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A. D. Margolin, P. F. Pokhil

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Abstract

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A. D. Margolin, P. F. Pokhil

Effect of Pressure on the Rate of Processes in the Reaction Layer of the Condensed Phase of Burning Gunpowder

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The combustion of gunpowders is accompanied, in total, by exothermic chemical reactions in the reaction layer of the condensed phase. The heat release in the reaction layer of this phase for some gunpowders amounts to 70% or more of the total quantity of heat q required to heat the condensed phase during steady combustion (^{1}).

$$q = c(T - T_0), \tag{1}$$

where T_0 is the initial temperature of the gunpowder, T is the surface temperature of the condensed phase, and c is the heat capacity.

The combustion process of gunpowders is completed in the smoke-gas or gas phase, where the maximum temperature for the given conditions is reached. Since the temperature in the gas phase is higher than in the condensed phase during combustion, a heat flux always passes from the gas phase into the condensed phase. However, the contribution of reactions occurring in the reaction layer of the condensed phase to the heat balance entering into the heating of this phase in a number of cases reaches $0.9q$ (^{2}), so that the process in the condensed phase may be the leading one or one of those determining the burning rate of gunpowder. The influence of one process or another on the burning rate is determined not only by the contribution of the given process to the heat balance, but also by the chemical kinetics, as well as by such physical processes as heat conduction, diffusion, evaporation, and dispersion.

In the general case, the burning rate depends not on any single stage, but on a combination of several or even all stages of combustion (^{1},^{3}); however, to understand the combustion process it is necessary to analyze each stage separately.

The influence of pressure on the burning rate of a gas mixture, or on the burning rate of a gunpowder whose leading combustion stage is located in the gas phase, has been analyzed in detail (^{4},^{5}). In many works on the theory of combustion of condensed systems it is assumed that the decomposition process of the condensed phase itself does not depend on pressure, and that its rate changes only as a result of the action of the heat flux entering from the gas phase. Only in some works are there indications that pressure directly affects the rate of processes in the reaction layer of the condensed phase ([3],[6]). Let us consider this question in greater detail.

The processes occurring during combustion in the reaction layer of the condensed phase are very diverse: homogeneous and heterogeneous chemical reactions, diffusion and heat transfer, dissolution, melting, transition from one crystalline modification to another, evaporation, dispersion, sublimation, and gasification. Pressure affects the rate and kinetics of chemical reactions involving gaseous substances formed as a result of decomposition of the condensed phase and present in the reaction layer in dissolved form, in bubbles, and in gaps between the grains of the gunpowder components. The influence of pressure on the equili-

···surface temperature and the rate of phase transitions, since the kinetics of chemical reactions changes during phase transitions; the effect of pressure on the surface temperature of the condensed phase is very significant, this temperature being determined by the conditions of evaporation, dispersion, and heat release in the reaction layer of the condensed phase.

Let us consider the regularities of dispersion, which, as is known, plays a major role in the combustion of powders ([1]).

Reactions in the condensed phase lead to the formation, in the reaction layer, of gaseous decomposition and combustion products. The gaseous products dissolve in the condensed phase. When the concentration of dissolved gaseous products reaches a limiting value, which for the given solution depends on pressure, temperature, physical state, and mechanical properties of the condensed substance, vigorous formation of gas bubbles occurs, causing dispersion of the reaction layer of the condensed phase. As the pressure increases, the solubility of gaseous products in the condensed phase increases and dispersion becomes more difficult; therefore, for bubble formation and dispersion to occur, more complete decomposition of the condensed phase in the reaction layer is necessary, which leads to an increase in the temperature T_p at the surface of the condensed phase and to an increase in the burning rate.

To illustrate the mechanism by which pressure affects the burning rate (as a consequence of changes in the dispersion conditions), let us consider the combustion of a powder model when the leading stage of combustion is located in the reaction layer of the condensed phase.

Let the surface layer of the condensed phase, where chemical reactions occur, be liquid. We shall neglect diffusion of the reaction products in the condensed phase; the concentration of gaseous combustion products beneath the liquid surface is proportional to the depth of reaction or to the heat release of the chemical reactions,

$$a \sim q = c\,(T_\mathrm{p} - T_0), \tag{2}$$

where a is the maximum concentration reached at the surface and dependent on temperature and pressure according to the law of dissolution

$$a \sim P \exp\left(\frac{L}{RT_{\text{p}}}\right), \tag{3}$$

where L is the heat of dissolution.

These two processes (chemical reaction and dissolution) determine the surface temperature of the condensed phase:

$$\alpha c\left(T_{\text{p}} - T_0\right) = P \exp\left(\frac{L}{RT_{\text{p}}}\right), \tag{4}$$

α is the proportionality coefficient.

The burning rate is determined by the chemical kinetics and the surface temperature. In the simplest case, when the reaction proceeds in the condensed phase without participation of gaseous products and intermediate products and its rate does not depend on pressure,

$$u \sim \exp\left(-\frac{E}{2RT_{\text{p}}}\right), \tag{5}$$

where E is the activation energy, and R is the gas constant.

From equations (4) and (5) one can establish the burning rate as a function of the physicochemical characteristics of the powder. Let us find the dependence of the burning rate on pressure and temperature

$$\nu = \frac{P}{u}\frac{du}{dP} = \frac{E}{2RT_{\text{p}}^2}\,\frac{T_{\text{p}} - T_0}{1 + \dfrac{L}{RT_{\text{p}}^2}\left(T_{\text{p}} - T_0\right)}, \tag{6}$$

$$\beta = \frac{1}{u}\frac{du}{dT} = -\frac{E}{2RT_p^2}\,\frac{1}{1 + \frac{L}{RT_p^2}\left(T_p - T_0\right)}, \tag{7}$$

$$\beta = \frac{\nu}{T_p - T_0}. \tag{8}$$

If $\dfrac{E}{2RT_p^2}\left(T_p - T_0\right) \gg 1$, then formulas (6), (7) are simplified:

$$\nu = \frac{E}{2L}, \tag{6a}$$

$$\beta = -\frac{E}{2L(T_p - T_0)}. \tag{7a}$$

In real systems, during combustion in the reaction layer of the condensed phase many substances of different solubility are dissolved; therefore the dependence of the burning rate on pressure may in individual cases become complex, non-monotonic.

The laws governing the dispersion of crystalline substances in which chemical reactions occur are more complex; they depend on the crystal lattice and its defects, but when the local concentration of reacted molecules whose chemical bonds have broken or weakened becomes sufficiently large, the crystal begins to crack and disperse. Dispersion of a mixture of fuel with oxidizer proceeds owing to chemical reactions at the boundary between oxidizer and fuel grains and to the decomposition of the oxidizer and fuel separately.

Thus, the burning rate of powder may depend on pressure also in the case when processes in the reaction layer of the condensed phase are the leading processes determining the burning rate of the system.

Institute of Chemical Physics
Academy of Sciences of the USSR

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REFERENCES

1. P. F. Pokhil, *Collection: Physics of Explosion*, No. 2, Publishing House of the Academy of Sciences of the USSR, 1953; P. F. Pokhil, L. D. Romodanova, M. M. Belov, *Collection: Physics of Explosion*, No. 3, Publishing House of the Academy of Sciences of the USSR, 1955.
2. V. M. Mal' tsev, P. F. Pokhil, *Journal of Applied Mechanics and Technical Physics*, No. 2, 173 (1963).
3. P. F. Pokhil, O. I. Nefedova, A. D. Margolin, *Doklady Akademii Nauk*, **145**, No. 4, 860 (1962).
4. Ya. B. Zel' dovich, D. A. Frank-Kamenetskii, *ZhFKh*, **12**, 100 (1938); Ya. B. Zel' dovich, N. N. Semenov, *ZhETF*, **10**, 1116 (1940); N. N. Semenov, *UFN*, **23**, 251 (1940); **24**, 433 (1940).
5. Ya. B. Zel' dovich, *ZhETF*, **12**, No. 12, 498 (1942); A. F. Belyaev, *ZhFKh*, **12**, 93 (1938); *Collection on the Theory of Explosive Substances*, 1940.
6. A. D. Margolin, *Doklady Akademii Nauk*, **141**, No. 5 (1961).