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## Modelling Synthesis *via* Combustion of Composites Based on Mechanoactivated Ti–C, Ti–B, and Ti–Si Powder Systems

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### Abstract

A model of synthesis was proposed and theoretically investigated *via* combustion of a composite in mechanically activated Ti–C, Ti–B, and Ti–Si powder mixtures. The effect of mechanical activation on synthesis modes was explored by introducing special activation parameter. As demonstrated by calculations, with its increase, the maximum temperature in the reaction wave is decreased during the reaction; combustion concentration limits are expanded and the propagation velocity of the reaction front is increased.

**Key words:** mechanical activation, composites synthesis, solid-phase combustion, modelling

### INTRODUCTION

In the last quarter of a century, composite materials have been produced by self-propagating high-temperature synthesis (SHS), and mechanical activation (MA) of the reaction mixture, which can significantly expand opportunities of gas-free combustion [1]. Mechanical activation allows expanding combustion concentration limits, using compounds that do not burn under normal conditions for synthesis and eliminating the need to pressing initial samples [2]. A significant decrease in the temperature of initiation of chemical interaction of reagents and expansion of the reaction surface area in mechanically activated compounds are also important in practice. However, as it is not always possible to identify and explain the reasons for the existence of different modes of synthesis by combustion in experimental works, it is required to involve mathematical modeling of processes proceeding in powder mixtures beginning with the reaction initiation step.

Among works devoted to the theoretical substantiation of MA influence on the kinetic regularities of chemical reactions, publications by several authors may be distinguished [3–12]. Paper [1] analyses mechanochemical process mechanisms that change contact melting and crystallization conditions and kinetic equations are suggested to describe transformation degrees in mechanochemical processes. In papers [8], kinetic regularities of mechanochemical reactions are explained from the standpoint of their correspondence to S. N. Zhurkov's formula suggested to describe the rupture of chemical bonds in polymers under load; the total energy yield of MA, and the relationship of the energy expended with the multiplication of dislocations and the formation of new surfaces are analysed. The interrelationship between different physical phenomena upon MA is observed in V. V. Boldyev's papers, *e.g.* [13].

In papers [11, 12, *etc.*], the authors are not far away from generalizations of S. N. Zhurkov's formula and try to interrelate excess energies with

broadening spectral lines and further bring together various processes to changing the effective activation energy of the total reaction. The authors of publications [5, 6] estimate energy contributions for different mechanisms of relaxation of the introduced mechanical energy with a view to explaining the chemical activity. As demonstrated by assessments of all types of local energies identified by the authors (the energy of residual elastic deformation; the elastic energy related to dislocations; the energy of newly created grain boundaries; and the energy of point defects), none of them can serve as a cause for a decrease in the effective activation energy of the reaction mixtures after MA in actual experiments.

As a matter of fact, the most diverse modern activation methods of initial mixtures in synthesis technologies for new materials are aimed towards making non-equilibrium states of materials and their surfaces [14]. The theoretical background of current modification methods of material states is non-equilibrium thermodynamics, within which it is possible not only to explain changing material properties under conditions of external effects but also predict the nature of their change [15, 16].

The objective of the present research work consists in the elaboration and exploration of the model SHS for the synthesis of the composite based on a mechanoactivated mixture of powders with an excess of titanium (Ti-C, Ti-B, Ti-Si). Based upon thermodynamic theory, changing microscopic and thermodynamic properties that can be a cause for the observed variation of chemical activity is taken into consideration.

#### GENERAL THEORETICAL STATEMENTS

In order to consider the effect of pre-mechanical activation of powders on the material synthesis process in the mode of combustion or thermal explosion, one may use the activation parameter and its interconnection with macroscopic properties.

This parameter is determined according to the deviation of the atomic volume of the activated material *vs* its equilibrium value:

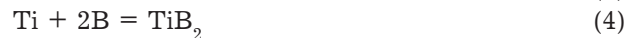
$$\eta = \frac{\Omega - \Omega_{\text{eq}}}{\Omega' - \Omega_{\text{eq}}} \quad (1)$$

where  $\Omega_{\text{eq}}$  is the maximum volume per the atom (molecule) in the equilibrium state, and  $\Omega'$  is the volume per the atom (molecule) in the non-equilibrium (activated) state. In the equilibrium state,  $\Omega = \Omega_0$  and  $\eta = \eta_0$ . Near equilibrium state,  $|\eta| \ll 1$ , whereas in the completely non-equilibrium state,

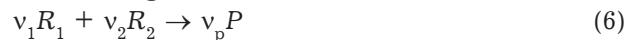
$\eta = 1$  ( $\Omega = \Omega'$ ). Upon this introduction method, this parameter corresponds to the concept of excess volume and, therefore, it can be considered as an additional parameter in the thermodynamic description of the effect of external influences on the state of materials and on the processes proceeding in them. Nevertheless, it is required to link the value of this parameter and the excess free energy corresponding thereto with conditions (*e.g.*, with ball mass in a mill ( $M_A$ )) and MA process time ( $t_A$ ). Assume that this dependence is known from the experiment:

$$\eta = \eta(M_A, t_A) \quad (2)$$

For the systems under study, let us limit ourselves to total schemes of chemical reactions:



Hence, under conditions of titanium excess, titanium-based composites with inclusions of carbide, boride, and silicide, respectively, are formed. Or in a single form



where  $v$  is stoichiometric coefficient;  $R$ ,  $P$  are molar concentrations of reagents and reaction product, respectively.

The law of conservation of mass in this reaction looks as follows:



Hereafter, everywhere in thermodynamic ratios, index "1" would correspond to titanium; "2" – to the second element; "p" – to the product of one of the reactions. Then, the main form the Gibbs equation for the local volume would take the form of:

$$du = Tds + \sigma_{ij}^e \rho^{-1} d\varepsilon_{ij} + g_1 dC_1 + g_2 dC_2 + g_p dC_p - Ad\eta \quad (8)$$

Herein the internal energy and potential  $A$  are computed per unit mass. Chemical potentials are also measured in J/kg. Measurement units counting on mole are more common in chemistry. All other dimensions are as follows:

$$[u] = \text{J/kg}, [\sigma_{ij}^e] = \text{n/m}^2; [s] = \text{J}/(\text{kg} \cdot \text{K}), \text{ etc.}$$

Self-sustaining combustion mode and thermal explosion may not be realised in systems with an excess of titanium due to the insufficiency of chemical heat. Nevertheless, pre-mechanoactivation changes the situation [2]. How is the excess energy related to the reaction rate under synthesis conditions?

It is known that the rate of a chemical reaction is determined by its affinity, whereas in the case of diffusion-controlled processes – also by the rate of movement of reagents through the reaction product layer. Both the chemical affinity

and transfer rates are defined *via* chemical potentials of components that are nothing but partial Gibbs energies of reaction mixture components:

$$g = g_1 C_1 + g_2 C_2 + g_p C_p \quad (9)$$

where

$$g = u - Ts - \rho^{-1} \sigma_{ij}^e \varepsilon_{ij} \quad (10)$$

Therefore:

$$dg = -sdT - \varepsilon_{ij} \rho^{-1} d\sigma_{ij}^e + g_1 dC_1 + g_2 dC_2 + g_p dC_p - Ad\eta \quad (11)$$

As the additional parameter is a function of the main parameters, it can be written:

$$d\eta = \left( \frac{\partial \eta}{\partial T} \right)_{\sigma, C_i} dT + \left( \frac{\partial \eta}{\partial \sigma_{ij}^e} \right)_{T, C_i} d\sigma_{ij}^e + \sum_{k=1}^n \left( \frac{\partial \eta}{\partial C_k} \right)_{T, \sigma} dC_k$$

or

$$d\eta = w_T dT + w_{ij}^\sigma d\sigma_{ij}^e + \sum_{(k)} w_k dC_k \quad (12)$$

where values

$$w_T = \left( \frac{\partial \eta}{\partial T} \right)_{\sigma, C_i}, w_{ij}^\sigma = \left( \frac{\partial \eta}{\partial \sigma_{ij}^e} \right)_{T, C_i}, w_k = \left( \frac{\partial \eta}{\partial C_k} \right)_{T, \sigma}$$

characterise the ‘‘sensitivity’’ of the activation parameter to changing thermodynamic state variables. Therefore, it can be found from (11) and (12):

$$dg^a = -s^a dT + \varepsilon_{ij}^a d\sigma_{ij}^e + \sum_{k=1}^n g_k^a dC_k \quad (13)$$

where superscript ‘‘a’’ indicates that this value refers to the activated state.

It is obvious that

$$g_1^a = g_1 - Aw_1; \quad g_2^a = g_2 - Aw_2; \quad g_p^a = g_p - Aw_p$$

$$s^a = s + Aw_T; \quad \varepsilon_{ij}^a = \varepsilon_{ij} + Aw_{ij}^\sigma$$

In a similar fashion, there are modified all other thermodynamic relations, including those using which the defining equations in continuum mechanics are written and macroscopic properties are determined [15].

As it follows from the system of state equations in the differential form (written on the basis of (11)):

$$ds^a = \left[ \frac{c_\sigma}{T} + w_T \omega \right] dT + \left[ \alpha_{ij}^T + \omega w_{ij}^\sigma \right] d\sigma_{ij}^e + \sum_{k=1}^n \left[ s_k + \omega w_k \right] dC_k \quad (14)$$

where  $\omega$  is specific volume;  $\alpha_{ij}^T$  is coefficient of heat expansion.

In this case, the heat capacity of the activated material is determined as follows:

$$c_\sigma^a = c_\sigma + Tw_T \omega = T \left( \frac{\partial s^a}{\partial T} \right)_\sigma \quad (15)$$

where

$$\omega = \left( \frac{\partial s}{\partial \eta} \right)_{T, \sigma, C_k} = \left( \frac{\partial A}{\partial T} \right)_{\sigma, C_k, \eta} = \left( \frac{\partial^2 g}{\partial \eta \partial T} \right)_{\sigma, C_k} \quad (16)$$

Ratio (16) is one of the thermodynamic Maxwell relations and suggests that as resulting from activation, the entropy change is described by the same coefficient as changing activation potential *vs* temperature. As it follows from the presented relations and the property of additivity of entropy [14]:

$$Aw_T = \omega \sum_{(k)} w_k C_k$$

In classical thermodynamics, if one knows heat capacity *vs* temperature (*i.e.* the so-called caloric equation of state is known), then it is possible to calculate the entropy:

$$s^a = \int_{T_0}^T \left( \frac{c_\sigma}{T} + w_T \omega \right)$$

Then

$$\begin{aligned} c_\sigma^a &= \sum_k c_{\sigma, k}^a C_k = \sum_k T \left( \frac{\partial s_k^a}{\partial T} \right)_\sigma C_k \\ &= \sum_k \left[ T \left( \frac{s_k}{\partial T} \right)_\sigma C_k + T \frac{\partial \omega w_k}{\partial T} \right] \\ &= \sum_k \left[ T \left( \frac{s_k}{\partial T} \right)_\sigma C_k + T w_k \frac{\partial^2 A}{\partial T^2} \right] \end{aligned} \quad (17)$$

Thus, an important factor that should be considered when explaining the effect of MA is heat capacity changes.

In a similar fashion, on the basis of theory [15], the relations for chemical potentials of components are derived. They allow computing changes in chemical affinity and the reaction enthalpy. The reaction (6) entropy is as follows:

$$\begin{aligned} \Delta s &= v_p s_p^a - v_1 s_1^a - v_2 s_2^a = v_p s_p - v_1 s_1 - v_2 s_2 \\ &+ \omega [v_p w_p - v_1 w_1 - v_2 w_2] \end{aligned}$$

For clarity, the partial enthalpies of the components

$$h_k = g_k - Ts_k$$

Therefore

$$h_k^a = g_k^a - Ts_k^a$$

or

$$\begin{aligned} h_k^a &= g_k - Aw_k - T \left( s_k + \left( \frac{\partial A}{\partial T} \right)_{\sigma, C_k, \eta} w_k \right) \\ &= g_k - Ts_k - w_k \left( A + T \left( \frac{\partial A}{\partial T} \right)_{\sigma, C_k, \eta} \right) \end{aligned}$$

Thus, already without apparent consideration of linkedness between thermal and mechanical processes, one should expect changes of heat capacity and formal kinetic reaction parameters determined according to thermodynamic data. Based on the linear relationship between an increase in activation parameter and the potential  $A$ , in the first approximation, let us limit ourselves to the

linear dependence of the reaction parameters and macroscopic properties on  $\eta$ , i.e.,

$$\Psi = \Psi_0(1 + \kappa\eta) \quad (18)$$

where  $\Psi_0$  is heat capacity, braking coefficient and the pre-exponential factor for non-activated powder systems;  $\kappa$  is a parameter that would be determined from the comparison of calculated and experimental data, whereas activation parameter  $\eta$  would be related to, in the first approximation, mechanical activation duration.

#### MATHEMATICAL FORMULATION OF THE PROBLEM

The mathematical model of the reaction initiation process in a powder mixture would be considered as follows. The sample is a cylinder of the radius ( $R$ ) consisting of two layers of powder fillings. Let us make the following assumptions: the temperature along the sample diameter is uniform; the igniter and the ignited mixture are gas-free. Assume that layer 1 (igniter) is a stoichiometric mixture of titanium Ti and Si powders, filling thickness is  $l$  (i.e.  $\zeta_0(\text{Ti}) = 73.9$  mass %,  $\zeta_0(\text{Si}) = 26.1$  mass %, or Ti/Si = 5/3 (in at. %)), which corresponds to reaction (5).

The second layer of thickness  $L$  (ignitable mixture) is a mixture of Ti and C (soot) powders or Ti + Si or Ti + B; however, the mixture is not stoichiometric. Let us assume that titanium in the second mixture is present in excess, hence not being completely consumed in the reaction.

In the equation of energy, heat losses to the environment at the expense of convection (if the synthesis is carried out under inert gas) and heat radiation. Thus, heat conduction equations become as follows:

$$c_k \rho_k \frac{\partial T_k}{\partial t} = \frac{\partial}{\partial x} \left( \lambda_k \frac{\partial T_k}{\partial x} \right) + Q_k \phi_k(\zeta, T) - \frac{2\alpha}{R} (T_k - T_0) - \frac{2\varepsilon_0 \sigma_0}{R} (T_k^4 - T_0^4)$$

where  $k = 1, 2$ , the indexes "1" and "2" refer to the igniter and the ignited mixture, correspondingly;  $T$  is the temperature;  $\zeta_k$  is the reagent fraction;  $t$  is time;  $x$  is spatial coordinate;  $\lambda_k$ ,  $c_k$ ,  $\rho_k$  are the effective thermal conductivity, heat capacity and density of compositions, respectively;  $Q_k$ ,  $\alpha$ ,  $\sigma_0$ ,  $\varepsilon_0$ , and  $R$  are the total heat effects of the reactions, the heat transfer coefficient into the environment; the Stefan-Boltzmann constant, the degree of blackness, and the radius of layers, accordingly.

The exponential law would describe inhibition of the reaction by a growing layer of solid-phase products [17]. Kinetic functions in the equations

for the igniter and for reaction mixtures are as follows:

$$\begin{aligned} \phi_1(\zeta, T) &= k_{01} \zeta_{\text{Ti}}^5 \zeta_{\text{Si}}^3 \exp\left(-\frac{E_{a1}}{R_g T_1} - b_1 \zeta_{\text{Ti}_5\text{Si}_3}\right) \\ \text{I } \phi_2(\zeta, T) &= k_{02\text{Ti}_5\text{Si}_3} \zeta_{\text{Ti}}^5 \zeta_{\text{Si}}^3 \exp\left(-\frac{E_{a2}}{R_g T_2} - b_2 \zeta_{\text{Ti}_5\text{Si}_3}\right) \\ \text{II } \phi_2(\zeta, T) &= k_{02\text{TiC}} \zeta_{\text{Ti}} \zeta_{\text{C}} \exp\left(-\frac{E_{a2}}{R_g T_2} - b_2 \zeta_{\text{TiC}}\right) \\ \text{III } \phi_2(\zeta, T) &= k_{02\text{TiB}} \zeta_{\text{Ti}} \zeta_{\text{B}}^2 \exp\left(-\frac{E_{a2}}{R_g T_2} - b_2 \zeta_{\text{TiB}}\right) \end{aligned} \quad (19)$$

where  $k_{0k}$ ,  $E_a$ ,  $R_g$ , and  $b_k$  are pre-exponents, reaction activation energies; the universal gas constant; and stagnation parameters, respectively ( $k = 1, 2$ ).

Kinetic equations for component concentrations are written on the basis of reactions (3)–(5) for the appropriate region and the selected mixture:

$$\begin{aligned} \text{I } \frac{d\zeta_{\text{Ti}}}{dt} &= -5\phi_1; \quad \frac{d\zeta_{\text{Si}}}{dt} = -3\phi_1; \quad \frac{d\zeta_{\text{Ti}_5\text{Si}_3}}{dt} = \phi_1 \\ \text{II } \frac{d\zeta_{\text{Ti}}}{dt} &= -\phi_2; \quad \frac{d\zeta_{\text{C}}}{dt} = -\phi_2; \quad \frac{d\zeta_{\text{TiC}}}{dt} = \phi_2 \\ \text{III } \frac{d\zeta_{\text{Ti}}}{dt} &= -\phi_2; \quad \frac{d\zeta_{\text{B}}}{dt} = -\phi_2; \quad \frac{d\zeta_{\text{TiB}}}{dt} = \phi_2 \end{aligned}$$

It is believed that there is heat contact between the layers:

$$x = l: \begin{cases} \lambda_1 \frac{\partial T_1}{\partial x} = \lambda_2 \frac{\partial T_2}{\partial x} \\ T_1 = T_2 \end{cases}$$

The reaction in the igniter is initiated by a spark.

$$x = 0: \lambda_1 \frac{\partial T_1}{\partial x} = q_0 \delta(t)$$

where  $q_0$  and  $\delta(t)$  are the power density of the source and the Dirac Delta function, correspondingly.

Away from the bedding interface, there is the adiabaticity condition:

$$x = l + L: -\lambda_2 \frac{\partial T_2}{\partial x} = 0$$

In the initial time moment:

$$t = 0: T_1 = T_2 + T_0, \quad \zeta_1 = \zeta_2 = \zeta_{10}, \quad \zeta_2 = \zeta_{20}$$

where  $T_0$ ,  $\zeta_{01}$ , and  $\zeta_{02}$  are the initial temperature and the initial concentrations of mixture components, correspondingly.

The melting of one of the reagents (titanium) is taken into account by changing the effective heat capacity and the density in the neighborhood of the melting temperature as follows:

$$(\text{cp})\eta = \begin{cases} (\text{cp})_s, & T < T_{\text{ph}}, \\ (\text{cp})_L, & T \geq T_{\text{ph}}, \end{cases} + Q_{\text{ph}} \rho_s \delta(T - T_{\text{ph}})$$

TABLE 1  
Thermophysical properties

Compounds	$\rho_s/\rho_L$ , kg/m <sup>3</sup>	$\lambda$ , W/(m <sup>2</sup> · K)	$c_s/c_L$ , J/(kg · K)	MP, K
Ti	4540/4120	22	498/687	1941
Si	2330/2520	150	690/979	1687
Ti <sub>5</sub> Si <sub>3</sub>	4320	26.8	430	2403
TiC	4900	21.9	696	3533
TiB <sub>2</sub>	4520	24	647	3466

where indexes  $s$  and  $L$ , and also  $Q_{ph}$  and  $T_{ph}$  are parameters of the solid and liquid phases, the heat of the phase transition, and the temperature of the phase transition, respectively.

As during the SVS process, the initial pressing of the reagents is porous, the structure of the powder system is changed, however, is unknown an arbitrary point of time, then calculations use the effective properties calculated according to the rule of the mixture and using the formula proposed in [18]:

$$c_1\rho_1 = [c_{Ti}\rho_{Ti}\zeta_{Ti} + c_{Si}\rho_{Si}\zeta_{Si} + c_{Ti_5Si_3}\rho_{Ti_5Si_3}\zeta_{Ti_5Si_3}](1 - \varepsilon_p)$$

$$\lambda_1 = \left[ \lambda_{Ti}\zeta_{Ti} + \lambda_{Si}\zeta_{Si} + \lambda_{Ti_5Si_3}\zeta_{Ti_5Si_3} \right] \left( \frac{1 - \varepsilon_p}{1 + 11\varepsilon_p} \right)$$

where  $\varepsilon_p$  is porosity. Analogously, effective properties for the second (reaction) layer were determined.

The problem was solved numerically. The algorithm for solving the problem and finding the rate of the reaction front is described in [19].

The reference data were used upon solving the problem [20]. Table 1 presents thermophysical properties of titanium, and also titanium silicide, titanium boride, and titanium carbide.

Table 2 represents the values of kinetic parameters for overall reactions, with which the calculations were performed [21–23]. It is adopted that  $l = 1$  cm,  $L = 5$  cm,  $R_1 = R_2 = 2.5$  cm,  $\alpha = 10^3$  W/(m<sup>2</sup> · K), and  $\sigma = 5.67 \cdot 10^{-8}$  W/(K<sup>4</sup> · m<sup>2</sup>); other parameters were varied.

TABLE 2  
Kinetic parameters of reactions

No.	Reaction	Heat ( $Q$ ), J/cm <sup>3</sup>	$k_0$ , s <sup>-1</sup>	$E_a$ , J/mol
1	5Ti + 3Si → Ti <sub>5</sub> Si <sub>3</sub>	7685	$0.374 \cdot 10^{15}$	205 200
2	Ti + 2B → TiB <sub>2</sub>	21 062	$0.354 \cdot 10^{14}$	178 700
3	Ti + C → TiC	15 155	$0.157 \cdot 10^{14}$	117 000

## RESULTS AND DISCUSSION

In order to determine a priori unknown parameters of reaction inhibition with products ( $b_k$ ) for the Ti + C system, dependencies of the propagation velocity of the reaction front and the maximum temperature in the second layer on the excess fraction of titanium at different values of  $b_2$  were plotted (Fig. 1) for compositions without MA. The acquired results were compared with experimental data.

As can be seen in Fig. 1,  $a$ , the propagation velocity of the reaction front agrees well with the experiment upon the value of  $b_2 = 10$  (curve 4). Calculations for two other compositions (Ti + Si, Ti + B) were carried out with this value of  $b_2$  having yielded a fairly satisfactory fit when comparing the maximum temperature in the combustion wave with the experiment (see Fig. 1,  $b$ ).

Thereafter, unknown parameters for assessing heat capacity and the braking coefficient, and also the pre-exponential factor for formula (19) were determined. The optimum values for parameters were found having given a satisfactory fit with experimental data [24] (Fig. 2 and Table 3,  $\kappa_c = -0.1$ ,  $\kappa_b = -0.2$ , and  $\kappa_{k_0} = 1$ . Indices  $c$ ,  $b$ , and  $k_0$  are referred to parameters for determining the heat capacity, the braking coefficient and the pre-exponential factor, respectively).

The determined parameters were used in calculations for the same system, *i.e.* titanium – carbon, but for a different mass ratio

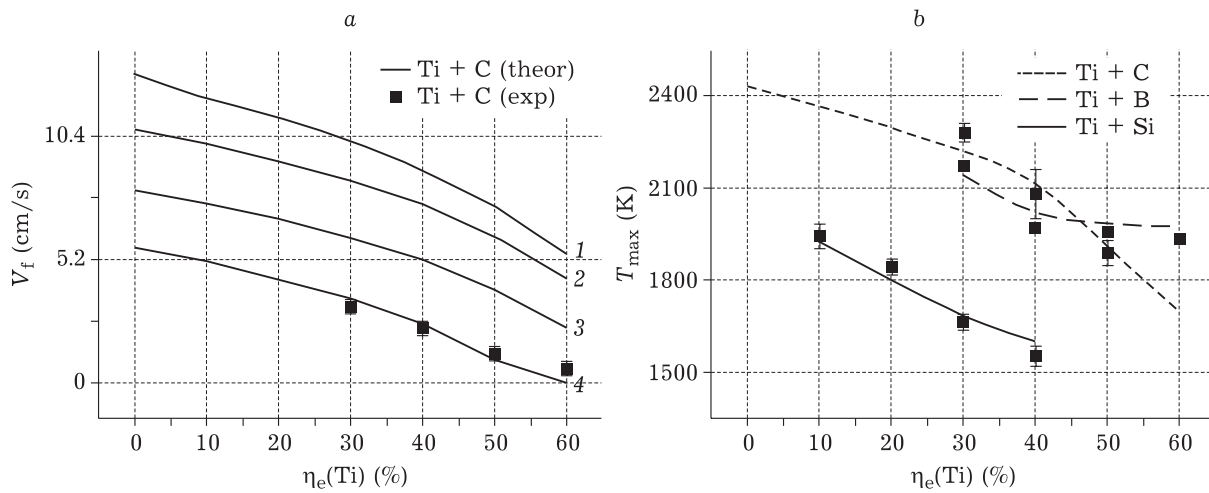


Fig. 1. Propagation rate of the reaction front (a) and the maximum temperature (b) vs braking parameters and calculated excess of titanium in reagents:  $b_1 = 10$ ,  $q_0 = 1.3 \text{ kW/cm}^2$ ;  $b_2$ : 1 (1), 2 (2), 5 (3), 10 (4).

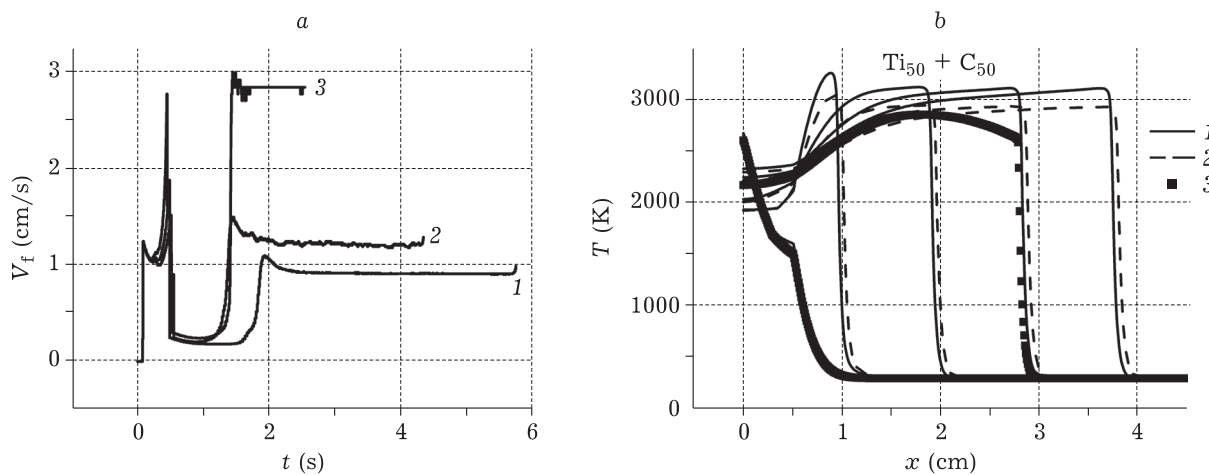


Fig. 2. Propagation rate of the reaction front (a) and temperature (b) vs time for different values of the activation parameter for the composition  $\text{Ti/C} = 50 : 50$  by mass.  $b_1 = 10$ ,  $q_0 = 1.3 \text{ kW/cm}^2$ ;  $\eta$ : 0 (1), 0.2 (2), 0.9 (3).

( $\text{Ti/S} = 70 : 30$ ). A satisfactory fit between experimental [24] and calculation data (see Table 3) was obtained.

Unknown parameters were similarly determined for two other two compositions ( $\text{Ti} + \text{Si}$ ,

$\text{Ti} + \text{B}$ ), proceeding from experimental data [25, 26]. This is not shown in the figures.

As demonstrated by the detailed research (see Fig. 3), if a powder mixture of reagents was not exposed to mechanical activation, then after the

TABLE 3

Maximum temperature of the reaction mixture and rate of the reaction front

Composition	MA time, min	$\eta$	$T_{\max}$ , K		$V_f$ cm/s	
			Theor.	Exp.	Theor.	Exp.
$\text{Ti}(50) + \text{C}(50)$	0	0.0	3025	2950	0.91	0.8
	150	0.2	2945	2900	1.20	1.1
	300	0.9	2905	2973	2.65	2.8
$\text{Ti}(70) + \text{C}(30)$	0	0.0	2512	2553	0.56	0.6
	150	0.2	2311	2323	0.75	0.7
	300	0.9	2355	2373	2.83	3.0

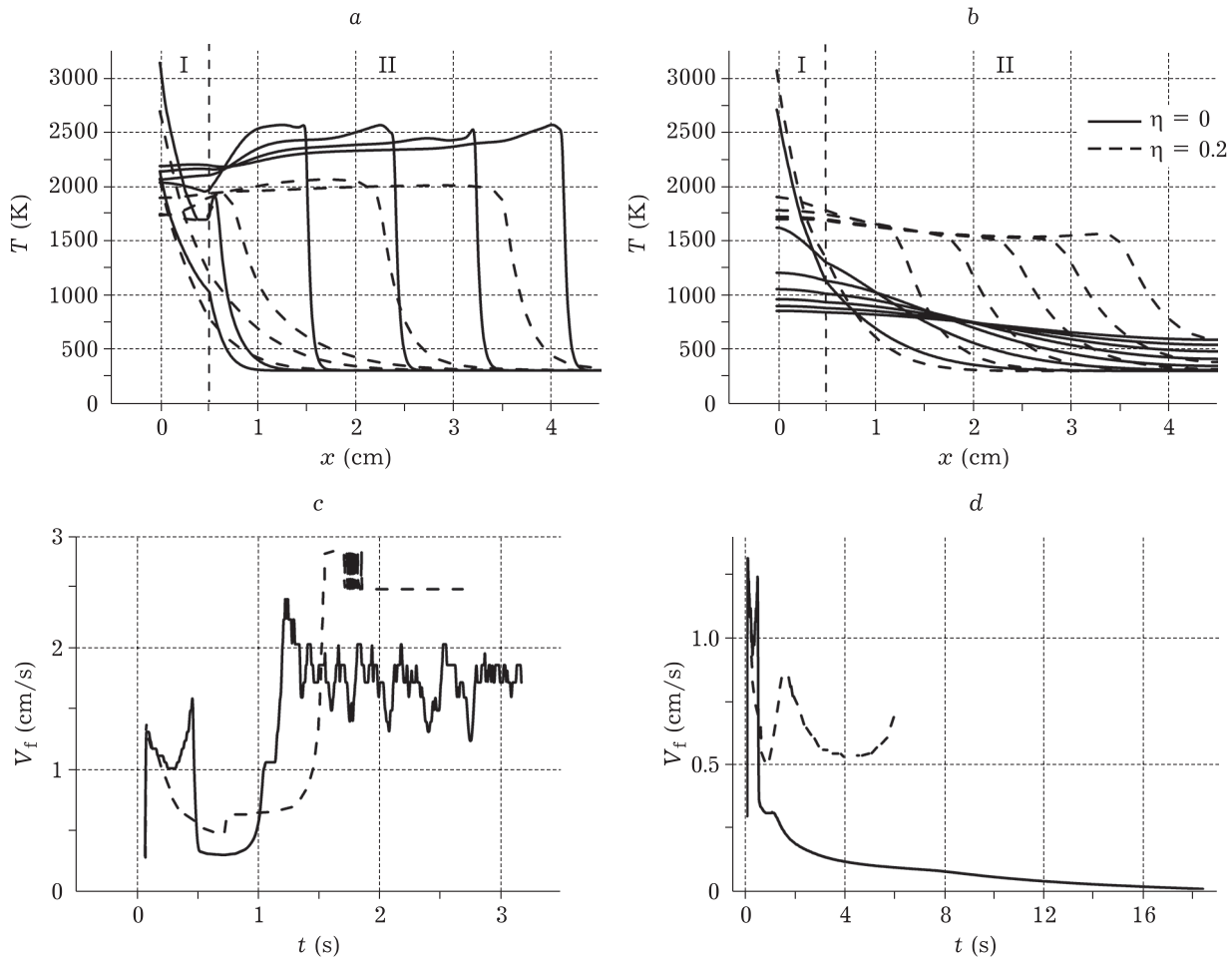


Fig. 3. Temperature  $X$  (a, b) and reaction front velocity (c, d) for the non-activated ( $\eta = 0$ ) and activated ( $\eta = 0.2$ ) compositions at successive time moments.  $q_0 = 1.3 \text{ kW/cm}^2$ ; the initial concentrations of components in a powder mixture: a, b -  $\zeta_{01,\text{Ti}} = 84 \%$ ,  $\zeta_{02,\text{C}} = 16 \%$  ( $\zeta_{e,\text{Ti}} = 30 \%$ ); c, d -  $\zeta_{01,\text{Ti}} = 96 \%$ ,  $\zeta_{02,\text{C}} = 4 \%$  ( $\zeta_{e,\text{Ti}} = 80 \%$ ).

initiation of the wave in the reaction mixture, the process proceed in an unstable self-oscillating mode (see Fig. 3 left, solid curves).

Synthesis for the activated system proceeds quite persistently after reaction initiation at  $\eta = 0.2$ . Furthermore, after low vibrations, the wave propagates in the reaction mixture at a constant rate (see Fig. 3 left, dashed curves). The maximum temperature in reaction wave is lower for activated compositions, whereas the propagation velocity of the reaction front is higher compared to the composition without MA. As demonstrated by experimental research, the percent composition of titanium not entered into the reaction was not higher than 60% upon the synthesis of clustered titanium carbide by SHS [15]. This refers to the theoretically calculated composition of titanium and carbon for the  $\text{Ti} + \text{C} = \text{TiC}$  reaction under the assumption that it would pass to the end (yielding stoichiometric carbide and remain-

ing unreacted Ti,  $\zeta_{e,\text{Ti}} = 60 \%$ ). Calculations have shown that the maximum value of unreacted titanium in the composite may be increased to 80% for  $\eta = 0.2$ .

As demonstrated by calculations for two other compositions (Fig. 4), the broadening of the concentration combustion limit is probable at  $\eta = 0.2$  compared to powder formulations without MA. Composite synthesis in the combustion mode after MA is likely in case of  $\zeta_{e,\text{Ti}} = 70 \%$  (the limit is 40% in experiments without MA). Combustion mode for Ti + B after mechanical activation may be implemented upon clustered titanium content to 75% (the limit in experiments without MA is 60%).

## CONCLUSION

Thus, as demonstrated by the synthesis model of a composite in Ti-C, Ti-Si, and Ti-B sys-

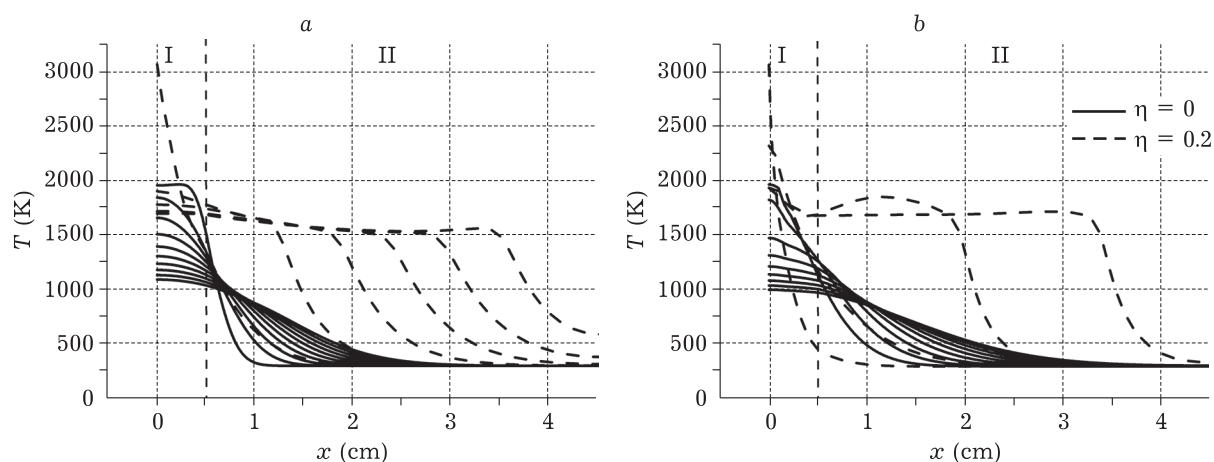


Fig. 4. Temperature for non-activated ( $\eta = 0$ ) and activated ( $\eta = 0.2$ ) compounds:  $q_0 = 1.3 \text{ kW/cm}^2$ ; the initial concentrations of components in a powder mixture: a -  $\zeta_{01,\text{Ti}} = 81.77\%$ ,  $\zeta_{02,\text{Si}} = 18.23\%$  ( $\zeta_{e,\text{Ti}} = 70\%$ ); b -  $\zeta_{01,\text{Ti}} = 95.4\%$ ,  $\zeta_{02,\text{B}} = 4.6\%$  ( $\zeta_{e,\text{Ti}} = 75\%$ ).

tems considering reaction inhibition with product layer and mechanical activation of reaction layers, preliminary MA significantly widens the concentration limit of combustion. It has been shown on an example of the Ti + C system that compounds exposed to preliminary mechanical activation burn more steadily than those without MA. The proposed model has predictive properties already in the first approximation. For example, it has been demonstrated that upon the value of  $\eta$  of 0.2, one may obtain composites for the titanium – carbon titanium rich ( $\zeta_{e,\text{Ti}} = 80\%$ ), titanium – silicon ( $\zeta_{e,\text{Ti}} = 70\%$ ), and titanium – boron ( $\zeta_{e,\text{Ti}} = 75\%$ ) systems.

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## REFERENCES

- Korchagin M. A., Lyakhov N. Z., *Khimicheskaya fizika*. 2008. Vol. 27, No. 1. P. 73–78.
- Korchagin M. A., Grigorieva T. F., Barinova A. P., Lyakhov N. Z., *Intern. J. Self-Propagating High-Temperature Synthesis*. 2000. Vol. 9, No. 3. P. 307–320.
- Urakaev F. Kh., Boldyrev V.V., *Powder Technology*. 2000. Vol. 107, No. 1–2. P. 93–107.
- Urakaev F. Kh., Boldyrev V.V., *Powder Technology*. 2000. Vol. 107, No. 3. P. 197–206.
- Khina B. B., *International Journal of SHS*. 2008. Vol. 17, No. 4. P. 211–217.
- Mukasyan A. S., Khina B. B., Reeves R. V., Son S. F., *Chemical Engineering Journal*. 2011. Vol. 174. P. 677–686.
- Buyanov R. A., Molchanov V. V., *Khimiya v interesakh ustojchivogo razvitiya*. 2001. Vol. 9, No. 3. P. 369–377.
- Butyagin P. Yu., *Uspekhi Khimii*. 1971. Vol. 40. P.1935.
- Butyagin P. Yu., Streletskij A. N., *Fizika tverdogo tela*. 2005. Vol. 47, No. 5. P. 830–836.
- Popov V. I., *PMTF*. 2012. Vol. 53, No. 6. P. 88–97.
- Smolyakov V. K., Lapshin O. V., and Boldyrev V. V., *International Journal of SHS*. 2007. Vol. 16, No. 1. P. 1–11.
- Lapshina O. V., Smolyakov V. K., *Combustion, Explosion, and Shock Waves*. 2017. Vol. 53, No. 5. P. 548–553.
- Boldyrev V. V., *Uspekhi khimii*. 2006. Vol. 75, No. 3. P. 203–216.
- Lotkov A. I., Psakh'e S. G., Knyazeva A. G., Koval' N. N., Korotaev A. D., Tyumentsev A. N., Sergeev V. P., Kul'kov S. N., Mejsner L. L., Grishkov V. N., Kolubaev A. V., Ivanov Yu. F., Ovcharenko V. E., Pribytkov G. A., Rotshhtejn V. P., Sivokha V. P., Zol'nikov K. P., Korosteleva E. N., Lapshin O. V., Ovchinnikov S. V., Pinzhin Yu. P., Savchenko N. L., Timkin V. N., Konovalenko I. S., Tyan A. V. *Nanoinzheneriya poverkhnosti. Formirovanie neravnovesnykh sostoyanij v poverkhnostnykh sloyakh materialov metodami elektronno-ionno-plazmennyykh tekhnologij*. Novosibirsk: Izd-vo SO RAN, 2008. 276 P.
- Knyazeva A.G., Psakh'e S.G., *Fizicheskaya mezomekhanika*. 2006. Vol. 9, No. 2. P. 49–54.
- Knyazeva A. G., Psakh'e S. G., *PMTF*. 2009. Vol. 50, No. 1. P. 118–126.
- Liu G., Li J., Chen K., *Int. Journal of Refractory Metals and Hard Materials*. 2013. Vol. 39. P. 90–102.
- Skorokhod V. V. *Reologicheskie osnovy teorii spekaniya*. Kiev: Naukova Dumka, 1976.
- Chumakov Yu. A., Knyazeva A. G., Pribytkov G. A., *Khimicheskaya fizika i mezoskopiya*. 2017. Vol. 19, No. 4. P. 524–537.
- Babichev A. P., Babushkina N. A., Bratkovskij A. M., Brodov M.E., Bystrov M. V., Vinogradov B. V., Vinokurova L. I., Gel'man E. B., Geppe A. P., Grigor'ev I. S., Gurtovoj K. G., Egorov V. S., Elets'kij A. V., Zarembo L. K., Ivanov V. Yu., Ivashintseva V. L., Ignat'ev V.V., Imamov R. M., Inyushkin A. V., Kadobiova N. V., Karasik I. I., Kikoin K. A., Krivoruchko V. A., Kulakov V. M., Lazarev S. D., Lifshits T. M., Lyubarskij Yu. E., Marin S. V., Maslov I. A., Mejlikhov E. Z., Migachev A. I., Mironov S. A., Musatov A. L., Nikitin Yu. P., Novitskij L. A., Obukhov A. I., Ozhogin V. I., Pisarev R. V., Pisarevskij Yu. V., Ptuskin V. S., Radtsig A. A., Rudakov V. P., Summ B. D., Syunyaev R. A., Khlopkin M. P., Khlyustikov I. N., Cherepanov V. M., Chertov A. G., Shapiro V. G., Shustr'yakov V. M., Yakimov S. S.,



- Yanovskij V. P. Fizicheskie velichiny: Spravochnik. M.: Energoatomizdat, 1991. 1232 P.
- 21 Yeh, C. L., Chou, C. C., Hwang P. W, *High Temperature Materials and Processes*. 2016. Vol. 35, No 8. P. 769–774.
- 22 Capaldi M. J., Said A. Wood J. V., *ISIJ International*. 1997. Vol. 37, No. 2. P. 188–193.
- 23 Makucha M., Kulkaa N., Keddama M., Taktak S., Ataibisc V., Dziarskia P., *Thin Solid Films*. 2017. Vol. 626. P. 25–37.
- 24 Maglia F., Anselmi-Tamburini U., Cocco, G., Monagheddu M., Bertolino N. and Munir Z., *Journal of Materials Research*, 2001. Vol. 16, No. 4. P. 1074–1082.
- 25 Maglia F., Anselmi-Tamburini U., Deidda C., Cocco G., Munir Z.A., *Journal of Materials Science*. 2004. Vol. 39. P. 5227.
- 26 Levashov E. A., Kurbatkina B. B., Kolesnichenko K. B., *Izvestiya vuzov. Tsvetnaya metallurgiya*. 2000. No. 6. P. 61–67.