Limits of applicability of the “diffusion-controlled product growth” kinetic approach to modeling SHS

B.B. Khina\textsuperscript{a,}\textsuperscript{*}, B. Formanek\textsuperscript{b}, I. Solpan\textsuperscript{c}

\textsuperscript{a}Physico-Technical Institute, National Academy of Sciences, 10 acad. Kuprevich St., Minsk 220141, Belarus
\textsuperscript{b}Silesian University of Technology, Katowice, Poland
\textsuperscript{c}Technical University of Moldova, Chishinau, Moldova

Abstract

In modeling SHS in condensed systems, it is typically considered that a solid and a liquid reactant (a molten metal) are separated by a solid product interlayer, and diffusion in this layer is the rate-controlling stage (a “solid–solid–liquid mechanism”). However, in most cases modeling is performed not with real diffusion data (activation energy $E$ and preexponent $D_0$) for the product phase but with fitting parameters which are chosen to match the calculated and measured thermal characteristics of the SHS wave. In this work, a system of kinetic, thermodynamic and structural estimates is developed for evaluating the validity of this approach for particular SHS systems/conditions using available experimental data on both diffusion in the product phase and characteristics of the SHS wave. A classical Ti–C system is chosen as an example. Change in geometry of a unit reaction cell due to melting and spreading of the metallic reactant is taken into account, and different situations arising within this concept are analyzed. It is demonstrated that the “diffusion-controlled growth” kinetics is not applicable to SHS of interstitial compounds in the wave propagation regime because it cannot provide sufficient heat release for sustaining SHS and the final product structure will disagree with experimental data known in literature. As an alternative, a “solid–liquid mechanism” of phase formation during SHS is grounded, which implies a direct contact of a metallic melt with a solid reactant. A micromechanistic criterion for a changeover of these interaction routes is obtained, which is important for SHS in the thermal explosion mode. © 2004 Elsevier B.V. All rights reserved.

PACS: 81.20.Ka; 66.30.Ny; 81.05.Je; 82.30.—b

Keywords: Self-propagating high-temperature synthesis (SHS); Reaction diffusion; Kinetics; Modeling

1. Introduction

Self-propagating high-temperature synthesis (SHS), or solid flame, is known as an effective
method for producing refractory compounds (carbides, borides, nitrides, intermetallics, etc.) and composite materials. Its advantages include short processing time, low energy consumption, high product purity due to volatilization of impurities, and unique structure and properties of the final products [1]. These features are ascribed to extreme conditions inherent in SHS, which may result in unusual phase-forming mechanisms: (i) high temperature, up to 3500 °C, (ii) fast heating, up to 10^9 K/s, (iii) steep temperature gradient in SHS waves, up to 10^5 K/cm, (iv) rapid cooling after synthesis, up to 100 K/s, and (v) fast accomplishment of conversion, from about 1 s to the maximum of 10 s [1–4]. It should be noted that traditional “furnace” synthesis of such compounds using the same initial particle sizes requires a much longer time, ~1–10 h. SHS can be carried out in the wave propagation mode and the thermal explosion mode. In the former case, a compact reactive powder mixture is ignited at one end to initiate an exothermic reaction which propagates through the specimen as a combustion wave. In the latter case, a pellet is heated up at a prescribed rate until at a certain temperature called the ignition point T_{ign}, the reaction becomes self-sustaining and the temperature rises to its final value T_{SHS} almost uniformly throughout the sample.

In modeling SHS, a formal homogeneous model [5,6] based on classical combustion theory is widely used. Heat transfer and the reaction rate in a sample are described as follows:

\[ \rho c_p \frac{\partial T}{\partial t} = \nabla (\lambda \nabla T) + Q \frac{\partial \eta}{\partial t}, \]  
\[ \frac{\partial \eta}{\partial t} = (1 - \eta)^n \cdot k \cdot \exp(-E/RT), \]  

where \( T \) is temperature, \( \rho \) is density, \( c_p \) is heat capacity, \( \lambda \) is thermal conductivity, \( Q \) is the heat release, \( \eta \) is the degree of chemical conversion from 0 in the unreacted state to 1 for complete conversion), \( n \) and \( k \) are formal parameters (the reaction order and preexponent) and \( E \) is the activation energy. This approach permitted modeling dynamic regimes of SHS, e.g. oscillating [5] and spin combustion [7,8], and was used for studying the effect of intrinsic stochasticity of heterogeneous reactions on the dynamic behavior of a solid flame [9]. However, this model is not linked to process-specific phase formation mechanisms.

Recently, new features of SHS were observed [10–13]. First, microscopic high-speed video recording [10,11] and photographing [12] demonstrated micro-heterogeneous nature of SHS which revealed itself in the roughness of the combustion wave front, chaotic oscillations of the local flame propagation rate and new dynamic behaviors such as relay-race, scintillation and quasi-homogeneous patterns. Second, the formation of non-equilibrium structure and composition of SHS products was examined experimentally and interpreted qualitatively in terms of relationships between characteristic times of reaction \( t_r \), structuring \( t_s \) and cooling \( t_c \) [13]. These features were attributed to two main factors: inhomogeneous heat transfer in the charge mixture and a specific reaction mechanism [12].

These results gave rise to new, heterogeneous models [14–16] involving heat transfer on the particle-to-particle basis [14,15] and percolation phenomena in a system of chaotically distributed reactive and inert particles [16]. However, they employ either thermal reaction kinetics as in Eq. (2) [14,16] or simplified stepwise kinetics using the Heaviside function \( 1(T - T_{ign}) \) instead of the Arrhenius exponent [15]. Thus, an urgent and still unresolved problem in SHS is an adequate description of fast interaction kinetics of a unit particle.

The most widely used kinetic model, which is connected to a phase forming mechanism, is a “solid-state diffusion-controlled growth” concept first applied to SHS in Ref. [17] for planar symmetry and in Ref. [18] for spherical symmetry of an elementary diffusion couple. As in a charge mixture there are contacts of unlike particles, a layer of an intermediate or final solid product forms upon heating thus separating the initial reactants. The growth rate of the reaction product and associated heat release necessary for sustaining combustion is controlled by solid-state diffusion through this layer. Then, the so-called “diffusion-type Stefan problem” is formulated instead of Eq. (2). However, as demonstrated below in more detail, in most cases modeling was
performed not with real diffusion data, which are known for many refractory compounds, but using either dimensionless coefficients varied in a certain range or fitting parameters chosen to match the calculated and measured results of the SHS temperature profile and velocity. Besides, in most of the SHS-systems fast interaction begins after fusion of a lower-melting-point reactant [1–3, 6] but within this approach melting does not alter the phase layer sequence in an elementary diffusion couple [17, 18].

Certain experimental results obtained by the combustion-wave arresting technique in metal–nonmetal (Ti–C [19, 20], (Ti + Ni + Mo)–C [21], Mo–Si [22]) and metal–metal (Ni–Al [23, 24]) systems gave rise to a qualitative notion of a non-traditional phase formation route. It involves dissolution of a higher-melting-point reactant (metal or non-metal) in the melt of a lower-melting-point reactant and crystallization of a final product from the saturated liquid.

Virtually the only kinetic model [25], which is based on this dissolution–precipitation mechanism, involves diffusion in the melt as a rate-limiting step but does not include kinetics of the final product formation. Besides, there is much controversy over the presence of an intermediate solid phase in the dissolution–precipitation route. In Ref. [23] it is concluded that during SHS in the Ni–Al system, solid Ni dissolves in liquid Al “through a continuous forming and dissolving of a reaction diffusion layer on the surface on the Ni particle”, which agrees with the phase diagram. But in Ref. [24] for the same system it is found that above 854 °C (the decomposition temperature of intermediate phase NiAl3) “the system consists of only solid nickel and liquid aluminum solution”, i.e. a solid interlayer is absent.

Hereinafter the situation where a reaction between condensed reactants proceeds through a solid layer, i.e. solid reactant (C for the Ti–C system or Ni for the Ni–Al system)/solid final or intermediate product (TiC or one of intermetallics of the Ni–Al system, respectively)/liquid (Ti or Al melt), will be provisionally called “solid–solid–liquid mechanism” since the interaction occurs at both solid/solid and solid/liquid interface. This term will be used both for the “solid-state diffusion-controlled growth” pattern where the product layer is growing and for dissolution–precipitation route where the interlayer remains very thin. As the diffusion coefficient in a melt is much higher than in solids, the rate-limiting stage in this mechanism is diffusion across the solid interlayer. The second route, viz. dissolution–precipitation without an interlayer, will be referred to as “solid–liquid mechanism” since the interaction of condensed reactants (solid C or Ni with molten Ti or Al, respectively) occurs at the solid/liquid interface while the product (TiC or NiAl) crystallizes from the melt.

To the best of the authors’ knowledge, the solid–liquid mechanism has not been validated theoretically, nor the solid–solid–liquid mechanism based on solid-state diffusion has ever been refuted with respect to SHS. This situation hinders the development of new microscopic models for fast interaction kinetics during SHS.

Thus, the main goal of this work is to develop a system of relatively simple estimates and evaluate the applicability limits of the “solid–solid–liquid mechanism” approach to modeling SHS basing our calculations on experimental data to the maximum extent possible. Below we present a brief discussion of the diffusion concept of SHS. Then we perform calculations for a particular system, viz. Ti–C, using available experimental data on both the diffusion coefficients in the growing phase and thermal characteristics of the SHS wave. We consider different situations that can arise during SHS within the frame of the above concept and, wherever possible, draw a quantitative and/or qualitative comparison between the outcome of calculations and experimental results. Emphasis is made on the structural characteristics of the SHS product emerging from this approach. We analyze the conditions for a change of the geometry of a unit reaction cell in the SHS wave due to melting of a metallic reactant and derive a micromechanistic criterion for a changeover of interaction routes. Finally, we justify the “solid–liquid mechanism” concept for SHS in a number of systems. To our knowledge, such investigation has not been previously reported in literature.
2. Brief review of the diffusion-based kinetic models of SHS

The interaction kinetics controlled by solid-state diffusion was used for numerical [17,18,26–33] and analytical [34] study of SHS for the case of planar diffusion couples (alternating laminae of reactants) [17,27,28,30,34] and spherical symmetry (growth of a product layer on the surface of a spherical reactant particle) [18,29,31–33].

Inherent in this concept are two basic assumptions: (i) the phase composition of the diffusion zone between parent phases corresponds to the isothermal cross-section of an equilibrium phase diagram, i.e. the nucleation of product phases occurs instantaneously over all contact surfaces and (ii) the interfacial concentrations are equal to equilibrium values. This results in the parabolic law of phase layer growth [35–37].

It should be noted that in many diffusion experiments the phase layer sequence deviates from equilibrium: the absence of certain phases was observed in solid-state thin-film interdiffusion [38,39] and in the interaction of a solid and a liquid metal (e.g., Al) [40,41]. These phenomena were ascribed to a reaction barrier at the interface of contacting phases [42] without considering the nucleation rate of a new phase. The effect of a nucleation barrier was examined theoretically using the thermodynamics of nucleation [43,44] and the kinetic mechanism of phase formation in the diffusion zone [45], and it was shown that in the field of a steep concentration gradient the formation of an intermediate phase is suppressed [43–45]. This effect has never been considered in the diffusion models of SHS. As in the theory of diffusion-controlled interaction in solids the nucleation kinetics is not included and it is assumed that critical nuclei of missing phases continuously form and dissolve [36,37], this qualitative concept is sometimes used in interpreting the results of SHS [23].

It will be fair to say that deviation of phase-boundary concentrations from equilibrium due to a reaction barrier was examined qualitatively for SHS [28] in the case of planar geometry. This effect is noticeable only in the low-temperature part of the SHS wave, and at high temperatures a strong barrier can only slightly decrease the combustion velocity [28]. Also, the influence of such barrier on self-ignition in the Ni–Al system at low heating rates, $dT/dt < 60$ K/min, was studied quantitatively using experimental data on both thin-film inter-diffusion in the NiAl$_3$ compound [46], which is the first phase to form in Ni–Al diffusion couples, and bulk diffusion data [47]. Similar calculations were performed using an experimental temperature profile of SHS to determine the NiAl$_3$ layer thickness formed below the melting point of aluminum $T_m(Al) = 660$ °C [31]. At a thick NiAl$_3$ layer (low heating rates) the reaction barrier is of little significance, but it can slow down the interaction for thin layers (higher heating rates) [31,47]: e.g. at $dT/dt > 35$ K/min the formation of the primary product can be suppressed [31]. But, as noted in Refs. [31,47], these results refer not to the SHS itself but only to a preliminary stage because fast interaction begins at $T > T_m(Al)$, the combustion temperature reaches 1400 °C and the final product is NiAl [31].

It should be outlined that in many works using the diffusion model of SHS the calculations were performed with dimensionless (relative) parameters varied in a certain range. A known or estimated value of the activation energy for diffusion in one of the phases was used only as a scaling factor and thus the results obtained revealed only qualitative characteristics of the process [17,18,26,30]. Besides, many of the modeling attempts [17,18] did not account for a change in the spatial configuration of reacting particles due to melting and spreading of a metallic reactant. The effect of melting was reduced to a change of interfacial concentrations and the ratio of diffusion coefficients in contacting phases [26].

In more recent papers [31,32], the parameter values (the activation energy $E$ and preexponent $D_0$) used for calculating the diffusion coefficient in a growing phase were presented. However, those were not the real values measured in independent works on solid-state diffusion but merely fitting parameters calculated from the characteristics of SHS. For example, the formation of NiAl above 640 °C was modeled using $D_0 = 4.8 \times 10^{-2}$ cm$^2$/s and $E = 171$ kJ/mol [31]. As noted in Ref. [31], this $E$ value was the experimentally determined
activation energy for the SHS process as a whole. Then the diffusion coefficient in NiAl at $T = 1273 \text{K}$ is $D = D_0 \exp(-E/RT) = 4.6 \times 10^{-9} \text{ cm}^2/\text{s}$. Let us compare it with experimental data on reaction diffusion in the Ni–Al system. For NiAl, $D = (2.5–3.6) \times 10^{-10} \text{ cm}^2/\text{s}$ at $T = 1273 \text{K}$ [48]. The parameters for interdiffusion in this phase are $E = 230 \text{kJ/mol}$ and $D_0 = 1.5 \text{cm}^2/\text{s}$ [49], hence at $T = 1273 \text{K}$, $D = 5.4 \times 10^{-10} \text{cm}^2/\text{s}$. Thus, the diffusion coefficient used in modeling SHS exceeds the experimental value by an order of magnitude.

SHS wave in the Ti–Al system with the Ti-to-Al molar ratio of 1:3 in the charge mixture was modeled using $E = 200 \text{kJ/mol}$ and $D_0 = 4.39 \text{cm}^2/\text{s}$ for phase TiAl$_3$ [32]. This $E$ value was obtained from experiments on combustion synthesis using Arrhenius plots, and $D_0$ was chosen to match the calculated and measured results of the propagation speed. Again, these values refer to the SHS wave as a whole but not to interdiffusion in TiAl$_3$. However, experimental data on SHS of TiAl$_3$ for the same starting composition, which were analyzed using the classical combustion model (see Eqs. (1) and (2)), gave a substantially higher activation energy: $E = 483 \text{kJ/mol}$ [50]. If solid-state diffusion in the TiAl$_3$ layer is really the rate-limiting stage of the process, then the values of apparent activation energy ought to agree (within an experimental error) regardless of the particular form of a model.

Since diffusion coefficients for many refractory compounds are known in literature, we can verify the validity of the diffusion-based kinetic model of SHS employing a somewhat opposite method: estimating the product layer growth and heat release using the experimental characteristics of SHS and independent diffusion data.

For this purpose, it makes sense to choose one of the “classical” SHS-systems, e.g., Ti–C, which was a subject of extensive theoretical and experimental studies [18–20,26,33]. It is a suitable candidate for the following reasons: (i) the Ti–C phase diagram [51] contains only one binary compound TiC whose melting temperature $T_m(\text{TiC}) = 3423 \text{K}$ exceeds the experimental SHS temperature $T_{\text{SHS}} = 3083 \text{K}$ [52] and (ii) numerous diffusion data for titanium carbide are available in literature [53–55]. We consider the case of spherical symmetry which better fits a typical configuration of reacting particles in SHS. With respect to the phase diagram, here the solid–solid–liquid mechanism (situation C(solid)/TiC(solid)/ Ti(liquid)) is quasi-equilibrium and the solid-liquid mechanism (situation C(solid)/Ti(liquid)) is truly non-equilibrium.

3. Formulation of the diffusion model for SHS of TiC

Let us consider solid-state diffusion-controlled formation of the product, titanium carbide, during heating of the Ti+C charge mixture in the SHS wave. Typical particle radii are 5–100 μm for Ti, about 0.1 μm for carbon black and 1–30 μm for milled graphite [19,20,33,52]. Two scenarios with a different geometry of a unit reaction cell are examined: (1) a solid Ti particle surrounded by carbon particles in a stoichiometric mass ratio at temperatures below the Ti melting point, $T_m(\text{Ti}) = 1940 \text{K}$ (Figs. 1a and d), and (2) a solid carbon particle surrounded by liquid titanium at $T > T_m(\text{Ti})$ (Figs. 1c and e). A condition for the change of the reaction cell geometry due to titanium melting (Fig. 1b) is analyzed later.
3.1. Scenario 1

In scenario 1, at $T < T_m(Ti)$ a thin uniform layer of TiC is formed on the surface of the Ti particle. This is due to fast surface diffusion of C atoms from the Ti/C contact spots in the charge mixture, which agrees with the idea expressed in Ref. [52]. Because of low carbon solubility in solid $\beta$–Ti and high diffusivity of C atoms in the $\beta$-phase as compared with that in TiC [54,55], we can consider the growth of only one product phase—titanium carbide, i.e. perform an upper-level estimate of the product thickness. Then the TiC layer growth in the SHS wave is described by a diffusion-type Stefan problem written in spherical symmetry neglecting a volume change at the Ti/TiC interface

$$\frac{\partial c_c}{\partial t} = \frac{D(T(t)) c_c}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_c}{\partial r} \right),$$  \hspace{0.5cm} (3)

$$(c_c^{22} - c_c^0) \frac{dR_1}{dt} = -D(T(t)) \frac{\partial c_c}{\partial r} \bigg|_{R(t)},$$  \hspace{0.5cm} (4)

where $D$ is the chemical diffusion coefficient in TiC, which is usually associated with the diffusion coefficient of carbon in the carbide layer, $c_c$ is the mass concentration of carbon, $R_1(t)$ is the current position of the TiC/Ti interface, $R_2$ is the outer radius of the Ti particle, and $c_1^0, c_2^1$ and $c_2^2$ are the interface concentrations (Fig. 1d) according to the equilibrium phase diagram. The boundary (at $r = R_2$) and initial conditions to Eq. (3) are

$$c_c(t, R_2) = c_{22}^0, c_c(t, r = 0) = c_1^0, c_c(t, R_1(t)) = c_2^1, R_1(t = 0) = R_2.$$ \hspace{0.5cm} (5)

In Refs. [26,27] the Stefan-type boundary condition, Eq. (4), was posed at both Ti/TiC and TiC/C interfaces. We should outline that in interstitial compounds such as nitrides, carbides and many borides, the partial diffusion coefficient of nonmetal species exceeds that of metal atoms by several orders of magnitude, which is due to the interstitial diffusion mechanism. Hence, the growth of titanium carbide occurs at the Ti/TiC interface and is controlled by the diffusion of C atoms across the TiC layer. But at the C/TiC interface the growth of TiC at the expense of graphite, which requires the supply of Ti atoms, cannot occur. Thus, the first-kind boundary condition, $c_c(t, R_2) = c_{22}^0$ (see Eq. (5)) is used for the C/TiC interface, which actually denotes an ideal “diffusion contact” of carbon particles with the outer surface of the growing TiC layer due to fast surface diffusion of the C atoms from the C/TiC contact spots.

3.2. Scenario 2

The physical background for scenario 2 (Fig. 1c) is the following. Spreading of molten titanium towards solid carbon in the SHS wave was observed experimentally [56,57]. Since it is accompanied with chemical interaction, for a sufficiently small C particle size the spreading velocity is not the rate-limiting stage [57,58]. Hence we consider that at $T \geq T_m(Ti)$ the carbon particles are completely enveloped with liquid titanium, and a thin TiC layer forms at the Ti/C interface separating the parent phases. The product growth occurs at the Ti(melt)/TiC interface, i.e. outwards, due to diffusion of carbon atoms across the TiC layer (Fig. 1c). Since the diffusion coefficient of carbon in the melt is at least an order of magnitude higher than in the carbide (Table 1), it is reasonable to presume that the titanium melt is saturated with carbon (otherwise the TiC layer will be dissolving). Then the boundary condition at $r = R_0$ to diffusion Eq. (3) and initial conditions to Eqs. (3) and (4) look as

$$c_c(t, R_0) = c_{22}^0, c_c(t, r > R_1) = c_1^0, R_1(t = 0) = R_0,$$ \hspace{0.5cm} (6)

where $R_0 = constant$ is the initial radius of the carbon particle.

3.3. Diffusion data

The parameters for calculating the diffusion coefficient in TiC in the Arrhenius form

$$D = D_0 \exp(-E/RT(t))$$  \hspace{0.5cm} (7)

are presented in Table 1. Since the extrapolation of $D$ to the whole temperature range of SHS may bring about overestimated values, the diffusion coefficients in TiC calculated at $T = T_m(Ti)$ and
species must be compared with the diffusion coefficient in molten titanium.

Because of the absence of experimental data, the diffusion coefficient of C in molten Ti is estimated by a simple Stokes–Einstein (or Sutherland–Einstein) formula, which was used for assessing the diffusion parameters of C, N, O and H in liquid metals (Fe, Co, Ni, etc.) [68,69]

\[ D_{m} = k_B T / (\pi n \alpha \mu), \]  

(8)

where \( n = 4–6 \), \( \alpha \) is the atomic radius in the melt, \( \mu = \xi \rho_{m} \) is the dynamic viscosity, \( \xi \) is the kinematic viscosity and \( \rho_{m} \) is the density of the liquid phase. For carbon atoms, the covalent radius is \( a = 0.077 \) nm [70], the density of molten Ti is \( \rho_{m} = 4.11 \) g/cm\(^3\) [71].

A typical value of the kinematic viscosity for such metals as Al, Fe, Co, Ni, etc. near the melting point is \( (0.5–1) \times 10^{-2} \) cm\(^2\)/s [70]. For liquid titanium saturated with carbon \( \xi = 0.94 \times 10^{-2} \) cm\(^2\)/s at \( T = T_{m}(Ti) \) [71], then \( D_{m}(T_{m}) \approx (4.8–7.2) \times 10^{-5} \) cm\(^2\)/s. For higher temperatures, the value \( \xi = 1.03 \times 10^{-2} \) cm\(^2\)/s at \( T = 2220 \) K is known [71]; using it at \( T = T_{SHS} \) gives \( D_{m}(T_{SHS}) \approx (6.9–10.4) \times 10^{-5} \) cm\(^2\)/s. It should be noted that since Eq. (8) does not account for chemical interaction in the melt, which may be substantial for the Ti–C system, these \( D_{m} \) values are upper estimates. Then the values of diffusion coefficients in TiC, which are close to or higher than the upper estimate of \( D_{m} \), are excluded from consideration (lines 10–14 in Table 1).

### 3.4. Temperature of the reaction cell in the SHS wave

Self-heating from ambient temperature \( T_{0} \) to \( T_{SHS} \) during the combustion synthesis is due to the adiabatic heat release of chemical reactions which are almost accomplished when maximal temperature is reached, and in the so-called after-burn zone (at \( T \approx T_{SHS} \)) only coalescence and sintering of the product particles occur with minor heat release [1–3]. Hence calculations of the product layer thickness and relevant heat release should be done in the time interval [0, \( t_{SHS} \)] corresponding to the attainment of \( T_{SHS} \).

To perform calculations, we have to know the time dependence of temperature in the reaction cell, \( T(t) \). We consider a steady-state combustion regime. For a low-temperature portion of the SHS wave, \( T_{0} < T < T_{m}(Ti) \), the temperature profile along a sample can be calculated using a known analytical solution [72]

\[ T(\xi) = T_{0} + (T_{m} - T_{0}) \exp(-v\xi/k), \quad \xi = x - vt, \]  

(9)

<table>
<thead>
<tr>
<th>Species</th>
<th>No.</th>
<th>( D_{0} ) (cm(^2)/s)</th>
<th>( E ) (kJ/mol)</th>
<th>( \Delta T ) (K)</th>
<th>( D(T_{m}(Ti)) ), cm(^2)/s</th>
<th>( D(T_{SHS}) ), cm(^2)/s</th>
<th>Refs.</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1</td>
<td>( 5 \times 10^{-2} )</td>
<td>235.6</td>
<td>2073–2973</td>
<td>2.3 \times 10^{-8}</td>
<td>5.1 \times 10^{-6}</td>
<td>[54,55,59,65]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6.98</td>
<td>398.7</td>
<td>1723–2973</td>
<td>1.3 \times 10^{-10}</td>
<td>1.23 \times 10^{-6}</td>
<td>[53,59,60,62] (TiC(_{0.97}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>10</td>
<td>438.9</td>
<td>1873–2573</td>
<td>1.5 \times 10^{-11}</td>
<td>3.7 \times 10^{-7}</td>
<td>[59,60] (TiC(_{0.9}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>45.44</td>
<td>447.3</td>
<td>1723–2553</td>
<td>4.1 \times 10^{-11}</td>
<td>1.2 \times 10^{-6}</td>
<td>[60,62] (TiC(_{0.85}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>114</td>
<td>460.2</td>
<td>2018–2353</td>
<td>4.6 \times 10^{-11}</td>
<td>1.8 \times 10^{-6}</td>
<td>[60,63] (TiC(_{0.67}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.1</td>
<td>259.4</td>
<td>1553–1773</td>
<td>1.0 \times 10^{-8}</td>
<td>4.0 \times 10^{-6}</td>
<td>[54,55]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>6.5 \times 10^{-2}</td>
<td>269.9</td>
<td>1673–1973</td>
<td>3.5 \times 10^{-9}</td>
<td>1.7 \times 10^{-6}</td>
<td>[54,66]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>4.2 \times 10^{-2}</td>
<td>307.1</td>
<td>1983–2573</td>
<td>2.3 \times 10^{-10}</td>
<td>2.6 \times 10^{-7}</td>
<td>[54,55] (TiC(_{0.9}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.48</td>
<td>328.42</td>
<td>1473–2023</td>
<td>6.9 \times 10^{-10}</td>
<td>1.3 \times 10^{-6}</td>
<td>[67] (TiC(_{1.0}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>99.48</td>
<td>328.42</td>
<td>1473–2023</td>
<td>1.4 \times 10^{-7}</td>
<td>2.7 \times 10^{-4}</td>
<td>[67] (TiC(_{0.5}))</td>
<td>( D(T_{SHS}) &gt; D_{m} )</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>77.8</td>
<td>338.9</td>
<td>1473–1673</td>
<td>5.8 \times 10^{-8}</td>
<td>1.4 \times 10^{-4}</td>
<td>[53]</td>
<td>( D(T_{SHS}) &gt; D_{m} )</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>220</td>
<td>405.8</td>
<td>2200–2600</td>
<td>2.6 \times 10^{-9}</td>
<td>2.9 \times 10^{-3}</td>
<td>[64] (TiC(_{x}), ( x = 0.86-0.91 ))</td>
<td>( D(T_{SHS}) &gt; D_{m} )</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>370</td>
<td>410.0</td>
<td>2200–2600</td>
<td>3.4 \times 10^{-9}</td>
<td>4.1 \times 10^{-3}</td>
<td>[64] (TiC(_{x}), ( x = 0.86-0.91 ))</td>
<td>( D(T_{SHS}) &gt; D_{m} )</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>1.31 \times 10^{3}</td>
<td>347.3</td>
<td>1173–1473</td>
<td>5.8 \times 10^{-7}</td>
<td>1.7 \times 10^{-3}</td>
<td>[54]</td>
<td>( D(T_{SHS}) &gt; D_{m} )</td>
</tr>
</tbody>
</table>

| Ti      |     | 4.36 \times 10^{4}       | 736.4           | 2193–2488     | 6.5 \times 10^{-16}         | 1.5 \times 10^{-8}          | [54,61] (TiC\(_{x}\), \( x = 0.67-0.97 \)) | \( D_{Ti} a D_{C} \) |
where \( v \) is the combustion velocity, \( x \) is a coordinate along the SHS-sample and \( \kappa \) is the thermal diffusivity. To determine \( T(t) \) for the reaction cell, a coordinate \( x_0 \) is chosen for which \( T(x_0, t = 0) = T_0 = T_0 + 0.01 T_m \), where \( T_0 = 298 \) K. Then the heating time, \( t_m \), from \( T_0 \) to \( T_m \) is

\[
t_m = - (\kappa / v^3) \ln[0.01 T_m / (T_m - T_0)].
\]  

(10)

For a stoichiometric Ti–C mixture (20 wt% C), \( \kappa \approx 0.04 \text{cm}^2/\text{s} \) [73] and \( v = 6 \text{cm/s} \) [20,52].

For higher temperatures, \( T_m \leq T \leq T_{\text{SHS}} \), we use the spline-approximation of the experimental temperature profile of a steady-state SHS wave in the Ti–C system, which was registered by a micro-thermocouple technique [52] (Fig. 2). It should be noted that the low-temperature tail (at \( T < T_m(Ti) \)) calculated by Eq. (9) lies slightly above the corresponding part of the experimental curve (not shown in Fig. 2). So, we use an upper estimate of temperature (and hence the grown product layer) in the reaction cell. In Fig. 2, \( x = 0 \) corresponds to the melting point of Ti, consequently the heating time from \( T_m(Ti) \) to \( T_{\text{SHS}} \) is

\[
\Delta t_{\text{SHS}} = t_{\text{SHS}} - t_m = x(T_{\text{SHS}})/v.
\]

3.5. Adiabatic heat release in the reaction cell

Having the heating law of the reaction cell, we can calculate the heat release due to diffusion-controlled phase layer growth in non-isothermal conditions and thus the maximal temperature attained, and then compare it with experimental \( T_{\text{SHS}} \). In adiabatic conditions, a heat balance equation for the formation of stoichiometric \( \text{TiC}_{1.0} \) is written as

\[
- \Delta H_{298}^0(\text{TiC}_{1.0}) m_{\text{TiC}(t)} =
\]

\[
= m_{\text{TiC}(t)} \int_{T_m}^{T_{\text{ad}}} c_p(\text{Ti}) \text{d}T
\]

\[
+ m_e(t) \int_{T_m}^{T_{\text{ad}}} c_p(\text{C}) \text{d}T + m_{\text{Ti}(t)}
\]

\[
+ \left( \int_{T_m}^{T_{\text{ad}}} c_p(\text{Ti}) \text{d}T + 1(T_{\text{ad}} - T_m(Ti)) \Delta H_m(\text{Ti}) \right),
\]

(11)

where \( T_{\text{ad}} \) is the adiabatic combustion temperature, \( c_p(t) \) is heat capacity, \( m_i(t) \) is a current mass of \( i \)-th substance, \( \Delta H_{298}^0(\text{TiC}_{1.0}) = -3.077 \text{kJ/g} \) is the standard enthalpy of \( \text{TiC}_{1.0} \) [74], \( \Delta H_m(\text{Ti}) = 0.305 \text{kJ/g} \) is the heat of fusion of \( \text{Ti} \) [74] and 1(\( T_m - T_m(Ti) \)) is the Heaviside step function. The masses of all the substances are determined using a solution of the Stefan problem for particular geometry of the reaction cell, and then \( T_{\text{ad}} \) is calculated from Eq. (11).

4. Growth of a TiC layer on the surface of a titanium particle

4.1. Analytical solution to scenario 1

Problems (3)–(5), (7) are non-linear and in a general case can be solved only numerically [75]. However, for a similar linear problem (with \( D = \text{const} \)) an asymptotic solution for the growth of a spherical phase layer, which is valid for a small layer thickness \( h = R_2 - R_1 < < R_2 \), is known [76–78]. To apply it, we linearize Eqs. (4) and (5) using substitution

\[
\tau(t) = \int_0^t D(T(\theta)) \text{d}\theta.
\]

(12)

Here \( t \) varies from 0 to \( t_{\text{SHS}} \), where \( t_{\text{SHS}} \) is time at which the temperature of the reaction cell reaches its maximal value \( T_{\text{SHS}} \). Then, according to Refs. [76,77], the asymptotic solution of Eqs. (3)–(5) with respect to the product layer

Fig. 2. Temperature profile of the SHS wave in the Ti–C system: (1) analytical solution for a steady-state SHS wave (Eq. (9)) for \( T \leq T_m(Ti); (2) \) cubic-spline approximation of experimental curve [52] in the range \( T_m(Ti) \leq T \leq T_{\text{SHS}} \).
thickess $h$, looks as
\[ h(t) = R_2 - R_1(t) = \beta_1 t^{1/2} + \beta_2 R_2^{3/2}(2R_2^3)^{1/2}, \]
(13)

where
\[ \beta_2 = 2\beta_1 - \beta_0^2 [24q/\beta + 4\beta(5 + 6q) + 2\beta^2(1 + q)] \]
\times [32 + 60q + \beta^3(18 + 20q) + 4\beta^4(1 + q)]^{-1},
\beta_1 = \frac{1}{2}(3 + \beta_2^2)/2, \quad q = (e_{32}^0 - e_{21}^0)/(e_{21}^0 - e_1^0),
(14)

and $\beta$ is a solution of a transcendental equation
\[ \pi^{1/2}(\beta/2) \exp(\beta/2) \text{erf}(\beta/2) = q \]
which arises in a similar Stefan problem for a semi-infinite sample.

For scenario 1 (Fig. 1a), $m_{TiC}(\tau) = (4/3)\pi (R_2^3 - R_1^3(\tau))\rho_{TiC}$. $m_{Ti}(\tau) = m_{TiC}(\tau)/2$, $m_{TiC}(\tau) = (4/3)\pi R_2^3(\tau)\rho_{Ti}$, where $\rho_i$ is the density of $i$th substance. For a stoichiometric composition, the initial C-to-Ti mass ratio is $m_{C0}/m_{Ti0} = 0.25$, where $m_{Ti0} = (4/3)\pi R_0^3\rho_{Ti}$. Then, ignoring the temperature dependence of heat capacities in Eq. (11), the maximal adiabatic heating of the reaction cell, $T_{ad} = T_{ad} - 298$, is estimated as
\[ T_{ad} = -\frac{-\Delta H^0_{298}(TiC_{1.0})\rho_{TiC}}{\rho_{Ti}[c_p(TiC) - 0.2c_p(C)] + \rho_{Ti}[c_p(Ti)R_2^3(\tau) + 0.25c_p(C)R_3^3]/[R_2^3 - R_3^3(\tau)]}. \]
(16)

4.2. Results of calculations

In the temperature range $T_0 \leq T \leq T_m(Ti)$, equilibrium interfacial concentrations $c_{21}^0 = 0.00138$ and $c_{21}^1 = 0.11$ corresponding to the Ti–TiC eutectic temperature $T_{eu} = 1918$ K [51] were used. For higher temperatures, $T_m \leq T \leq T_{SHS}$, it was assumed that molten titanium remains inside the spherical TiC shell, and the interfacial compositions were taken for an intermediate temperature $T = 2673$ K: $c_{21}^0 = 0.065$, $c_{21}^1 = 0.14$ [51]; at the C/TiC interface $c_{23}^0 = 0.2$ (maximal solubility of C in the carbide). Calculations have shown that varying the $c_{21}^0$ and $c_{21}^1$ values along the solidus and liquidus lines of the Ti–C phase diagram in the range $T = T_m - T_{SHS}$ has a negligible effect on the TiC layer thickness and associated heat release.

For the temperature range $T_0 \leq T \leq T_m$ the calculations were performed with all the diffusion data listed in Table 1 (Figs. 3a and b). For the whole temperature range, $T_0 \leq T \leq T_{SHS}$, only the data giving $D(T_{SHS}) < D_m$ (lines 1–9 in Table 1) were used (Figs. 3c and d). A maximal TiC layer thickness attained by the time of reaching the titanium melting temperature is small, $h(T_m) = 0.068$ μm (Fig. 3a), and corresponds to diffusion data No.14 in Table 1. The relevant adiabatic heating is insignificant, $\Delta T_{ad} = 57$ K for $R_2 = 10$ μm (Fig. 3b), and decreases with increasing the particle radius. For the temperature range $T_0 \leq T \leq T_{SHS}$, the maximal TiC layer thickness corresponds to the set of diffusion parameters $E = 235.6$ kJ/mol, $D_0 = 5 \times 10^{-2}$ cm$^2$/s (line 1 in Table 1), and this value is small, $h(T_{SHS}) \approx 1.6$ μm (Fig. 3c). The corresponding adiabatic heating is only $\Delta T_{ad} = 1064$ K for the Ti particle radius of 10 μm and sharply drops with increasing $R_2$ (Fig. 3d). Thus, heat release due to product growth is insufficient to sustain the SHS wave (i.e. to reach $T_{SHS} = 3083$ K).

The obtained result, viz. a small thickness of TiC grown in the temperature range below $T_m(Ti)$, qualitatively agrees with experimental data [19,20]: in rapidly cooled samples almost no interaction was observed in the so-called “preheating zone” of the SHS wave.

However, at the attainment of $T = T_m(Ti)$ the melting of titanium can bring about the rupture of the primary TiC shell and the spreading of the metallic melt.

It should be noted that in Ref. [33] the diffusion-controlled TiC formation was assessed using 6 different sets of the diffusion data, but only an isothermal situation below the titanium melting point was examined. Besides, the TiC layer growth was considered on the surface of a carbon particle
Fig. 3. Thickness of the TiC layer formed on the surface of a titanium particle by the time of attainment of $T_m(Ti)$ (a) and $T_{SHS}$ (c), and relevant adiabatic heating (b and d). Numbers at curves correspond to diffusion data sets in Table 1.
whereas, as mentioned above, the initial TiC film at \( T<T_m(Ti) \) will most probably form on the surface of solid Ti particles due to fast surface diffusion of C atoms.

### 5. Rupture of the primary TiC shell

The density of solid \( \beta\)-Ti at \( T=T_m \) is \( \rho_s=4.18 \text{g/cm}^3 \) while for molten titanium at the same temperature \( \rho_m=4.11 \text{g/cm}^3 \) [71]. The conditions for the rupture of the TiC case because of the dilatation of the titanium core during melting can be determined from a continuity equation written for spherical symmetry [79]:

\[
\text{grad div } U_t = 0. \tag{17}
\]

The boundary conditions at \( r=R_1 \) (expansion due to melting implying that liquid titanium is an incompressible fluid) and \( r=R_2 \) are written as:

\[
U_t(r=R_1) = R_1[(\rho_s/\rho_m)^{1/3} - 1], \quad \sigma_{rr}(r=R_2) = p_0, \quad \tag{18}
\]

Here \( U_t \) is the radial displacement, \( \sigma_{rr} \) is the radial stress and \( p_0=0.1 \text{ MPa} \) is the outer pressure. As the plasticity of TiC is low, we consider only elastic deformation. A solution to Eq. (17) is

\[
U_t(r) = Ar + B/r^2, \quad u_{rr}(r) = \partial U_t/\partial r = A - 2B/r^3, \quad u_{00}(r) = U_t/r = A + B/r^3, \tag{19}
\]

where \( u_{rr} \) and \( u_{00} \) are the radial and shear strain, correspondingly, and \( A \) and \( B \) are constants which are determined from boundary conditions (18).

Hooke’s law for spherical symmetry looks as

\[
\sigma_{rr} = \frac{Y}{(1+v)(1-2v)}[(1-v)u_{rr} + 2vu_{00}], \quad \sigma_{00} = \frac{Y}{(1+v)(1-2v)}(u_{00} + vu_{rr}), \tag{20}
\]

where \( \sigma_{rr} \) and \( \sigma_{00} \) are the radial and shear stress, correspondingly, \( Y \) is the elastic modulus and \( v \) is the Poisson’s ratio [79]. Then the solution for \( \sigma_{00} \) is obtained from Eqs. (18)–(20)

\[
\sigma_{00}(r) = \frac{Y}{1-2v} \left( \frac{\rho_s}{\rho_m} \right)^{1/3} - 1 \left( 1 + f_{0} - p_0 \gamma f - f'_{0} \right) \\
\gamma f_{0} = \frac{R_1^3}{2R_0^3}, f'_{0} = 2R_0^3 \gamma = 1 + v. \tag{21}
\]

Rupture of the primary TiC shell occurs when the maximal shear stress in the spherical layer (at \( r=R_2 \)) exceeds the ultimate tensile stress \( \sigma_{\text{uts}} \). Then from Eq. (21) we obtain a critical thickness, \( h_{cr} = R_2 - R_1 \), of the TiC layer

\[
h_{cr} = R_2 \frac{\phi - 1}{\phi} \cdot \phi = \frac{[\psi - 2\sigma_{uts} + p_0]^{1/3}}{[\gamma(\sigma_{uts} + p_0)]}, \quad \psi = \frac{3Y}{1-2v} \left( \frac{\rho_s}{\rho_m} \right)^{1/3} - 1. \tag{22}
\]

The TiC case can burst at \( h<h_{cr} \). This is an upper estimate because we do not take into account partial dissolution of TiC in molten titanium due to the eutectic reaction at 1645 °C.

To calculate the \( h_{cr} \) value, we have to determine the mechanical properties of TiC at the melting temperature of titanium. The temperature dependencies of the elastic modulus \( Y \) and shear modulus \( G \), for TiC are known in the following form [60]

\[
Y(T) = Y_0 - b_Y T \exp(-T_0/T), \quad G(T) = G_0 - b_G T \exp(-T_0/T), \tag{23}
\]

where \( T_0=320 \text{ K}, Y_0=461 \text{ GPa}, b_Y=0.0702 \text{ GPa/K}, G_0=197 \text{ GPa} \) and \( b_G=0.0299 \text{ GPa/K} \). Then at \( T_m=1940 \text{ K} \) we have \( Y=346 \text{ GPa} \) and \( G=148 \text{ GPa} \), thus the Poisson’s ratio is \( v=Y/(2G)-1=0.17 \). As for \( \sigma_{uts} \) values for TiC at elevated temperatures, there are only disembodied data, e.g., \( \sigma_{uts}(T=1073 \text{ K}) \approx 380 \text{ MPa}, \sigma_{uts}(T=1273 \text{ K}) \approx 280 \text{ MPa} \) [54]. However, available are data on the bending strength \( \sigma_b \), of titanium carbide over a wide temperature range because it is a typical test for brittle refractory compounds; \( \sigma_b \) has a maximum of approximately 500 MPa around \( T=2000 \text{ K} \) [60, p. 233]. Then,
using an estimate $\sigma_{\text{uts}} \approx \sigma_b/2 = 250$ MPa, from Eq. (22) we obtain $h_{\text{cr}} \approx 0.6 R_2$. Since the calculated value $h(T = T_m(Ti))$ is very small, for any initial size of Ti particles used in SHS ($R_a = 5–100$ μm) melting of the titanium core will inevitably bring about the rupture of the primary TiC shell and spreading of the melt. This changes the geometry of a unit reaction cell as shown in Figs. 1a–c.

6. Growth of a TiC layer on the surface of a carbon particle

6.1. Analytical solution to scenario 2

For scenario 2 (Figs. 1c and e), an asymptotic solution to Eqs. (4),(5)–(7) with respect to the TiC layer thickness, $h$, can be obtained similarly to Eq. (13) \cite{76–78}

$$ h(\tau) = R_i(\tau) - R_0 = \beta_1 \tau^{1/2} - \beta_1 \tau / R_0 - \beta_2 \tau^{3/2} / (2R_0^3), $$

(24)

Here coefficients $\beta$, $\beta_1$ and $\beta_2$ are defined, as previously, by Eqs. (14),(15) and $\tau$ is determined according to Eq. (12) where integration is performed over the time range $0 \leq t \leq \Delta t_{\text{SHS}}$, which corresponds to the temperature range $T_m \leq T \leq T_{\text{SHS}}$ (Fig. 2).

To calculate adiabatic heating, we turn to Eq. (11). For the reaction cell shown in Fig. 1c, $m_{\text{TiC}}(\tau) = (4/3)\pi (R_i(\tau) - R_0) \rho_{\text{TiC}}$, $m_C(\tau) = m_0^C - 0.2 m_{\text{TiC}}(\tau)$, $m_C = (4/3)\pi R_0^3 \rho_C$ and $m_{\text{Ti}}(\tau) = 4 m_0^C - 0.8 m_{\text{TiC}}(\tau)$. Then, ignoring the temperature dependence of heat capacities and neglecting the melting enthalpy of titanium (because $\Delta H_m(\text{Ti}) < | \Delta H_{298}(\text{TiC}_{1.0})|$) \cite{74}), the adiabatic heating of the reaction cell is estimated as

$$ \Delta T_{\text{ad}} = \frac{-\Delta H_{298}^{0}(\text{TiC}_{1.0}) \rho_{\text{TiC}}}{\rho_{\text{TiC}} [c_p(\text{TiC}) - 0.2 c_p(C) - 0.8 c_p(\text{Ti_m})] + \rho_C [c_p(C) + 4 c_p(\text{Ti_m})]/[R_i^3(\tau)/R_0^3 - 1]}, $$

(25)

where subscript “m” denotes melt. For calculations, the values of heat capacities (according to Ref. \cite{74}) were taken at $T = T_{\text{SHS}}$. Eq. (25) refers to incomplete conversion of carbon into titanium carbide, i.e. when $0 < \eta_{\text{TiC}} < 1$, where the degree of conversion is expressed as

$$ \eta_{\text{TiC}} = 1 - \frac{m_C(\tau)}{m_0^C} = 0.2 (R_i^3(\tau)/R_0^3 - 1) \rho_{\text{TiC}}/\rho_C. $$

(26)

For complete conversion $\eta_{\text{TiC}} = 1$, the maximal adiabatic heating is $\Delta T_{\text{ad}}^{(\text{max})} = -\Delta H_{298}^{0}(\text{TiC}_{1.0})/c_p(\text{TiC}) = 3095$ K, and the adiabatic SHS temperature $T_{\text{ad}}^{(\text{max})} = 298 + \Delta T_{\text{ad}}^{(\text{max})} = 3393$ K. It is somewhat higher than the value $T_{\text{ad}} = 3210$ K calculated taking into account the temperature dependence of heat capacities \cite{3,80}. Thus, Eq. (25) gives an upper estimate for $\Delta T_{\text{ad}}$.

6.2. Results of calculations

Numerical results are presented in Fig. 4. The TiC layer thickness, which can form in the SHS wave with the temperature profile shown in Fig. 2, was calculated using Eq. (24) not accounting for the exhaustion of reactants (Fig. 4a). The maximal value is $h \approx 1.5$ μm for a sufficiently large carbon particle size, $R_0 = 12.5$ μm, at the 1st set of diffusion data in Table 1.

Adiabatic heating (Fig. 4b) was calculated taking into account the degree of conversion of carbon into carbide (Eqs. (25) and (26)). A plateau with $\Delta T_{\text{ad}} = \Delta T_{\text{ad}}^{(\text{max})}$ for small $R_0$ values corresponds to complete conversion ($\eta_{\text{TiC}} = 1$). Thus, from Fig. 4b it is seen that the diffusion-controlled growth mechanism can provide sufficient adiabatic heating to sustain the SHS process, which results from almost complete conversion, only for small-sized carbon particles: $R_0 < 3$ μm.

This contradicts numerous experimental works where SHS of TiC was performed with coarse-grained graphite: 7 μm \cite{33,81,82}, 20 μm \cite{33,81}, and up to 63 μm \cite{83} in diameter. The results obtained regarding the above concept suggest that fast and complete conversion of reactants into the final product providing the required heat release can be achieved via a different route (without diffusion control of the product formation). For
From Fig. 4a it is seen that at $R_0 \geq 5 \mu m$ the effect of curvature is minor: raising $R_0$ from 5 to 12.5$\mu m$ increases the TiC thickness by less than 10%. Thus the diffusion problem can be considered for a semi-infinite rod. The diffusion equations are written for both C and Ti atoms

$$\frac{\partial c_i}{\partial t} = D_i(T(t))\frac{\partial^2 c_i}{\partial r^2}, \quad i = C, Ti.$$  \hfill (27)

The Stefan-type boundary conditions to Eq. (27) are formulated at interfaces Ti(melt)/TiC ($r = R_i$) and C/TiC ($r = R_0$) taking into account that here $R_0 = R_0(t)$ and $c_C + c_T = 1$

$$\left(c_{21}^i - c_{1}^i\right) \frac{dR_i}{dt} = -D_C(T(t)) \frac{\partial c_C}{\partial r} \bigg|_{R_i(t)}.$$  \hfill (28)

The initial conditions are

$$R_0(t = 0) = R_i(t = 0) = R_0^0.$$  \hfill (29)

Here $D_C$ and $D_Ti$ are the partial diffusion coefficients of C and Ti atoms in TiC (see Table 1), $r$ is the linear coordinate and $R_0^0$ is the initial position of the C/Ti(melt) interface at which a thin TiC layer originates at $t = 0$. Using substitution

$$\tau_i(t) = \int_0^t D_i(T(\theta)) d\theta, \quad i = C, Ti,$$  \hfill (30)

the non-isothermal problem (27)–(29) is reduced to an isothermal (linear) case which has an analytical solution [84] for the displacement of phase boundaries Ti/TiC ($h$) and C/TiC ($\delta$)

$$h(\tau_C) = R_i(\tau_C) - R_0^0 = \beta_C \tau_C^{1/2},$$  \hfill (31)

$$\delta(\tau_{Ti}) = R_0(\tau_{Ti}) - R_0^0 = \beta_{Ti} \tau_{Ti}^{1/2}.$$  \hfill (31)

The coefficients $\beta_C$ and $\beta_{Ti}$ are determined from transcendental equations

$$\pi^{1/2}(\beta_C/2) \exp(\beta_C/2)\left[\text{erf}(\beta_C/2)ight. \right.$$  

$$+ \text{erf}(\beta_{Ti}/\tau_{Ti}/\tau_C/2)\left[\text{erf}(\beta_{Ti}/2)$$

$$= (c_{23}^i - c_{21}^i)/(c_{21}^i - c_{1}^i),$$

$$\pi^{1/2}(\beta_{Ti}/2) \exp(\beta_{Ti}/2)\left[\text{erf}(\beta_{Ti}/2)$$

$$+ \text{erf}(\beta_C(\tau_C/\tau_{Ti}/2)\left[\text{erf}(\beta_C/2)$$

$$= (c_{23}^i - c_{21}^i)/(1 - c_{23}^i).$$  \hfill (32)
The calculated displacement of the C/TiC$x$ interface during interaction in the SHS wave (at $T_m < T < T_{SHS}$) is negligibly small: $\delta = 4.7\,\text{nm} < h$, i.e. only about 10 lattice periods of TiC. This is due to the smallness of the partial diffusivity of Ti atoms, $D_T < D_C$ (Table 1). That is, the inward growth of the TiC layer is insignificant, and we can reasonably assume $R_0 = \text{constant}$.

6.4. Porosity of the product formed via the diffusion mechanism

Now let us make an upper-level estimate (for TiC$_{1.0}$) of the apparent density of titanium carbide particles formed through the above-described route implying that the starting charge composition also corresponds to the TiC$_{1.0}$ stoichiometry (20 wt% C). Then the mass of TiC formed per single carbon particle is $m_{\text{TiC}} = (4/3)\pi(R_1^3 - R_0^3)\rho_{\text{TiC}} = (4/3)\pi R_0^3 \rho_C/0.2$, and its volume is $V_{\text{TiC}} = (4/3)\pi R_0^3 (1 + 5\rho_C/\rho_{\text{TiC}})$. Thus the apparent density of hollow TiC particles is $\rho_{\text{eff}} = [1/\rho_{\text{TiC}} + 1/(5\rho_C)]^{-1} \approx 3.3\,\text{g/cm}^3$ (where $\rho_{\text{TiC}} = 4.91\,\text{g/cm}^3$ for TiC$_{1.0}$ [53,54,60] and $\rho_C \approx 2\,\text{g/cm}^3$ for graphite), which is only 67% of the density of TiC$_{1.0}$. That is, closed porosity of titanium carbide produced by SHS will be $\varepsilon_{\text{cl}} = 1 - \rho_{\text{eff}}/\rho_{\text{TiC}} \approx 0.33$ and the pore size must be about the initial diameter of carbon particles.

However, microstructure investigations [19,56,82,83,85] have revealed that as-synthesized TiC samples possess mainly open porosity, $\varepsilon_{\text{op}} \approx 0.5\sim 0.6$. This is ascribed to the presence of green porosity, $\varepsilon_0 = 0.3\sim 0.65$ [58], melt spreading and gas release [56,85]. The fraction of closed porosity is usually small: about 1% for SHS in vacuum [83]. Besides, dense titanium carbide articles (with relative density above 95%) can be readily produced by SHS under high pressure [80,82] or by short-term compaction of a hot pellet immediately after the completion of SHS [1,2 and literature cited therein]. If as-synthesized TiC particles were hollow, which follows from the above-described route, the attainment of such relative density would require prolonged pressure sintering at a high temperature.

Thus the structural characteristic of the SHS product emerging from the diffusion model disagrees with experimental observations, which therefore supports an idea of a dissolution–precipitation route capable of producing dense TiC particles, which includes dissolution of carbon in molten titanium and subsequent crystallization of the product grains.

It should be noted that a conclusion in favor of the diffusion-controlled growth of hollow TiC shells on the surface of carbon particles having a size of $2R_0 = 7\,\mu\text{m}$ (initial porosity of a sample was $\varepsilon_0 = 0.2$) and $20\,\mu\text{m}$ ($\varepsilon_0 = 0.4$) was made in Ref. [81] basing solely on the porosity measurements and microstructures of as-synthesized specimens. Let us analyze these experimental data. For all of the samples the initial temperature, $T_0$, was 293 K, and the total porosity measured after SHS was almost the same, $\varepsilon^{(m)}_t = 0.46\sim0.5$. As shown above, SHS of TiC via this mechanism is possible for small-sized carbon particles, $R_0 \approx 3.5\,\mu\text{m}$, but closed porosity will be $\varepsilon_{\text{cl}} = 0.33$ which greatly exceeds the measured value $\varepsilon_{\text{cl}}^{(m)} = 0.06\sim0.08$ [81]. Besides, total porosity of an as-synthesized sample for the formation of TiC$_{1.0}$ is estimated as

$$\varepsilon_t = 1 - (1 - \varepsilon_0)[\rho_{\text{TiC}}(0.8/\rho_T + 0.2/\rho_C)]^{-1}$$

implying that the specimen volume does not change during SHS, which is true for strongly compacted green pellets (as in Ref. [81]). Here $\rho_T = 4.51\,\text{g/cm}^3$ [70] is the density of initial $\alpha$-Ti particles. Then for samples with 7 $\mu\text{m}$ diameter carbon particles the formation of dense TiC grains ($\rho_{\text{TiC}} = 4.91\,\text{g/cm}^3$) yields the total final porosity $\varepsilon_t = 0.41$, which is close to experimental data. But if hollow TiC particles are formed via the diffusion mechanism, then, substituting into Eq. (33) $\rho_{\text{eff}} = 3.3\,\text{g/cm}^3$ instead of $\rho_{\text{TiC}}$ we obtain $\varepsilon_t \approx 0.13$. In this case $\varepsilon'_t$ signifies the fraction of pores between the hollow particles. But this value is less than 0.154 ± 0.005 (the Scher–Zallen criterion), which is required by the percolation theory [86] for the existence of open porosity. Thus, the sample will contain only closed pores (inside the TiC particles and between them) whereas in Ref. [81] high open porosity was observed: $\varepsilon_{\text{op}}^{(m)} = \varepsilon_t^{(m)} - \varepsilon_{\text{cl}}^{(m)} \approx 0.4$. 
For larger carbon particles (2R0 = 20 μm), as demonstrated above, SHS via the diffusion mechanism is impossible (for T0 ≈ 298 K) because of low heat release per unit reaction cell (Fig. 4b). If dense TiC particles are formed, from Eq. (33) for e0 = 0.4 we have 
\[ e_t = 0.56 \]
which is close to experimental porosity 
\[ e_t^{(m)} = 0.46–0.5 \]. For the formation of hollow particles (ecl = 0.33), Eq. (33) gives 
\[ e_t' = 0.34 \]
and then the total porosity will be 
\[ e_t = e_t' + e_{cl} = 0.67 \], which substantially exceeds the measured value. Maximal closed porosity in the experiments was 
\[ e_{cl}^{(m)} = 0.22 \] for samples with the particle diameter 17 μm (Ti) and 20 μm (carbon) [81]. Since SHS was performed under isostatic gas pressure, the origin of closed pores should be ascribed to partial sintering of dense TiC grains (presumably precipitated from melt) around voids formed on the sites of outflown titanium particles. This is supported by the fact that the closed porosity was noticed to increase with raising the 
\[ p \] pressure (from 
\[ e_{cl}^{(m)} = 0.12 \] at 1 bar to 0.22 at 70 bar) while the total porosity remained almost the same, 
\[ e_t^{(m)} = 0.47–0.5 \] [81].

7. Analysis of the dissolution–precipitation route

Let us discuss a dissolution–precipitation route of the TiC formation, which can produce 100% dense particles. According to the idea first proposed in Ref. [87] and used for studying SHS in the Ni–Al [31] and Nb–C [88] systems, as soon as a metallic melt spreads and engulfs solid particles, a thin film of an intermediate phase (here TiC) forms around them instantaneously. Then the product particles (TiC) precipitate from the saturated melt due to diffusion of carbon atoms across this film. The film thickness remains constant: it is believed that its growth rate at the C/TiC interface is equal to the dissolution rate at the melt/TiC interface. Thus, the TiC film shrinks to the center of the carbon particle as the latter dissolves. This pattern is sometimes called “the shrinking-core mechanism”. It corresponds to the solid–solid–liquid mechanism which, for the Ti–C system, is truly quasi-equilibrium. However, the film thickness has not been previously estimated using realistic diffusion data.

The concentration profile of carbon in the reaction cell is similar to that shown in Fig. 1a but with 
\[ R_0 = R_0(t) \]; final TiC particles precipitate from the melt in domain 
\[ (R_1, R_2) \]. In a general case, the displacement of the melt/TiC and C/TiC interfaces is determined by Eqs. (27)–(29) with the only difference that Eq. (27) should be written in spherical symmetry. But since the TiC film thickness is small and 
\[ D_C \gg D_{Ti} \], outdiffusion of carbon atoms through the film is not the rate-limiting stage. Thus the process is controlled by indiffusion of Ti atoms across the TiC layer, and radial shrinking of the film is described as

\[ (1 - c^{(2)}_{Ti}) \frac{dR_0}{dt} = DTi(T(t)) \frac{c^{(2)}_{C}}{c^{(2)}_{Ti}} |_{R_0(t)}, \]

\[ R_0(t = 0) = R_0^0, h_0 = R_1(t) - R_0(t) = \text{constant}, \]

(34)

where 
\[ h_0 \]
is the layer thickness. For a thin film, a steady-state concentration profile can be used to determine the concentration gradient at 
\[ r = R_0(t) \] in Eq. (34)

\[ c_C(r) = c^{(2)}_{C23} R_0/r + (1 - R_0/r)(R_1 c^{(2)}_{21} - R_0 c^{(2)}_{23})/h_0, \]

\[ R_0(t) \leq r \leq R_1(t). \]

(35)

Using 
\[ \tau_{Ti} \]
defined by Eq. (30) and introducing 
\[ z = R_0/R_0^0 \], from Eqs. (34) and (35) we obtain

\[ z \frac{dz}{(z R_0^0/h_0 + 1)} = -q \, dt \tau_{Ti}. \]

\[ q = (R_0^0)^{-2} (c^{(2)}_{23} - c^{(2)}_{21})/(1 - c^{(2)}_{23}), \]

(36)

By the attainment of the maximal SHS temperature 
\[ T_{SHS} \], which corresponds to time 
\[ t = t_{SHS} \], the carbon particle completely dissolves, i.e. 
\[ R_0(t_{SHS}) = 0. \] Then, integrating Eq. (36) from 0 to 
\[ t_{SHS} \], we receive a non-linear equation linking the initial radius of the carbon particle 
\[ R_0^0 \] with the thickness of the TiC film

\[ h_0[R_0^0 - h_0 \ln(R_0^0/h_0 + 1)] = \tau_{Ti} t_{SHS} \times (c^{(2)}_{23} - c^{(2)}_{21})/(1 - c^{(2)}_{23}). \]

(37)

The results of the numerical solution of Eq. (37) are shown in Fig. 5. It is seen that the thickness of the TiC film for the initial radius of carbon particles 
\[ R_0^0 = 0.5 \mu m \] is close to the crystal lattice period: 
\[ h_0 = 0.5 \text{ nm} \sim a_{TiC} = 0.4327 \text{ nm} \] [53], and still decreases with increasing 
\[ R_0^0 \]. Hence the aforesaid solid–solid–liquid mechanism loses its physical
meaning: a minimal thickness of a crystalline phase must be about the size of a critical nucleus which is of the order of 10 lattice periods.

8. Discussion and conclusions

The above-presented consistent analysis of the solid–solid–liquid (diffusion-controlled) mechanism, which was performed using available experimental data on both solid-state diffusion in the product phase and characteristics of the SHS wave, has demonstrated that this widely used concept is actually not applicable to modeling SHS of titanium carbide. This is because the physical meaning of the results obtained within this approach (e.g., the product structure and density) disagrees with experimental data.

It is shown that formal calculation of the product-layer thickness and associated heat release for small particles of a nonmetallic reactant (for scenario 2) can bring about numerical data supporting the diffusion model. Thus the comparison of theoretical and experimental results should be performed using structural characteristics of SHS products, e.g. porosity.

Therefore, only the solid–liquid mechanism, which for the Ti–C system is truly non-equilibrium, can operate during SHS to produce dense product particles. It involves direct contact of solid carbon with molten titanium without the presence of a continuous TiC interlayer. The product formation occurs via dissolution of carbon in liquid titanium at the C/Ti(melt) interface and precipitation of TiC grains. Because of fast diffusion in high-temperature melts \( (D_m \sim 10^{-5} - 10^{-4} \text{cm}^2/\text{s}) \), diffusion in liquid is not the rate-limiting stage and the phase-forming process responsible for major heat release is crystallization of the product particles. Because of the presence of the solid/liquid interface and strong chemical interaction between the C and Ti atoms, crystallization of the TiC particles will occur via heterogeneous nucleation at the C/Ti(melt) interface rather than through homogeneous nucleation in the melt. Besides, the activation energy for the former is generally lower than for the latter. The nucleated TiC grains must detach from the carbon particle surface, otherwise a thin TiC layer separating the parent phases will form and the situation will reduce to the solid–solid–liquid (quasi-equilibrium) pattern considered above. This process continues until complete consumption of solid carbon is achieved. Further, in the after-burn zone of the SHS wave, growth and coalescence of the TiC particles in the metallic melt can occur. In this case, the final size of product particles will depend on the conditions of crystallization and subsequent coalescence/sintering but not on the size of initial reactants. An important factor is the melt lifetime which depends on the Ti-to-C ratio in the charge, structure of a green pellet determining the melt spreading conditions and heat exchange with the environment.

This solid–liquid mechanism qualitatively agrees with the results obtained in experiments on arresting SHS wave in the binary Ti–C [20] and multi-component Ti–C–Ni–Mo [21] systems where in rapidly quenched samples the formation of small uniform-sized TiC particles was observed in the molten metal around a graphite particle. This mechanism may also be valid for other interstitial compounds such as carbides, borides, etc. for which the SHS temperature exceeds the melting point of a metallic reactant but is below the melting temperatures of the non-metal and product, and for certain intermetallics, e.g. NiAl [23–25].
It should also be noted that in this situation the critical thickness, \( h_{cr} \), of the layer of a primary product formed on the surface of a metal particle before the attainment of the melting temperature, which is determined by Eq. (22), acquires a precise physical meaning. This parameter becomes a criterion for the changeover from the solid–solid–liquid (diffusion-controlled) mechanism (a “slow” route of product formation) to the solid–liquid mechanism (a “fast” route). As stated above, in the wave propagation mode this thickness is small \( (h < < h_{cr}) \) due to high heating rate, and hence the changeover will always take place. But this criterion is important in the thermal explosion mode when the heating rate is small, \( \sim 1-10 \text{ K/min} \) [31,45], and a sufficiently thick case of the primary product can be formed to prevent the liquid core from spreading. Besides, it clearly illustrates the difference in the interaction routes between SHS and traditional furnace synthesis where the heating rate may be still lower.

Acknowledgements

This work was partly supported by the Belarusian Fundamental Research Foundation (Grant X02P-037). The authors thank Prof. O.S. Rabinovich at the Luikov Heat/Mass Transfer Institute of the National Academy of Sciences of Belarus for helpful discussion.

References