

DOI: 10.17516/1997-1397-2020-13-6-708-717

УДК 536.46

A Coupled Mathematical Model for the Synthesis of Composites

Anna G. Knyazeva*

Natalia V. Bukrina†

Institute of Strength Physics and Materials Science SB RAS

Tomsk, Russian Federation

Received 10.07.2020, received in revised form 25.08.2020, accepted 20.09.2020

Abstract. The work proposes a model for synthesizing a composite "metallic matrix–reinforcing inclusions". The solution is based on two algorithms demonstrating similar results. It is shown that, like in classic models of combustion, there is a domain of model parameters where a transition to the stationary regime is possible. It is demonstrated that taking into account the thermal and mechanical processes alters the effective properties (thermal capacity and thermal effects of the reaction) and provokes the formation of a new heat source conditioned by the interaction of different physical processes.

Keywords: composite synthesis, pulsed heating, consecutive-parallel reactions, comparison of algorithms.

Citation: A.G. Knyazeva, N.V. Bukrina, A Coupled Mathematical Model for the Synthesis of Composites, J. Sib. Fed. Univ. Math. Phys., 2020, 13(6), 708–717. DOI: 10.17516/1997-1397-2020-13-6-708-717.

Introduction

Currently, there are numerous methods for synthesizing composites [1–3 and other]. One of them is based on combustion synthesis or SHS [4]. The chemical reactions in powder mixtures are diverse. The obtained multi-component and multi-phase reaction products, depending on the conditions of synthesis, can possess different properties. In general case, the deformation and stress field formation processes accompanying the chemical transformations are inherent stages of the synthesis and may impact the effective properties and structure. Such mathematical models, taking into account the processes of different physical nature, are called coupled models. From this perspective, the models of classic combustion theory—taking into account the effect of heat liberation from the reactions on the temperature field—also belong to coupled models. Taking into account the mutual influence of thermal phenomena, chemical reactions and deformation, in the elementary case, affects the effective formal-kinetic parameters [5, 6]. In the case of more detailed investigation, it leads to the occurrence of new transformation regimes [7]. However, before the detailed accounting of mechanical and mechanochemical phenomena, the sequence and mutual influence of the chemical stages should be elucidated. This work is aimed at studying the regimes of transformation using a non-stationary model of composite synthesis that includes consecutive-parallel stages at the moment of powder mixture reaction initiation by a heat pulse applied from a side end.

*anna-knyazeva@mail.ru

†bnv@ispms.tsc.ru

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1. Mathematical statement of problem

Let us assume that the composite synthesis can be described by a simple scheme of chemical reactions. The result of the first reaction are reinforcing particles and an intermediate product consumed in the second reaction. The second reaction immediately forms the matrix. The general reaction scheme can be expressed as



This scheme can be exemplified by the synthesis of composites in systems $Al + Cr_2O_3 + Ti$ and $Al + Fe_2O_3 + Ni$. According to scheme (1), the reagent Y (oxides) takes part in the first reaction, consequently changing its rate, while the concentration of the component Z (titanium or nickel) in the initial mixture changes the rate of the second reaction. Therefore, these substances may not be included into the kinetic equations. The resulting set of kinetic equations, corresponding to the said reaction scheme, is as follows:

$$\begin{aligned} \frac{dP_1}{dt} &= k_1(T)\bar{X}^2, \\ \frac{dP_2}{dt} &= 2k_1(T)\bar{X}^2 - 2k_2(T)P_2^2\bar{X}, \\ \frac{dP_1}{dt} &= k_2(T)P_2^2\bar{X}, \end{aligned} \quad (2)$$

where $\bar{X} = 1 - P - P_1 - P_2$ is the total number of reagents, $k_1(T) = k_{10} \exp\left(-\frac{E_1}{RT}\right)$ and $k_2(T) = k_{20} \exp\left(-\frac{E_2}{RT}\right)$ are the rates of reactions 1 and 2. Assuming that the synthesis is initiated from the surface by a uniformly distributed heat source (heat pulse) and the side surfaces are heat-insulated, in the thermal section of the problem we will stick to the one-dimensional thermal conductivity equation with chemical sources:

$$c\rho \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + Q_1\Phi_1 + Q_2\Phi_2, \quad (3)$$

where $\Phi_1 = k_1(T)\bar{X}^2$, $\Phi_2 = k_2(T)P_2^2\bar{X}$.

The boundary conditions are:

$$x = 0 : -\lambda \frac{\partial T}{\partial x} = q_0, \quad t < t_{imp}, \quad \text{and} \quad -\lambda \frac{\partial T}{\partial x} = 0, \quad t > t_{imp}, \quad (4)$$

$$x \rightarrow \infty : \frac{\partial T}{\partial x} = 0. \quad (5)$$

To reduce the number of variables and number of necessary numerical calculations, let us introduce the following dimensionless variables: $\theta = \frac{T - T_*}{T_* - T_0}$, $\tau = \frac{t}{t_*}$, $\xi = \frac{x}{x_*}$, where $t_* = \frac{c\rho RT_*^2}{k_{10}E_1Q_1} \exp\left(\frac{E_1}{RT_*}\right)$, $T_* = \frac{Q_1}{c\rho} + T_0$ and $x_*^2 = \frac{\lambda t_*}{c\rho}$ are the characteristic scales.

Then, the problem (2)–(5) will take the following form:

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial \xi^2} + W_{ch}, \quad (6)$$

$$\frac{\partial P_1}{\partial \tau} = \bar{X}^2 \gamma \exp\left(\frac{\theta \sigma}{\beta(1 + \theta \sigma)}\right), \quad (7)$$

$$\frac{\partial P_2}{\partial \tau} = 2\bar{X}\gamma \left[\bar{X} \exp\left(\frac{\theta\sigma}{\beta(1+\theta\sigma)}\right) - zP_2^2 \exp\left(\frac{\theta\sigma + \varepsilon}{\beta(1+\theta\sigma)}\right) \right], \quad (8)$$

$$\frac{\partial P}{\partial \tau} = z\bar{X}P_2^2\gamma \exp\left(\frac{\theta\sigma + \varepsilon}{\beta(1+\theta\sigma)}\right), \quad (9)$$

$$\xi \rightarrow 0 : -\frac{\partial \theta}{\partial \xi} = Q_e, \quad \tau < \tau_* \quad \text{and} \quad -\frac{\partial \theta}{\partial \xi} = 0, \quad \tau > \tau_* \quad (10)$$

$$\xi \rightarrow \infty : \frac{\partial \theta}{\partial \xi} = 0, \quad (11)$$

$$\tau = 0 : \theta = -1, \quad P = P_1 = P_2 = 0,$$

where $\tau_* = \frac{t_{imp}}{t_*}$, $W_{ch} = \frac{\beta}{\sigma} \bar{X} \left(\bar{X} \exp\left(\frac{\theta\sigma}{\beta(1+\theta\sigma)}\right) + K_Q z P_2^2 \exp\left(\frac{\theta\sigma + \varepsilon}{\beta(1+\theta\sigma)}\right) \right)$.

The problem, along with the pulse duration, includes dimensionless parameters $\sigma = \frac{T_* - T_0}{T_*}$, $\beta = \frac{RT_*}{E_1}$ is the lesser parameter of the combustion theory, $\gamma = \frac{c\rho RT_*^2}{E_1 Q_1} \ll 1$ is the lesser parameter of the combustion theory that characterizes the sensitivity of the reaction rate to burning-out, $\theta_0 = \frac{\sigma}{\beta}$ is the temperature head, while the parameters $K_Q = \frac{Q_2}{Q_1}$, $z = \frac{k_2}{k_1}$, $\varepsilon = \frac{E_1 - E_2}{E_1}$ characterize the relations between the kinetic reaction parameters, $Q_e = \frac{q_0}{Q_1} \sqrt{\frac{t_*}{\kappa}}$ is the relation of heat accumulated in the layer x_* to the reaction heat Q_1 , $\kappa = \frac{\lambda}{c\rho}$.

2. Method of solution

The thermal conductivity equation (6) was solved using an implicit difference scheme of first-order approximation in time and second-order approximation in spatial coordinates and implementing the sweep method [8]. The kinetic equations for the total reactions were solved by an explicit-implicit method, which efficacy was shown elsewhere [9]. For instance, let us express eq. (7) for the numerical solution as

$$\frac{P_{1i} - \check{P}_{1i}}{\Delta\tau} = \gamma (1 - \check{P}_i - \check{P}_{1i} - \check{P}_{2i})(1 - \check{P}_i - P_{1i} - \check{P}_{2i}) \exp\left(\frac{\theta\sigma}{\beta(1+\theta\sigma)}\right)$$

or

$$P_{1i} = \frac{\check{P}_{1i} + (1 - \check{P}_i - \check{P}_{2i})Z}{1 + Z}, \quad (12)$$

where $Z = \Delta\tau\gamma (1 - \check{P}_i - \check{P}_{1i} - \check{P}_{2i}) \exp\left(\frac{\theta\sigma}{\beta(1+\theta\sigma)}\right)$. In eq. (10), the numerator is, obviously, always less than the denominator. Similarly for eqs. (8) and (9):

$$P_{2i} = \frac{\check{P}_{2i} + (1 - \check{P}_i - \check{P}_{1i})Z}{1 + 2Z + 2Z_2}, \quad (13)$$

$$P_i = \frac{\check{P}_i + (1 - \check{P}_{1i} - \check{P}_{2i})Z}{1 + Z_3}, \quad (14)$$

where $Z_2 = \Delta\tau\gamma z \check{P}_{2i} (1 - \check{P}_i - \check{P}_{1i} - \check{P}_{2i}) \exp\left(\frac{\theta\sigma + \varepsilon}{\beta(1+\theta\sigma)}\right)$, $Z_3 = \Delta\tau\gamma z \check{P}_{2i}^2 \exp\left(\frac{\theta\sigma + \varepsilon}{\beta(1+\theta\sigma)}\right)$.

In eq. (12), the following notations were accepted: \check{P}_{1_i} is the value P_1 in point i of the difference grid at the moment of time $j\Delta\tau$; P_{1_i} is the value P_1 in point i of the difference grid at the moment of time $(j+1)\Delta\tau$.

To confirm the correctness of the results, the problem was solved using two algorithms: (1) consecutive calculations at each of the layers in time with the verification of the convergence with decreasing step in time and number of decompositions of the calculation domain; (2) using the iteration at each of the layers in time. In the second case, the iterations are repeated until the result ceases to change (in the selected points) with a given accuracy:

$$\left[\sum_{(k)} (\tilde{\theta}_k - \theta_k)^2 \right]^{-1/2} \leq \varepsilon,$$

where $\tilde{\theta}_k$ is the solution for the temperature obtained in the previous iteration, θ_k is current calculation.

Tabs. 1 and 2 contain the data on the temperature at specific moments of time in point $\xi = 0$ for $h = 0.005$ and different steps in time $\Delta\tau$. Both the tables illustrate satisfactory convergence with decreasing step in time. Both the algorithms demonstrate satisfactory convergence also with increasing number of decompositions of the calculation domain (i.e. with decreasing spatial step), which is not shown in the tables.

Table 1. Temperature and conversion degree in point $\xi = 0$ for different time steps for the problem solution as per the first algorithm

	dt	t=0.5s.	t=1s.	t=2s.
θ	0.0025	3.9386	10.7376	67.9454
	0.005	3.9153	10.6336	65.6274
	0.01	3.8695	10.4418	62.4896
P	0.0025	$1.5441 \cdot 10^{-4}$	0.0697	0.4722
	0.005	$1.5252 \cdot 10^{-4}$	0.00684	0.4702
	0.01	$1.488 \cdot 10^{-4}$	0.00658	0.466
P_1	0.0025	0.02591	0.09022	0.4876
	0.005	0.02589	0.08982	0.4856
	0.01	0.02584	0.08906	0.4826
P_2	0.0025	0.0515	0.1664	0.037
	0.005	0.0514	0.1657	0.04
	0.0512	0.0513	0.1645	0.046

The iteration method converges, on average, on the 2–6th iteration, depending on the process stage: heating, reaction initiation, or process stabilization. The advantage of the iteration method is in the possibility to use in calculations quite large time steps with satisfactory convergence of the kinetic subproblem. The results below were generally obtained with the following parameters of the problem: $\sigma = 0.9$, $\varepsilon = 0.01$, $\gamma = 0.035$, $K_Q = 0.3$, $z = 5$.

3. Results and discussion

A typical distribution of the temperatures and concentrations in the surface layer at different moments of time is shown in Fig. 1 for different external pulse durations. The small duration

Table 2. Temperature and conversion degree in point $\xi = 0$ for different time steps using iterations

	dt	t=0.5s.	t=1s.	t=2s.
θ	0.1	4.0828	12.3788	43.2305
	0.04	4.2018	11.3522	51.7492
	0.025	3.9876	11.1474	55.5466
P	0.1	0.00015	0.0111	0.4089
	0.04	0.00018	0.0084	0.4462
	0.025	0.0015	0.0078	0.4566
P_1	0.1	0.02912	0.1164	0.4655
	0.04	0.02879	0.0989	0.4744
	0.025	0.02666	0.0955	0.4776
P_2	0.1	0.05746	0.2015	0.0998
	0.04	0.05701	0.1786	0.0676
	0.025	0.05291	0.1740	0.0574

of the external pulse is insufficient for the reaction in the mixture to continue. Disabling the source inhibits the reaction, after which the reaction stops (Fig. 1, left side). With increased pulse duration, there is a self-sustained reaction and stabilization of the process (Fig. 1, right side). We suppose that the stationary regime was caused by the conditions when the maximum temperature does not change with the accuracy of 3–5%. Other criteria—connected with the analysis of various thermodynamic characteristics are also possible. The figures in the center correspond to some intermediate case, when the stabilization of the process takes long time. In this case, there are fluctuations in the composition at the initial stage of the process evolution.

The maximum temperature, evidently, grows with the increase of the pulse duration. However, during the stabilization process, the maximum temperature decreases and approaches some asymptotic limit. The same is applicable to the fraction of particles in the reaction products P_1 and the fraction of the matrix P. The intermediate product exists in a considerable concentration in the reaction front; however, then, the concentration P_2 appreciably drops due to the end product formation. In the combustion theory, the stationary regime is a limit that should not depend on the initiation conditions and properties of a system under study. In the investigation of the stabilization process, it cannot be shown. Having a short pulse, the reactions in the surface layer stop (Fig. 2b, solid lines). In the stationary regime, they condition some end composition of the composite that depends on the initial composition of the reagents and other parameters. In our model, the variation of the initial composition is bound with altered relation of pre-exponential factors of the reactions.

Fig. 3 demonstrate changed composition of the products. The alteration of parameter is connected with the change to the stationary velocity of the front that can be defined using various methods (though, all the methods are equivalent to each other). For instance, the velocity can be calculated from Fig. 3 using the data on the location of the point with fixed value of the product P concentration at different moments of time. For three values of $z = 0.5, 3$ and 5 , we get $V = 0.365, 0.592$ and 0.735 , respectively.

After changing parameters γ or β , we get the stationary regime of the composite synthesis with different velocity and different temperature in the front. However, the composition of the products remains unchanged.

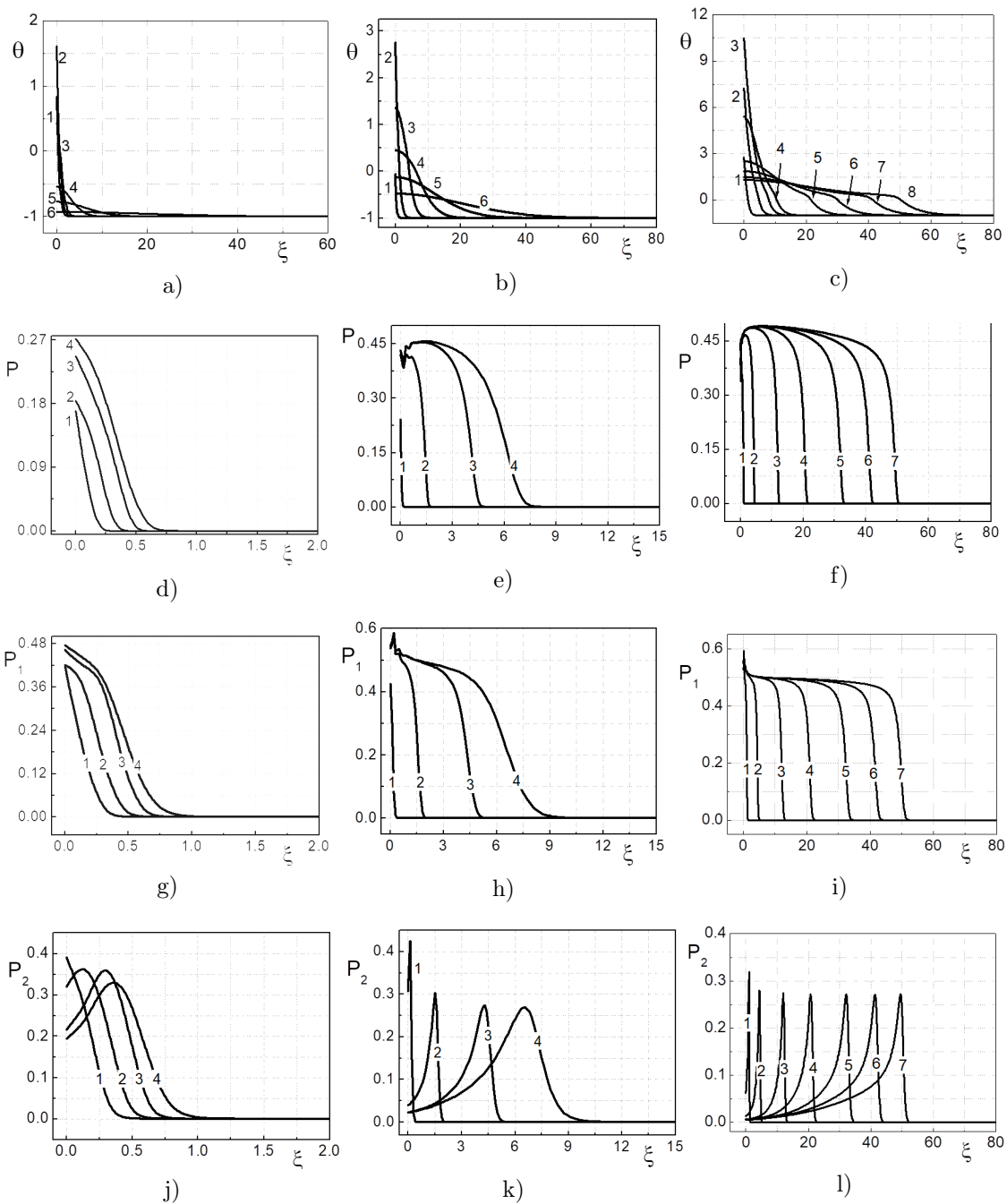


Fig. 1. Temperature and concentration distribution for different pulse durations τ_* at different moments of time. a), d), g) and j) correspond to $\tau_* = 0.5$; b), e), h) and k) correspond to $\tau_* = 2$; c), f), i) and l) correspond to $\tau_* = 10$. Moments of time: a) $t = 1) 0.3, 2) 0.5, 3) 0.8, 4) 5, 5) 20, 6) 200$; b) $t = 1) 0.3, 2) 2, 3) 2.5, 4) 5, 5) 50, 6) 200$; c) $t = 1) 1, 2) 5, 3) 10, 4) 15, 5) 50, 6) 90, 7) 150, 8) 200$; d, g, j) $t = 1) 0.3, 2) 0.4, 3) 0.5, 4) 200$; e, h, k) $t = 1) 0.3, 2) 1.5, 3) 7, 4) 200$; f, i, l) $t = 1) 1, 2) 5, 3) 20, 4) 50, 5) 105, 6) 155, 7) 200$

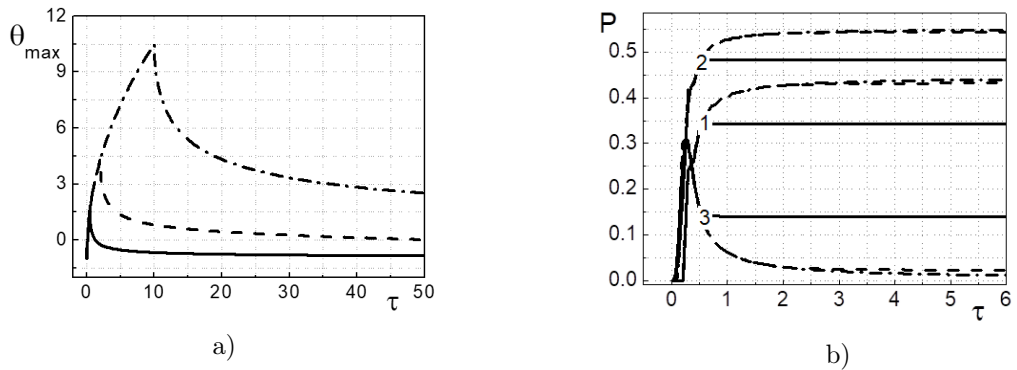


Fig. 2. Time dependence of the maximum temperature and concentrations in the surface layer. The solid line corresponds to the calculation of the pulse duration $\tau_* = 0.5$; the dashed line corresponds to $\tau_* = 2$; the dash-dotted line corresponds to $\tau_* = 10$. Curves 1 in b) correspond to product P , the curves 2 correspond to product P_1 , the curves 3 correspond to product P_2

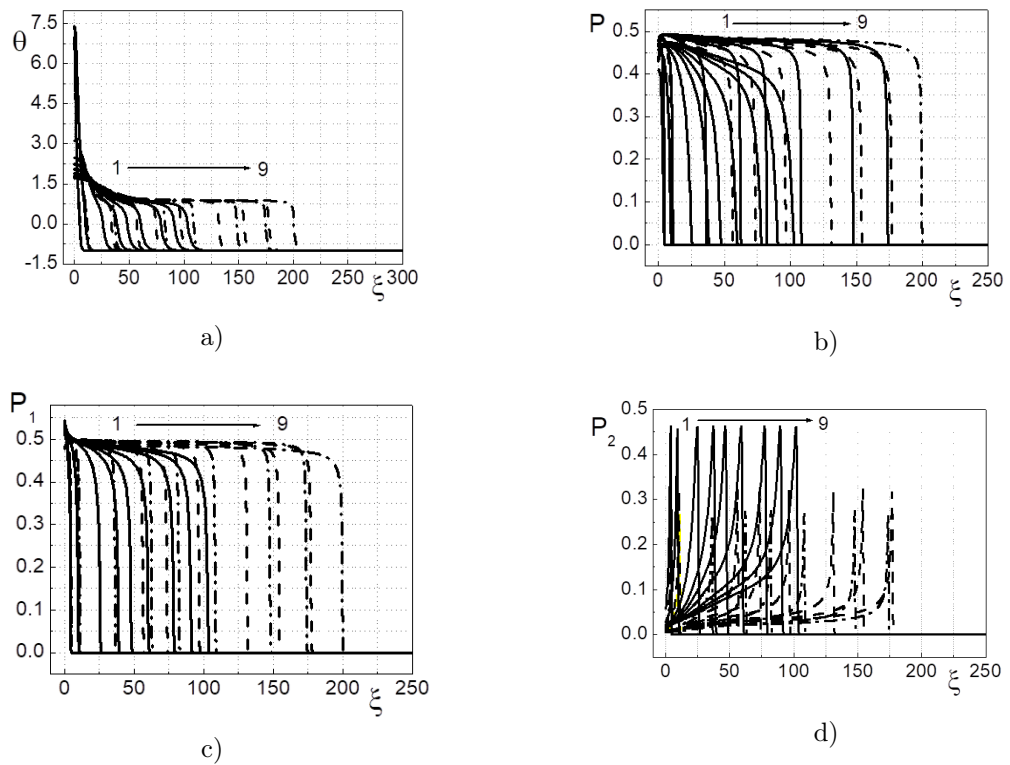


Fig. 3. Temperature and concentration distribution for different values of parameter z at different moments of time. The solid line corresponds to the parameter value of $z = 0.5$, the dashed line corresponds to $z = 3$, the dash-dotted line corresponds to $z = 5$, $\gamma = 0.025$. Moments of time: $t = 1) 4, 2) 12, 3) 50, 4) 90, 5) 120, 6) 160, 7) 220, 8) 260, 9) 300$

4. Transition to the coupled model

The mathematical model that takes into account the mutual influence of thermal, chemical and mechanical phenomena for the described reaction scheme and built similarly to [10,11]

includes an equation that is similar to eq. (3), but including an additional nonchemical source of heat:

$$c'_\varepsilon \rho \frac{dT}{dt} = \lambda \frac{\partial^2 T}{\partial x^2} - W(t, x) + Q'_1 \Phi_1 + Q'_2 \Phi_2$$

where

$$c'_\varepsilon = c_\varepsilon \left(1 + 3 \frac{K \alpha_T^2 T}{\rho c_\varepsilon} \frac{1 + \nu}{1 - \nu} \right),$$

$$Q'_1 = Q_1 - 3K \alpha_T T \frac{1 + \nu}{1 - \nu} [(\alpha_1 - \alpha_x) + 2(\alpha_2 - \alpha_x)],$$

$$Q'_2 = Q_2 - 3K \alpha_T T \frac{1 + \nu}{1 - \nu} [(\alpha - \alpha_x) - 2(\alpha_2 - \alpha_x)],$$

$$W(t, x) = 2K \alpha_T \frac{2 - 4\nu}{1 - \nu} \left(\frac{x}{h} - 1 \right) T \frac{d}{dt} F(t, x),$$

$$F(t, x) = \frac{2}{h^2} \int_0^h w(t, x) x dx - \frac{4}{3h} \int_0^h w(t, x) dx,$$

$$w = 3 [\alpha_T (T - T_0) + (\alpha_1 - \alpha_x) (P_2 - P_{2_0}) + (\alpha - \alpha_x) (P - P_0)],$$

K is the isothermal volume elasticity modulus, ν is the Poisson's ratio; α_T is the linearly coefficient of thermal expansion (averaged in the properties of the reagents and products); α , α_1 , α_2, α_x are the coefficients of concentration expansion of the reagents and reaction products; h is the sample dimensions along 0X. The alteration of the effective properties (thermal capacity and thermal effects of the reaction), compared to the uncoupled model, can be interpreted as the expansion of the variation domain of the model parameters (6)–(11). However, the introduction of the additional heat source may introduce its own peculiarities; for instance, lead to the expansion of the domain of existence of stationary conversion regime, as compared to the classic works [12–15 and other] even with due account for the peculiarities in the kinetic functions that reflect the specificity of the reactions in heterogeneous systems. This should be investigated further.

Conclusions

Therefore, the work proposed the model of composite synthesis with reinforcing inclusions. The synthesis of the matrix and inclusions is determined by two total parallel-consecutive stages. Two algorithms for the problem solution on the reaction initiation give similar results. It was shown that in the model, there is a domain of parameters, where a stationary synthesis regime is possible. The composition of the products depends on the relation of the model parameters, including the changes to the initial composition, which in the model is connected with the alteration of the relation of the reaction pre-exponential factors. The paper presented a coupled model of the composite synthesis, including the effective properties (depending on the mechanical characteristics) and an additional heat source, conditioned by the interaction of different physical processes. The role of the new factors requires additional investigation.

The reported study was funded by RFBR, project no. 20-03-00303.

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Связанная математическая модель синтеза композитов

Анна Г. Князева

Наталья В. Букрина

Институт физики прочности и материаловедения СО РАН
Томск, Российская Федерация

Аннотация. В работе предложена модель синтеза композита «металлическая матрица – упрочняющие включения». Решение осуществлено с помощью двух алгоритмов, показывающих близкие результаты. Показано, что, как и в классических моделях горения, существует область параметров модели, в которой возможен переход к стационарному режиму. Продемонстрировано, что учет связанности тепловых и химических процессов приводит к изменению эффективных свойств (теплоемкости и тепловых эффектов реакции) и появлению дополнительного источника тепла, обусловленного взаимодействием процессов разной физической природы.

Ключевые слова: синтез композитов, импульсный нагрев, последовательно-параллельные реакции, сравнение алгоритмов.

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