Modeling of the combustion synthesis of titanium based composite with detailed reaction schema

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Abstract. The model of composite synthesis from powders of titanium and boron is proposed in this paper. Mathematical model takes into account the dependence of effective properties powders mixture on the composition and structure of reaction mixture. The ignition stage, the formation irreversible phases and reaction retardation by reaction product are also considered in the model. The reaction scheme of the composite synthesis process includes the system of four kinetic equations describing the formation of different titanium borides. Results of modeling for non-stoichiometric composition of the reaction mixture are presented and discussed.

1. Introduction

Self-propagating high-temperature synthesis (SHS) is one of the methods of composite manufacturing based on titanium including titanium borides. However, this process is nonequilibrium one and it is not possible to predict the composition of the synthesized product due to the presence of a wide range of homogeneity on the phase diagrams of some systems. Experimental investigation the synthesis of titanium borides in the combustion regime by the SHS method [2] have shown that titanium interacts with boron in a wide range of changes in boron content from 8.3 to 56% and three boride phases have been detected in this system: TiB, Ti3B4 with orthorhombic structure and TiB2 with a hexagonal structure. Hence, it is necessary to develop a mathematical model that takes into account the specifics of the interaction mechanisms of the reagents and the detailed kinetics of the process to understand the mechanism of solid-phase synthesis and chemical transformations in similar heterogeneous systems.

The features of structural transformations in a combustion wave based on the models of mechanics of heterogeneous media and including the continuity equation and the heat conduction equation for refractory and low-melting components was investigated in [3, 4]. The actual chemical reaction was described in terms of the formal kinetic law. The balance equations for the components in the solid and liquid phases, the equation of motion for the solid phase and the Darcy law for the flow of the melting point component penetrating into the pores, and the total energy equation were used for describing the process of synthesis by combustion [5]. Thermal and chemical stress components, the distribution of pores by size, the dependence of properties on porosity and temperature were not taken into account. However, the calculations were presented only for a simplified thermokinetic problem in which the calculation of the enthalpy changes for each temperature interval in accordance with the equilibrium state diagram. The really coupled models of solid-phase combustion using the approach of a homogeneous medium with averaged properties were proposed, for example, in [6-10].
The aim of this work is to develop a model and a theoretical study the synthesis of the titanium-based composites in the combustion regime with detailed reaction kinetics.

2. Problem formulation

To investigate the influence of the excess (non-reacted) titanium fraction in reaction products on the propagation regimes of the combustion wave the mathematical model of the process of the reaction initiation in the powder mixture of metal (Ti) and boron (B) is presented. The sample is a cylinder of radius \( R \) consisting of two layers of pressing powders (figure 1). We assume that first layer (igniter) is a stoichiometric mixture of Ti and Si powders and the thickness of this layer is \( l \). The second layer (reaction mixture) has thickness \( L \) and it consists of the mixture of titanium and boron powders. We assume also that titanium in the second mixture is presented in excess, so that it is not completely consumed in the reaction.

![Figure 1. Scheme of process.](image)

We consider the chemical transformations in the first system corresponds to the global reactions scheme “reagent-reaction product”

I. \( 5Ti+3Si \rightarrow Ti_5Si_3 \).

In accordance with the phase diagram of the Ti-B system we can write a system of chemical reactions for second layer

II. \( Ti+2B \rightarrow TiB_2 \); III. \( Ti+B \rightarrow TiB \); IV. \( TiB+B \rightarrow TiB_2 \); V. \( 2TiB+TiB_2 \rightarrow Ti_3B_4 \).

In the energy equations we take into account the heat losses to the environment due to convection and thermal radiation. Thus, the energy equations are written in the form

\[
\begin{align*}
\frac{\partial T_1}{\partial t} & = \frac{1}{\rho_1 c_1} \frac{\partial}{\partial x} \left( \lambda_1 \frac{\partial T_1}{\partial x} \right) + Q_1 \phi_1(\eta_1, T) - \frac{2\alpha_1}{R} (T_1 - T_0) - \frac{2\sigma_0 \varepsilon_0}{R} (T_1^4 - T_0^4), \quad x \leq l; \\
\frac{\partial T_2}{\partial t} & = \frac{1}{\rho_2 c_2} \frac{\partial}{\partial x} \left( \lambda_2 \frac{\partial T_2}{\partial x} \right) + \sum_{i=2}^{5} Q_i \phi_i(\eta_i, T) - \frac{2\alpha_2}{R} (T_2 - T_0) - \frac{2\sigma_0 \varepsilon_0}{R} (T_2^4 - T_0^4), \quad l < x < L,
\end{align*}
\]

where indexes \( \langle 1 \rangle, \langle 2 \rangle \) are the igniter and reaction mixture properties, respectively; \( T \) is the temperature; \( \eta \) is the molar concentration; \( t \) is the time; \( c, \rho \) and \( \lambda \) are the effective heat capacity, density and thermal conductivity, respectively; \( \alpha \) is the coefficient of heat transfer; \( Q \) is the heat effect of the reactions; \( \sigma_0 \) is the Stefan-Boltzmann constant; \( \varepsilon_0 \) is the emissivity; \( R \) is the layers radius.

We introduce the notation for the molar concentration of reagents and reaction products: \( \eta_1=[Ti], \eta_2=[Si], \eta_3=[Ti_5Si_3], \eta_4=[B], \eta_5=[TiB], \eta_6=[TiB_2], \eta_7=[Ti_3B_4] \). Then, the kinetic functions for the four reactions have the form
\[ \phi_1(T, \eta) = k_1 \eta^2 \eta_1, \quad \phi_2(T, \eta) = k_2 \eta^2 \eta_2, \quad \phi_3(T, \eta) = k_3 \eta \eta_4, \quad \phi_4(T, \eta) = k_4 \eta \eta_5, \quad \phi_5(T, \eta) = k_5 \eta \eta_6. \]

We assume the kinetic equations corresponding to the reaction with strong retardation by layer reaction product. The fraction of the reaction products in the layers satisfies the exponential law
\[
\phi_k(\eta_k, T_k) = \phi_k(\eta_k) k_{ok} \exp \left( -\frac{E_{ak}}{R_k T_k} \right) \exp (-m_{ak}),
\]
where \( k_{ok} \) is the pre-exponential factor; \( E_{ak} \) is the activation energy; \( R_k \) is the universal gas constant; \( m_{ak} \) is the retardation parameters; \( k = 1, \ldots, 5 \).

The equations of kinetics for the concentrations of the components have the form:
\[
0 \leq x \leq l: \quad \frac{d\eta_1}{dt} = -5\phi_1, \quad \frac{d\eta_2}{dt} = -3\phi_1, \quad \frac{d\eta_3}{dt} = \phi_2 - \phi_3, \quad \frac{d\eta_4}{dt} = \phi_4, \quad \frac{d\eta_5}{dt} = \phi_5.
\]

The ideal thermal contact between the layers is considered
\[
x = l: \quad T_1 = T_2; \quad \lambda_1 \frac{dT_1}{dx} = \lambda_2 \frac{dT_2}{dx}.
\]

The initiation of the reaction in the igniter is carried out by the heat flux
\[
x = 0: \quad \lambda_1 \frac{dT_1}{dx} = \begin{cases} q_0, & t \leq t_i, \\ 0, & t > t_i. \end{cases}
\]

The adiabatic condition is taken into account at the bottom boundary
\[
x = L: \quad -\lambda_2 \frac{dT_2}{dx} = 0.
\]

The initial conditions
\[
t = 0: \quad T_1 = T_2 = T_0, \quad \eta_1 = \eta_{01}, \quad \eta_2 = \eta_{02}, \quad \eta_3 = \eta_{03}.
\]

The melting of the components is considered by taking into account the changing of effective heat capacity and density in the vicinity of the melting temperature
\[
(c_p)_h = \begin{cases} (c_p), & T < T_{ph}, \\ (c_p)_s, & T \geq T_{ph}, \end{cases} + Q_{ph} \rho_s \delta(T - T_{ph}),
\]
where indexes «s», «L» are the parameters of the solid and liquid phase, \( Q_{ph} \) is the heat of phase transition, \( T_{ph} \) is the melting temperature, \( \delta \) is the Dirac’s delta.

Since the structure of the powder system is changing and unknown at any time, we use the rule of the mixture to calculate the effective properties of initial substance and synthesized composite \([12]\). The effective coefficient of thermal conductivity of the initer and reaction mixture was calculated similarly
\[
0 \leq x \leq l: \quad c_i = \left[ c_{i, 1} \rho_1 \eta_1 + c_{i, 2} \rho_2 \eta_2 + c_{i, 3} \rho_3 \eta_3 + c_{i, 4} \rho_4 \eta_4 \right] \left( \frac{1 - \epsilon_p}{1 + 11 \cdot \epsilon_p} \right), \quad \lambda_i = \left[ \lambda_{i, 1} \eta_1 + \lambda_{i, 2} \eta_2 + \lambda_{i, 3} \eta_3 \right] \left( \frac{1 - \epsilon_p}{1 + 11 \cdot \epsilon_p} \right);
\]
\[
1 \leq x \leq l: \quad c_i = \left[ c_{i, 1} \rho_1 \eta_1 + c_{i, 2} \rho_2 \eta_2 + c_{i, 3} \rho_3 \eta_3 + c_{i, 4} \rho_4 \eta_4 + c_{i, 5} \rho_5 \eta_5 \right] \left( \frac{1 - \epsilon_p}{1 + 11 \cdot \epsilon_p} \right), \quad \lambda_i = \left[ \lambda_{i, 1} \eta_1 + \lambda_{i, 2} \eta_2 + \lambda_{i, 3} \eta_3 + \lambda_{i, 4} \eta_4 + \lambda_{i, 5} \eta_5 \right] \left( \frac{1 - \epsilon_p}{1 + 11 \cdot \epsilon_p} \right),
\]
where \( \epsilon_p \) is the porosity.
To evaluate the porosity change, we use the relation obtained in the sintering theory for the case of the action only capillary forces [12, 13].

3. Algorithm of numerical solution and model parameters

The problem was solved numerically. The finite-difference approximation of differential equations by implicit scheme was used. The energy equations were approximated by finite-difference scheme to the four-point pattern. Further, the system of linear algebraic equations was solved by a sweep method. The implicit Euler method was used for solution the equations of chemical kinetics. In our calculations, we determined the temperature and concentration of components.

The material properties of titanium, boron and titanium borides used in the calculations [14] are presented in table 1.

| Material | $\rho/\rho_L$, kg/m$^3$ | $\lambda$, W/(m$^2$K) | $c_s/c_L$, J/(kg·K) | $T_{\text{melting}}$, K |
|----------|----------------------|---------------------|-------------------|------------------|
| Ti       | 4540/4120            | 22                  | 498/687           | 1941             |
| B        | 2340/2120            | 27.4                | 1280/2597         | 2348             |
| TiB      | 5090                 | 23.2                | 511               | 2423             |
| TiB$_2$  | 4520                 | 24                  | 647               | 3466             |
| Ti$_3$B$_4$ | 3240               | 26                  | 800               | 2473             |

The kinetic parameters of the total reactions are presented in table 2 [15, 16].

| Reaction | $Q$, W/(cm$^3$) | $k_0$, $c^{-1}$ | $E_a$, J/mol |
|----------|----------------|----------------|--------------|
| I        | 7685           | 0.374·10$^{15}$ | 193000       |
| II       | 21034          | 0.354·10$^{14}$ | 123000       |
| III      | 14332          | 0.269·10$^{14}$ | 178710       |
| IV       | 10655          | 0.431·10$^{14}$ | 123000       |
| V        | -3244          | 0.491·10$^{14}$ | 204000       |

The calculations were carried out with the parameters: $l=0.5$ cm, $L=4.5$ cm, $R=2.5$ cm, $\alpha=10^3$ W/(m$^2$K), $\sigma=5.67·10^{-8}$ W/(K$^4$·m$^2$), other parameters were varied.

The initial mass concentrations of titanium ($\eta_{01}$) and boron ($\eta_{04}$) were selected according reaction scheme Ti+2B→TiB$_2$, composition of this reaction mixture is non-stoichiometric and the fraction of unreacted titanium in the reaction products is $\eta_{Ti}$.  

4. Results and Discussion

The coordinate of wave front was determined from the value of the point on the temperature curve corresponding to the half melting point of titanium (approximately 970 K). The $x_{T1}$ coordinate was determined at the first moment of time and $x_{T2}$ was determined at the next time moment (figure 2a). The velocity was calculated by the formula

$$V_f = \frac{x_{T2} - x_{T1}}{t_2 - t_1} \quad \text{or} \quad V_f(t) = \frac{dx(t)}{dt}.$$ 

As calculations showed if the mixture of titanium and boron powders is stoichiometric, the front of the reaction wave propagates in an oscillatory regime (figure 2b, curve 1). The oscillatory regime of propagation of the combustion wave is also observed at $\eta_{Ti}=20\%$ and until $\eta_{Ti}<40\%$. Further increase of the mass fraction of titanium in the reaction products up to 40\% leads to a steady state of propagation of the combustion wave after initiation of the reaction (figure 2b, curve 3). A single peak
of the maximum velocity is observed on the velocity curves at $\eta_{Ti}$ equal from 40% to 60% then decrease of velocity occurs and after about 1 second the wave begins to propagate with constant rate (figure 2b, curves 3, 4, figure 3). Further increase in fraction of non-reacted titanium in the reaction product leads to a drop in the velocity of practically to zero and termination of the reaction after initiation (figure 2b, curve 5), which is due to the rapid consumption of reagents in the reactions and insufficient heat release in these reactions for its further spread.

Figure 2. Scheme for determining the wave velocity (a) and dependence wave velocity on $\eta_{Ti}$ (b). $\eta_{01}=73.9\%$, $\eta_{02}=26.1\%$, $q_{0}=1500\text{ W/cm}^2$, $t_i=1\text{ s}$, $m=5$, $\epsilon_p=0.2$. (a): $\eta_{Ti}=30\%$. (b): $\eta_{Ti}=1–0\%$; 2 – 20%; 3 – 40%; 4 – 60%; 5 – 70%.

Total consumption of boron occurs at $\eta_{Ti}=40\%$ in the reaction wave and its concentration drops to zero (Figure 3c). The value of titanium concentration drops to approximately 27% by mass, which is lower than one theoretically calculated ($\eta_{Ti}=40\%$). The concentrations of TiB and TiB$_2$ take the maximum value in the reaction wave and then that of value decreases. The concentration of Ti$_3$B$_4$ takes the maximum value at the "igniter-reaction mixture" boundary. The titanium diboride (TiB$_2$) takes maximum integral value of concentration and Ti$_3$B$_4$ takes the minimum one in reaction products.
Figure 3. Temperature (a), molar concentration of titanium (b) and boron (c) and products of reaction (d-f) in different moments, $q_0=1500$ W/cm$^2$, $t_1=1$ s, $m=5$, $\varepsilon=0.2$, $t$: 1 – 0.5 s; 2 – 1.0 s; 3 – 1.5 s; 4 – 1.8 s; 5 – 2 s. I is the igniter $\eta_1=73.9\%$, $\eta_{02}=26.1\%$, II is the reaction mixture $\eta_{01}=48.22\%$, $\eta_{04}=51.78\%$, $\eta_2=40\%$.

5. Conclusion
The model of SHS synthesis of composite material in the titanium-boron system was proposed. It was shown that for $\eta_{Ti}<40\%$ the mode of propagation of the reaction wave is oscillatory regime, with $\eta_{Ti}$ from 40% to 60% the wave goes to a stationary regime, with $\eta_{Ti}\geq 70\%$ the termination of the process after initiation occurs. As calculations shown the titanium diboride (TiB$_2$) takes maximum integral value of concentration and Ti$_3$B$_4$ takes the minimum one in the reaction products.

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