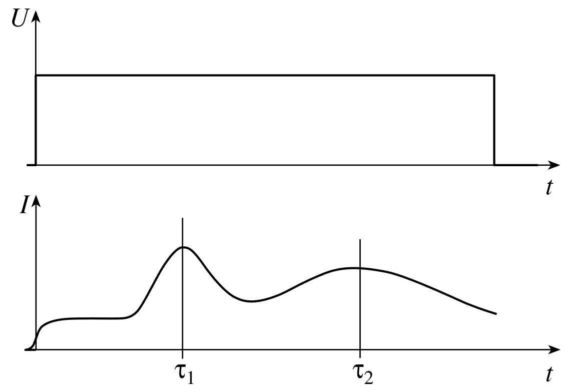

Fig. 1. Voltage U and current I diagrams.

The studies were performed in the spectral range 400–1100 nm. Our experiments showed that the number densities of the fine and coarse grains were N_{d1} = $(3 \pm 1) \times 10^{11}$ cm^{-3} and $N_{d2} = (2 \pm 1) \times 10^9$ cm^{-3}.

Let us consider the technique for estimating the magnitude and sign of the charge of the magnesium oxide particles in a smoke plasma. The metallic magnesium block was placed in the electric field of a plane capacitor formed by two parallel plates at a distance exceeding the flame size and was ignited. When a stable burning of magnesium was established, a rectangular voltage pulse with an amplitude of 1.5–2.5 kV was applied to the plates. During the experiment, we recorded the current in the capacitor circuit, which was also rectangular in shape in the absence of a burning magnesium particle. Obviously, the electric field of the capacitor triggers the motion of charged particles toward the plate surface. In this case, the conduction current does not flow through the smoke plasma, since the plasma is not in contact with the plates. It thus follows that the emerging current surges in the capacitor circuit are attributable to the charge transport by condensed particles.

As we see from the time dependence of the current (Fig. 1), there are two time-shifted current surges. This can be explained by the fact that oppositely charged grains have different mobilities that are determined by the particle masses. The integrals of the current dependence for the first and second surges define the charges transported by particles. We established that the fine and coarse grains settled on the plates with negative and positive voltages, respectively. Thus, we concluded that the smaller particle have positive charges, while the larger magnesium oxide particles are charged negatively.

Based on the pattern of the oxide particle distribution on the plate surface, we determined the regions of flame space in which they were formed. Analysis showed that the smaller oxide particles were formed near the zone of chemical reaction, while the larger particles were formed far from the reaction zone, i.e., at lower temperatures.

Comparing the transported charge with the mass of the particles settled on the capacitor plate and with the results of our dispersion analysis, we will obtain the mean charge number of the condensed particles. The small and large particles turned out to have the mean charges $Z_1 = 30 \pm 10$ and $Z_2 = -(900 \pm 200)$ (in units of electron charge), respectively. Thus, we conclude that the small and large magnesium oxide particles in the thermoemission smoke plasma have opposite electric charges.

4. CALCULATING THE PARTICLE CHARGES

The experimentally studied system may be considered in the condensation zone of the burning products as a thermoemission plasma, since the temperature is not enough for a noticeable ionization of atmospheric atoms. The system may be assumed to consist of condensed particles and electrons emitted by them. According to the model of neutralizing charges [19], a set of $n + 1$ equations with the system's electrical neutrality equation as the closure one must be solved to determine the charge numbers of the particles constituting n fractions in the thermoemission plasma. In our case, the charge numbers of the condensed particles are defined by

$$Z_j = n_0(V_W - V_j) \pm \frac{\sqrt{2}a_j kT}{e^2}\sqrt{\frac{n_{sj}}{n_0} - \ln\frac{n_{sj}}{n_0} - 1}, \tag{4}$$

where $V_W = (N_{d1} + N_{d2})^{-1}$ is the Wigner–Zeitz cell volume, V_j is the particle volume, and n_{sj} is defined by Eq. (1), $j = 1, 2$.

The system's electrical neutrality condition is given by the relation

$$Z_1 N_{d1} + Z_2 N_{d2} = 5n_0. \tag{5}$$

Equations (4) and (5) allow the unperturbed number density to be calculated. For our experimental data at the electron work function $W = 3.9$ eV, we obtain n_0 = 3×10^{12} cm^{-3}. Accordingly, the charge of the fine fraction is $Z_1 = 33$, which matches the measured value.

In our experiment, we recorded the coarse negatively charged grains formed on the flame periphery, at lower temperatures. The lower temperature of the coarse grains probably has an effect on their emission properties. Since the number density of the fine grains is much higher than that of the coarse ones, it determines the unperturbed number density and the neutralizing background. The thermoelectron emission flux from the surface of a large grain is lower than the flux on the surface of a neutral large grain due to the thermal

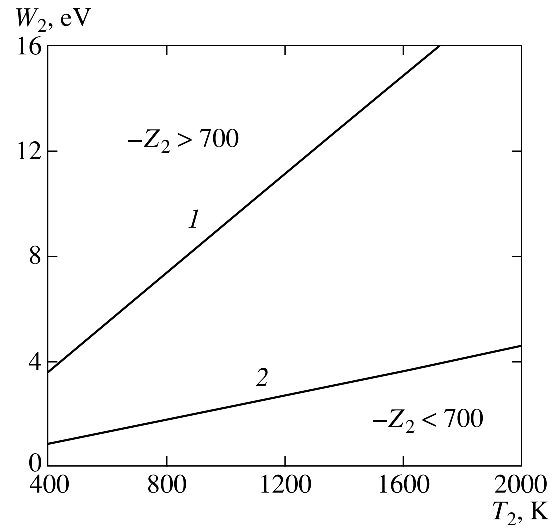

Fig. 2. Domains of temperatures and work function for a large particle corresponding to the charge $Z_2 = -700$: $a_2 =$ 0.3 (a) and 1 (2) μm.

motion of the plasma electrons. Consequently, for these fluxes to be balanced, a negative barrier must arise near the surface of the large grain that reduces the electron flux on it.

The number density of the oxygen molecules in the ambient medium is considerably higher on the flame periphery, far from the reaction zone, which may lead to oxygen adsorption on magnesium oxide. As was shown in [22], this effect causes the electron work function from the particle surface to increase.

Thus, when the charges of large particles are calculated, both factors leading to a reduction in thermoelectron emission, the decrease in temperature and the increase in work function, should be taken into account. Unfortunately, an accurate calculation cannot be performed due to the absence of accurate values of these parameters. Therefore, let us determine the ranges of T_2 and W_2 at which the calculated particle charge falls within the admissible interval of measured charges of large particles. The results of our calculations are presented in Fig. 2.

Analytically, this dependence can be represented as

$$W_2 \approx kT_2\left[\ln\frac{\nu_e(T_2)}{n_0} + \frac{-Z_2}{4\pi r_D^2 a_2 n_0}\right],$$

where $r_D = \sqrt{kT/4\pi e^2 n_0}$ is the screening length.

We thus see that the particle size plays a significant role—$W_2(T_2)$ decreases with increasing size. This fact is reflected in Fig. 2. As follows from the plot, the region of charges corresponding to the measured value for particles 1 μm in radius is observed at much lower values of the work function.

5. CONCLUSIONS

It follows from the presented results that unlikely charged condensed particles are formed in the thermoemission plasma produced through the burning of a magnesium block.

In the case considered, one of the particle fractions, charging positively due to its emission properties, determines the electronic gas density in the plasma. Because of their thermal motion, free electrons collide with dust grains; this electron flux on the particle surface should be in equilibrium with the thermoelectron emission flux. The latter is ensured by the acquisition of a charge by the particle and by the formation of a potential barrier at the electronic gas–condensed particle boundary.

The coarse particles do not provide a sufficient thermoelectron emission flux and, hence, are charged negatively. We can assume that there exist at least two causes of the reduction in the emission properties of the condensed particles. The first is the cooling of large particles on the flame periphery. The second is probably related to an increase in electron work function when oxygen molecules are adsorbed on the particle surface [22]. Other causes related both to a change in the chemical composition of the particles themselves and to a modification of their surface are possible. Only further studies will give the exact answer to this question.

In any case, the existence of unlikely charged dust grains in a thermoemission plasma can be explained in the model of neutralizing charges.

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