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SHS-SYSTEM COMBUSTION MODELS ACCOUNTING FOR MACROSTRUCTURAL TRANSFORMATIONS

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Based on the concepts of the mechanics of heterogeneous media, combustion models were constructed that take into account macrostructural transformations associated with liquid-phase sintering, the loosening action of gas filtering in the pores, and the difference in the densities of the initial substances and products. The combustion of systems with a partially gaseous product is investigated analytically. The rate of combustion and final porosity as well as the conditions for the formation of cracks are determined.

Present-day theoretical concepts about the combustion of heterogeneous systems that form condensed products presuppose the invarability of structural characteristics. This prevents an adequate description of the combustion of many SHS systems in which a substantial change in the macrostructure takes place, i.e., in the porosity, dimensions, and shape of the sample. Such changes are most perceptible when one of the reagents melts in the course of interaction and the substance becomes fluid. In this case the change in the macrostructure is caused by liquid-phase sintering, the loosening action of gas filtering in the pores, and the difference in the densities of the initial substances and products.

The appearance of a liquid leads to a sharp increase in the rate of reaction due to enlargement of the interaction surface and intensification of transfer processes. Therefore the melting temperature can be considered as a natural "cutting off" [1] of the heat release source, and it can be assumed that chemical reaction, just as structural variations, occurs after the appearance of the liquid phase. The initial mixture of two reagents (coarser low-melting one B uniformly surrounded by a high-melting one A (see Fig. 1a)) can be represented, after the melting of B, by a set of solid-liquid drops of radius R_0 (see Fig. 1b).

Limiting the discussion to a qualitative analysis, we consider a one-dimensional model of quasistationary adiabatic combustion [2-4]. The model is based on the mechanics of multiphase media [5]. It involves equations of the mass balance of the gaseous and condensed phases, heat balance, and chemical reaction and boundary conditions

$$\frac{d}{dz}[m\rho_1(u+v_1)] = \mu I, \tag{1}$$

$$\frac{d}{dz}[(u-m)\rho_2(u+v_2)] = -\mu I, \tag{2}$$

$$\frac{d}{dz}[(u-m)\rho_2\alpha(u+v_2)] = I, \tag{3}$$

$$m\rho_1(u+v_1)\frac{dv_1}{dz} = -m\frac{dP}{dz} - F_1 - F_2 + \mu I(v_2 - v_1), \tag{4}$$

$$(1-m)\rho_2(u+v_2)\frac{dv_2}{dz} = -(1-m)\frac{dP}{dz} + F_1 + F_2 + \frac{d\sigma_*}{dz}, \tag{5}$$

$$[c_1\rho_1 m(u+v_1) + (1-m)c_2\rho_2(u+v_2)]\frac{dT}{dz} = \frac{d}{dz}\left(\lambda\frac{dT}{dz}\right) + QI, \tag{6}$$

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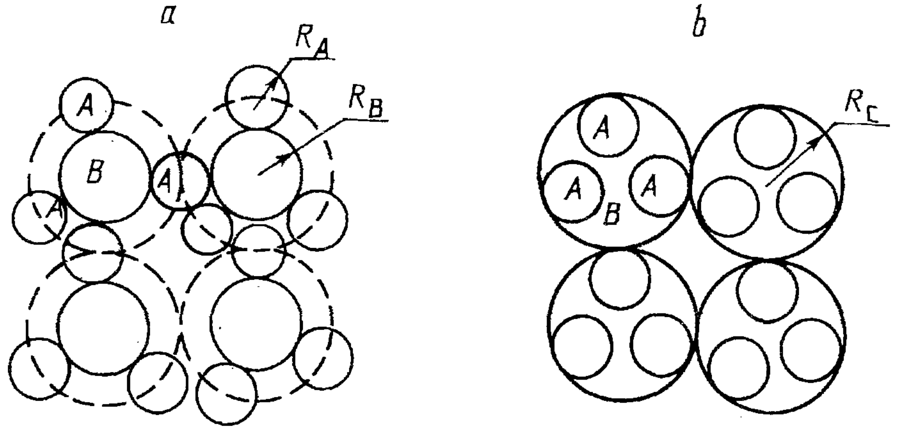

Fig. 1. Model of the original structure.

$$(u+v_2)\frac{d\alpha}{dz} = k(T)\,F(\alpha), \tag{7}$$

$$\begin{gathered} z=-l_2: v_2=0,\quad T=T_0,\quad m=m_0,\quad \alpha=0,\ P=P_0, \\ z=l_1: \alpha=1,\quad P=P_0,\quad dT/dz=0. \end{gathered} \tag{8}$$

In Eqs. (1)-(8) the following designations are adopted: m is the porosity; α is the conversion depth; v_i and ρ_i are the rate and density of the gaseous (i = 1) and condensed (i = 2) phases; $\rho_2 = \rho_m\rho_p/[\alpha\rho_m + (1-\alpha)\rho_p]$; ρ_m and ρ_p are the densities of the mixture and the product; $P = \rho_1 RT$ is the gas pressure; T is the temperature; σ, $\sigma_* = (1-m)\sigma + (1-m)P + P_L$ are the full and reduced stresses in the condensed phase (σ_* characterizes momentum transfer through the contacting surfaces); I is the rate of product formation; u is the rate of combustion; $P_L \approx 3\varepsilon(1-m)^2/R_0$ is the effective Laplace pressure in the condensed phase, determining the intensity of sintering [6]; ε is the surface tension; R_0 is the radius of the drops; $F(\alpha)$ is the kinetic law; c_1, $c_2 = c_p\alpha + c_m(1-\alpha)$ are the heat capacities of the phases; c_p, $c_m = c_k + (1-c_0)L_{mel}\delta(T_{mel}-T)$ are the heat capacities of the product and the mixture; T_{mel} and L_{mel} are the temperature and heat of melting; $\delta(T_{mel}-T)$ is the delta-function; $\lambda = \lambda_0(1-m)$ is the thermal conductivity; c_k and λ_0 are constants; $F_1 \approx (1-m)\mu I(v_2-v_1)$, $F_2 \approx 150\mu_1\mu(1-m)^2(v_1-v_2)/4mR_0^2$ are the forces of inertial and viscous interaction of the phases [5]; Q is the thermal effect of the reaction; μ_1 is the gas viscosity; $k(T) = k_0(-E/RT)$, k_0, and E are a constant, the preexponential factor, and the activation energy of the chemical reaction, respectively; l_1 and l_2 are the coordinates of the sample end faces; μ is the fraction of gas in the product.

In the simplest case of a Newtonian fluid, the rheological law, which couples the stress in the condensed phase with the rate of deformation, is

$$\sigma = -P - P_L + 2\eta\frac{dv_2}{dz}, \tag{9}$$

where $\eta = \eta_* f(\varphi)$ is the viscosity of the solid-liquid suspension; $f(\varphi)$ is the restriction function, reflecting the effect of the volumetric concentration of the solid component $\varphi(\alpha)$; $\eta_* = \eta_0\exp(E_*/RT)$, η_0, and E_* are the viscosity, the preexponential factor, and the viscosity activation energy of the liquid phase, respectively. For $f(\varphi)$ we adopt the expression [6] $f(\varphi) = 1/(1-5\varphi/2)$.

Analysis of Eqs. (4) and (5) shows [3] that in a wide range of governing parameters it is possible to neglect the source and inertia terms. The equation of momentum conservation in the gas is reduced to the equation of steady filtration

$$\frac{dP}{dz} = \frac{150(1-m)^2\mu_1}{4m^2R_0^2}(v_2-v_1), \tag{10}$$

and the sum of Eqs. (4) and (5) yields the equation of equilibrium

$$\frac{d}{dz}[(1-m)\sigma + P_L - P_m] = 0. \tag{11}$$

Integration of Eq. (11) with allowance for boundary conditions (8), rheological law (9) and the relation for the condensed phase velocity, resulting from Eqs. (1)-(3), gives an equation

$$\frac{dm}{dz} = \frac{[\rho_p(1+\mu)-\rho_m]\rho_2(1-m)}{\rho_m\rho_p(1+\alpha\mu)}\frac{d\alpha}{dz} + \frac{(P-P_0-P_L m)(1-m)\rho_2(1+\alpha\mu)}{2\eta(1-m_0)u\rho_m}, \tag{12}$$

which determines the change in the porosity due to the effect of all the factors investigated, i.e., liquid-phase sintering, the loosening action of gas, and the change in the condensed phase volume.

From the general model (6)-(8), (11), (12) one can obtain specific models that consider both the effect of separate factors (sintering, loosening, volumetric changes) and the specific features of the combustion regime (gas-free, filtrational, combined). For example, in carrying out the analysis for gas-free combustion, it is necessary to assume that $\mu = 0$, and for filtrational combustion that $\mu = -\mu$.

As an example, we consider the combustion of an SHS system with a partially gaseous product. Due to the smallness of the thickness of the front as compared with the filtration length, the gas pressure in the wave can be assumed constant. In a linear approximation, with escape of gas through the initial mixture,

$$P_* \approx P_0 + \frac{150(1-m_0)^3\rho_m\mu\mu_1 u l_2}{4m_0^3R_*^2(1+\mu)\rho_0}, \tag{13}$$

where R* is the effective dimension of a mixture of two powders [7]. With escape of gas through the products

$$P_* \approx P_0 + \frac{150(1-m_k)^2(1-m_0)\mu\mu_1\rho_m u T_{com} l_1}{4m_k^3R_0^2\rho_0(1+\mu)T_0}, \tag{14}$$

where the combustion temperature is

$$T_{com} = T_0 + \frac{\rho_m u(1-m_0)[Q/(1+\mu) - L_{mel}(1-c_0)]}{c_1 m_0\rho_0(u+v_{10}) + c_k\rho_m(1-m_0)u}.$$

In the case of long nonarmored samples, gas exchange takes place through the side surface. For a qualitative analysis we adopted $l_1 = l_2 \approx d/2$, where d is the sample diameter. Analysis of Eq. (12) and calculations show that at the initial instant the second term is several orders of magnitude larger than the first one, i.e., at the initial instant the change in the porosity occurs as a result of sintering and loosening, with the depth of conversion being virtually equal to zero. This allows one to consider, instead of Eq. (12), the equilibrium condition $P_* - P_0 - P_L m_{k0} = 0$ at the first stage, from which one determines the porosity m_{k0} after the establishment of equilibrium between the forces of sintering and loosening. Since $\varphi(0) \sim 0.3$, $\varphi(1) \sim 1$ for the systems considered, the depth of conversion at which fluidity terminates is small, and at the second stage the change in the porosity is associated with the difference in densities. Integration of Eq. (12) for $\eta = \infty$ with the condition $\alpha = 0$: $m = m_{k0}$ yields

$$m = 1 - (1-m_{k0})[1 + \alpha(\rho_m - \rho_p)/\rho_p]/(1+\alpha\mu). \tag{15}$$

The rate of combustion for $F(\alpha) = 1 - \alpha$ is defined by the expression

$$u^2 = \frac{\lambda_0 k(T_{com})RT_{com}^2(1-m_{k0})^2(1+\mu)(\rho_m-\rho_p)}{Q\rho_m\rho_p\ln(\rho_m/\rho_p)E(1-m_0)^2}. \tag{16}$$

Use of Eqs. (13) and (16) yields m_{k0} in the case of filtration through the mixture:

$$m_{k0} = \frac{1}{2} - \sqrt{\frac{1}{4} - \frac{(1-m_0)^2}{m_0^2}\frac{dA_1}{R_*^2}},$$

$$A_1 = \frac{25\rho_m \mu \mu_1 R_0}{4\rho_0 \varepsilon (1+\mu)} \sqrt{\frac{\lambda_0 k(T_{\text{com}}) R T_{\text{com}}^2 (1+\mu)(\rho_m - \rho_p)}{Q E \rho_m \rho_p \ln(\rho_m/\rho_p)}}. \tag{17}$$

With escape through the products, m_{k0} is determined from the equation

$$A_1 \frac{(1+\mu)^2 \rho_m^2 T_{\text{com}} d}{R_0^2 \rho_p^2 T_0} = \frac{m_{k0}}{1-m_{k0}} \left[1 - (1-m_{k0})\frac{\rho_m}{\rho_p(1+\mu)}\right]^3. \tag{18}$$

Which of Eqs. (17) and (18) is valid follows from the inequality resulting from Eqs. (13) and (14). If

$$m_0^3 (1-m_k)^2 R_*^2 T_{\text{com}} u_2 > (1-m_0)^2 m_k^3 R_0^2 T_0 u_1,$$

where u_1 and u_2 are the rates of combustion with escape of gas through the mixture and the products, then Eq. (17) is valid. When the pressure is relieved through the mixture, there are critical values of the parameters m_0, R_*, and d for which no solution exists. This means that the porous medium loses continuity. Cracks appear in it through which gas exchange takes place. The sample diameter at which continuity is violated is

$$d_* = \frac{R_*^2 m_0^3}{4A_1(1-m_0)^3},$$

and the critical pressure for the formation of cracks is

$$P^* \approx P_0 + \frac{150(1-m_0)^3 \rho_m \mu \mu_1 u_1 d_*}{4 m_0^3 R_*^2 \rho_0 (1+\mu)}.$$

Comparison of P^* with the pressure at which gas escapes through the products yields the spacing between the cracks:

$$l_* \approx m_k^3 R_0^2 T_0 / [8A_1 (1-m_k)^2 (1-m_{k0})(1-m_0) \cdot T_{\text{com}}],$$

where m_{k0} is determined from Eq. (18).

In the example given, the initial structure is formed by particles of close dimensions. In practice, especially in the synthesis of carbides and borides, the dimensions of the powders may differ by orders of magnitude. In this case it is necessary to analyze the conditions for formation of solid-liquid drops [3].

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