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MATHEMATICAL SIMULATION OF COMBUSTION OF THREE-COMPONENT SHS SYSTEMS

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Based on the concepts of the mechanics of heterogeneous media, a model of the combustion of a three-component mixture is constructed. The model describes the macrostructural laws that govern the process of combustion and that are associated with the processes of heterogeneous chemical transformation at the microlevel. The dynamics of the concentration and temperature fields in the process of ignition was studied as a function of variations in the characteristics of the initial mixture.

In SHS metallurgy, for obtaining cast refractory inorganic materials use is made of combustion of high-caloric mixtures consisting of oxides of metals, metallic reducers, and nonmetals [1].

A mathematical model describing the process of combustion is based on the conservation laws in chemically active multicomponent solid media. The medium itself is modeled by a periodic cellular structure, each period (fragment) of which contains all of the initial reagents with preservation of their initial percentage content and which reflects to the utmost the typical features of the real structure of a multicomponent mixture. The dimensions of the fragment are assumed to be rather small, and it is possible to neglect the temperature difference over the dimension of one fragment. Active media that are homogeneous in temperature and heterogeneous in composition are considered [2]. In contrast to two-component models (see, for example, [3]) the description of multicomponent cellular media meets with great difficulties at the stage of cell structure formation. In many respects success here depends on intuition and insight into the physics of the process. We shall start with the hypothesis that real multicomponent media behave like periodic model systems. We shall investigate the process of mass exchange within the scope of one fragment and, making further simplifications, reduce its analysis to a one-dimensional problem. Such an approach will allow us to describe the processes at the microlevel and determine the macrokinetic laws governing chemical conversions in heterogeneous active media.

Mathematical Model. Below we will consider the process of frontal exothermal transformation of a three-component mixture system on the basis of local chemical interaction

$$\mathrm{Al} + \mathrm{MeO}_x \xrightarrow{+Q} \mathrm{Me} + \mathrm{Al_2O_3}, \tag{1}$$

$$\mathrm{C} + \mathrm{MeO}_x \xrightarrow{-q} \mathrm{Me} + \mathrm{CO}, \tag{2}$$

$$\mathrm{Me} + \mathrm{Al}_x\mathrm{O}_y\mathrm{C} \longrightarrow \mathrm{MeC} + \mathrm{Al_2O_3}. \tag{3}$$

We shall proceed from the fact that the processes of heterogeneous chemical interaction at the microlevel can be described by taking as a basis a typical fragment. We assume that the reaction zone represents a melt of $\mathrm{MeO_x}$ involving spherical carbon and aluminum particles. The processes near the particles are rather well described with allowance for spherical symmetry. Knowing the mass fraction of the reagents and the mean dimensions of the particles R_c and R_a, we can determine the mean distance between them R. In Fig. 1 a fragment is depicted schematically for the case where there are fewer aluminum than carbon particles. As a result half of the carbon particles contact only a certain fraction of the aluminum particles through the $\mathrm{MeO_x}$ melt, which is determined by the ratio of the numbers of particles N_c and N_a. The place of contact R_s is determined by the condition of the equality of the contact surface:

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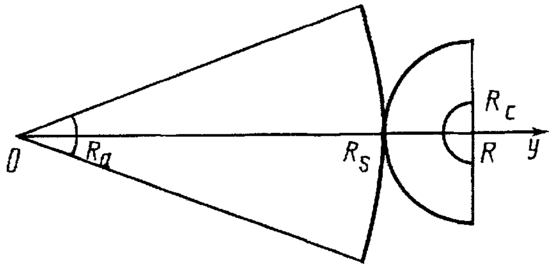

Fig. 1. View of the regular cellular structure of a multicomponent solid medium.

$$N_a R_s^2 = N_c (R - R_s)^2.$$

Although the possibilities of this mathematical model of chemical interaction are limited, other versions are also possible. In our case the process is described by the following system of differential equations:

$$\frac{\partial m}{\partial t} = \frac{1}{S(y)} \frac{\partial}{\partial y} \left(S(y) D(T) \frac{\partial m}{\partial y} \right), \tag{4}$$

$$\frac{\partial b}{\partial t} = \frac{1}{S(y)} \frac{\partial}{\partial y} \left(S(y) D(T) \frac{\partial b}{\partial y} \right), \tag{5}$$

$$\frac{\partial c}{\partial t} = \frac{1}{S(y)} \frac{\partial}{\partial y} \left(S(y) D(T) \frac{\partial c}{\partial y} \right); \tag{6}$$

the boundary conditions in an Al particle ($y = R_a$) are

$$\frac{R_a^3}{3} \frac{\partial a}{\partial t} = - K(T) m a R_a^2, \tag{7}$$

$$\frac{R_a^3}{3} \frac{\partial c}{\partial t} = D(T) b \frac{\partial c}{\partial y} R_a^2, \tag{8}$$

$$D(T) \frac{\partial m}{\partial y} = \nu_2 K(T) m a, \tag{9}$$

$$D(T) \frac{\partial b}{\partial y} = - \nu_6 K(T) m a; \tag{10}$$

the boundary conditions in a C particle ($y = R - R_c$) are

$$\frac{R_c^3}{3} \frac{\partial c}{\partial t} = - D(T) b \frac{\partial c}{\partial y} R_c^2 - K_1(T) m c R_c^2, \tag{11}$$

$$D(T) \frac{\partial m}{\partial y} = - \nu_4 K_1(T) m c, \tag{12}$$

$$D(T) \frac{\partial b}{\partial y} = 0. \tag{13}$$

To construct the model, we assumed that in the reaction scheme (2) the gas freely leaves an "elementary cell" (fragment) the area of the variable cross section of which is described approximately by the formula

$$S(y) = \min (N_a y^2, N_c (R - y)^2), \tag{14}$$

where N_a and N_c are the number of aluminum and carbon particles per unit volume.

The rate of chemical conversion

$$K(T) = K_0 \exp(- E_0/RT), \quad K_1(T) = K_1 \exp(- E_1/RT)$$

and diffusion

$$D(T) = D\exp(-E/RT)$$

are known functions, i.e., K_0, K_1, D, E_0, E_1, and E are known.

The coefficients ν_i characterize the stoichiometry of the chemical interaction. We also assume that the exothermal interaction characteristics are known, namely Q, kal/g, is evolved in Eq. (1) and q, kal/g, is absorbed in Eq. (2). The nonisothermicity of the process of carbidization is ignored.

The process of heat transfer at the macrolevel takes into account the overall dynamics of chemical heat release in the interior of each fragment. In the present case this dynamics is associated with the change in the aluminum mass and with the formation of CO (i.e., with the change in the mass of the condensed component):

$$\frac{\partial}{\partial t}(C\rho T) = \frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right) - Q\rho_a\frac{4}{3}\pi R_a^3 N_a\frac{\partial a}{\partial t} + q\frac{\partial \rho}{\partial t}, \tag{15}$$

$$\frac{\partial}{\partial t} = -4\pi R_c^2 N_c \rho_{CO}\nu_5 K_1(T)\, mc, \tag{16}$$

$$\frac{\partial a}{\partial t} = -\frac{3\,K(T)}{R_a} ma. \tag{17}$$

We are studying a one-dimensional nonstationary process of ignition at the end face of a semiinfinite mixture sample by a high-temperature wall. In conformity with this, the initial conditions are

$$\begin{gathered}(t = 0,\ 0 < x < \infty,\ \ R_a < y < R - R_c);\\ a(x,\ 0) = a_0;\ \ b(x,\ y,\ 0) = b_0;\ \ m(x,\ y,\ 0) = m_0;\\ c(x,\ y,\ 0) = c_0;\ \ y > R - R_c;\ \ \rho(x,\ 0) = \rho_0;\ \ T(x,\ 0) = T_0.\end{gathered} \tag{18}$$

The boundary condition for the temperature is $T(t, 0) = TW$.

Method of Solution. The mathematical model considered represents a nonlinear system of differential equations in the space (t, x, y). The presence of essentially different characteristic time and space dimensions in the problem as well as its nonlinearity offer considerable difficulties for numerical investigation. Employing the specific properties of the chemical process (the laws governing heterogeneous exothermal transformation), we constructed an effective stable difference algorithm to obtain the solution of the system. It is based on an implicit difference approximation of differential equations, separation of linear and nonlinear parts of the corresponding difference system of equations, and the use of the factorization method for solving the linear portion of the system [4].

The difficulties due to the different scales of the process were overcome by applying a new modification of the method [5] for constructing a spatially nonuniform time-varying difference grid adapting to the solution. The nonstationary ignition process was calculated up to emergence into the steady regime of burning. The elements of the stationary front structure were obtained on the basis of the established regime of burning.

Results of Mathematical Simulation. Using the values of the parameters characteristic for the mixture system considered, we determine the dynamics of the temperature and concentration fields in the process of ignition. One of the examples of the calculation is presented in Fig. 2. It contains mainly the characteristics of the process at the microlevel, i.e., the spatial-time distribution of temperature along the sample. By igniting the sample at the end face at a temperature close to the combustion temperature, we obtain a rather fast emergence to the steady-state combustion regime. The temperature profile is displaced in parallel in the form of a travelling wave whose velocity is equal to the rate of burning. The transformation depth and the condensed medium density behave similarly. The latter changes due to the formation of gas-phase reaction products (CO). The dynamics of the rate of heat release at successive instants of time is presented in a relatively enlarged scale. Here, one portion characterizes the exothermal interaction of aluminum with the metal oxide, and the other (negative) represents the endothermal process of CO formation.

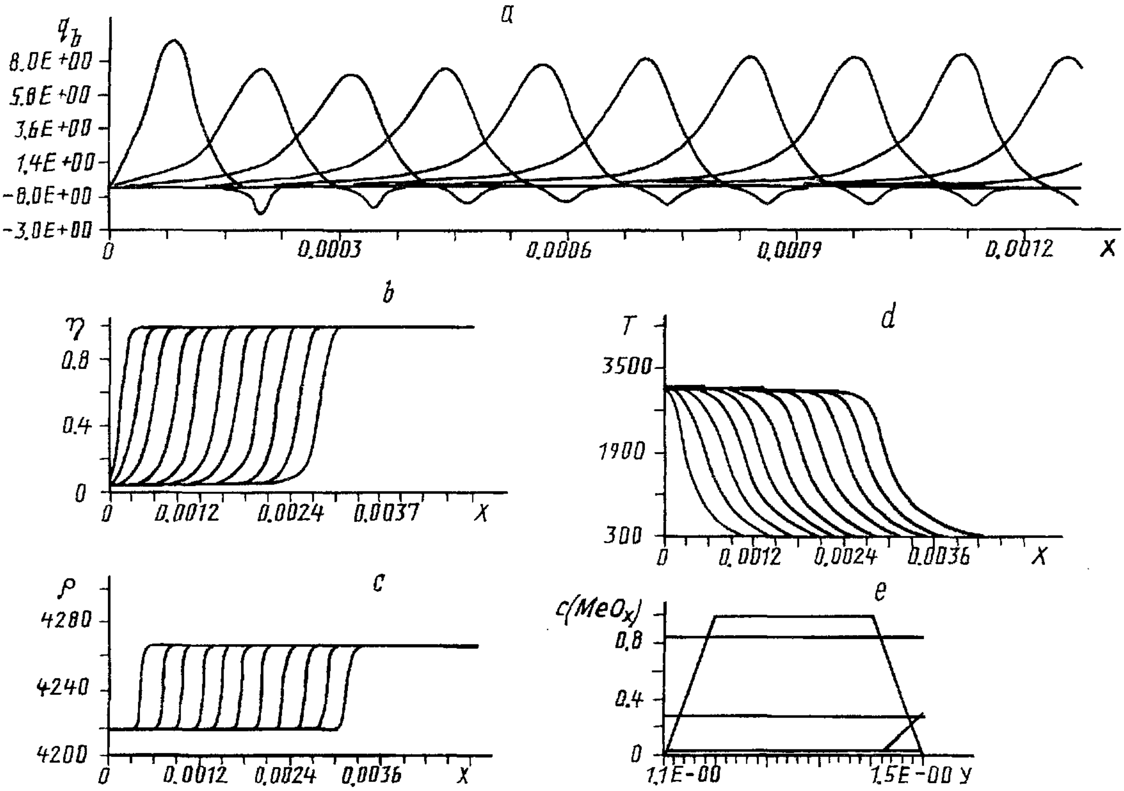

Fig. 2. Dynamics of the rate of heat release (a), degree of aluminum conversion (b), density of the condensed medium (c), temperature of combustion (d), and degree of conversion of the metal oxide and carbon (e). X, Y, m; T, K; η, %; ρ, kg/m^3.

The macrokinetic characteristics of chemical interaction in the combustion front are determined as integral characteristics from the study of the processes of heterogeneous interaction at the microlevel. The dynamics of the change in the metal oxide within one typical cell is also presented in this figure.

Depending on the percentage content of the components and the size of their particles, the constant fundamental parameters of heterogeneous chemical interaction of reagents (Al, MeO_x, C) give a varying gross kinetics at the macrolevel. The proportions between the degrees of transformations of separate components and the gross exothermics of chemical transformation also undergo variations. The quantitative and qualitative characteristics of such a change can be obtained by varying the dimensions of the aluminum and carbon particles. The results of such calculations are presented in Fig. 3. For example, in Fig. 3a the decrease in the combustion temperature with an increase in the size of aluminum particles is shown. An increase in the radius of aluminum particles with a preservation of the percentage content of reagents reduces the effective value of the exothermal heterogeneous interaction surface and promotes a higher degree of the endothermal interaction of carbon with the formation of CO. The inverse process of the increase in combustion temperature with the size of the carbon particles is presented in Fig. 3b. A reduction in the effective surface of heterogeneous endothermal interaction between carbon and the metal oxide with the formation of CO leads to an increase in the degree of exothermal transformation of aluminum with a corresponding increase in the combustion temperature.

In addition to such factors that are relatively simply observed in experiments, the mathematical model allows one to study the process of the metal carbidization and the change in the chemical composition of the combustion products. Nevertheless, one should take into account the inadequacy of the mathematical model and the real process. On the one hand, the proposed model has, for example, limitations on the initial percentage content of reagents and cannot describe all actually existing compounds. On the other hand, we can consider it in a wider range of change in the parameters, departing from their specific physical values. In this way, calculations by the

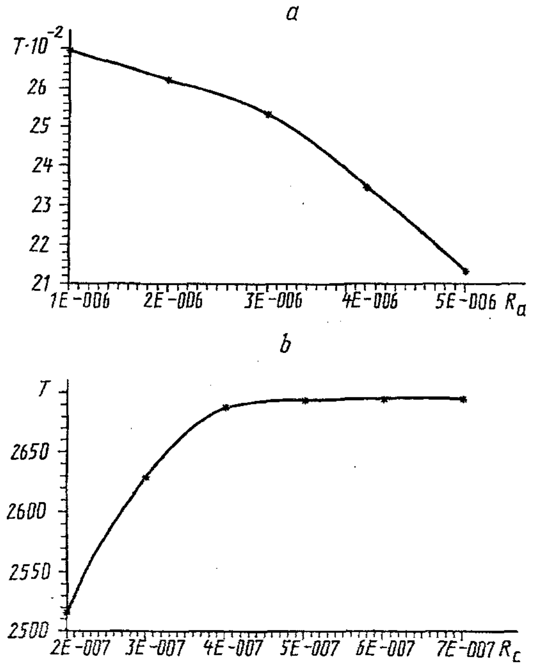

Fig. 3. Combustion temperature vs the dimensions of aluminum and carbon particles. R_a, R_c, m.

mathematical model predict possible mechanisms at the microlevel and disclose their nature. For example, the model considered points to the possible existence of combustion fronts with wide transformation zones having a fundamentally different nature of their origination from those described earlier in the literature. This mechanism is based on the process of preliminary fast solution of one of the reagents in an oxide and its subsequent relatively slow reaction.

In conclusion it may be said that the present work should be considered as a first step on the way to the mathematical simulation of the frontal regimes of the exothermal transformation of multicomponent heterogeneous media (the number of components exceeds two) with account for the specific properties of interaction at the microlevel (competing, successive, parallel, etc. processes). We think that an integral account for such an interaction will yield real macrokinetic trends typical of many systems of SHS metallurgy.

NOTATION

R_a and R_c, dimensions of aluminum and carbon particles, respectively; N_a and N_c, number of aluminum and carbon particles per unit volume; R_s, place of contact; a, c, b, m, concentrations of aluminum, carbon, and aluminum and metal oxides.

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