

Titanium-based composite synthesis in the combustion regime

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Abstract

The model of composite synthesis on the base of titanium with inclusions of carbides, borides and silicides is analyzed numerically. It was assumed that synthesis is carried out from the mixtures Ti-C, Ti-B and Ti-Si containing the excess of titanium in comparison with stoichiometric relation of components necessary for the formation of TiC, TiB and Ti₅Si₃. The model is based on the classical ideas of the combustion models with summary reaction. However, it takes into account nonstoichiometric composition of green mixture, dependence of properties on the composition changing during the synthesis and the reaction initiation stage in the igniter. Temperature distribution, conversion level, maximal combustion temperature, reaction zone thickness, and the rate of reaction propagation are determined numerically. The results of the product temperature calculation qualitatively agree with experimental data.

Keywords: composite synthesis, nonstoichiometric mixture, gasless combustion, reaction retardation by reaction product, combustion transition through interface

1. Introduction

Combustion synthesis is an intensively developed scientific field [1,2]. Combustion application to modern technologies connects with the possibility to use the energy of chemical reactions and to obtain the final product with slow energy losses. This method attracts attention by numerous researchers. For example, the combustion synthesis of composite with TiC-inclusions of various phase composition was carried out in [3]. Composite from Ni, Ti and B₄C powder blends was synthesized in [4]. Method SHS was used in [5] to obtain composites from Ni₃Al with inclusions TiC, WC, TaC, etc. Authors [6] studied the physical and chemical phenomena in the reaction of TiO₂, C, Al and the TiC/Alumina composite synthesis. Self sustaining high temperature synthesis (SHS) together with following disintegration is one of possible variants to obtain the powder systems with required structure for application for surface modification and object creation in additive technologies [7]. However irreversible conditions of the synthesis lead to the problems of theoretical and experimental character. For example, when the synthesis is carried out in the regime of layered combustion from the mixtures containing inert component (the component does not participate in the reaction), there is limiting concentration of inert above that reaction front stops. In the double systems Ti-C, Ti-Si, Ti-B, excess titanium powder should play a role of inert addition and should form titanium binder in the product. Dependencies of the maximal product temperature and combustion rate on the elemental composition of the green mixture were investigated in numerous papers; however detailed phase composition of the reaction product does not correspond to theoretical predictions. Temperature and combustion rate decrease monotonically when titanium content increases. Second feature inherent to all three systems consists in the liquid phase formation in the reaction front that plays an ambiguous

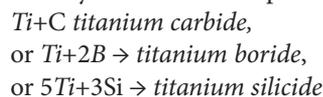
role in the combustion mechanism. Reversible state diagram of Ti-C differs from two other systems because there is a wide area of homogeneity for titanium carbide shifted to titanium. This leads to the formation of nonstoichiometric titanium during the synthesis from powder mixtures with titanium excess instead of the predicted composition Ti-TiC: instead 60 volume % of titanium binder real composition gives 26 V% [8] of titanium. Several intermediate compounds present at the reversible state diagram for the systems Ti-Si, Ti-B (three borides and five silicides); however not all phases are observed experimentally after the synthesis.

To study the dynamics of reaction front formation, in this paper, the process of composite synthesis in the systems Ti-C, Ti-Si, Ti-B with Ti excess is investigated numerically in terms of classical concept with summary reaction scheme taking into account reaction retardation with product accumulation in the special kinetic function.

2. Problem formulation

To calculate theoretically the combustion rate and product temperature in studied systems we use the model suggested in [9] adding it by the stage the reaction initiation in the igniter and properties dependence on the composition. Generalized model for three systems contains the thermal conductivity equations for igniter (stoichiometric mixture 5Ti+3Si) and for the mixture where composites form. Specimen is two-layer cylinder with radius *R*. First layer has the thickness *l*, second layer thickness is *L* (Fig. 1).

The second mixture contains the Ti-excess with mass concentration η_c . In a first approximation, we assume that summary reactions correspond to simple reaction schemes



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or summary scheme “Reagent-Product”. Reaction initiation in the igniter is carried out by spark. Hence, for reaction depth description only two kinetical equations are necessary – for first and for second layers.

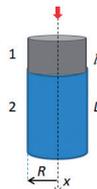


Fig.1. Illustration to the problem formulation: 1- igniter; 2. pressed-powder compact (reagent)
1. ábra. Illusztráció a probléma értelmezéséhez: 1- a gyújtófész; 2. a préselt (reagens) test

As a result, we come to the mathematical model:

$$c_1 \rho_1 \frac{\partial T_1}{\partial t} = \frac{\partial}{\partial x} \left(\lambda_1 \frac{\partial T_1}{\partial x} \right) + Q_1 \phi_1(\eta_1, T_1) - \frac{2\alpha}{R} (T_1 - T_0) - \frac{2\epsilon\sigma_0}{R} (T_1^4 - T_0^4), \quad x \leq l;$$

$$\frac{d\eta_1}{dt} = \phi_1(\eta_1, T_1) = z_{01}(1 - \eta_1) \exp\left(-\frac{E_{a1}}{R_g T_1}\right) \exp(-m_1 \eta_1);$$

$$c_2 \rho_2 \frac{\partial T_2}{\partial t} = \frac{\partial}{\partial x} \left(\lambda_2 \frac{\partial T_2}{\partial x} \right) + Q_2(1 - \eta_c) \phi_2(\eta_2, T_2) - \frac{2\alpha}{R} (T_2 - T_0) - \frac{2\epsilon\sigma_0}{R} (T_2^4 - T_0^4), \quad l < x < L;$$

$$\frac{d\eta_2}{dt} = \phi_2(\eta_2, T_2) = z_{02}(1 - \eta_2) \exp\left(-\frac{E_{a2}}{R_g T_2}\right) \exp(-m_2 \eta_2);$$

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

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

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

$$t = 0: T_1 = T_2 = T_0, \eta_1 = \eta_2 = 0,$$

where index «1» relates to igniter, index «2» relates to the mixture under study, T – is the temperature, η_k , $k=1,2$, – is the product concentration or conversion level; t – is the time; x – is the spatial coordinate; λ_k, c_k, ρ_k – are the effective thermal conductivity, - unwanted coefficients, heat capacities and densities depending on the current composition; Q_k – are chemical heats of summary reactions; α – is effective heat exchange coefficient in Newton law; σ_0 – is Stephen-Boltzmann constant; ϵ_0 – is blackness level; $\delta(t)$ – is delta function; E_{ak} – are activation energies; z_{ok} – pre-exponential factors; m_k are the retardation coefficient in formal kinetical laws.

Titanium melting is taken into account through the heat capacity change. Then we can write

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

where indexes s and L correspond to the parameters of solid and liquid phases; Q_{ph} - is melting heat; T_{ph} - is melting temperature. Because the powder mixture structure changes during the synthesis and it is not known a priori, we restrict the effective properties calculation by mixture rule, for example, for first layer

$$c_1 \rho_1 = [c_{Ti} \rho_{Ti} \eta_{Ti} + c_{Si} \rho_{Si} (1 - \eta_{Ti})] (1 - \eta_1) + c_{Ti_5Si_3} \rho_{Ti_5Si_3} \eta_1.$$

The problem was solved numerically. Temperature and concentration fields were found for different time moments that

had allow to find the product temperature and combustion rate for different parameters of the model. The data presented in [10] where used for the calculation (Table 1). Formal-kinetical parameters that used for calculations are presented in Table 2 [10-13]. It was assumed: $l=1$ cm, $L=5$ cm, $R=2.5$ cm, $a=10^3$ W/(m²K), $s=5.67 \times 10^{-8}$ W/(K⁴m²). Other parameters are varied.

Substance	$r_s/r_L, \text{kg/m}^3$	$\lambda, \text{W}/(\text{m}^2\text{K})$	$c_s/c_L, \text{J}/(\text{kg} \times \text{K})$	$T_{\text{melting}}, \text{K}$
Ti	4540/4120	22	498/687	1941
C(graphite)	2250	1.6	712	4620
Si	2330/2520	150	690/979	1687
B	2340	27.4	1280	2075
TiC	4900	21.9	696	3533
Ti₅Si₃	4320	26.8	140	2403
TiB₂	4500	24	656	3503

Table 1. Thermal-physical properties
1. táblázat Hőfizikai tulajdonságok

Reaction	$\Delta H_{\text{react}}, \text{kJ/mol}$ (MJ/kg)	$E_a, \text{kJ/mol}$	$k_0, 1/\text{s}$	Molar mass, g/mol
Ti + C → TiC	209 (3.5)	117	10 ⁸	60 (TiC)
Ti + 2B → TiB₂	295.4(4.25)	123.3	10 ⁸	69.5
5Ti + 3Si → Ti₅Si₃	579.3(1.8)	204.2	10 ¹²	324(Ti ₅ Si ₃)

Table 2. Kinetical parameters for the reactions
2. táblázat Reakció-kinetikai paraméterek

3. Result analysis

Reaction front coordinate X_p reaction front rate (combustion rate) V_f and thickness of the reaction zone X_{ch} were determined similarly to [14]. The retardation parameters were found based on experimental data. It was ascertained for all three systems $m_2=10$. The comparison of numerical results with experimental data (the experimental method was described, for example, in [8,14]) is presented in Fig. 2. For the systems Ti-Si, Ti-B the agreement is very well. For the system Ti-C, there is the deviation of theory from experiment that connects probably with reductive character of the model, where the existence of wide area of homogeneity is not taken into account. Second cause for the deviation connects obviously with the measure of the combustion temperature for the synthesis conditions in air. Titanium oxidation can effect on summary heat release that is confirmed with the data [9], where the presence of titanium dioxide to 8% was detected. With titanium excess η_c increase the combustion temperature decreases.

Calculation for the reaction mixture Ti-B show that the part of titanium excess η_c affects only maximal temperature and this practically does not change the combustion rate (curve 2 in Fig. 2.b).

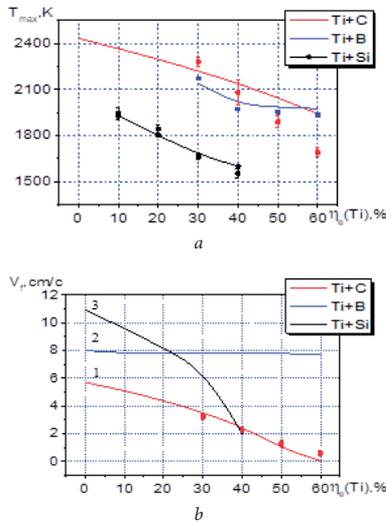


Fig. 2. The dependencies of maximal temperature (a) and reaction front propagation (b) on the titanium excess in green mixture. $m_1=10, q_0=1.3 \text{ MW/m}^2, m_2=10$; points – experimental data

2. ábra A nyers (zöld) keverékben a maximális hőmérséklet (a) és az reakció (égési) frontvonal terjedése (b) a titánban $m_1 = 10, q_0 = 1,3 \text{ MW/m}^2$; kísérleti adatok $m_2=10$

For various systems different combustion regimes were found. Typical qualitative picture for stationary combustion regime is presented in Figs. 3.a and 3.b. for the system Ti+Si. For chosen composition, the reaction proceeds in the solid phase, melting temperature is not achieved. For $\eta_c=40\%$, the periodic regimes could be observed: after some reaction front delay, reaction can be renewed. This did not be observed for other systems. To demonstrate the difference in the combustion regimes, maximal temperature and average conversion versus time level are suitable. Average conversion level is calculated by the formula

$$\eta_{\Sigma}(t) = \frac{1}{(L-l)} \int_l^L \eta(x,t) dx$$

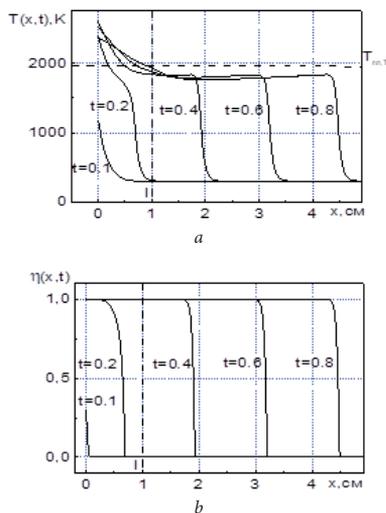


Fig. 3. Temperature (a) and conversion level (b) for the stationary combustion regime. $\eta_c=20\%$; $q_0=1.3 \text{ MW/m}^2$, system Ti+Si; time moments: $t=1. 0.1; 2. 0.2; 3. 0.4; 4.0.6; 5. 0.8; 6.2.95 \text{ s}$

3. ábra A hőmérséklet (a) és a konverziós szint (b) stacionális égési rendszer esetén a Ti-Si anyagrendszerben. $\eta_c = 20\%$; $q_0 = 1,3 \text{ MW/m}^2$; idő pillanatok: $t = 1. 0,1; 2. 0,2; 3. 0,4; 4.0,6; 5,8; 6,2,95 \text{ s}$

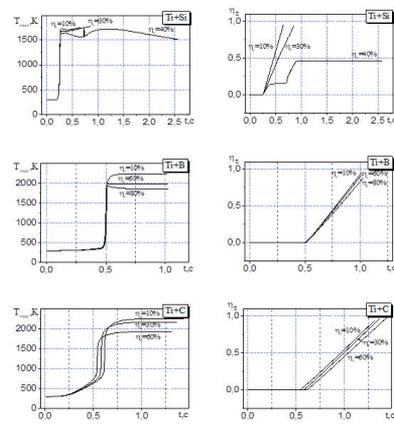


Fig. 4. Maximal temperature and average conversion level versus time for various systems
4. ábra A maximális hőmérséklet és az átlagos konverziós szint az eltérő titán alapú anyagrendszerekben

The results are presented in the Fig. 4. For the system Ti-Si (Fig. 4.a), practically stationary regimes with various rates are observed for $\eta_c = 10$ and 30%. Maximal temperature is not constant, the rate of the reaction front propagation can be determined as the slope of the curve $\eta_{\Sigma}(t)$. If $\eta_c = 40\%$, the phenomena of the repeated reaction initiation takes place, but after $\eta_{\Sigma}(t) \approx 0.49$ reaction stops. Reaction front coordinate is presented in Fig. 5 for various regimes. Quasistationary regime with total conversion was found only for $\eta_c = 10\%$; 5; for $\eta_c = 80\%$, the repeated reaction initiation does not occur.

For the system Ti-B (Fig. 4.b), the quasistationary regimes are characterized by different maximal temperatures. The reaction front rate determined as in [14] does not change; the reaction front rate determined as the slope of the curve $\eta_{\Sigma}(t)$ decrease very weakly. If $\eta_c = 10\%$, maximal temperature grows slowly to stationary value when quasistationary regime establishes; if $\eta_c = 40\%$, combustion temperature reaches to maxima and then diminishes to stationary value.

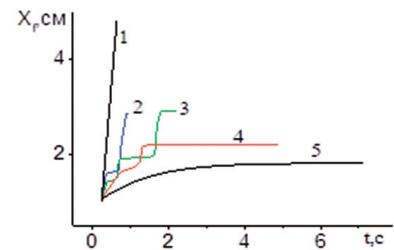


Fig.5. Reaction front coordinate versus time for the system Ti-Si; $m_1=10, m_2=10, q_0=1.3 \text{ MW/m}^2$
Curves: 1. 10%; 2. 40%; 3. 50%; 4. 60%; 5. 80%

5. ábra A reakció frontvonal terjedése az idő függvényében a Ti-Si rendszerben; $m_1=10, m_2=10, q_0=1,3 \text{ MW/m}^2$; Konverziós szintek: 1. 10%; 2. 40%; 3. 50%; 4. 60%; 5. 80%

For the system Ti-C (Fig. 4.c), the rise of titanium excess leads to the reaction zone expansion, quick maximal temperature decrease, however the reaction starts earlier. Reaction front rate decreases, if it is determined by the method [14], however it does not change, if it calculated as the slope of the curve $\eta_{\Sigma}(t)$. To understand the difference in the physical mechanism of the synthesis and the reaction front propagation the additional experimental and theoretical study are necessary.

4. Conclusions

So, the solid-phase combustion model with summary reaction scheme was realized numerically for three systems: titanium-carbon, titanium-boron, titanium-silicon. Taking into account nonstoichiometric composition of initial powder mixture, reaction retardation by reaction product, and dependence of properties on composition, the qualitative compliance between theory and experiment was obtained. The various combustion regimes for different systems were detected. Following study should include the detailed reaction scheme corresponding to irreversible conditions and porosity evolution during composite synthesis.

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Titán alapú kompozit szintézise égési rendszerben

Jelen munkában a szerzők numerikusan modellezik a karbid, borid és szilicid zárványokat tartalmazó titán alapú kompozit szintézisét. Modellje numerikusan valósul meg. Feltételezik, hogy a fém titán többletet tartalmazó Ti-C, Ti-B és Ti-Si porkeverékek termikus szintetizálása során sztöchiometrikusan képződnek a TiC, TiB és Ti₅Si₃ komponensek – létrehozva ezáltal egy új kompozit anyagszerkezetet. Az általuk alkalmazott módszer az „égető modellek” klasszikus ötletén alapszik, ahol a kémiai átalakulások és reakciók mint a „közvetlen égés” eredménye mennek végbe. Mindazonáltal az alkalmazott módszer figyelembe veszi a nyers (zöld) keverék nem-sztöchiometrikus összetételét, a tulajdonságok függését a szintézis során változó összetételre és a gyújtóreakció kezdeti szakaszára. A hőmérséklet-eloszlást, a konverziós szintet, a maximális égési hőmérsékletet, a reakciózónák vastagságát és a reakció terjedésének sebességét numerikusan határozzák meg. A termék-hőmérséklet számítás kapott eredményei minőségi szempontból jól megegyeznek a mért kísérleti adatokkal.

Kulcsszavak: kompozit szintézis, nem-sztöchiometrikus keverék, gázmentes égés, reakciókésleltetés reakciótermékkel, égés átmenet határfelületen

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