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INFLUENCE OF THE POLARIZATION OF MOLECULES OF METAL OXIDES ON THE DIFFUSION COEFFICIENT IN SMOKY PLASMAS

We study the influence of the polarization of molecules of metal oxides on the diffusion coefficient in a smoky plasma that is formed by the combustion of a metal powder in air. It is shown that the electrostatic dipole–charged grain interaction leads to a decrease in the diffusion coefficient. The values of the diffusion coefficients of aluminum and magnesium oxides in a smoky plasma as functions of the plasma temperature and the size and the charge of grains are determined.
Keywords: smoky plasma, diffusion coefficient, dipole.

The composition of a plasma of the combustion products of metallized fuels [1] and gas-dispersion flames [2] (the so-called smoky plasmas [3]) is determined by the conditions of combustion of metal particles in a torch and by the processes of nucleation and condensation of metal oxide grains. At the formation stage of smoky plasmas, the decisive role is played by the combustion of a dispersed metal (iron, aluminum, or magnesium) in a gaseous oxidizer (oxygen), which results in the appearance of the molecules of metal oxides. In the molecular gas of metal oxides during the cooling of a torch, the condition of a phase transition is created, and the grains of the condensed phase are formed. Then the grains grow up to the exhaustion of the gas, and, thus, a fraction of the smallest smoky grains of a plasma is formed. Note that, along with the processes of chemical transformation of molecules, the processes of ionization and recombination are running as well, so the gas phase contains free electric charges. As a result of the interfacial interaction, a charge appears on the surface of grains, which can lead subsequently to the electrostatic grain–molecule dipole interaction. It is known that the molecules of metal oxides have a dipole moment due to the inner structure of the electron shells, as well as the impact of an external electric field. Thus, the charged grains may interact with the dipole that will affect the diffusive flow in the direction of the grain. Accordingly, the diffusion coefficient will be sensitive to the condensational growth of particles. The effect of the electrostatic interaction on the diffusion coefficient was considered in [4], but without accounting for molecules of a buffer gas such as air. The purpose of the present work is to determine the effect of the polarization of molecules of metal oxides on the diffusion coefficient in the atmospheric-pressure smoky plasma formed by the combustion of aluminum- and magnesium-fuel compositions. We use Einstein's formula for the diffusion coefficient:

$$D = \frac{1}{2}\lambda\frac{kT}{mv}, \tag{1}$$

where λ – free path length, m – mass, v – velocity of molecules, T – temperature, k – the Boltzmann constant.

The free path length of a molecule in the gas mixture can be approximated by the expression

$$\lambda = \frac{1}{\sqrt{2}\sum_i n_i\sigma_i},$$

where n_i and σ_i are the concentration and the transport cross-section of the i-component of the mixture, respectively. The transport cross-section of the electroneutral i-th molecule can be represented in the first approximation as πr_i^2. Then the free path length for the considered vapor mixture of metal oxides and nitrogen can be written as

$$\lambda = \frac{1}{\sqrt{2}\pi(n_m r_m^2 + n_N r_N^2)},$$

where n_m and n_N are the concentration of the metal oxide vapor and nitrogen molecules, respectively, r_m,

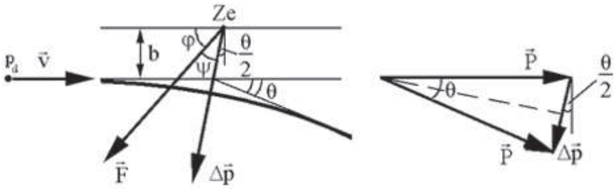

Fig. 1. Scheme of the motion of a dipole in the electric field of a grain (*a*) and the dipole momentum change (*b*)

r_N – their radii. Substituting these expressions in (1), we obtain that the diffusion coefficient of an electrically neutral gas mixture reads

$$D_0 = \frac{kT}{2\sqrt{2}\pi mv(n_m r_m^2 + n_N r_N^2)}. \quad (2)$$

Assume that the oxide molecule has some dipole moment, whose interaction with a charged grain leads to the scattering of a dipole in the electric field of the grain charge. By considering the interaction of an electrostatic dipole and a grain charge according to the method in [5], we obtain the following expression for the interaction force:

$$F_d = \frac{p_d Ze}{4\pi\epsilon\epsilon_0 r^3}. \quad (3)$$

Here, p_d – the dipole moment of a molecule, Z – charge of a condensed grain in units of electron charge, r – distance between the dipole and the grain. Consider the motion of a dipole in the electric field of a charged grain (Fig. 1) with the impact parameter b and the scattering angles θ, φ, ψ.

Let us write the conservation laws of energy and momentum for a dipole that flies in the field of a grain charge:

$$\begin{cases} \frac{m}{2}(r'^2 + r^2\varphi') + \frac{p_d Ze}{8\pi\epsilon\epsilon_0 r^2} = \frac{m\nu^2}{2}, \\ mr^2\varphi\prime = mvb. \end{cases} \quad (4)$$

Here, b – sighting option.

The system of equations (4) yields

$$r^2\varphi' = vb.$$

Given $dt = \frac{d\varphi}{\varphi'}$, we can write the expression for a change in the momentum of a dipole in the field of a point charge:

$$\Delta\mathbf{p} = \int F_{\Delta p} dt = \int F\cos(\psi) dt =$$

$$= \frac{p_d Ze}{8\pi\epsilon\epsilon_0 rvb} \int\limits_0^{\pi-\theta} \sin\left(\varphi + \frac{\theta}{2}\right) = \frac{p_d Ze}{8\pi\epsilon\epsilon_0 rvb} 2\cos\left(\frac{\theta}{2}\right).$$

From Fig. 1, we have

$$\psi = \frac{\pi}{2} - \varphi - \frac{\theta}{2}, \quad \cos(\psi) = \sin\left(\varphi + \frac{\theta}{2}\right).$$

On the other hand,

$$p = 2mv\sin\left(\frac{\theta}{2}\right),$$

where θ, φ, ψ – scattering angles.

From the last two equations, we can find the sighting option and its differential:

$$b = \frac{p_d Ze}{4\pi\epsilon\epsilon_0 rv^2 m}\,\mathrm{ctg}\left(\frac{\theta}{2}\right),$$

$$db = -\frac{p_d Ze}{4\pi\epsilon\epsilon_0 rv^2 m}\frac{1}{2\sin^2(\frac{\theta}{2})}d\theta.$$

The relation between the scattering angle θ and the sighting option b is determined explicitly, the range of scattering angles from θ to $\theta + d\theta$ matches a range of sighting options from b to $b + db$. We now calculate the proportion of the scattering angles of dipoles that are within θ and $\theta + d\theta$. Dipoles that satisfy this condition get in the ring with the inner and outer radii b and $b + db$, respectively (Fig. 1). Given the smallness db, the area of the ring is $2\pi bdb$. If one grain is a target in the unit area, omitting the sign "–" before the transport scattering cross-section of dipoles on the charged grains, we obtain

$$d\sigma = \frac{dn}{n} = 2\pi bdb = 2\pi\left(\frac{p_d Ze}{4\pi\epsilon\epsilon_0 rmv^2}\right)^2 \frac{\mathrm{ctg}(\frac{\theta}{2})}{2\sin(\frac{\theta}{2})}d\theta. \quad (5)$$

The expression for the transport scattering cross-section is

$$\sigma_t = \int (1-\cos\theta) d\sigma =$$

$$= \pi\left(\frac{p_d Ze}{4\pi\epsilon\epsilon_0 rmv^2}\right)^2 \int (1-\cos\theta)\frac{\mathrm{ctg}(\frac{\theta}{2})}{\sin^2(\frac{\theta}{2})}d\theta, \quad (6)$$

where the integral

$$\int (1-\cos\theta)\frac{\mathrm{ctg}(\frac{\theta}{2})}{\sin^2(\frac{\theta}{2})}d\theta = 4\ln\left(\sin\left(\frac{\theta}{2}\right)\right).$$

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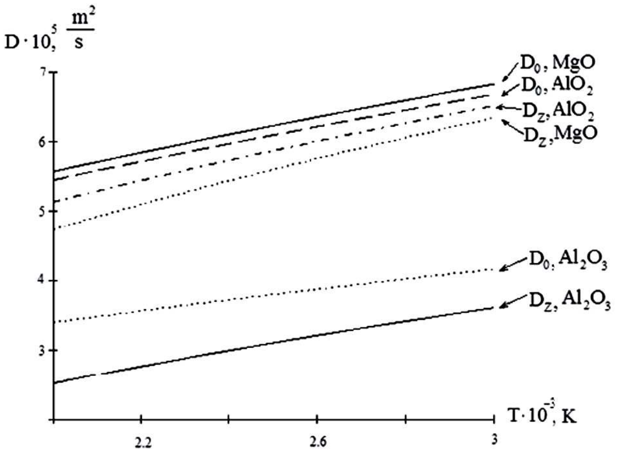

Fig. 2. Diffusion coefficients of molecules of metal oxides in nitrogen for electrically neutral molecules D_0 and for polarized molecules D_z

For small angles, $\sin(\frac{\theta}{2}) = \frac{\theta}{2}$. Averaging the function $\ln(\frac{\theta}{2})$ between $\frac{\pi}{150}$ and $\frac{\pi}{180}$, we obtain a numerical value of 0.017.

Then the final equation for the transport scattering cross-section reads

$$\sigma_t = 0.017\pi \left(\frac{p_d Ze}{4\pi\epsilon\epsilon_0 rmv^2}\right)^2. \tag{7}$$

From expressions (1) and (7), we obtain the equation for the diffusion coefficient in the case of the charged grain–dipole interaction for small scattering angles,

$$D_Z = \frac{kT}{2\sqrt{2}mv(n_\mathrm{d}\sigma_t + \pi n_\mathrm{N} r_\mathrm{N}^2)}, \tag{8}$$

where n_d and n_N are the concentrations of metal oxide dipoles and nitrogen molecules, respectively, and r_N is the radius of nitrogen molecules.

Consider the results of calculation of the diffusion coefficient of the molecules of aluminum and magnesium oxides as a function of the temperature for electrically neutral molecules and polarized ones (Fig. 2). The calculations were carried out for the temperature range 2000–3000 K, which is characteristic of a smoky plasma produced by the combustion of metal powders in air. As follows from the plots, the dependences are linear, and the dipole–charged grain interaction leads to a decrease in the value of diffusion coefficient. We also note that the diffusion

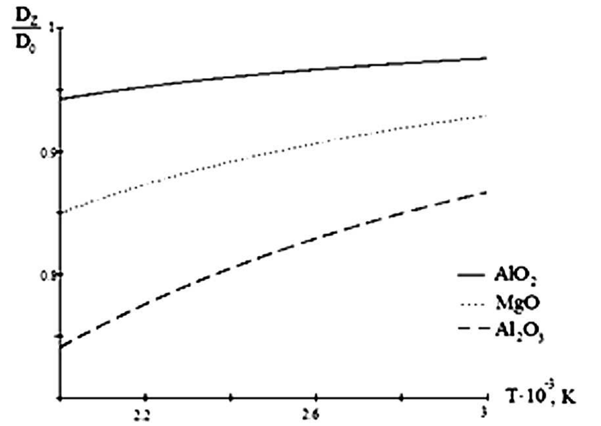

Fig. 3. Dependence of the relative diffusion coefficient $\frac{D_z}{D_0}$ on the temperature for various molecules of oxides

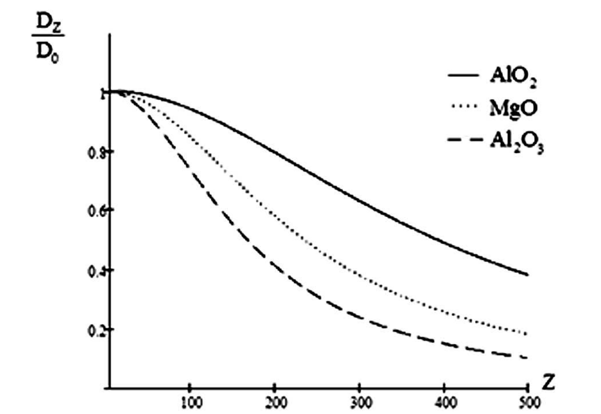

Fig. 4. Dependence of the ratio $\frac{D_z}{D_0}$ on the particle charge Z (in units of electron charge)

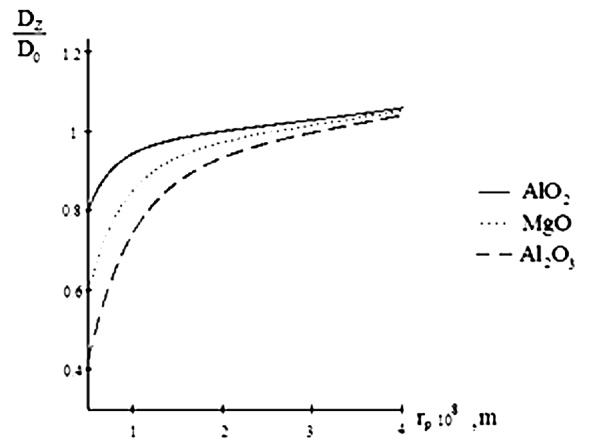

Fig. 5. Dependence of the ratio $\frac{D_z}{D_0}$ on the grain size for different molecules

coefficients of the lighter molecules such as MgO and AlO_2 are higher than that for molecules Al_2O_3.

For clarity, Fig. 3 shows the influence of the electrostatic dipole interaction with charged particles on the temperature dependences of the diffusion coefficient relative to its value for the electrically neutral gas. The relatively strong influence of the electrostatic interaction is observed for molecules Al_2O_3, which can be explained by their strong polarization. However, with as the temperature increases, this effect is reduced, since the average energy of thermal motion of molecules increases.

The charge on the grain surface significantly affects the relative diffusion coefficient, as it affects the transport scattering cross-section of dipoles. As follows from Fig. 4, as the charge of particles increases, the relative influence of electrostatic interaction increases significantly, and the diffusion coefficient is reduced by several times.

Similar dependences of the relative diffusion coefficient on the grain size are shown in Fig. 5. For the grains with smaller sizes, the dipole interaction leads to a decrease in the coefficient of diffusion. However, as the grain size increases, we arrive at the situation where the diffusion coefficient of neutral molecules becomes more than the diffusion coefficient of a dipole.

As a result, we can conclude that, in the study of the condensing growth of particles in a smoky plasma, the dipole moments of molecules and their interaction with charged grains of the condensed phase should be considered.

1. V.I. Vishnyakov, D.S. Dragan, and S.V. Margashchuk, in it Plasma Chemistry (Energoatomizdat, Moscow, 1990), Issue 16, p. 98 (in Russian).
2. A.N. Zolotko, Ya.I Vovchuk, N.I. Poletaev, A.V. Florko, and I.S. Al'tman, Fiz. Goren. Vzryva **32**, No. 3, 24 (1996).
3. G.S. Dragan, JETP **125**, 570 (2004).
4. G.S. Dragan, A.I. Goremulta, K.V. Kolesnikov, D.V. Spodarets, and V.M. Ulyanitskiy, *Contr. 4th Int. Conf. "Dusty plasma in applications"* (Odessa, Ukraine, 2013).
5. E.M. Lifshitz and L.P. Pitaevskii, *Physical Kinetics* (Pergamon Press, Oxford, 1981).
6. B.M. Smirnov, Uspekhi Fiz. Nauk **92**, 75 (1967).

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ВПЛИВ ПОЛЯРИЗАЦІЇ МОЛЕКУЛ ОКСИДІВ МЕТАЛІВ НА КОЕФІЦІЄНТ ДИФУЗІЇ В ДИМОВІЙ ПЛАЗМІ

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Досліджено вплив поляризації молекул оксидів металів на значення коефіцієнта дифузії в димовій плазмі, утвореної спалюванням металевого порошку в повітрі. Показано, що електростатична взаємодія диполь–заряджена частинка призводить до зменшення значення коефіцієнта дифузії в димовій плазмі. Визначено коефіцієнти дифузії оксидів алюмінію і магнію в димовій плазмі залежно від температури, розмірів і зарядів частинок.