Mathematical model of gas-free combustion of a binary powder mixture with allowance Marangoni convection

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Abstract. A macroscopic mathematical model has been developed for the gas-free combustion of a binary reaction mixture with allowance for thermocapillary convection of a low-melting reagent. The model includes equations as follows: mass balance of reaction substances, chemical transformation, melt motion, thermal conductivity. Melt formed during the melting of one of the components is believed to move in the porous carcass of the mixture due to thermocapillary forces. The dynamics of changes in temperature, chemical conversion depth, melt fraction and porosity are numerically calculated in a gasless combustion wave. Depending on the main parameters characterizing the process, conductive, convective, and mixed modes of synthesis front propagation are revealed. Analytical relationships are derived to estimate the combustion rate for these modes. An approximate criterion that reveals the synthesis mode from the structural and physicochemical parameters of the binary mixture is found.

1. Introduction

For the majority of reaction mixtures with a low-melting reagent, combustion is accompanied by melting and, therefore, by capillary spreading of one or several components in a structure consisting of solid reagents and solid-phase reaction products [1 - 10]. Capillary or convective melt flow is caused by the surface tension forces in a porous reaction medium. In particular, Marangoni convection (or thermocapillary flow) occurs due to the difference in surface tension forces caused by the temperature gradient [11].

The effect of the capillary flow of a liquid metal on the combustion of gas-free mixtures was first considered in [12]. The effect of melt spreading on the combustion modes of condensed systems was experimentally studied in the works [13, 14]. In addition, the effect of thermocapillary convection on heat transfer in a gas-free combustion wave with a melting reagent for an inertialess flow was analytically and numerically studied in [15].

The goal of this work was to theoretically study the effect of structural parameters on the velocity and modes of propagation of a gas-free combustion wave in a binary powder mixture containing a low-melting component.

2. Computational approach

Let us consider a reaction sample consisting of a porous two-component powder mixture of reagents A and B, which form a refractory product F in the one-stage irreversible synthesis reaction according to the following interaction scheme

$$(1-v)A(\text{solid})+v(\text{solid, liquid})=F(\text{solid}),$$
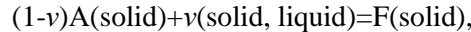
where v is the mass (stoichiometric) concentration of B in the reaction product F.

The synthesis wave is induced by applying a heated wall with a temperature of T_W to the sample end, t_W is the time of contact with the sample. It is also assumed that the melt formed by the melting of component B starts moving in the layer of the reaction mixture exposed to thermocapillary forces (the Marangoni effect).

The assumptions are taken as follows:

1. The densities of the mixture components and product are assumed to be equal, and as a result, the sample sizes remain unchanged.

2. It is assumed that the heat capacity and heat conductivity of the mixture components and product are equal. Heat capacity is a constant, and heat conductivity depends on porosity according to the law

$$\lambda(m) = \lambda_0 (1-m)^n . \qquad (1)$$

The mass fraction of substance (i) in the mixture is represented as the ratio of the initial mass of the mixture to its mass. Under assumption 1, the mass fractions of the components (m_A, m_B) and reaction product (α) in the mixture are related to their volume concentrations ((μ_A, μ_B, μ_F) by the relationship as follows

$$\mu_A = (1-m_0)m_A , \quad \mu_B = (1-m_0)m_B , \quad \mu_F = (1-m_0)m_F \quad (2)$$

where m_0 is the initial porosity of the mixture. Note that $m_F = \alpha$.

Porosity is determined by the relation

$$m = 1 - (\mu_A + \mu_B + \mu_P) . \quad (3)$$

The equations of mass conservation of substances A and B are written as

$$\frac{\partial(m_A)}{\partial t} = -(1-v)J , \quad (4)$$

$$\frac{\partial(m_B)}{\partial t} + \frac{\partial(v_L m_B)}{\partial x} = -vJ . \qquad (5)$$

The rate of formation of the reaction product introduced in (4) and (5) will be given as follows

$$J = \frac{\partial\alpha}{\partial t} = f(\alpha)k_0 \exp\left(-\frac{E}{RT}\right). \quad (6)$$

(4) - (6) contain the parameters as follows: t is time; x is the spatial coordinate; T is temperature; E is the activation energy of a chemical reaction; R is the universal gas constant; k_0 is a pre-exponential factor $f(\alpha)$ is a kinetic law.

The equation of motion of the melt exposed to thermocapillary forces

$$v_L = \frac{r}{2\mu(T)}\frac{\partial\sigma}{\partial T}\frac{\partial T}{\partial x}, \quad (7)$$

where r is the diameter of the capillary; σ is surface tension; $\mu = \mu_0 exp(U/RT)$ is viscosity; μ_0 is a pre-exponential factor; U is the activation energy of a viscous flow.

Temperature distribution in the powder mixture with the assumptions 1 and 2 will be described by the equation of heat conductivity

$$\rho(1-m)[c + \varphi(m)m_B L\delta(T-T_L)]\frac{\partial T}{\partial t} + (1-m_0)m_B\rho v_L[c + L\delta(T-T_L)]\frac{\partial T}{\partial x} = \quad (8)$$

$$= \lambda\frac{\partial}{\partial x}\left(\lambda(m)\frac{\partial T}{\partial x}\right) + \rho(1-m_0)[Q + vLe(T-T_L)]J$$

where ρ, c is the density and heat capacity of the mixture; T_L, L is the temperature and heat of melting; Q is the heat of synthesis reaction;

$$\delta(T-T_L) = \begin{cases} 0, T \neq T_L \\ \infty, T = T_L \end{cases} \text{ - Dirac } \delta\text{-function;}$$

$$e(T-T_L) = \begin{cases} 0, T < T_L \\ 1, T \geq T_L \end{cases} \text{ - Heaviside function; } \varphi(m) = (1-m_0)/(1-m).$$

The initial and boundary conditions are given by:

$t=0$: $T(x)=T_0$, $m_A(x)=m_{A0}$, $m_B(x)=m_{B0}$, $\alpha(x)=0$, $m=m_0$, $0 \leq x < +\infty$ (9)

$x=0$: $T=T_W$ ($t<t_W$), $\partial T/\partial x=0$ ($t \geq t_W$); $x=+\infty$: $T=T_0$. (10)

In order to reduce the number of parameters, select the main ones, and simplify the analysis and calculations, dimensionless quantities are used as follows:

$Td=cRT_*^2/QE$, $\theta=E(T-T_*)/RT_*^2$, $\theta_L=E(T_L-T_*)/RT_*^2$, $\theta_0=E(T_0-T_*)/RT_*^2$, $Ar=RT_*/E$ $\xi=x/x_*$,

$x_*=(\lambda_0 t_*/c\rho)^{1/2}$, $t_*=Tdk_0^{-1}exp(E/RT_*)$, $\tau=t/t_*$, $\tau_W=t_W/t_*$, $Ph=vL/QTd$, $\zeta=U/E$, $\mu_*=\mu_0 exp(U/RT_*)$,   (11)

$\eta=v_L t_*/x_*$ $\phi(\theta)=exp(\zeta\theta/(1+Ar\theta))e(\theta-\theta_L)$, $c_{eff}(\alpha,\theta)=1+(1-\alpha)Ph\delta(\theta-\theta_L)$, $\psi(\theta)=1+TdPhe(\theta-\theta_L)$,

$\omega=Kr_*T_*^2c\rho/2\mu_*E\lambda_0$, $d=r/r_*$ (r_* is the size of a low-melting particle, therefore the value $d = 1$ corresponds to the case when particles A and B are of equal size).

In (11), the combustion temperature is taken for the characteristic temperature: $T_*=T_f=T_0+Q/c$.

In dimensionless quantities, the governing equations and ratios of the mathematical model described above take the form

$$c_{eff}(\alpha,\theta)\frac{\partial\theta}{\partial\tau} + \delta dc_B\omega c_{eff}(\alpha,\theta)\phi(\theta)\left|\frac{\partial\theta}{\partial\xi}\right|\frac{\partial\theta}{\partial\xi} = (1-m)^{-1}\frac{\partial}{\partial\xi}\left((1-m)^n\frac{\partial\theta}{\partial\xi}\right) + \frac{\Psi(\theta)}{\beta(\xi)}|\Psi(\theta)|\frac{1}{Td}\frac{\partial\alpha}{\partial\tau}, \text{ (12)}$$

$$\frac{\partial c_A}{\partial\tau} = -(1-v)\frac{\partial\alpha}{\partial\tau}, \quad (13)$$

$$\frac{\partial(c_B)}{\partial\tau} + \frac{\partial(\eta c_B)}{\partial\xi} = -v\frac{\partial\alpha}{\partial\tau}, \quad (14)$$

$$\eta = d\omega\phi(\theta)exp\left(\frac{\varsigma\theta}{1+Ar\theta}\right)\left|\frac{\partial\theta}{\partial\xi}\right|, \quad (15)$$

$$\frac{\partial\alpha}{\partial\tau} = Tdf(\alpha)exp\left(\frac{\theta}{1+Ar\theta}\right). \quad (16)$$

After simple but lengthy transformations, taking into account the accepted assumptions, the equation for porosity (2) can be rewritten as

$$m = 1 - [c_B + c_{A0} + v\alpha](1-m_0). \quad (17)$$

Initial and boundary conditions:

$\tau=0$: $\theta=\theta_0=1/Td$, $c_A(\xi)=c_{A0}$, $c_B(\xi)=c_{B0}$, $\alpha(\xi)=0$, $m(\xi)=m_0$, $0 \leq \xi < +\infty$.   (18)

$\xi=0$: $\theta=\theta_W$ ($\tau \leq \tau_W$), $\partial\theta/\partial\xi=0$ ($\tau>\tau_W$), $\xi=+\infty$: $\partial\theta/\partial\xi=0$.   (19)

The system of equations (12) - (19) was solved by a finite difference method using an author's numerical code that included an implicit scheme and approximation of the convective term by differences against the flow with constant coordinate and time steps.

To solve the difference analog of equation (12), the sweep method was used in combination with an iterative process. In the numerical solution of equation (12), smoothing of the delta function was applied.

The choice of integration steps $h=0.25$ and $\Delta\tau=0.005$ ensured the stability of numerical calculations. Verification of numerical results included testing the used method to solve the classical problem of gas-free combustion and checking for mesh convergence.

The combustion rate in numerical calculations was determined by the displacement of the points of the combustion front with a temperature equal to the melting point θ_L for the second order of approximation.

In numerical calculations, the parameters of the problem, which determine thermocapillary convection, varied in the intervals as follows: $0.2 \leq m \leq 0.8$, $0.2 \leq Ph \leq 01$, $0.1 \leq \zeta \leq 0.8$, $-4 \leq \theta_L \leq -1$, $0 \leq \omega \leq 0.5$, $c_{B0} = 0.5$, $c_{A0} = 0.5$, $n = 2$.

The conservativeness of the difference scheme was controlled by the law of energy conservation and mass concentration of substance in the entire computational domain.

3. Analytical estimates

The propagation velocity of a stationary combustion wave is determined in two limiting modes: conductive and convective. According to [11], in the conductive mode of combustion, the velocity of the synthesis front will mainly be determined by heat transfer in the system due to heat conductivity. In this case, it can be assumed that $\omega \approx 0$, $\eta \approx 0$. When the combustion wave propagates in the mode determined by the thermocapillary flow of the melt, in (12) it can be assumed that $\partial^2 \theta / \partial \xi^2 \approx 0$.

Following the methodology proposed in [11] and assuming $Ar << 1$, in the approximation of a narrow zone of a chemical reaction, analytical relations for the stationary velocity of the combustion wave propagating in the conductive mode take the form

$$w_t = \exp\left(\frac{\theta^*}{1 + Ar\theta^*}\right)(1 + Ar\theta^*)(1 - m_0)^{\frac{n-1}{2}} \sqrt{\frac{Td}{(1 + TdPh)} \left\{ \int_0^{\alpha^*} \frac{(1-\alpha)}{f(\alpha)} d\alpha \right\}^{-1}} , \quad (20)$$

and in the convective mode

$$w_c = c_B \delta d\omega \exp\left(\frac{\varsigma\theta^*}{1 + Ar\theta^*}\right)(Td\theta^* - 1)\left(\frac{Td(\theta^* - \theta_L) + Ph}{1 - Td(\theta^* - \theta_L)}\right). \quad (21)$$

In (20), (21), the introduced parameters were as follows: $\theta^* = (\alpha^* - 1)/Td$, α^* are the combustion temperature and the final depth of transformation. With an excess of component A: $\alpha^* = m_{0B}/\nu = \delta$; with its deficiency: $\alpha^* = m_{0A}/(1 - \nu) = (1 - \delta\nu)/(1 - \nu)$. In formula (20), the expression under integral sign is given by:

$$I(\alpha) = \int_0^{\alpha^*} \frac{(1-\alpha)}{f(\alpha)} d\alpha .$$

For the case when $f(\alpha) = 1 - \alpha$, the integral $I(\alpha) = \alpha^*$.

For $f(\alpha) = c_A c_B$, the integral $I(\alpha)$ has an accurate but lengthy analytical solution. Therefore, assuming that $c_{A0} c_{B0}$, $(1 - \nu)c_{B0}\alpha$, $\nu c_{A0}\alpha >> (1 - \nu)\nu\alpha^2$, the final expression takes the form

$$\int_0^{\alpha^*} \frac{(1-\alpha)}{c_A c_B} d\alpha \approx \frac{\alpha^*}{\Omega} + \frac{c_{A0} c_{B0} - \Omega}{\Omega^2} \ln\left[\frac{|c_{A0} c_{B0} - \Omega\alpha^*|}{c_{A0} c_{B0}}\right]$$

where $\Omega = (1 - \nu) c_{B0} + \nu c_{A0}$.

Using analytical dependencies (20) and (21), the approximate estimation criterion characterizing the modes of gas-free combustion in a mixture with a low-melting component is given by

$$Kr = \frac{w_c}{w_t} . \quad (22)$$

When $Kr << 1$, the combustion of the sample is determined by conductive heat transfer; for $Kr >> 1$ - by convection of heat due to the thermocapillary flow of melt B.

4. Computational results

Figure 1 shows a typical structure of a combustion wave in a porous powder sample containing a low-melting component.

It is seen that during chemical reaction, an intensive increase in temperature (1, a) and the depth of chemical transformation (2, a) is observed.

After melting B, the thermocapillary melt flow with a velocity of η (1, b) occurs due to a temperature gradient in the combustion zone (2, b). In this case, redistribution of the low-melting component takes place in the high-temperature region (3, a, melt is indicated by a dotted line): its content increases and the porosity of the mixture decreases (4, a).
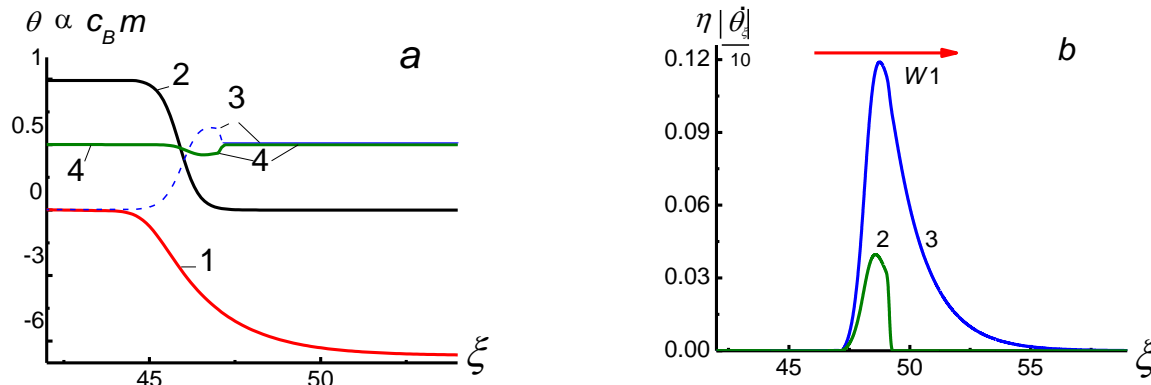

Figure 1. Structure of the combustion wave for Td=0.15, Ar=0.08, Ph=0.2, θ_L=-3, δ=1, d=1, ω=0.05, $f(\alpha)$=1-α: (a) 1 –temperature , 2 - depth of chemical transformation, 3 - mass fraction of a low-melting component (dotted line indicates the melt), 4 - porosity; (b) 1 — melt flow rate, 2 — temperature gradient.

The regions of different combustion modes as a function of the parameter d, which characterizes the structure of the powder mixture, are shown in Fig. 2. Curve 1 determines the velocity of the combustion wave in the sample. Vertical line 2, corresponding to the condition Kr=1 for d=d^*, is the boundary separating the different modes of synthesis.

Figure shows that the conductive combustion mode is predominantly implemented (region I) for refractory particles of small size with respect to low-melting ones $(d<<d^*)$. In this case, the true propagation velocity of the synthesis wave will be close to the value w_t. For refractory particles of large size $(d>>d^*)$, the combustion wave significantly depends on convective heat transfer, and as a result, its propagation velocity approaches the value w_c (region III).

In the range of d~d^* $(Kr$~1) values a mixed combustion mode is implemented, when both conductive thermal conductivity and convective heat transfer have a significantly effect on the velocity of the synthesis wave due to the movement of hot melt in a porous medium (region II).
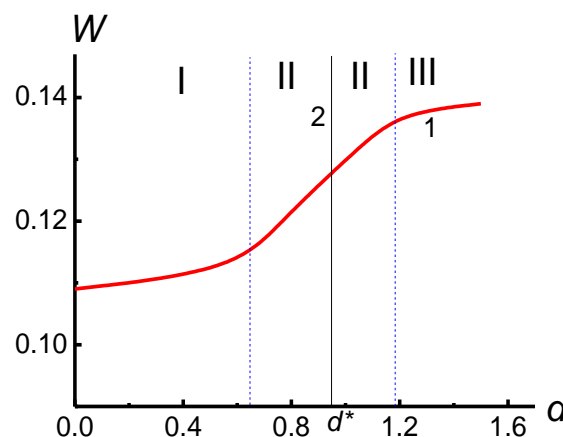
Figure 2. Combustion rate as a function of the structural parameter d. The calculation parameters correspond to those shown in Figure 1.

5. Conclusion

1. Based on the developed mathematical model, the numerical calculations of gas-free combustion were conducted in a binary powder mixture containing a low-melting component, and the dynamics of the process was determined.

2. It was revealed that, depending on the structure of the powder mixture, three combustion modes controlled by the rate of chemical transformation, thermocapillary flow of the melt, or both can be implemented.

3. Analytical relations were obtained to calculate the propagation velocity of the combustion wave depending on the parameters determining the process in the two different synthesis modes: conductive and convective.

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