NON-STEADY-STATE THEORY OF VAPOR-PHASE IGNITION AND COMBUSTION OF A METAL PARTICLE

M. A. Gurevich, A. Ya. Lukin,
G. I. Sirkunen, and A. M. Stepanov

UDC 662.612.2,3

The boiling point of metals (Mg, Al), as distinct from hydrocarbon fuels, is relatively high. Hence, the interaction of metal particles with a gaseous oxidant initially, i.e., at low temperatures of the metal, occurs almost entirely on the particle surface; in addition, the oxide film formed during the heterogeneous reaction (or beforehand) also strongly prevents (in the case of Al, for instance) the development of the homophasic reaction until the film melts. The conditions of ignition of a metal particle (whether there is a sharp increase in its temperature or not) depend, consequently, on the relative rates of heat production due to the heterogeneous reaction and heat transfer from the particle to its surroundings. Experimental investigations of the mechanism of ignition of magnesium particles and dense conglomerates of them [1] provide direct evidence that the primary ignition of the particle is heterogeneous. Since the experiments in [1] showed that limit of heterogeneous ignition (determined from the appearance of red tracks) agreed closely with the results of measurements in [2], these latter authors probably also observed the limits of heterogeneous ignition.

The theory of heterogeneous ignition of metal particles has now been fairly well developed for the following: a linear law of oxidation of the metal (Mg) [3]; the presence of changes in the structure of the oxide film (its recrystallization) during heating (Al) [4, 5]; and any power law of oxidation (Mg, Al) [6]. This question is not considered in the present paper.

In the experiments in [1] purely surface combination of Mg specimens was observed only in atmospheres with very low oxidant contents (1-4% O_2); the difference in the limits of heterogeneous and vapor phase ignition did not exceed 25°C. In all other known investigations the combustion of the magnesium (particles, wires, etc.) always took place in the gas phase. This indicates that from the viewpoint of practical problems we can regard the accomplishment of surface ignition of Mg particles as a perfectly adequate condition for their vapor-phase ignition and combustion. The question of transfer of the chemical reaction from the surface of the metal particle to the gas phase was investigated theoretically in [7] and more rigorously in [8]. In each case the authors concluded that for particles this transfer must occur in superlimit conditions. It should be noted that in [7, 8] the problem was regarded in a quasisteady formulation; the calculations were made for only one value of the Arrhenius constants (k* and E) for a homogeneous reaction. The value of k* was calculated on the basis of the gas-kinetic theory of double molecular collisions, and E was arbitrarily assumed equal to the activation energy for the heterogeneous reaction; such values of k* and E can, of course, differ significantly from the actual values.

We consider the problem of ignition of a metal particle, the formation of a diffusion combustion front close to it, and developed vapor-phase combustion in a non-steady-state formulation. The temperature distribution near the particle T(r, t) is given by the equation

$$c_p(\rho+\rho_{\mathrm{ox}})\left[\frac{\partial T}{\partial t}+v\frac{\partial T}{\partial r}\right]-\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\lambda\frac{\partial T}{\partial r}\right)=qk+l_{\mathrm{ox}}m, \qquad (1)$$

where

$$k=k^*\rho^2 n_{\mathrm{V}} n_{\mathrm{O}}\exp\left(-\frac{E}{RT}\right).$$

The first term on the left-hand side of this equation takes into account the buildup in unit volume of the enthalpy of the gas and condensed oxide (ρ and ρ_{ox} are their densities; the local temperature and specific heats of the gas and condensed oxide are assumed equal); the second term takes into account convective heat transfer in the gaseous and condensed phases (the velocity of the oxide particles is assumed equal to the gas velocity v); the third term

---

Leningrad. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 5, pp. 108-116, September-October, 1977. Original article submitted September 8, 1976.

takes into account conductive heat transfer through the gas. The first term on the right-hand side of Eq. (1) represents the evolution of heat due to chemical reaction of the metal vapor with the oxidant before formation of the gaseous oxide (the reaction rate k is described by the Arrhenius law); the second term represents the evolution (or absorption) of heat due to local volume condensation (or evaporation) of oxide at rate m.

As in [9], we assume that at each point the partial pressure of the gaseous oxide p_{ox} is equal to the saturation pressure at the local temperature

$$p_{ox} = p^*_{ox} \exp(-l^*_{ox}/RT), \tag{2}$$

and its content is

$n_{ox} = \mu_{ox} p_{ox}/\mu_V P$ (V is the subscript denoting the surroundings).

On this assumption the phase transition rate m of the oxide can be calculated from its transport equation

$$\frac{\partial(\rho n_{ox})}{\partial t} + \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(\rho v n_{ox} - \rho D \frac{\partial n_{ox}}{\partial r}\right)\right] = (1+\beta)k - m. \tag{3}$$

The distribution of the concentrations of metal vapor $n_V(r, t)$ and oxidant $n_O(r, t)$ are given by similar equations:

$$\begin{cases} \dfrac{\partial(\rho n_V)}{\partial t} + \dfrac{1}{r^2}\dfrac{\partial}{\partial r}\left[r^2\left(\rho v n_V - \rho D \dfrac{\partial n_V}{\partial r}\right)\right] = -\beta k, \\ \dfrac{\partial(\rho n_O)}{\partial t} + \dfrac{1}{r^2}\dfrac{\partial}{\partial r}\left[r^2\left(\rho v n_O - \rho D \dfrac{\partial n_O}{\partial r}\right)\right] = -k. \end{cases} \tag{4}$$

Some of the gaseous oxide produced by the reaction condenses. The density of the condensed oxide ρ_{ox} is given by its mass-balance equation

$$\frac{\partial \rho_{ox}}{\partial t} + \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 \rho_{ox} v) = m. \tag{5}$$

The mass velocity of the gas can be calculated from the continuity equation

$$\frac{\partial \rho}{\partial t} + \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 \rho v) = -m. \tag{6}$$

The gas density at each point is calculated from the equation of state

$$\rho = \mu_V P/RT, \tag{7}$$

the total pressure P and molecular weight μ_V of the gas are regarded as constant and equal to their values in the surroundings. The temperature dependence of the thermal conductivity of the gas $\lambda = \lambda^*(T/T^*)^\gamma$ is taken into account, and the Lewis number is assumed equal to unity.

We formulate the boundary and initial conditions for the compiled system of equations (1), (3)-(6).

1. On the particle surface ($r = r_s$):

a) the metal vapor is saturated

$$p_{Vs} = p^*_V \exp(-l^*_V/RT_s), \quad n_{Vs} = \frac{\mu_m p_{Vs}}{\mu_V P};$$

b) the flux of oxidant is equal to the rate of the heterogeneous reaction

$$\left(\rho v n_O - \rho D \frac{\partial n_O}{\partial r}\right)_s = -k_s = -k^*_s \rho_s n_{Os} \exp\left(-\frac{E_s}{RT_s}\right);$$

c) there is no flux of neutral gases

$$\rho_s v_s = -k_s + \left(\rho v n_V - \rho D \frac{\partial n_V}{\partial r}\right)_s + \left(\rho v n_{ox} - \rho D \frac{\partial n_{ox}}{\partial r}\right)_s;$$

d) the gas temperature is equal to the particle surface temperature $T = T_s$;

e) the condensed oxide is not removed from the particle surface; i.e., if $v_s > 0$, then $\rho_{ox} = 0$.

The radius of the particle and its temperature (we assume that there are no temperature gradients within the particle) at each instant are given by the balance equation for its mass

$$-\rho_{\mathrm{m}}\frac{dr_s}{dt}=\beta k_s+\left(\rho v n_{\mathrm{v}}-\rho D\frac{\partial n_{\mathrm{v}}}{\partial r}\right)_s \tag{8}$$

and heat

$$\frac{c_p\rho_{\mathrm{M}}r_s}{3}\frac{dT_s}{dt}=\lambda_s\left(\frac{\partial T}{\partial r}\right)_s+q_sk_s-l_{\mathrm{m}}\left(\rho v n_{\mathrm{v}}-\rho D\frac{\partial n_{\mathrm{v}}}{\partial r}\right)_s-l_{\mathrm{ox}}\left(\rho v n_{\mathrm{ox}}-\rho D\frac{\partial n_{\mathrm{ox}}}{\partial r}\right)_s, \tag{9}$$

where q_s is the specific heat of formation of the condensed oxide; the specific heat of the particle is assumed equal to the specific heat of the gas, and its density before and after melting is assumed to be the same. We note that if the particle temperature reaches the melting point T_{mp} of the metal, then $T_s = T_{mp}$ for a subsequent period t_{mp}, and the time t_{mp} is determined from the heat balance for the melting particle.

2. On the outer boundary $(r = \infty)$;

a) there is no metal vapor

$$n_{\mathrm{v}}=0;$$

b) we know the temperature

$$T=T_{\mathrm{v}}$$

c) and oxident content

$$n_{\mathrm{o}}=n_{\mathrm{ov}};$$

d) the condensed oxide is removed by the external flow; i.e., if $v < 0$, then $\rho_{ox} = 0$.

3. The initial conditions $(t = 0)$ are as follows:

a) $r_s = r_0$, $T_s = T_{s0}$;

b) when $r_s < r < \infty$, $T = T_V$, $n_o = n_{oV}$, $n_V = \rho_{ox} = 0$.

Thus, to calculate the seven unknowns (T, n_V, n_o, n_{ox}, m, ρ_{ox}, v) characterizing the heat and mass transfer near the particle we compiled the system of seven equations (1)-(7); for the six differential equations (1), (3)-(7) we write the boundary (1a-e, 2a-d) and initial (3b) conditions; to calculate the relations $r_s = r_s(t)$ and $T_s = T_s(t)$ we use (8) and (9) with initial conditions (3a).

We introduce the dimensionless variables

$$\Theta=\frac{T}{T^*};\quad u=\frac{\rho v r_0 c_p}{\lambda^*};\quad y=1+\frac{\rho_{\mathrm{ox}}}{\rho};\quad x=\frac{r}{r_0};$$

$$\tau=\frac{\lambda^* t}{c_p\rho^* r_0^2};\quad M=\frac{c_p r_0^2 m}{\lambda^*};\quad x_s=\frac{r_s}{r_0}$$

and parameters

$$L_{\mathrm{v}}=\frac{l_{\mathrm{v}}}{c_pT^*};\ L_{\mathrm{v}}^*=\frac{l_{\mathrm{v}}^*}{RT^*};\ L_{\mathrm{ox}}=\frac{l_{\mathrm{ox}}}{c_pT^*};\quad L_{\mathrm{ox}}^*=\frac{l_{\mathrm{ox}}^*}{RT^*};\quad H=\frac{q}{c_pT^*};\quad H_s=\frac{q_s}{c_pT^*};$$

$$\Pi=-\frac{E}{RT^*};\quad \Pi_s=-\frac{E_s}{RT^*};\quad \psi=k_s^*\frac{r_0c_p\rho^*}{\lambda^*};\quad \Phi=k^*\frac{r_0^2c_p(\rho^*)^2}{\lambda^*};\ \varepsilon=\frac{\rho^*}{\rho_{\mathrm{m}}}.$$

The system of equations (1)-(7) takes the form

$$\frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\Theta^{\nu}\frac{\partial\Theta}{\partial x}\right)-yu\frac{\partial\Theta}{\partial x}-y\frac{1}{\Theta}\frac{\partial\Theta}{\partial\tau}=-Hf-L_{\mathrm{ox}}M,$$

$$\frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\Theta^{\nu}\frac{\partial n_{\mathrm{v}}}{\partial x}\right)-u\frac{\partial n_{\mathrm{v}}}{\partial x}-\frac{1}{\Theta}\frac{\partial n_{\mathrm{v}}}{\partial\tau}=\beta f-n_{\mathrm{v}}M,$$

$$\frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\Theta^{\nu}\frac{\partial n_{\mathrm{o}}}{\partial x}\right)-u\frac{\partial n_{\mathrm{o}}}{\partial x}-\frac{1}{\Theta}\frac{\partial n_{\mathrm{o}}}{\partial\tau}=f-n_{\mathrm{o}}M,$$

$$\frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\Theta^{\nu}\frac{\partial n_{\mathrm{ox}}}{\partial x}\right)-u\frac{\partial n_{\mathrm{ox}}}{\partial x}-\frac{1}{\Theta}\frac{\partial n_{\mathrm{ox}}}{\partial\tau}=-(1+\beta)f+(1-n_{\mathrm{ox}})M,$$

$$\frac{1}{\Theta}\frac{\partial y}{\partial\tau}+u\frac{\partial y}{\partial x}=yM,$$

$$\frac{\partial}{\partial\tau}\left(\frac{1}{\Theta}\right)+\frac{2}{x}u+\frac{\partial u}{\partial x}=-M.$$

Here

$$f = \Phi n_{\mathrm{V}} n_{\mathrm{O}} \frac{1}{\Theta^2} \exp\left(\frac{\Pi}{\Theta}\right).$$

The boundary conditions are

when $x = x_s$

$$n_{\mathrm{V}} = \frac{\mu_{\mathrm{m}} p_{\mathrm{V}}^*}{\mu_{\mathrm{V}} p} \exp\left(-\frac{L_{\mathrm{V}}^*}{\Theta_s}\right); \qquad \frac{1}{\varepsilon} \frac{dx_s}{d\tau} = -\beta\psi n_{\mathrm{O}} \frac{1}{\Theta_s} \exp\left(\frac{\Pi_s}{\Theta_s}\right) + \Theta_s^{\gamma} \frac{\partial n_{\mathrm{V}}}{\partial x} - u n_{\mathrm{V}};$$

$$\Theta_s^{\gamma} \frac{\partial n_{\mathrm{O}}}{\partial x} - u n_{\mathrm{O}} = \psi n_{\mathrm{O}} \frac{1}{\Theta_s} \exp\left(\frac{\Pi_s}{\Theta_s}\right);$$

$$u\,(n_{\mathrm{OX}} + n_{\mathrm{V}} + n_{\mathrm{O}} - 1) = \Theta_s^{\gamma} \frac{\partial\,(n_{\mathrm{OX}} + n_{\mathrm{V}} + n_{\mathrm{O}})}{\partial x};$$

$$\frac{x_s}{3\varepsilon} \frac{d\Theta_s}{d\tau} = \Theta_s^{\gamma} \frac{\partial\Theta}{\partial x} + H_s \frac{\psi}{\Theta_s} \exp\left(\frac{\Pi_s}{\Theta_s}\right) + L_{\mathrm{V}}\left(\frac{\partial n_{\mathrm{V}}}{\partial x} - u n_{\mathrm{V}}\right) + L_{\mathrm{OX}}\left(\frac{\partial n_{\mathrm{OX}}}{\partial x} - u n_{\mathrm{OX}}\right),$$

if $u > 0$, then $y = 1$;

when $x = \infty$

$$\Theta = \Theta_{\mathrm{V}};\ n_{\mathrm{O}} = n_{\mathrm{OV}};\ n_{\mathrm{V}} = 0, \text{ if } u < 0, \text{ then } y = 1.$$

The initial conditions ($\tau = 0$) are

$$x_s = 1,\ \Theta_s = \Theta_{s0};$$

$$\text{when } x_s < x < \infty, \Theta = \Theta_{\mathrm{V}},\ n_{\mathrm{V}} = 0;$$

$$\text{when } x = x_s, n_{\mathrm{V}} = n_{\mathrm{V}s};$$

$$\text{when } x_s \leqslant x < \infty, n_{\mathrm{O}} = n_{\mathrm{OV}},\ y = 1.$$

The problem was solved numerically on an electronic computer by new methods, developed in [10, 11], for integration of systems of differential equations. The calculations were made for the case of a magnesium particle (r_0 = 25 μ) in air. The kinetic constants of the heterogeneous reaction were found in [3] from the experimental values of the ignition limits for magnesium particles of different size [2]: E_s = 45,120 cal/mole, k_s^* = 8.6 · 10^{10} cm/sec (Π_s = —22.56; ψ = 2.7 · 10^8); these constants were used in the present calculation. As in [8], for the homogeneous reaction we took $E = E_s$, but the value of k* was varied in the range from 5 · 10^{15} to 4 · 10^{19} cm³/g·sec (Φ = 8.4 · 10^6–6.7 · 10^{10}); the latter was used in [8]. As in the model example [8], H_s = 1.2, H = 10.04, L_{OX}^* = 66.34, p_{OX}^* = 4.4 · 10^8, L_{V}^* = 15.8, p_{V}^* = 10^5, L_{OX} = 12.4, L_{V} = 4.815, ε = 4.44 · 10^{-3}, β = 1.57.

It was found that if the particle undergoes heterogeneous ignition, then when k^* = 5 · 10^{15} cm³/g·sec (Φ = 8.4 · 10^6) vapor-phase ignition must occur and the process develops in the same way as ignition of a hydrocarbon drop. Far from the particle, where the gas temperature is practically the same as the ambient temperature, and diffusion supplies metal vapor, there is a small temperature maximum; it begins to move rapidly toward the particle, and the gas temperature at the maximum point increases. At a distance of approximately 1-1.5 times the particle radius from its surface the maximum stops and there is a rapid increase in gas temperature at the maximum point — the particle ignites in the vapor phase. If the gas temperature is sufficiently high (above the limit for the particular particle size), the transfer of the reaction from the particle surface to the volume takes a very small part of the total induction time; there is practically no condensed oxide in the volume, since the particle after the induction period does not succeed in burning up appreciably.

When k^* < 5 · 10^{15} cm³/g·sec the qualitative picture of transfer of the reaction from the particle surface to the vapor phase is not altered, and only the transfer time is increased. Values of k^* less than 5 · 10^{15} cm³/g·sec are of no practical interest, since the rate constant of the homogeneous reaction in such cases is extremely low; at temperatures of ∿1000°C itis many orders below the experimentally determined value [14].

If the value of k^* is increased without the other kinetic constants being altered, the coordinate of the initial position of the temperature maximum, the coordinate of its stopping point and sharp increase in maximum temperature, and also the times from the start of the process to each of these events are reduced. Finally, for some value of the kinetic factor for the homogeneous reaction (k^* ∿ 2 · 10^{17} cm³/g·sec) the metal vapor ignites directly at the particle surface; the rate of reaction of the vapor with oxygen is so rapid that the vapor

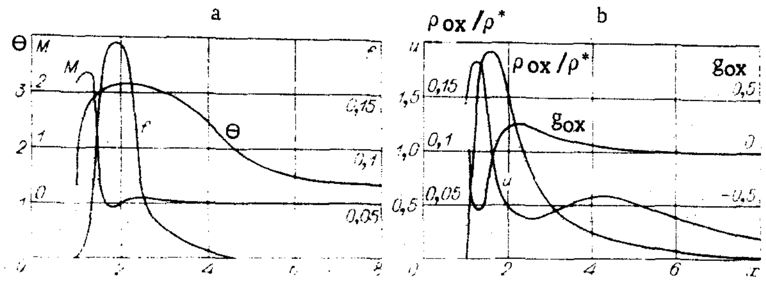

Fig. 1

cannot move very far from the particle by diffusion and mass flow of the gas (directed toward the surroundings). For the value of the factor k^* used in [8] ($4 \cdot 10^{19}$ cm^3/g·sec) vapor-phase ignition begins near the pargicle surface, and not at the boundary with the surroundings, as was found in the quasi-steady-state approximation [8].

The calculated induction times (from 8 to 22 msec for particles of diameter 30-50 μ in air at atmospheric pressure and temperature 850°C) are in good agreement with experimental data [12]. The good agreement between calculation and experiment is simply explained. For instance, for a particle of diameter 50 μ in the indicated conditions the time of heating to the start of melting and the duration of melting did not depend greatly on the value of $k^* = 5 \cdot 10^{15}$-$4 \cdot 10^{19}$ cm^3/g·sec and was ∿11 and ∿10 msec, respectively; the melting of the particle was always followed almost immediately (within about 1 msec) by a sharp increase in its temperature — heterogeneous ignition. The time for transfer of the reaction from the surface to the gas phase was short; it depended significantly on the value of the kinetic factor k^*: It decreased from ∿2 to ∿0.2 msec with increase in k^* from $5 \cdot 10^{15}$ to $4 \cdot 10^{19}$ cm^3/g·sec. Hence, the total induction time of the particle is determined mainly by the kinetics of the heterogeneous reaction (particularly near the ignition limit); its constants were calculated as already mentioned, by using experimental data for the heterogeneous ignition limits.

In [13, 14] the temperature variant of the dilute diffusion flame method was used to investigate the kinetics of the reaction of alkali-earth metal (Mg, Ca, etc.) vapor with molecular oxygen. Here we analyze the possible competition of two types of processes: the usual gas-phase reaction followed by condensation and transfer of the reaction to the phase interface between the dispersed product and the initial substance. The first mechanism of metal vapor oxidation was assumed in the cited works, and the second was considered for magnesium in [15]. Kashireninov et al. [13, 14] give preference to the first reaction mechanism; they found the following values for the kinetic constants of the bimolecular reaction of magnesium vapor with oxygen: $E = 15.3 \pm 2.8$ kcal/mole, $k^* = 1.7 \cdot 10^{14}$ cm^3/mole·sec.

Calculations with these values of the kinetic constants of the homogeneous reaction showed that vapor-phase ignition of the particle must begin right at the surface: The temperature maximum occurs directly at the particle surface, after which it moves a little away from it. The temperature at the maximum point increases rapidly — a diffusion combustion front is formed. Thus, although combustion of the magnesium particle occurs in the gas phase, it must ignite heterogeneously.

As calculations showed [9], the quasi-steady-state diffusion model of vapor-phase combustion of a metal particle allows us in general to determine correctly its combustion rate at atmospheric pressure. Calculations [16] indicate that even simpler models can be used for calculation of particle combustion rates alone. In our calculations of the combustion of a magnesium particle by the non-steady-state model we have several other aims: first, to find the particle combustion rate at increased pressures, when the quasi-steady-state approximation may become inapplicable; second, to determine the "fate" of condensed combustion products formed near the burning particle, which is very important for gasdynamic calculations of the flow in rocket motor jets. In the calculations we used the values found for the constants of the homogeneous reaction in [14].

The results of calculation for a typical case are given in Figs. 1-4. For clearer illustration and comparison with experiment we give not only the dimensionless, but also the dimentional, times corresponding to a magnesium particle with initial diameter 50 μ, burning in air at atmospheric pressure and temperature 1000°C. After the temperature maximum has been formed in the immediate vicinity of the particle surface it begins to move away from the particle, and the temperature at the maximum increases. At a distance of approximately 2.4 times

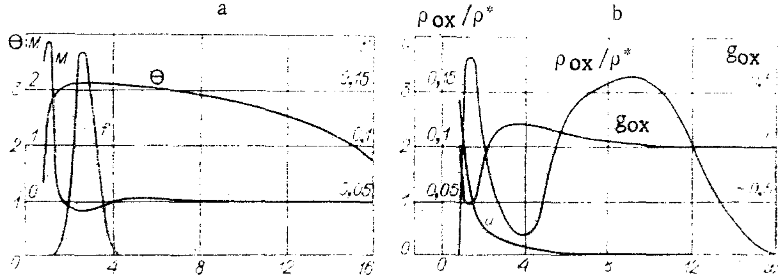

Fig. 2

the initial radius of the drop from its center, the velocity of motion of the temperature maximum sharply decreases.

By the time $\tau = 35.2 \cdot 10^3$ ($t = 15.25$ msec, Fig. 1) a diffusion flame of characteristic structure is formed: The zone of heat production due to the chemical reaction (f is the reaction rate) is narrow and is localized near the maximum of the temperature θ (see Fig. 1a); the concentrations of metal vapor and oxygen in this zone are negligibly small. The mass velocity of the gas u at every point is directed away from the particle, the flow of gaseous oxide g_{ox} from the zone of its formation is directed away from the particle and also toward it, but does not reach its surface (see Fig. 1b). The oxide condensation rate M is significant only near the particle itself, where the temperature gradients are large; in the zone of the temperature maximum the condensation rate is negative — the oxide evaporates (see Fig. 1a). The mass of condensed oxide is still very small; its density ρ_{ox} differs appreciably from zero only near the particle, where the condensation rate is high. The rate of formation of the gaseous oxide and its condensation in the whole gas volume are quantities of the same order.

The flame structure at time $\tau = 37.27 \cdot 10^3$ ($t = 16.15$ msec) is shown in Fig. 2a, b. The combuation zone becomes narrower, and the temperature profile on the right of it becomes more gentle. The distributions of the rates of condensation and flow of oxide vapor are not greatly altered — they vary little during the whole combustion time of the particle. The mass velocity of the gas changes sign at $r \approx 25r_0$. The distribution of the density of the condensed oxide is of interest (Fig. 2b). In the zone of intense condensation in the immediate vicinity of the particle the condensed oxide cannot accumulate — it is carried away by the great mass flow of gas. In the combustion zone the oxide evaporates — its amount becomes less and less with time. A large part of the oxide is found in the region between 4 and 15 times the initial radius of the drop.

The point at which the mass velocity of the gas changes sign subsequently begins to approach the particle. The result of this is that the zone where the condensed oxide accumulates becomes narrower, the maximum of the distribution of ρ_{ox}/ρ^* approaches the drop, and the density at the maximum increases. Thus, in Fig. 3 ($\tau = 38.88 \cdot 10^3$, $t = 16.85$ msec) $u = 0$ at $r \approx 12r_0$, $\max \rho_{ox}/\rho^* \approx 1$; in Fig. 4 ($\tau = 40.69 \cdot 10^3$, $t = 17.63$ msec) $u = 0$ at $r \simeq 6r_0$, $\max \rho_{ox}/\rho^* \approx 200$ ($\rho^* = 0.388 \cdot 10^{-3}$ g/cm³). By the time of almost complete combustion of the particle ($\tau = 41.61 \cdot 10^3$, $t = 18.03$ msec) the gas velocity changes sign at $r \approx 5r_0$; practically all the condensed oxide is concentrated at the accumulation surface, whose position depends on the point at which u changes sign; the oxide density ρ_{ox} at the maximum point is 0.143 g/cm³.

The experimental data confirm the calculated nature of the formation and evolution of the zone of oxide accumulation. Thus, according to the data of [17], the width of the luminous zone near a magnesium particle (∿100 μ) at the initial stage of combustion increases, is practically constant during established combustion, and decreases toward the end of combustion; the maximum external radius of the luminous zone during combustion of the particle is $(8\text{-}12)r_0$; according to calculation (see Fig. 2b) it is $\sim 12r_0$. Pokhil et al. [18] observed a similar movement of the outer boundary of the luminous zone during combustion of aluminum particles (100-200 μ) at increased pressure (20-40 atm). It was reported in [1] that the external diameter of the luminous zone around a magnesium conglomerate burning in air is approximately 10 times greater than its initial diameter. According to the track width (∿1 mm) of a burning magnesium particle with initial diameter ∿84 μ [19] the value of the diameter is approximately the same ($\sim 12d_0$).

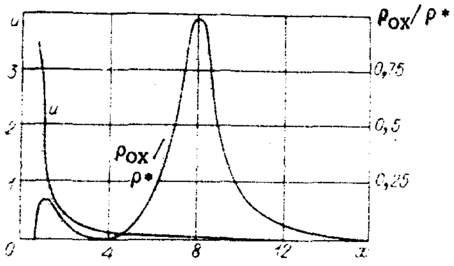

Fig. 3

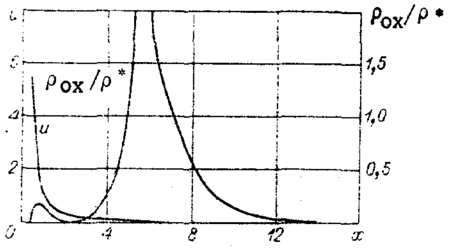

Fig. 4

The diameter of the combustion zone varies with time in the same way as for a hydrocarbon drop. After the formation of an almost-diffusion flame the radius of the combustion surface (where the reaction rate is greatest) increases from 2.4 to 2.7 times the initial particle radius; by the time that ∿80% of the metal has evaporated, the radius of the combustion surface, having reached a value of $2.7r_0$, begins to decrease and by the end of combustion becomes equal to $2.2r_0$.

Calculations showed that during the entire combustion time of a magnesium drop of any diameter (10-500 μ) the relation $r_s^2 \sim t$ is fairly accurately fulfilled; hence, the duration of complete combustion is proportional to the square of the initial diameter; $t_c \sim d_0^2$. The rate constant $\varkappa$ of combustion in air at atmospheric pressure and 1000°C was found to be 0.896 mm/sec. According to a quasi-steady-state calculation [9] for the same conditions it is a little lower (0.752 mm/sec), and according to experimental data $\varkappa = 0.75$-1.35 mm/sec.

With increase in pressure in the atmosphere the surfaces of combustion and oxide accumulation move a little closer to the drop. Thus, with increase in pressure from 1 to 25 atm the maximum radius of the combustion surface decreases from 2.7 to 2.3 times the initial drop radius, and the radius of the accumulation surface decreases from $5r_0$ to $4.4r_0$. The combustion rate constant increases with increase in pressure (at P = 1, 5, and 25 atm $d_0^2/t_c = 0.896, 1.02$, and 1.12 mm²/sec, respectively), and more appreciably than was obtained from calculation in the quasi-steady-state approximation. Thus, the hypothesis of Gurevich et al. [16] that the experimentally obtained [20] decreasing dependence of $\varkappa$ on P can be obtained by calculation (including consideration of the non-steady-state processes near the burning particle) has not been confirmed.

LITERATURE CITED

1. E. S. Ozerov and I. I. Skvortsov, "Combustion of a conglomerate of magnesium particles," Fiz. Goreniya Vzryva, 7, No. 2 (1971).
2. H. M. Cassel and J. Liebman, "The cooperative mechanism in the ignition of dust dispersions," Combust. Flame, 3, No. 4 (1959).
3. M. A. Gurevich and A. M. Stepanov, "Limiting conditions of ignition of a metal particle," Fiz. Goreniya Vzryva, 4, No. 2 (1968).
4. T. I. Alekseeva, M. A. Gurevich, and E. S. Ozerov, "Ignition of an aluminum particle," Tr. Leningr. Politekh. Inst., No. 280 (1967).
5. M. A. Gurevich, G. E. Ozerova, and A. M. Stepanov, "Heterogeneous ignition of an aluminum particle in oxygen and water vapor," Fiz. Goreniya Vzryva, 6, No. 3 (1970).
6. B. I. Khaikin, V. N. Bloshenko, and A. G. Merzhanov, "Ignition of metal particles," Fiz. Goreniya Vzryva, 6, No. 4 (1970).
7. M. A. Gurevich and B. I. Sotnichenko, "Transfer of combustion from surface of a metal particle to the vapor phase," Tr. Leningr. Politekh. Inst., No. 280 (1967).
8. M. A. Gurevich and A. M. Stepanov, "Ignition of a metal particle," Fiz. Goreniya Vzryva, 4, No. 3 (1968).
9. M. A. Gurevich, G. E. Ozerova, and A. M. Stepanov, "Calculation of combustion rate of metal particle with due regard to condensation of oxide," in: Combustion and Explosion [in Russian], Nauka, Moscow (1972).
10. Yu. V. Rakitskii, "Method of successive increase in step of numerical integration of systems of ordinary differential equations," Dokl. Akad. Nauk SSSR, 207, No. 4 (1972).
11. Yu. V. Rakitskii, "New numerical methods of solution of systems of ordinary differential and difference equations," Tr. Leningr. Politekh. Inst., No. 332, No. 3 (1973).
12. M. A. Gurevich, G. V. Ignatov, E. S. Ozerov, and B. I. Sotnichenko, "Statistical method of obtaining combustion characteristics of metal particles," Fiz. Goreniya Vzryva, 5, No. 3 (1969).

13. O. E. Kashireninov, V. A. Kuznetsov, and G. B. Manelis, "Calculation of kinetic parameters of fast, gas-phase, highly exothermal reactions, accompanied by formation of condensing products, from data of diffusion-flame method," Dokl. Akad. Nauk SSSR, 215, No. 4 (1974).
14. O. E. Kashireninov, V. A. Kuznetsov, and G. B. Manelis, "Kinetic investigation of gas-phase reaction of magnesium with oxygen by the diffusion-flame method," Zh. Fiz. Khim., 49, No. 4 (1975).
15. G. H. Markstein, "Analysis of a dilute diffusion flame maintained by heterogeneous reaction," in: Heterogeneous Combustion (edited by H. G. Wolfhard), Academic Press (1964).
16. M. A. Gurevich, E. S. Ozerov, and L. S. Rybina, "Calculation of rate of vapor-phase diffusion combustion of a metal particle," Fiz. Goreniya Vzryva, 10, No. 3 (1974).
17. C. K. Law and F. A. Williams, "Combustion of magnesium particles in oxygen-inert atmospheres," Combust. Flame, 22, No. 3 (1974).
18. P. F. Pokhil, A. F. Belyaev, Yu. V. Frolov, V. S. Logachev, and A. I. Korotkov, Combustion of Powdered Materials in Active Media [in Russian], Nauka, Moscow (1972), p. 125.
19. J. Leibman, J. Corry, and H. E. Perlee, "Ignition and incendivity of laser-irradiated single micron-size magnesium particles," Combust. Sci. Technol., 5, 21 (1972).
20. G. K. Ezhovskii, A. S. Mochalova, E. S. Ozerov, and A. A. Yurinov, "Ignition and combustion of a magnesium particle," in: Combustion and Explosion [in Russian], Nauka, Moscow (1972), p. 234.

EXPERIMENTAL DETERMINATION OF THE KINETICS OF RELAXATION PROCESSES DURING THE SHOCK COMPRESSION OF CONDENSING MEDIA

G. I. Kanel'

UDC 534.222.2:662.215

Introduction

The compression of condensing media by shock waves can be accompanied by such relaxation processes as phase changes, chemical reactions, etc. For a quantitative analysis of the evolution of a shock wave one must know the dependence of the rate of the process on the parameters of state of a particle of the specimen at each time. Two methods of finding the kinetic data directly from the experimental results are discussed in the present report.

In [1, 2] it is shown that if a series of profiles of the pressure p(t) or the mass velocity u(t) are determined for different fixed coordinates in a specimen through which a one-dimensional compression wave propagates then from these data one can reconstruct the dependence of the variation of the pressure and the specific volume V for each layer of the specimen; from the experimental data one determines the trajectory of the change of state of fixed layers of the substance in the coordinates p—V, with each point of this trajectory corresponding to a certain (and known) time. Then if the equations of state of the initial and final products are known one can construct in the same coordinates a grid of curves of the compression of mixtures with different concentrations of the final product. One thereby determines the concentration of the final product at each point of the trajectory of the change of state; i.e., for a chosen layer one determines the law of variation of the concentration of the initial and final products with time. By varying the parameters of the shock wave introduced into the specimen one can obtain a set of kinetic curves and from them choose a single empirical dependence of the rate of the relaxation process on the parameters of state of a particle of the substance.

A set of trajectories of the change of state provides complete information on the process, but to construct them one must make a large number of measurements with increased demands on the accuracy. At the same time, there are reasons to assume that in a number of cases (such as in the analysis of the propagation of shock waves in explosive materials), it is sufficient to know the initial rate of the process. In the present report it is shows that the initial behavior of the trajectory of the change of state can be determined from the experimentally measured profiles of the pressure or the mass velocity and from the law of variation of the

---

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 5, pp. 117-122, September-October, 1977. Original article submitted August 2, 1976.

0021-8944/77/1805-0685$07.50