SUPERSONIC REGIMES IN THE SOLID PHASE COMBUSTION MODELS WITH REGARD TO THE THERMOMECHANICAL PROCESSES

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ABSTRACT

The non-diffusion models of the solid-phase combustion wave accompanied by stresses and deformations (which are able to affect the chemical reaction course and the regimes of the front propagation) are presented in this paper. It was shown that two solutions exist at least in the coherent nonlinear models, this are subsonic and supersonic solutions. The influence of the thermal and concentration stresses and the relaxation time of heat flux on the characteristics of the front was examined here. The solution was carried out by the method of joint asymptotical expansion and numerically.

NOMENCLATURE

t	time
x, x'	space coordinate
v_n	rate of the chemical reaction wave
T, T_0, T_b	temperature, (initial, burning)
y	part of reaction product
q	heat flux
σ	stress
ε	strain
u	displacement
c_ε	heat capacity at the constant strain

ρ	density
Φ	heat realise function
k_0	preexponent
Π	work of the deformation forces
E	activation energy
R	gas constant
Q_0	heat realise during the chemical reaction
w	specific volume
μ_0	molecular weight
λ_T	thermal conductivity coefficient
a_T	thermal diffusivity coefficient
α_{BA}, α_T	coefficients of the concentration and heat expansion
K	coefficient of the isothermal volume compression
k_a	sensitivity coefficient of the chemical reaction rate to the mechanical action
λ, μ	Lamer's coefficients
t_r	relaxation time of the heat flux

INTRODUCTION

It is known that the all physical chemical processes in solid are interrelate. So, the change of temperature field leads to the advent of the thermal stresses. The relaxation of stresses occurs in the differ channel. This are the change of the specific volume of body (deformations), the heat release and the destruction. The similar processes accompany any solid-phase chemical reaction proceeding with the release and the absorption of the heat and are the reason of the differ regimes of the front propagation.

The known models of solid-phase combustion ignore, as a rule, the interrelation of differ physical phenomena, that does not allow to interpret unambiguously the various experimental facts which do not correspond to habitual guides. The high rate processes of the polymerization in solid phase, the various type of reactions at the conditions of high pressure and deformations (there are non-diffusion reactions and processes limited by diffusion at such conditions), low temperature radical reactions in polycrystalline matrices are the examples of such processes. It can be said in some cases on two mechanisms of the acceleration of the solid phase reactions - heat mechanism (due to the temperature rise) and deformation mechanism (due to losses of the free energy of the system), that should lead to the various regimes of the solid-phase combustion. The greatest amount of paper is devoted to low temperature radical reactions [1-5]. The influence of the destruction in the reaction zone on the initiation conditions of reactions was taken into account in [1] with the formal substitution the customary Arrenius source of the heat release by source which is differ from zero only at the critical temperature gradient corresponding to the destruction condition. The model of other type was suggested in [2]. The heat release rate is assumed to depend obviously on the temperature gradient, on the concentration of reactive centres. The severe influence of the heat capacity on the thermal wave propagation at the low temperature was indicated here. It was claimed in [3] that the regimes with high rate exist in autowave model with the source of type [1] only due to presence in medium of the effects of the heat relaxation. The heat model of the combustion with additional nonchemical heat release [4] may be also interpreted as one of possible models of the reactions with the destruction in the front. The explicit destruction waves or the stresses wave do not consider in this paper. The model of process of the propagation of the thermal decomposition front was investigated in [5] with take into account the finite relaxation time and the stresses wave following the heat wave .It was detected there also that the rate of such processes may be as more so less then the sound rate in solid. Let us shown that the interrelation of the heat and deformation processes is the reason of the nonuniquity of the regime of the stationary front propagation for exothermal reactions. But the effect of the coherence (the influence of stresses on the chemical reaction) absent in this model, therefore such conclusion of author [5] is incorrect.

THE BASIC CORRELATIONS

In present paper, we analyze the model including the energy equation in form of generalized thermal conductivity equation

$$c_{\varepsilon}\rho_0 \frac{\partial T}{\partial t} = -\mathrm{div}q + Q_0 k_0 \Phi(y, T, \Pi) - T\frac{\partial}{\partial T}\left\{\varepsilon_{kk}\frac{\partial}{\partial T}(K\omega)\right\},$$

the motion equations

$$\sigma_{ij\cdot k} = \rho \frac{\partial^2 u}{\partial t^2},$$

and the equation for the change of conversion extend y (the part of the reaction product)

$$\frac{\partial y}{\partial t} = k_0\Phi(y, T, \Pi) = k_0(1-y)\exp\left[-\frac{E - k_a\,\mu_0\Pi/\rho}{RT}\right],$$

where $K = \lambda+2\mu/3$ is the coefficient of the isothermal volume compression, λ, μ are Lamer's coefficients; ε_{kk} is the first invariant of the deformation tensor which is equal to the change of the specific volume w:

$$w = 3\left[\alpha_T(T - T_0) + \alpha_{BA}\,y\right]$$

at the absence the all stresses, where $\alpha_{BA} = (\alpha_B - \alpha_A)C_{A0}$, α_B, α_A are the coefficients of the concentration expansion of product and reagent; C_{A0} is the part of the reagent in nondeformed substance, Π is the work of deformation forces, k_a is the sensitivity coefficient of the chemical reaction rate to the mechanical actions.

The employment of the linear Fourier low leads to the usual thermal conductivity equation with the additional items due to connection between the thermal conductivity process and the deformation of the substance. If we use the nonlinear correlations [6]

$$q = -\lambda_T \nabla T + t_r\,\partial q/\partial t,$$

which take into consideration the finite relaxation time of the heat flux, we receive the generalized hyperbolic thermal conductivity equation.

The stresses connect with deformations by generalized Hooke low

$$\sigma_{ij} = 2\mu\varepsilon_{ij} + \left[\lambda\,\varepsilon_{kk} - \frac{v - v_0}{v_0}\right]\delta_{ij} \tag{1}$$

where δ_{ij} - is Kronecker symbol. In principle, the similar correlations have a place for stresses and deformations of any type, therefore the employment (1) does not belittle the community of the reasoning. We have

$$\sigma_{22} = \sigma_{33} = \lambda\varepsilon_{11} - Kw, \qquad \sigma_{11} = (\lambda + 2\mu)\varepsilon_{11} - Kw,$$

$$\sigma_{12} = \sigma_{13} = \sigma_{23} = 0,$$

and the unique motion equation $\sigma_{11,x} = \rho\,\partial^2 u_1/\partial t^2$ in the simplest case of one-axis deformation. To move up to the coordinate system connecting with the reaction front we will make the replacement the variable x on x'. We accept the following boundary conditions

$$x' \to \infty: \quad \partial T/\partial x = 0$$
$$x' \to -\infty: \quad T = T_0, \quad y = 0, \quad u = \partial u/\partial x = 0$$

for the nonstationary combustion model. The question of the existence of the automodel solutions is the greatest interest for us. The corresponding automodel problems are received with the help of the formal equation the time derivatives to zero in the equations system which are written in the variables x', t.

THE EXAMPLES OF THE SPECIAL MODELS

1. If the temperature deformations are the basic in the system, the problem may be reduced to the more simple mathematical formulation. The stresses and deformations follow the change of the temperature field in this case, and the model of the stationary wave of the solid-phase combustion take a form

$$a_T \frac{d^2T}{dx'^2} - v_n \frac{dT}{dx'}\left[1 + \frac{(3K\alpha_T)^2}{\lambda + 2\mu}\frac{T}{c_e\rho}\frac{1}{1 - M^2}\right] - \frac{Q_0 k_0}{c_e\rho}\Phi(y,T) = 0, \qquad (2)$$

$$-v_n \frac{dy}{dx'} + k_0\Phi(y,T) = 0, \qquad (3)$$

where

$$\Phi(y,T) = (1-y)\exp\left\{-\left(E - \frac{\mu_0}{\rho}k_n\frac{(3K\alpha_T)^2}{\lambda+2\mu}\frac{M^2}{1-M^2}(T-T_0)^2\right)\Big/RT\right\}, \qquad (4)$$

$$x \to \infty: \partial T/\partial x = 0, y \to 1; \quad x \to -\infty: T - T_0, y = 0, \qquad (5)$$

$M = v_n/((\lambda + 2\mu)/\rho)^{1/2}$ is the ratio of the front rate to the sound rate in the solid (it is the analogy of Mach-number). It had been received in [8] at the analysis of linearized model (when we assumed $T \approx T_b$ in the square bracket of (2)) the unique value of the front rate v_n exists in the model at the condition M << 1. The value of v_n increase sharply with regard to the dependence of the chemical reaction rate on the work of the deformation forces:

$$\frac{v_n}{v_{n0}} = \left[\frac{\exp\left(g\, c_\varepsilon \mu_0 k_a (T_b - T_0)^2 / R T_b^2\right)}{1 + g c_\varepsilon \mu_0 k_a \left(T_b^2 - T_0^2\right) / T_b E_0} \right]^{1/2}, \tag{6}$$

where

$$g = \frac{(3K\alpha_T)^2}{\lambda + 2\mu} \frac{T_b}{c_\varepsilon \rho} \frac{M^2}{\left(1 - M^2\right)^2} << \quad 1,$$

v_{n0} is the rate of the stationary front corresponding to the pure heat model. The nonuniquity solution appears at the attempt to connect the temperature in combustion front with the conditions of the stationary propagation of the cracks system in this case. In general case, the ununiquity of the solution inherent in the properties of the equations system (2),(3).

2. The starting equation system for the case $w = 3\alpha_T(T - T_0)$ is differ from the equation system of the usual coherent equation system of the thermal elasticity by the presence the source item and the presence the nonlinearity in the dissipative item of thermal conductivity equation. It have been assumed in classical works that the examination may be restricted by the linearized problem substituting $T \approx T_0 + o(\partial T/\partial t)$ for the small temperature drop and for the slow temperature field change. The solutions of the problems on the heat shock (they are known as the Danilovskaya's problems) are presenting in form of the thermal elasticity wave attenuating quickly at the removing from the heating boundary. The automodels solutions absent in such problems. Taking into account the nonlinearity in inert thermal conductivity equation we will receive the automodel solutions.

Really, assuming $\Phi = 0$ in (2), we have the nonlinear equation which coincides in form with the Burgers equation [8] which is written in automodel variables. Using the conditions (5) we find the temperature behind the front of wave T_s. The infinitely many values of rate v_n which satisfy to the condition

$$v_n^2 > \frac{\lambda + 2\mu}{\rho} + \frac{(3K\alpha_T)^2}{\rho} \frac{T_0}{c_\varepsilon \rho}$$

exist. If the temperature T_s and T_0 are given the thermal mechanical autowave runs with the rate

$$v_n^2 = \frac{\lambda + 2\mu}{\rho} + \frac{(3K\alpha_T)^2}{c_\varepsilon\rho}\frac{T_s + T_0}{2\rho} \tag{7}$$

Adding the thermal conductivity equation by the heat release caused by the chemical reaction we determine practically T_s as the product temperature T_b.

3. The first integral of the equation system (2),(5) has a view

$$a_T\frac{dT}{dx'} - v_n\left[(T - T_0) + \frac{(3K\alpha_T)^2}{\lambda + 2\mu}\frac{1}{2c_\varepsilon\rho}\frac{T^2 - T_0^2}{1 - M^2}\right] + \frac{Q_0 v_n}{c_\varepsilon\rho}y = 0,$$

and allows us to determine the temperature of the reaction products. Introducing the designations

$$\theta_b = (T_b - T_0)/(T_{b0} - T_0), \quad B = \delta_0/2(M^2 - 1),$$

$$\delta_0 = \frac{(3K\alpha_T)^2(T_{b0} - T_0)}{c_\varepsilon\rho(\lambda + 2\mu)},$$

where $T_{b0} = T_0 + Q_0/(c_\varepsilon\rho)$, $\gamma_1 = 2(1-\sigma)/\sigma$, $\sigma = (T_{b0} - T_0)/T_{b0}$, we find

$$B\theta_b^2 + (B\gamma_1 - 1)\theta_b + 1 = 0, \tag{8}$$

The equations system for the temperature and the conversion extend take a form

$$r^2\frac{dy}{d\xi} = (1 - y)\ f(\theta),$$
$$\frac{d\theta}{d\xi} = \theta - \frac{\delta_0}{2}\frac{\theta}{M^2 - 1}(\theta + \gamma_1) - y, \tag{9}$$

$\xi \to -\infty$: $y \to 0, \theta \to 0$;
$\xi \to \infty$: $y \to 1, \theta \to \theta_b$,

with using the first integral, where

$$\xi = a_T x'/v_n, \quad \theta = (T - T_0)/(T_b - T_0),$$

$$r^2 = \frac{v_n^{\ 2}}{k_0 a_T}\exp\left[\frac{E_0}{RT_{bo}}\right], \qquad f(\theta) = \exp\left[\frac{\theta_0(\theta - 1)}{1 + \sigma(\theta - 1)}\right], \qquad \theta_0 = \frac{T_{bo} - T_0}{\left(RT_{bo}^{\ 2}/E_0\right)}$$

The solution of the problem (9) with help of joint asymptotical expansion method leads to the expression

$$r^2 = \frac{\sigma^2}{\theta_b}\left[\gamma_1/2 + \theta_b\right]^2 \exp\left\{\frac{\theta_0}{\sigma}\frac{\theta_b - 1}{\theta_b + \gamma_1/2}\right\} \qquad (10)$$

for the front rate. The analysis of (8),(10) has shown that the two regimes - subsonic and supersonic exist in this problem, and two differ value of the temperature θ_b correspond to the rates which are more the sound rate

$$r^2 > v_x^{\ 2} = \frac{\lambda + 2\mu}{\rho}\exp\left[\frac{E_0}{RT_{bo}}\right],$$

Practically, we have two supersonic combustion regimes. The low-temperature regime is nonstable due to character of singular point ($\theta_b = \theta_1, y=1$).The since of such result could be understandable with help of the numerical examination.

The typical temperature and concentration profiles for the various regimes of the propagation of the combustion wave are presented on the fig 1,2. The calculation was carried out for the parameters values: $\theta_0 = 10, v_x^{\ 2} = 0.01, \sigma = 0.9, \delta_0 = 1$

The wave propagating with subsonic rate $r^2 \approx 5,5 \times 10^{-4} (M^2 \approx 0,055)$ is characterized by the product temperature $\theta_b = 0,677$.The supersonic wave has the rate $r_1^{\ 2} \approx 0,162 (M^2 \approx 16,2)$ and the temperature which is equal to the lesser temperature $\theta_b = \theta_1 \approx 1,04$ from two solutions of (8) (fig. 1). Selecting the θ_2 as the product temperature we receive the temperature profile in the reaction zone which reminds the detonation wave (fig. 2). The thermal mechanical wave propagates with the rate which is equal to the reaction front r_1 . The temperature θ_2 may be estimated from (7)

$$\theta_2 = 2\frac{M^2 - 1}{\delta_0} - \gamma_1, \quad M = \frac{r_1^{\ 2}}{v_x^{\ 2}}.$$

Unlike the detonation wave the thermomechanical wave "push" the chemical wave. The existence of new wave are stipulated by the interrelation of heat and deformation processes in the front of the solid-phase chemical reaction wave.

The results of the numerical determination of the rates of the subsonic and supersonic regimes agree well with the calculations from the formulas (8),(10).

4. Taking into account the concentration stresses and deformations, we arrive to the problem on the propagate of the stationary front with the thermal conductivity equation

$$v_n c'_\varepsilon \rho \frac{dT}{dx'} = \lambda_T \frac{d^2T}{dx'^2} + Q'_0 v_n \frac{dy}{dx'}, \qquad (11)$$

where

$$c'_\varepsilon = c_\varepsilon\left[1+\delta\frac{T}{T_b}\right], \quad Q'_0 = Q_0\left[1-\delta g\frac{T}{T_b}\right], \quad g = \frac{c_\varepsilon \rho}{Q_0}\frac{\alpha_{BA}}{\alpha_T}$$

Hence, the change of the heat capacity and the heat effect of the reaction connect immediately with the stresses and deformations which are the result of the reaction. If the reaction proceeds with the volume expansion, we have the apparent parallel endothermic reaction ($g > 0$) In the opposite case, "dissipative" heat from concentration stresses and deformations appears as the heat release in the parallel reaction. Let us give the result of the asymptotical analysis of the problem for $k_a = 0$:

$$B\theta_b^2 + [B(2g+\gamma_1)]\theta_b + 1 - B\gamma_1 g = 0, \qquad (12)$$

$$r^2 = \frac{\sigma^2}{\theta_0}\left[\frac{\gamma_1}{2}+\theta_b\right]^2 \exp\left\{\frac{\theta_0}{\sigma}\frac{\theta_b - 1}{\theta_b + \gamma_1/2}\right\}\left[1+2Bg(\theta_b+\frac{\gamma_1}{2})\right]^{-1}. \qquad (13)$$

The calculations from formulae (12),(13) shown that negative g leads to the increase of the subsonic front rate ($M < 1$) and to the decrease of the values of the supersonic wave ($M > 1$). Influence of the positive g has the opposite nature.

5. Accepting the nonlinear connection between the heat flux and the temperature gradient we receive following thermal conductivity equation [9]

$$v_n c'_\varepsilon \rho \frac{dT}{dx'} = \lambda'_T \frac{d^2T}{dx'^2} + Q'_0 \Phi' + t_r v_n Q'_0 \frac{d\Phi}{dx'}, \qquad (14)$$

where

$$c'_\varepsilon = c_\varepsilon\left[1+\frac{\delta_0}{1-M^2}\frac{1}{T_{b0}-T_0}\left(T+t_r v_n\frac{dT}{dx'}\right)\right],$$

$$\lambda'_T = \lambda_T\left[1-\frac{t_r v_n{}^2}{a_T}\left(1+\frac{\delta_0}{1-M^2}\frac{T}{T_{b0}-T_0}\right)\right],$$

$$\Phi' = \Phi\left[1-\frac{\delta_0 g}{1-M^2}\frac{1}{T_{b0}-T_0}\left(T+t_r v_n\frac{dT}{dx'}\right)\right].$$

The equation (14) includes the all known models for the low temperature radical reactions. Really, the dependence of the reaction rate on the work of the deformation forces (or on the excess of the free energy presenting in the system [1,4]), the dependence of the preexponent (or the heat release of the reaction) on the temperature [2], the influence of the temperature change on the heat capacity of substance [5] are taken into consideration in the model obviously. The individual items in Φ', c'_ε , the change of the thermal conductivity coefficient and the additional source item in (14) reflect the influence of effect of the heat relaxation [3]. Unlike [4], the additional heat release has a chemical nature. One of the conditions of the existence of the heat autowave is $\lambda'_T > 0$.

The solution of the problem was carried out also by the method of the joint asymptotical expansion and numerically. We have, for example,

$$r^2 = r^2(\tau_r{=}0)\times\exp\left\{-\frac{\tau_r r^2\theta_0}{\sigma^2(\theta_b+\gamma_1/2)^2}\left(1-\frac{\delta_0 g}{1-M^2}\left(\theta_b+\frac{\gamma_1}{2}\right)\right)\right\},$$

in particular case $k_a = 0$ and at the conditions

$$\tau_r \approx o(\theta_0{}^{-1}) << 1,$$

with the exponentially small accuracy to θ_0.

The equation for the product temperature θ_b (with the same accuracy) does not change. The estimation shown that the stationary front rate (for any regimes) increases with the relaxation time $\tau_r = t_r k_0 \exp\left(E_0/(RT_{b0})\right)$.

Let us make in conclusion, that the coherent equations which are analogous to presented above have a place for the stresses and deformations of any type [10].

Hence, we may expect the appearance of supersonic regimes and thermomechanical autowaves at the other connections between $\sigma_{ij}, \varepsilon_{ii}, w$.

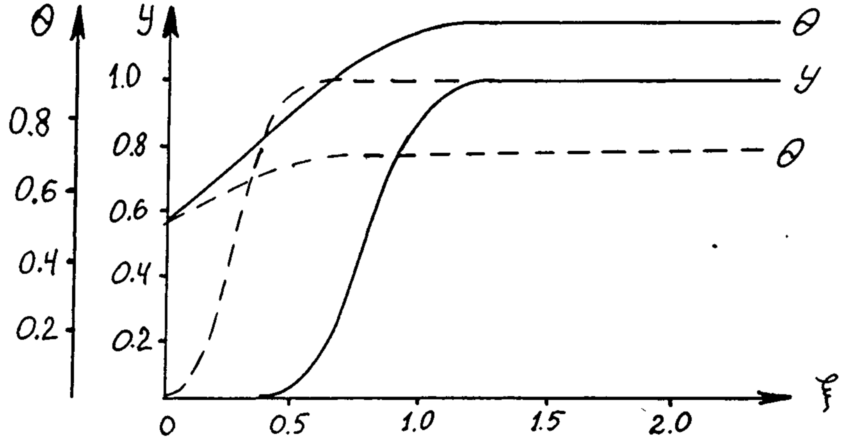

Fig.1. The profiles of temperature (1) and conversion extend (2) in the reaction zone of solid-phase combustion wave

- - - - - - - subsonic regime

————supersonic regime (thermomechanical wave absents)

$\theta_0 = 10, v_x^2 = 0.01, \sigma = 0.9, \delta_0 = 1.$

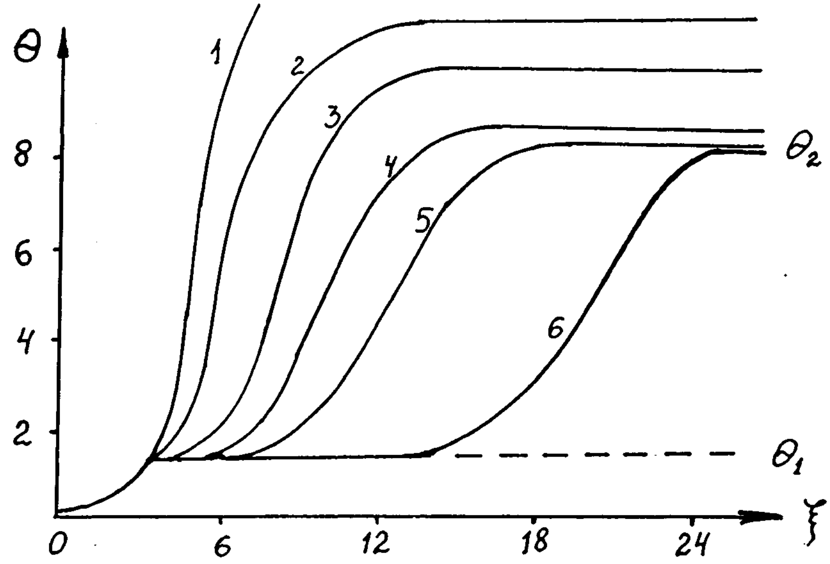

Fig.2. The temperature profile for the supersonic combustion wave
$\theta_0 = 10, \delta_0 = 1, \sigma = 0.9(\gamma_1 = 2/9), v_x^2 = 0.1.$

v_n^2 = 1. - 0.965; 2. - 0.6433; 3. - 0.6031; 4. - 0.5780; 5. - 0.5742; 6. - 0.5735.

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