THEORY OF THE COMBUSTION OF SMALL DROPS OF METAL

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The article discusses the combustion of small drops of metal. It is postulated that the formation of an oxide in the liquid phase starts with the origin of a condensed phase and continues as the result of a reaction between the vapors of the drop and the oxidizer at the surface of the forming particles of the condensed phase. It is shown that the process of the formation of particles of condensed oxide in the gas, for very small drops, has an essentially unsteady-state character. Under these circumstances, a considerable fraction of the vaporization products of a drop does not succeed in condensing after the complete gasification of the drop and remains in the gaseous state.

The most significant special characteristic of the combusion of metallic drops is the formation of condensed combustion products. The question of the formation mechanism and the spectrum of the oxide particles formed can be determined only with an explicit consideration of the structure of the zone of the reaction between the vapors of the drop and the oxidizer. In a quasisteady-state approximation, for metals with difficulty volatilizing oxides (of the type of Al, Mg, Be, etc.), this question was discussed in [1]. It was found that with steady-state combustion of a drop, at great distances from its surface the velocity of the steady-state flow reverts to zero, and, as a result of this, in this region there is an accumulation of particles of the oxide. It was noted, however, that for small drops a steady-state distribution of the particles in the neighborhood of the point at which the Stefan flow reverts to zero is established after a time which is considerably greater than the time of the complete combustion of a drop of metal. Therefore, it is of interest to examine the manner in which the particles of the oxide are formed and move in space during the time of the unsteady-state process of the formation of the structure of the reaction zone.

Let there be a drop of metal with an initial radius R in an oxidizing medium with a temperature T_0, a pressure P_0, and a relative mass concentration of the oxidizer a_{ox}^0. Analogously to [1], we shall assume that the combustion of the drop is spherically symmetrical and that the process of the formation of the oxide in the gas starts with the formation of nuclei of the condensed phase, consisting of molecules of the metal and the oxidizer, and continues as the result of a heterogeneous reaction between vapors of the drop and the oxidizer, even at the surface of the oxide particles. Under these circumstances, let the rate of condensation Φ and the rate of formation of the nuclei, respectively, have the form

$$\Phi = k_1\rho^2 a_f a_{\text{ox}} s; \quad d_t n = k_2\rho^2 a_f a_{\text{ox}},$$

where a_f and a_{ox} are the relative mass concentrations, respectively, of the vapors of the metallic drop and the oxidizer; ρ is the density of the gas; s is the specific (for a unit of volume) surface of the oxide particles formed; n is the number of oxide particles in unit volume; and k_1 and k_2 are the reaction-rate constants of condensation and nucleus-formation, which, by virtue of the small value of the activation energy of these reactions and the high level of the temperatures of the medium, are assumed to be independent of the temperature. The rate of consumption of vapors of the drop of metal and the oxidizer going to the formation of nuclei of the condensed phase (by virtue of their smallness) is assumed to be negligibly small in comparison with the rate of condensation.

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The picture of the combustion of a drop of metal described in [1] has the following appearance. The products of the vaporization of the drop flow away from its surface and enter into a heterogeneous reaction with the oxidizer at large distances from the drop, forming condensed particles of oxide. This reaction has only a weak effect on the distribution of the vapors of the drop and the oxidizer at large distances and almost does not prevent the penetration of the oxidizer to the surface of the drop. The heat evolved as a result of the reaction between the oxidizer and the metal at the surface of the drop goes for further vaporization of the metal and heating of the drop.

The condensed oxide, which is a combustion product of the metallic drop, is formed both at the surface of the drop of metal and in the gas surrounding the drop. The entrainment of small condensed particles of oxide, forming in the gas phase, is effected by a Stefan flow, which is assumed to be directed away from the surface of the drop. By the velocity of the Stefan flow in diffusion problems there is usually understood the mean volumetric velocity of the gas, while in hydrodynamics by the velocity of the motion of the liquid there is understood the mean mass velocity [2-4]. The difference between the mean mass and mean volumetric velocities of the gas is connected with the varying density and can be very considerable if the molecular weights of the counterdiffusing components differ greatly. The transport of condensed particles in the gas takes place at the velocity of the gas; therefore, here by the velocity of the Stefan flow there is understood the mean mass velocity of the gas.

We shall assume that the characteristic combustion time of a drop of metal R^2/α, where α is the coefficient of proportionality in the Sreznevskii law ($r_0^2 = R^2 - \alpha t$), is much greater than the characteristic time of the heterogeneous reaction at the surface of the nuclei $(k_1 \rho s_0)^{-1}$, where $s_0 = [4\pi(\rho/\rho_c)^2 k_2 \rho / k_1]^{1/4}$ is the characteristic specific surface of the forming particles of oxide, and much greater than the characteristic diffusion time R^2/D, which leads to the ratios $R^2 > \alpha/k_1 \rho s_0$ and $\alpha/D \ll 1$. Under this assumption, the distributions of the concentrations of the gaseous substances around the drop can be assumed to be steady-state.

We introduce the following dimensionless variables and parameters: $\tau = \alpha t/R^2$ is the time; $\zeta = r/R$ is the distance from the drop; $\beta = ur_0/D$ is the Stefan flow (at the surface of the drop $\beta = \beta_0 = u_0 r_0/D$); $\delta^2 = k_1 \rho R^2 s_0/D$ is the ratio of the characteristic diffusion time to the characteristic time of the heterogeneous reaction at the surface of the nuclei; $\gamma = \alpha/D$ is the ratio of the characteristic diffusion time to the characteristic combustion time of the drop; and $S = s/s_0$ is the dimensionless specific surface of the particles of oxide in the gas phase.

Assuming that the binary diffusion coefficients are equal to each other, the dimensionless diffusion equations for the products of the vaporization of the drop and for the Stefan flow can be written in the form

$$\partial(\beta a_f \sqrt{1-\tau} - \zeta^2 \partial a_f/\partial\zeta)/\partial\zeta = -(\nu_f \mu_f/\mu_c)\delta^2 \zeta^2 a_f a_{ox} S; \tag{1}$$

$$\zeta_0 \partial\beta/\partial\zeta = -\delta^2 \zeta^2 a_f a_{cx} S. \tag{2}$$

Here the partial derivatives are written, since it is assumed that the specific surface of the particles of the condensate S, the concentration a_f, and the Stefan flow β depend not only on the coordinate, but also on the time. The quantity $\sqrt{1-\tau} = r_0/R = \zeta_0$ is the coordinate of the surface of the drop of metal. Analogous diffusion equations can be written for the concentration of the oxidizer a_{ox}, the decomposition products of the oxidizer a_p, and the inert gas a_i. The parameters ν and μ, with the corresponding subscripts, introduced into the equations, are the stoichiometric coefficients of the heterogeneous reaction at the surface of the nuclei and the molecular weights of the components participating in the reaction.

The boundary conditions for Eqs. (1), (2) can be written in the form

$$\zeta = \zeta_0,\ a_f = a_f^0,\ a_{ox} = 0,\ \beta = \beta_0,\ (u_0 a_i^0 - \partial a_i/\partial\zeta) = 0,$$
$$(\nu_p \mu_p/\nu_{ox} \mu_{ox})(\partial a_{ox}/\partial\zeta) = -(u_0 a_p^0 - \partial a_p/\partial\zeta),\ \zeta = \infty,$$
$$a_f = a_p = 0,\ a_{ox} = a_{ox}^0,\ a_i = (1 - a_{ox}^0),$$

where it is assumed that at the surface of the metallic drop a heterogeneous reaction takes place at a high rate and that the equilibrium between the vaporization products of the drop and the condensed substance of the drop is established very rapidly.

To determine the dependence of the specific surface of the oxide particles S on the coordinate and the time, let us consider the equation of the rate of formation of nuclei of the condensed phase and the equation of the rate of growth of the forming particles of condensate. The dimensionless equation of the change in the diameter φ of an individual particle of condensate in the gas phase is written in the form

$$\gamma \partial\varphi/\partial\tau + (\beta\zeta_0/\zeta^2)(\partial\varphi/\partial\zeta) = 2(\rho/\rho_c)(\delta^2/s_0)a_f a_{ox}, \tag{3}$$

and the dimensionless equation of the formation of nuclei of the condensed phase in the form

$$\gamma \partial n/\partial\tau + (\zeta_0/\zeta^2)(\partial\beta n/\partial\zeta) = (k_2\rho/k_1)(\delta^2/s_0)a_f a_{ox}. \tag{4}$$

In distinction from the diffusion equations (1), in which by virtue of the assumption $\gamma \ll \delta^2$ the derivative with respect to the time was neglected, in Eqs. (3), (4) the derivatives with respect to the time are retained, since it is assumed that $\gamma \sim \delta^3$ (in [1] it was assumed that $\gamma \ll \delta^3$).

The boundary conditions for Eqs. (3), (4) are as follows: at the surface of the drop of metal

$$\zeta = \zeta_0 = \sqrt{1-\tau},\ n = 0;$$

at the point of formation of a nucleus of the particle of condensate under consideration

$$\zeta = \zeta',\ \varphi = 0.$$

The initial conditions are as follows:

$$\tau = 0,\ n = 0,\ \varphi = 0.$$

To simplify the equations presented, we introduce the function $\theta = \theta(\zeta, \tau)$, which satisfies the equation

$$\gamma \partial\theta/\partial\tau + (\beta\zeta_0/\zeta^2)(\partial\theta/\partial\zeta) = \delta^2 a_f a_{ox}, \tag{5}$$

with the initial conditions $\tau = 0$, $\theta = 0$, $\xi = \xi_0$, and $\theta = 0$. In its physical meaning, the function θ corresponds to the diameter of a particle of the condensate, whose nucleus was formed near the surface of the drop of metal.

The solutions of Eqs. (3), (4) can be written in terms of the function θ:

$$\varphi = 2(\rho/\rho_c)(1/s_0)(\theta - \theta');$$

$$n = (k_2\rho/k_1 s_\theta)\exp\left(\int_{\theta'}^{\theta} S d\theta\right)\int_{\theta'}^{\theta}\exp\left(-\int_{\theta'}^{\theta} S d\theta\right)d\theta,$$

where the function θ' corresponds to the coordinate and the moment of time of the formation of the nucleus of the particle of condensate under consideration.

Integrating with respect to θ' from zero to θ the product of the surface of a particle of condensate $\pi\varphi^2$ by the function $dn/d\theta'$, we can obtain an expression for the value of S:

$$S = \int_0^{\theta}(\theta - \theta')^2\exp\left(\int_{\theta'}^{\theta} S d\theta\right)d\theta'.$$

The solution of this equation is

$$S = \mathrm{tg}\,\theta/2^{1/4} - \mathrm{th}\,\theta/2^{1/4}.$$

Thus, the problem of investigating the structure of the zone of the reaction around a drop of metal, i.e., the problem of determining the value of the Stefan flow, the concentration and the specific surface of the particles of the condensate, and the distributions of the concentrations of the gaseous substances, reduces to finding the dependence of the function θ on the coordinate and the time.

We use the postulation, introduced in [1], with respect to the smallness of the characteristic time of the heterogeneous reaction at the surface of the nuclei in comparison with the characteristic diffusion time $\delta^2 \ll 1$. Then at small distances from the surface of the drop ($\zeta\delta \ll 1$) the solution of the diffusion equations (1), with an accuracy up to quantities of the zero order with respect to δ, will be as if there were no condensation reaction at all in the gas around the drop. Such a situation corresponds to a situation in which the reaction in the gas phase has no effect on the combustion rate of the drop during the process of the combustion of a metallic drop. The combustion reaction of a drop of metal takes place at its surface due to the diffusion of the oxidizer into it.

Solving the diffusion equation (1) with a zero right-hand part, and using the condition of the equality to unity of the sum of the concentrations of all the gaseous substances at the surface of the drop, we obtain the following expressions for the concentration and the flow I_f^0 of the products of the vaporization of a drop at its surface:

$$a_f^0 = 1 - \left[1 - (1 - \nu_p\mu_p/\nu_{ox}\mu_{ox})\,a_{ox}^0\right]e^{-\beta_0};$$
$$I_f^0 = \zeta_0 a_f^0\beta_0/(1 - e^{-\beta_0}). \tag{6}$$

Eliminating the right-hand part in Eqs. (1), (2), and integrating the equation obtained with respect to the coordinate, taking account of the boundary conditions at the surface of the drop (6), we obtain

$$\beta\zeta_0 a_f^0 - \zeta^2 (\partial a_f/\partial\zeta) = \nu_f \mu_f \zeta_0 (\beta - \beta_\infty)/\mu_c, \tag{7}$$

where

$$\beta_\infty = \beta_0 \left[(1 - \mu_f \nu_f/\mu_c) + (1 - \mu_p \nu_p/\mu_{ox}\nu_{ox})\, a_{ox}^0 e^{-\beta_0}/(1 - e^{-\beta_0})\right]$$

corresponds to the value of the Stefan flow at infinity in the steady-state problem [1]. The value of β_∞ is negative, independently of the medium in which the combustion of the drop takes place: in oxygen, water vapor, or carbon dioxide.

At large distances from the drop ($\zeta\delta \sim 1$) we introduce the new variable $\eta = \zeta\delta$ and the parameter $\omega = \gamma/\delta^3$. Neglecting terms of the order δ in Eq. (7) and expressing the concentration of the vaporization products of the drop a_f in terms of the function θ, from (5), taking account of the fact that at great distances $a_{ox} = a_{ox}^0 + 0(\delta)$, we obtain the equation

$$\eta^2 [\omega\partial\theta/\partial\tau + (\beta\zeta_0/\eta^2)(\partial\theta/\partial\eta)]/\partial\eta = -(\nu_f\mu_f/\mu_c)\, a_{ox}^0 (1/2)^{1/4} \zeta_0 (\beta - \beta_\infty). \tag{8}$$

An equation for determining the change in the Stefan flow at large distances from the drop is obtained by substituting the concentration of the vaporization products of the drop a_f from (5) into Eq. (2):

$$\partial\beta/\partial\eta = -S\eta^2/\zeta_0 [\omega\partial\theta/\partial\tau + (\beta\zeta_0/\eta^2)(\partial\theta/\partial\eta)]. \tag{9}$$

The initial and boundary conditions for Eqs. (8), (9) can be written in the form

$$\tau = 0,\ \theta = 0;\ \eta = 0,\ \theta = 0;\ \eta \to \infty,\ \omega\partial\theta/\partial\tau + (\beta\zeta_0/\eta^2)(\partial\theta/\partial\eta) \to 0.$$

The latter condition means the equality to zero at infinity of the concentration of the vaporization products of the drop.

We shall solve Eqs. (8) and (9) with the assumption $\omega/\beta_0 \gg 1$, which corresponds to the condition

$$R < [\alpha D^{1/2}/\beta_0 (k_1 \rho s_0)^{3/2}]^{1/3}.$$

Together with the condition of the quasisteady-state distribution of the concentrations of the gaseous substances around a drop of the metal $R > (\alpha k_1 \rho s_0)^{1/2}$, evaluations using this condition give a range of diameters of the metallic drops, in which the dependences given are valid, equal to from 3 to 40 μ.

At great distances from the surface of the drop, the solution of Eq. (8) is $\theta \sim \beta_0/\omega$. From this, substituting the solution into Eq. (9), we find that with an accuracy up to quantities on the order of (β_0/ω) the Stefan flow can be regarded as constant at such large distances. At small distances $\eta \sim \beta_0/\omega$ we introduce the following new variables: $z = \theta\omega^{2/3}$ and $x = \eta\omega^{1/3}$, where the value of θ is on the order of β_0/ω and, consequently, the Stefan flow can be assumed constant and equal to β_0, by virtue of the connection with the solution near the drop. Finally, after connecting the solutions at large distances from the drop and at distances on the order of β_0/ω, we obtain the solution of Eq. (8):

$$\begin{gathered} \eta \leqslant \eta^*,\ \theta = (\nu_f\mu_f/\mu_c)\, a_{ox}^0 (1/2)^{1/4} [(\beta_0 - \beta_\infty)/2\beta_0]\, \eta^2, \\ \eta \geqslant \eta^*,\ \theta = (\nu_f\mu_f/\mu_c)\, a_{ox}^0 (1/2)^{1/4} [(\beta_0 - \beta_\infty)/2\beta_0]\, [\eta^2 - (\eta^3 - \eta^{*3})^{2/3}], \end{gathered} \tag{10}$$

where

$$\eta^* = \left(\frac{3\beta_0}{\omega}\int_0^\tau \zeta_0 d\tau\right)^{1/3} = \left\{\frac{2\beta_0}{\omega}[1 - (1 - \tau)^{3/2}]\right\}^{1/3}$$

is a coordinate, corresponding to the maximum of the specific surface of the particles of condensate. In obtaining this solution, it was taken into consideration that the coordinate of a particle of the condensate, reaching the coordinate η after a time τ ($\eta' = (\eta^3 - \eta^{*3})^{1/3}$), is greater than or equal to zero and cannot be negative.

The dependence of the Stefan flow on the coordinate and the time can be determined from Eq. (9). Substituting the solution (10) into this equation, we find

$$\begin{gathered} \eta \leqslant \eta^*,\ \beta = \beta_0 - \frac{4}{\beta}\beta_0 \left[\frac{1}{4}\frac{\nu_f\mu_f}{\mu_c} a_{ox}^0 \frac{(\beta_0 - \beta_\infty)}{\beta_0}\right]^4 \eta^8, \\ \eta \geqslant \eta^*,\ \beta = \beta_1 - \left[\frac{1}{3}\frac{\nu_f\mu_f}{\mu_c} a_{ox}^0 \frac{(\beta_0 - \beta_\infty)}{\beta_0}\right]^4 \beta_0 \eta^{*8}\left(1 - \frac{\eta}{\eta^*}\right), \end{gathered}$$

where β_1 is the value of the Stefan flow with $\eta = \eta^*$. It can be seen that for the small drops under consideration here ($\beta_0/\omega \ll 1$) the Stefan flow is always directed away from the surface of the drop and does not revert to zero. For larger drops, the formation of the stationary reaction front in the gas phase, described in [1], at which the maximum of the specific surface of the particles of condensate (a maximum of θ) coincides with the point at which the velocity of the Stefan flow reverts to zero, takes place in the following manner. At some moment of time, the velocity of the Stefan flow reverts to zero at infinity and, with the development of the process of the combustion of the drop, moves toward its surface. Such a situation is similar to the development of a gas-phase reaction front with the combustion of a drop of a hydrocarbon fuel [5]. On the other hand, the maximum of the specific surface of the particles of condensate originates near the surface of the drop and, with the passage of time, moves away fron it, approaching the point where the Stefan flow reverts to zero, which is in agreement with visual observations of the process of the ignition of metallic particles. For drops of the metal with a diameter of 100-200 μ, the formation of a stationary reaction front in the gas takes place in a time which is considerably less than the combustion time of a drop. With the combustion of smaller drops, such as are under consideration in the present case, a stationary reaction front is not able to form in the gas during the time of the complete gasification of the drop.

With the steady-state combustion of a drop of metal, the Stefan flow at infinity is equal to β_∞, and the flow of vaporization products of the drop reverts to zero. In [6] it was shown that the fraction of the oxide forming in the gas phase from the vaporization products of a drop is 70-80% of the whole mass of oxide forming with combustion, while the remaining part of the oxide is formed at the surface of the burning metallic drop. In the present case of the combustion of small drops of metal, the Stefan flow at infinity is greater than β_∞, and the flow of vaporization products of the drop does not revert to zero. This is evidence that only part of the vaporization products of the drop succeeds in condensing in the time of the complete gasification of the drop in the gas. The remaining part remains in the gaseous state in the form of suboxides. An expression for the fraction of oxide which succeeds in condensing in the gas phase in the combustion time of the drop, out of the whole mass of oxide which should be formed, can be written in the form

$$\sigma = \sigma_0 (3/11)[1 + (3/4)^3][(\beta_0 - \beta_\infty)/\beta_0]^3 \left[\nu_f \mu_f/3\mu_c) a^0_{\mathrm{ox}}\right]^4 (2\beta_0/\omega)^{8/3}.$$

It can be seen that for all cases of the combustion of drops of aluminum in the above range of sizes, the fraction of oxide condensing in the gas phase amounts to fractions of a percent. However, this fraction rises very sharply with an increase in the drop size (as R^8).

Thus, the process of the formation of condensed particles of oxide in the gas with the combustion of drops of metal with a diameter less than 40 μ takes place under essentially unsteady-state conditions, under which a stationary zone of the reaction of the chemical condensation of the oxide does not succeed in forming in the gas phase in the time of the complete gasification of the drop. The vaporization products of a drop of metal in the gas phase are not able to condense in the combustion time of a drop, and thus, they remain in the gaseous state (for example, with the combustion of aluminum [6]) in the form of aluminum monoxide and polyoxide AlO and Al_2O.

LITERATURE CITED

1. V. M. Gremyachkin, A. G. Istratov, and O. I. Leipunskii, "The formation of condensed particles of oxide with the combustion of small drops of metal," Zh. Prikl. Mekh. Tekh. Fiz., No. 4, 70-78 (1974).
2. V. N. Bloshenko and B. I. Khaikin, "Stefan flow with heterogeneous chemical reactions," Zh. Fiz. Khim., No. 12 (1967).
3. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, The Molecular Theory of Gases and Liquids, Wiley (1964).
4. L. D. Landau and E. M. Lifshits, The Mechanics of Continuous Media [in Russian], Izd. Gostekhteorizdat, Moscow (1953).
5. V. N. Bloshenko, A. G. Merzhanov, N. I. Peregudov, and B. I. Khaikin, "The theory of the gas-phase ignition of a drop," in: Combustion and Explosion, Materials from the Third All-Union Symposium on Combustion and Explosion [in Russian], Izd. Nauka, Moscow (1972).
6. V. M. Gremyachkin, A. G. Istratov, and O. I. Leipunskii, "Model of the combustion of small drops of metal," Fiz. Goreniya Vzryva, No. 3 (1975).