Mathematical modeling of the formation and decomposition of a metastable product during MSHS

O V Lapshin

Tomsk Scientific Center of the Siberian Branch of the Russian Academy of Sciences,
10/4 Akademicheskii Pr., Tomsk, 634055, Russia

E-mail: ovlap@mail.ru

Abstract. Synthesis and decomposition of nonequilibrium phases are studied in a thin-layer gas-free system that forms metastable products, using a developed mathematical model and numerical methods. The model uses the chemical transformation equation, which takes into account the possibility of the formation and decomposition of a metastable product, as well as the energy equation with the possibility of external heating and cooling of the reaction sample. The development of a chemical reaction is considered under two extremely different conditions: wave synthesis and thermal explosion. Characteristic modes of the process are found. The possibility of multiple synthesis of a metastable product, determined by external heat input and heat removal in a reacting condensed system, is shown. It is revealed that for the reaction wave propagation, three modes of formation and decomposition of metastable phases can take place: breaking, merging, and quenching.

1. Introduction
Equilibrium synthesis of materials in the SHS mode is well studied. These studies are based on equilibrium state diagrams that characterize the thermodynamic parameters of obtained products [1 – 8].

At the same time, the equilibrium approach cannot explain many experimental facts which indicate that in most cases the parameters of the products formed during SHS differ from their equilibrium values [1, 9 – 15].

At present, multiple cycles of synthesis and decomposition, called by the authors [16] “multiple self-propagating high-temperature synthesis (hereinafter, MSHS)”, are found to be conducted in some systems (for example, Al-Si, Al-S, Al-Zn, Au-Ge), using thin-film samples. The authors of the work [16] report the important hypotheses that the MSHS phenomenon is related to the formation and decomposition of metastable phases.

At present, for the analysis of chemical interaction in reacting media, it is important to use mathematical models that can describe not only processes under study, but also solve certain problems, searching for optimal modes of obtaining the final reaction product and thereby significantly reducing the number of experiments.

The purpose of the work is to develop a MSHS model for the modes of thermal explosion and frontal combustion of a composition consisting of alternating reagent layers.
To achieve this goal, the second section of the paper represents a mathematical macroscopic model that was built to describe the processes of synthesis and decomposition of a metastable product for the reaction volume and wave propagation. The model uses a phenomenological approach to continuum mechanics, using the continuity hypothesis, which allows the basic equations of the problem under consideration to be written in differential form. The third section represents, on the basis of the developed computer code, numerical calculations with dimensionless parameters and variables obtained using the Euler method and the TDMA method (tridiagonal matrix algorithm). The fourth section summarizes the main findings.

2. Computational approach
A pore-free mixture consisting of the layers of A and B substances is considered in the work. During reaction, either a stable phase F or a metastable phase M may form in the mixture. The synthesis of an unstable product will be considered. In this case, an increase in the temperature of the system above $T_0$ leads to the formation of the M phase that decomposes into initial substances under cooling below $T_0$ [17]. During the further heating, the process repeats: above $T_0$, the M phase may form again, and during cooling below $T_0$ the A+B mixture may form. In this case $T_0$ is a temperature at which thermodynamic parameters change. In contrast to typical reversible reactions, the reversible chemical transformation in a condensed system described in [17] takes place in different temperature ranges. It is worth noting that rapid cooling (quenching) can preserves a metastable phase.

Two methods are considered for the synthesis of a metastable product: thermal explosion and frontal combustion. In the first case, the entire volume of the sample is uniformly heated by an external heat flux with a constant power $W$, and the heat is removed by a cooler with a constant power $W$. In the second case, combustion is initiated by a heated wall.

The rate of chemical transformation during the formation and decomposition of the metastable product M can be written in the simplest form

$$\frac{d\alpha}{dt} = \begin{cases} k_{0+}\exp\left(-\frac{E_+}{RT}\right), & T > T_0, \\ -k_{0-}\exp\left(-\frac{E_-}{RT}\right), & T \leq T_0, \end{cases}$$

where $t$ is time; $k_{0+}, k_{0-}, E_+$ are the pre-exponential factors and activation energy of chemical reactions, which characterize the formation (index +) and decomposition (index -) of the metastable phase, respectively; $R$ is the universal gas constant; $\alpha$ is the depth of chemical transformations.

2.1 Bulk reaction
The heat balance equation describing the temperature change in the sample volume is given by

$$\rho c \frac{dT}{dt} = \rho Q \frac{d\alpha}{dt} + W,$$

where $c$ is the heat capacity of the mixture; $\rho$ is the density of the mixture, $Q$ is the thermal effect of reaction.

The external energy flux:

- during heating: $W = \begin{cases} W_s S / V, & t \leq t_+, \\ 0, & t > t_+ \end{cases}$, (3)
- during cooling: $W = \begin{cases} -W_s S / V, & t \leq t_-, \\ 0, & t > t_- \end{cases}$, (4)

In (3), (4): $S, V$ are the surface area exposed to the flow of energy and the volume of the sample; $t_+, t_-$ are the operation time of heating and cooling sources in one cycle. Initial conditions for the synthesis of the product: $t=0; T=T_n, \alpha=0$; for the decomposition of product:
t=0: T=T\textsubscript{m}, \alpha=1. \quad (5)

In (5): \(T_n\) is the initial temperature of the mixture, \(T_m\) is the temperature of the sample after the product was synthesized and the external energy source was switched off.

2.2 Frontal reaction

The temperature distribution in the sample is described by the equation

\[ c\rho \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + Q\rho \frac{\partial \alpha}{\partial t} - \chi (T - T_n), \quad (6) \]

where \(\lambda\) is the coefficient of thermal conductivity; \(x\) is a coordinate; \(\chi\) is a heat transfer coefficient. In (6), the heat capacity and density of all substances were considered to be equal. The latter assumption is made not to consider the movement of a substance due to the difference in the density of the initial substances and the phase transformation products. Initial and boundary conditions are written in the form

\[ t=0: T=T_{m}, \alpha(x)=0; \quad (7) \]
\[ x=0: T=T_{\text{system}}(t), \partial T/\partial x=0 \quad (t>t_{w}); \quad x=+\infty: T=T_{m}. \quad (8) \]

In (7), (8) \(T_n\) is the initial temperature of the mixture; \(T_\text{system}, t_w\) are the temperature of the wall heated above \(T_0\) and the time of its contact with the sample. As it follows from (1), chemical reactions and synthesis of products are not observed in the range of \(T_n\leq T\leq T_m\); the substances are heated only by the heat flux from a high-temperature wave. In the temperature range of \(T_0 \leq T \leq T_m\), the phase does not decompose, and the substance is cooled exchanging the heat with the environment.

To reduce the number of parameters, dimensionless quantities are introduced: \(\tau=tK_s(T_0)\) \((K_s(T_0)=k_0*exp(-E_s/RT))\), \(\alpha=tK_s(T_0)\), \(\theta=E_s/(RT_0)\), \(\theta_0=E_s(T_n)/RT_0\), \(\theta_n=E_s(T_m)/RT_0\), \(\gamma=C_rT_0^2/(Q.E_s)\), \(\beta=RT_0/E\), \(q_\text{a}=W_aSE_s/(K_s(T_0)p_vC_rT_0^2)\), \(q_\text{s}=W_SSE_s/(K_s(T_0)p_vC_rT_0^2)\), \(q_\text{e}=E_s/E_u\), \(\varepsilon=K(T_0)/K_s(T_0)\) \((K(T_0)=k_0*exp(-E_s/RT))\), \(\tau_0=t_0K_s(T_0)\), \(\zeta=a(c_0K_s(T_0)/\beta)^{1/2}\), \(\psi=\gamma/(c_0K_s(T_0))\).

3. Computational results

The mathematical model (1) - (5) was numerically studied using the Euler difference scheme and dimensionless parameters: \(\gamma=0.11 - 0.15\), \(\beta=0.03\). It was assumed that \(q=q_\text{a}=q_\text{s}, \varepsilon=1, \varphi=1\). The mathematical model (1), (6) - (8) was numerically studied using the sweep method and an implicit difference scheme.

The equations written above were numerically integrated according to the Euler scheme of the first order accuracy. The stability of the difference scheme was provided by limiting the time step in accordance with the condition \(\Delta\tau<2(\theta/\theta_{n+1} - \theta_n)\), where \(\theta_n, \theta_{n+1}\) are the function values in the previous and subsequent time steps. The main advantage of the TDMA method used in this work is its weak sensitivity to errors in setting the initial conditions and to computational errors.

The rates of combustion and decomposition were calculated from the surface velocity of chemical transformations at which \(\alpha=0.5\). Approximation convergence was checked by condensing the nodes of the computational mesh. The conservativeness of the difference scheme was controlled by the energy conservation law in the computational domain.

3.1 Bulk chemical reaction

Fig. 1 shows a thermogram of temperature \((a)\) and depth of chemical transformation \((b)\), reflecting the multiple synthesis of a metastable product. It is considered the case when the external energy source is turned off at the time when the system reaches the temperature of the onset of the reaction: \(\tau_\text{a}=\tau_{0,\text{on}}, \tau_\text{a}=\tau_{0,\text{on}}\).

Figure 1 demonstrates that the heating of the sample consisting of the initial components to the temperature of the onset of the reaction is conducted in an inert mode and chemical transformations are absent. When the system reaches the point at which the thermodynamic state changes \((\theta=0)\), it
leads to intensive chemical interactions accompanied, due to heat release, by a rapid increase in the temperature and depth of transformation of initial components into a metastable product.

Figure 1. Dynamics of temperature (a) and depth of bulk chemical transformation (b) during MSHS for $\gamma=0.15$, $q=0.1$.

After the synthesis is completed ($\alpha=1$), an external cooling source is switched on. During cooling to the temperature of the onset of decomposition reaction, the product M is stable (the horizontal line in Fig. 1 (b)) and decomposes with heat absorption at $\theta\leq0$. Moreover, the rate of the nonequilibrium phase decomposition into the initial components decreases exponentially with decreasing temperature, and the duration of the reaction increases significantly.

3.2 Wave mode of chemical reaction
The structure of waves, in which, unlike [9], combustion and decomposition simultaneously occur, is shown in Fig. 2.

Figure 2. Distribution of temperature (solid line) and chemical transformation depth (dashed line) in the wave of synthesis and decomposition $\theta_0=-4.5$, $\sigma=1$, a) $\varepsilon=1$, $\psi=0.0009$, $\tau=500$; b) $\varepsilon=1$, $\psi=0.005$, $\tau=500$; c) $\psi=0.005$, $\varepsilon=10$, $\tau=60(1)$, $160(2)$, $220(3)$, $250(4)$
Depending on the parameters, the main of which are the rate of synthesis and decomposition of the phase and the intensity of heat exchange with the environment, three characteristic modes can be selected.

The separation mode (Fig. 2a) takes place at the values $\kappa$ close to 1 and during the relatively low heat exchange with the environment. At the same time, with a decrease of $\kappa$ and (or) $\psi$ the distance between the fronts of combustion and decomposition increases. Finally, for $\psi=0$ (adiabatic case), there is only a combustion wave (synthesis of product).

The second mode is the merge mode (Fig. 2b) that is characterized by a small distance between synthesis and decomposition waves. This mode is observed in a narrow range of main parameters. The temperature profile of this mode is similar to a soliton, when a temperature pulse separates an initial mixture.

In above Figures, the synthesis and decomposition of a metastable product can be judged by the profile of chemical conversion depth (dashed line): the synthesis wave increases the amount of the product to its maximum value, and the decomposition wave almost completely decomposes it.

The third characteristic mode is the quenching mode (Fig. 2c). It takes place at relatively intensive heat exchange and a rate of decomposition that is faster than that of synthesis. This relation between the rates leads to the fact that after ignition with an external source the decomposition wave reaches the synthesis wave and quenches it.

The front of synthesis, as with a single-stage irreversible reaction, can spread in a self-oscillatory mode. The difference is in the impossibility of the existence of a self-oscillatory mode, when during depressions the temperature drops below the value that characterizes the stability of a non-equilibrium phase. In this case, temperature decreases (intensification of depression) due to heat absorption during the decomposition of the metastable phase and quenching of the wave.

The self-oscillatory mode is conducted in another way in the temperature range when the unstable phase decomposes (Fig. 3). Depending on the maximum temperature, the stationary mode (Fig. 3, curve 1) changes for to self-oscillatory one (Fig. 3, curve 2).

![Figure 3](image)

**Figure 3.** Decomposition front velocity ($\omega_{ph}$) as a function of the coordinate at $\psi = 0$, the wall temperature $\theta_w = -3$, $\varepsilon = 1$, $\sigma = 1$ and different values of the final synthesis temperature $\theta_m$: 1 – 5.7, 2 – 5.8.

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Under accepted assumptions, the described modes can be observed in the systems the state diagram of which does not contain equilibrium phases. The analysis of possible situations in systems in which there are equilibrium phases requires special consideration.
4. Conclusion
A mathematical model of non-isothermal chemical transformations of a metastable product was developed and numerically studied in two reaction modes: bulk and wave.

The multiple formation and decomposition of a metastable product were shown can be conducted both in the bulk and wave mode, using the same reaction sample.

During the wave chemical reaction, the characteristic modes were found as follows: separating, merging, and quenching. Modes differ in the location of synthesis and decomposition fronts of the metastable phase. Self-oscillatory modes in this system were shown to be separated by a threshold of temperature stability of the product. The self-oscillatory mode, in which the product is simultaneously synthesized (during temperature peaks) and decomposed (during stagnation), cannot be implemented. It was revealed that the self-oscillatory mode was the intermediate mode between the stationary and degenerated modes in the decomposition zone of the metastable phase.

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