

A micromechanistic criterion for changeover of interaction mechanisms during SHS of refractory interstitial phases (carbides, nitrides)

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Introduction

Self-propagating High-temperature Synthesis (SHS), or Combustion Synthesis (CS) is used as a efficient versatile method for producing a wide range of refractory compounds, e.g., carbides, nitrides, borides, intermetallics and composite materials with fine-grain structure and superior properties.

SHS can be performed in two regimes: (i) the thermal explosion (TE) mode when a mixture of reactive powders is heated by an external heat source until the rate of an exothermal reaction becomes high enough to provide self-heating of a specimen resulting in fast and uniform completion of interaction throughout the whole volume, and (ii) the wave propagation (WP), or true SHS mode when an exothermal reaction, being initiated at the end of a specimen by local heating, propagates through the cold charge mixture as a combustion wave leaving behind a glowing solid product. The combustion temperature depends on the heat release of an exothermal reaction and can reach 4000 K. In the TE mode, a typical heating rate from the initial temperature, T_0 , to the ignition point, T_{ign} , is within 1-100 K/s depending on a heating method. The value of T_{ign} in many systems is close to the melting point of a lower-melting reactant. In the WP mode, as well as in the TE mode above T_{ign} , the heating rate is $\sim 10^5$ - 10^6 K/s and the interaction accomplishes in about or even less than 1 s; the temperature gradient in the thermal reaction zone of the SHS wave is $\sim 10^5$ K/cm [1,2].

The main drawback of SHS is impossibility of controlling transformations in the SHS wave *in situ* after the specimen is ignited; the product structure can only be influenced by varying the composition of the charge mixture and initial temperature. Development of controllable SHS processes is a complex task that can be solved only through elaboration of mathematical models adequately describing intricate physicochemical phenomena inherent in SHS. Modeling and simulation plays an important part in the development of CS processes, as well as in the investigation of reaction kinetics and intricate physicochemical mechanisms of phase formation that operate in CS. The most widely used model for the product-phase growth kinetics during CS and hence for the heat release rate employs the diffusion-type Stefan problem. It implies the formation of a solid product interlayer at the interface of starting reactant particles and its diffusion-controlled growth in non-isothermal conditions. This kinetic model was used for studying SHS of metal carbides [3,4] and intermetallics [5].

This approach had gained wide acceptance the Materials Science for modeling phase and structure formation during interdiffusion in many binary and multi-component systems. It is based on the assumption of local quasi-equilibrium at the interfaces, where the phase composition of the diffusion zone corresponds to the equilibrium phase diagram [6]. Actually, this interaction route corresponds to a long-term annealing in isothermal or weakly non-isothermal conditions below the melting temperature of a system. At small interaction time or thin layers of solid reactants, certain intermediate compounds are known to be missing from the diffusion zone [7,8]; a similar effect is known at interaction of a solid and a liquid metal, e.g., Fe-Al [9]. This phenomenon is attributed to an interfacial reaction barrier [10] and the existence of a thermodynamic [11,12] and kinetic [13] barrier for the nucleation of an equilibrium phase in the field of a steep concentration gradient at initial stages of interaction. However, modeling in non-isothermal conditions has demonstrated that the influence of the reaction barrier is noticeable only at low heating rates at temperatures below T_{ign} , i.e. only on the

stage of preheating [14] while at high temperatures ($T > T_{\text{ign}}$), when a sufficiently thick product layer can be grown in a short time due to a high interdiffusion coefficient, this effect is negligible [15].

Recent experimental studies have demonstrated non-equilibrium nature of phase and structure formation during CS, which is currently a subject of discussion [16,17]. The observed effects are attributed to specific features of heat transfer in SHS waves [18] and an “unusual” reaction mechanism in non-isothermal conditions. The latter was revealed in the Ti-C [19], Ti-Ni-Mo-C [20,21], Ni-Al [22,23] and some other systems using quenching of SHS-samples by rapid cooling, as well as in model experiments employing the electrothermography (ETG), or electrothermal explosion (ETE) method-controlled heating (at a rate of $1-10^5$ K/s) by electric current of a metal wire clad by a second reactant, e.g. in the Ti-C [24], Mo-Si [25] and some other systems. A non-conventional interaction route found in such experiments involves dissolution of a higher-melting reactant particles (e.g., C or Ni, in the Ti-C and Al-Ni systems, correspondingly) in a metallic melt (here Ti and Al) and precipitation of a solid product (TiC and NiAl, respectively) from the supersaturated liquid.

It should be outlined that for a binary system, e.g., Ti-C, this pathway implies the presence of a two-phase zone in contact with a pure solid reactant (here C): solid TiC particles in the titanium melt at the experimental CS temperature ($T_{\text{CS}} = 2937$ [26] to 3083 K [27]) which is below the TiC-Ti eutectic temperature $T_{\text{eu}}=3323$ K (Fig.1). This contradicts the Gibbs phase rule, i.e. the reaction route is substantially non-equilibrium; such a pattern is quasi-equilibrium only in a ternary system (e.g., in internal oxidation). Hence, to comply with the assumption of local quasi-equilibrium at the interfaces, a thin film of a product phase (in this example, TiC) is supposed to exist to separate the solid reactant from the two-phase zone [28]. This concept was used in modeling CS of NiAl [29] and niobium carbide [30]. In this situation, the rate-limiting stage is atomic diffusion across the film whose thickness remains constant, and the model formulation is close to that for the aforementioned “quasi-equilibrium diffusion-controlled growth” approach.

In literature, there is a controversy about the existence of a thin interlayer of a product phase (or phases) that corresponds to an equilibrium phase diagram at the solid/liquid interface in the dissolution-precipitation mechanism: e.g., in [22] the presence of thin films of all the intermediate phases during SHS in the Ni-Al system is postulated while in [23] the absence of such films in the same system is concluded. Recently, it has been demonstrated theoretically on the example of the Ti-C system that the dissolution-precipitation mechanism ought to proceed without a thin interlayer of an intermediate phase (here TiC) on the surface of carbon particles dissolving in molten Ti, i.e. it really has non-equilibrium nature [31]. Almost simultaneously, a new model has been developed to describe this reaction route in the SHS of titanium carbide [32,33], which includes direct dissolution of non-metal (C) particles in the melt, diffusion in the liquid phase and crystallization of the product grains.

As there are two radically different reaction mechanisms, viz. the “quasi-equilibrium solid-state diffusion-controlled growth” and “non-equilibrium dissolution-precipitation”, there ought to exist a condition for the changeover between these interaction pathways as applied to non-isothermal conditions and, specifically, to SHS of refractory compounds. Also, it seems necessary to determine the domains of applicability of the two corresponding models. Earlier, a micromechanistic criterion was proposed to determine the conditions for spreading of a metallic melt in the SHS wave for the Ti-C system [31]. In this work, this parameter will be used for constructing a diagram of phase formation mechanisms for SHS in the TE mode, which will illustrate the effect of heating rate on the reaction route. The applicability of the developed approach to CS in other binary systems will be discussed.

Model formulation

The Ti-C system provides a good example for studying a transition between the reaction routes in a condensed system in non-isothermal conditions because it contains only one compound phase, TiC, and, as mentioned above, the experimental CS temperature exceeds the titanium melting point, $T_{\text{m}}(\text{Ti})=1940$ K but is below the melting temperature of the TiC-C eutectic (Fig. 1). In this case, non-isothermal interaction can be divided into two stages: (i) at $T < T_{\text{m}}(\text{Ti})$ where only solid-state diffusion-

controlled growth of the titanium carbide can occur, and (ii) at $T_m(\text{Ti}) < T < T_{\text{CS}} = 2937\text{-}3083\text{ K}$ where fast formation of the solid reaction product proceeds via the dissolution-precipitation route: dissolution of solid carbon particles in the titanium melt and crystallization of the TiC grains [24,19]. This mechanism was analyzed theoretically considering a thin interlayer of the equilibrium phase, titanium carbide, at the Ti(melt)/C(solid) interface [31]. It has been proved, using experimental data on both solid-state diffusion across the product (TiC) interlayer and the temperature profile of the SHS wave in the Ti-C system, that the thickness of this film (if it really exists) must be below the lattice period. That is, the dissolution-precipitation mechanism of phase formation in this system ought to proceed in the non-equilibrium manner (without a quasi-equilibrium solid interlayer) during CS to provide completion of the heterogeneous reaction within the experimentally observed (i.e. very short) time.

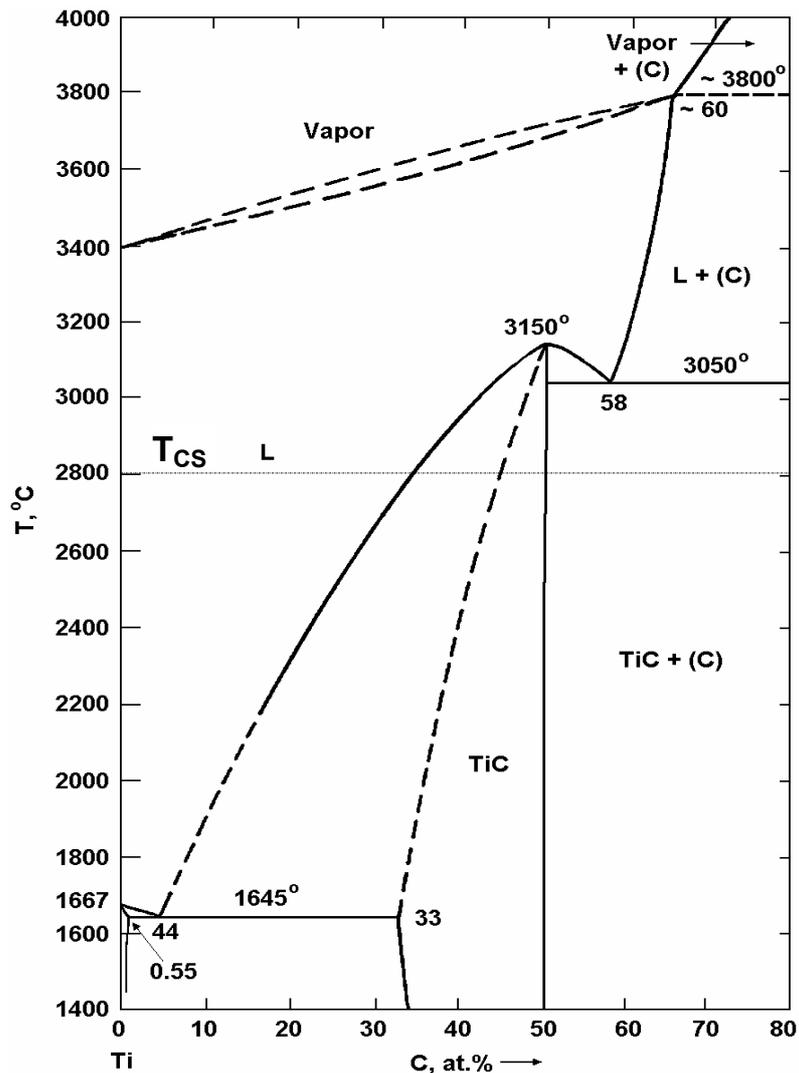


Figure 1. The equilibrium Ti-C phase diagram [34].

Hence, immediate contact of a solid reactant particle (carbon in the Ti-C system) with a metallic melt (here Ti) is a necessary condition for the non-equilibrium dissolution-precipitation mechanism to operate in the CS. However, during heating of the reactive powder mixture from the ambient temperature T_0 to the melting point of a lower-melting reactant (Ti in our example), a continuous shell of a primary refractory product (here TiC) can be grown on the metal particle surface due to solid-state interdiffusion thus preventing this contact. At the attainment of $T_m(\text{Ti})$, titanium melting inside the particle can result in the rupture of this layer due to a volume change associated with the phase

transition and subsequent melt spreading towards the solid reactant. The burst of the shell was supposed to be a criterion for the changeover of the interaction routes in the SHS wave where the heating rate is very high, $\geq 10^5$ K/s [31].

At CS in the TE mode, the heating rate from T_0 to T_{ign} can be low, ≤ 1 K/s. As the diffusion coefficient in solids increases with temperature according to the Arrhenius law, the grown refractory shell may be rather thick. Thus, to built a diagram of the interaction mechanisms in the Ti-C system it is necessary to examine the competition of two factors: diffusion-controlled growth of the primary TiC spherical shell on the surface of a starting Ti particle in non-isothermal conditions and a possibility of the rupture of this shell due to melting of the titanium core at $T=T_m(\text{Ti})$.

Diffusion-controlled growth of the primary TiC shell

The Stefan problem formulation

For CS in the Ti-C powder mixture, a solid titanium particle surrounded with smaller-size carbon grains (milled graphite or carbon black) in the stoichiometric mass ratio constitutes a unit reaction cell. A uniform spherical film of the primary product, TiC_x , on the Ti particle is formed due to fast surface diffusion of C atoms, and its further growth is controlled by solid-state diffusion across the TiC layer. Solid β -Ti is characterized by low solubility of carbon (Fig.1) [34] and high diffusion coefficient of C atoms in comparison with TiC [35], hence β -Ti can be treated as saturated with carbon.

For TiC_x at $T=T_0=293$ K the density varies from 4.51 ($\text{TiC}_{0.5}$) to 4.91 g/cm^3 ($\text{TiC}_{1.0}$) and the thermal expansion coefficient of in the range $T=293-1273$ K is $\alpha_{\text{TiC}}=10.94 \cdot 10^{-6}$ K^{-1} [37]. Then for the TiC_x phase contacting with solid β -Ti in the diffusion zone, the density at high temperatures is estimated as

$$\rho_{\text{TiC}_x}(T) = \rho_{\text{TiC}_x}(T_0)/[1 + 3\alpha_{\text{TiC}}(T-T_0)]. \quad (1)$$

At $T=T_m(\text{Ti})=1940$ K Eq. (1) gives $\rho_{\text{TiC}_x}=4.28$ g/cm^3 (for $x=0.5$) whereas the density of solid β -Ti at the same temperature is 4.18 g/cm^3 [38], i.e. the relative difference is about 2%. Hence we can neglect the volume change at the β -Ti/ TiC_x interface in the diffusion zone during the TiC phase layer growth.

In this case, the Stefan problem in spherical symmetry for the diffusion-controlled growth of the primary TiC shell on the surface of a solid titanium particle in non-isothermal conditions is written as

$$\frac{\partial c}{\partial t} = \frac{D(T(t))}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right), \quad (c_{21}^0 - c_1^0) \frac{dr_1}{dt} = -D(T(t)) \frac{\partial c}{\partial r} \Big|_{r_1(t)}, \quad c(r_0, t) = c_{23}^0. \quad (2)$$

The initial conditions to Eqs.(2) are

$$r_1(t=0) = r_0, \quad c(0 < r < r_1, t=0) = c_1^0. \quad (3)$$

Here c is the mass concentration of carbon atoms, r_1 is the current coordinate of the Ti/ TiC_x phase boundary, r_0 is the initial radius of a titanium particle, c_1^0 and c_{21}^0 are the equilibrium concentrations of carbon in β -Ti and TiC_x , correspondingly, at the β -Ti/ TiC_x interface, c_{23}^0 is the equilibrium concentration at the TiC_x /C interface, D is the interdiffusion coefficient in TiC. It should be outlined that since titanium carbide is an interstitial compound in which the partial diffusion coefficient of C atoms exceeds that of Ti atoms by several orders of magnitude, the 1st order boundary condition is posed at the TiC_x /C boundary (at $r=r_0$), i.e. the TiC phase layer grows at the β -Ti/ TiC_x interface.

The interdiffusion coefficient obeys the Arrhenius law

$$D(T) = D_0 \exp[-Q/(RT)], \quad (4)$$

where D_0 is the preexponential factor and Q is the activation energy.

Here, continuous heating of the charge mixture at a constant rate v_T , which corresponds to CS in the TE mode below T_{ign} , is considered. As the difference between $T_m(Ti)$ and the Ti-TiC eutectic temperature is small, about 20 K (Fig. 1), we neglect this value and consider the temperature range [$T_0=298$ K, $T_m(Ti)=1940$ K]. The equilibrium concentrations c_{1}^0 , c_{21}^0 and c_{23}^0 are assumed constant because their variation in this temperature range is small (Fig.1).

Asymptotic solution

For the Stefan problem in spherical symmetry, an asymptotic solution for the product layer thickness $h(t) = r_0 - r_1(t)$ was found in a linear case (i.e. when $D=const$) for small h ($h \ll r_0$) [6,39]. Non-linear problem (2)-(4) can be linearized using substitution

$$\tau(t) = \int_0^t D(T_0 + v_T \xi) d\xi. \quad (5)$$

Then the analytical solution for the TiC shell thickness assumes the form

$$h_{TiC}(\tau(t)) = \beta_0 \tau^{1/2} + r_0^{-1} \beta_1 \tau + (2r_0^2)^{-1} \beta_2 \tau^{3/2}. \quad (6)$$

Coefficient β_0 is found from the following equation known in the Stefan problem for planar symmetry

$$\pi^{1/2}(\beta_0/2) \exp(\beta_0/2)^2 \operatorname{erf}(\beta_0/2) = g, \quad g = (c_{23}^0 - c_{21}^0)/(c_{21}^0 - c_1^0), \quad (7)$$

and parameters β_1 and β_2 are calculated by the following formulas:

$$\beta_1 = \beta_0^2 / (3 + 0.5\beta_0^2), \quad (8)$$

$$\beta_2 = 2\beta_0\beta_1 - \beta_1^2 [24g/\beta_0 + 4\beta_0(5+6g) + 2\beta_0^3(1+g)] / [32 + 60g + \beta_0^2(18+20g) + \beta_0^4(1+g)]. \quad (9)$$

The asymptotic solution (6)-(9) was originally derived for the case of a small layer thickness $h \ll r_0$ [6,39]. A comparison of calculated results, which were obtained by us using Eqs. (6)-(9), with a direct numerical solution of the same problem found by the finite-volume method [40] have demonstrated that this approach gives adequate results for a substantially larger thickness, up to $h \approx 0.75r_0$.

Rupture of the spherical shell

As metal melts are incompressible, the volume dilatation associated with melting of the titanium core at the attainment of $T_m(Ti)$ may result in the disruption of the spherical shell of a primary refractory product unless the thickness of the latter is large enough to withstand the arising stress. Let's determine the critical thickness of the TiC layer that can keep the metallic melt inside the particle; this will be a condition for the changeover of the interaction routes.

For an isotropic solid in the absence of volume-distributed forces, the continuity equation looks as [41]

$$\Delta \operatorname{div} \mathbf{u} = 0, \quad (10)$$

where \mathbf{u} is the displacement vector. In spherical symmetry there is only radial displacement, $\mathbf{u} = u_r$. Then Eq. (10) is rewritten in a simple form

$$d[(1/r^2)d(r^2 u_r)/dr]/dr = 0, \quad (11)$$

which has a simple analytical solution

$$u_r = ar + b/r^2, \quad \varepsilon_{rr} = du_r/dr = a - 2b/r^3, \quad \varepsilon_{\theta\theta} = u_r/r = a + b/r^3. \quad (12)$$

Here ε_{rr} and $\varepsilon_{\theta\theta}$ are the radial and tangential strain, respectively, a and b are constants that are to be determined from the relevant boundary conditions to Eq. (12).

At the titanium core melting, the displacement of the point $r=r_1$ (the Ti/TiC boundary) is determined from the mass conservation law: $(4/3)\pi r_1^3 \rho_s = (4/3)\pi (r_1')^3 \rho_m$, where r_1' is the new position of this point (after melting), ρ_s and ρ_m are the densities of solid and molten Ti at $T_m(\text{Ti})$. Thus, boundary conditions to Eq. (12) are formulated as

$$u_r(r=r_1) = r_1' - r_1 = r_1 [(\rho_s/\rho_m)^{1/3} - 1], \quad \sigma_{rr}(r=r_0) = p_0 = 0.1 \text{ MPa}, \quad (13)$$

where p_0 is pressure at the outer surface of the particle, which is equal to the ambient pressure.

Rupture of the refractory shell occurs when the shear stress at the outer surface $r=r_0$ reaches the ultimate tensile strength:

$$\sigma_{\theta\theta}(r=r_0) = \sigma_{UTS}. \quad (14)$$

As titanium carbide, like many other refractory compounds, is brittle even at $T=T_m(\text{Ti})$, only elastic strain is considered. Thus, we use the Hooke's law written in spherical symmetry

$$\sigma_{rr} = q[(1-\nu)\varepsilon_{rr} + 2\nu\varepsilon_{\theta\theta}], \quad \sigma_{\theta\theta} = q[\nu\varepsilon_{rr} + \varepsilon_{\theta\theta}], \quad q = E/[(1+\nu)(1-2\nu)], \quad (15)$$

where E is the elastic modulus and ν is the Poisson's ratio.

Taking into account that $p_0 \ll \sigma_{UTS}$, from Eqs. (12)-(15) the following solution is obtained for a critical thickness, h_{cr} , of the refractory product shell that can keep the metallic melt inside the particle, i.e. prevent it from contacting the pure solid reactant:

$$h_{cr} = r_0(F-1)/F, \quad F = \left[\frac{3E((\rho_s/\rho_m)^{1/3} - 1)}{(1+\nu)\sigma_{UTS}} - \frac{2(1-2\nu)}{1+\nu} \right]^{1/3}. \quad (16)$$

Let's calculate the value of h_{cr} for the system under consideration. At the melting point, the densities of solid and liquid titanium are $\rho_s=4.18 \text{ g/cm}^3$ and $\rho_m=4.11 \text{ g/cm}^3$, correspondingly [38]. For TiC at $T=T_m(\text{Ti})$, the elastic and shear moduli are $E=346 \text{ GPa}$ and $\mu=148 \text{ GPa}$, correspondingly [37], then $\nu = E/(2\mu)-1 = 0.17$. As consistent data on σ_{UTS} for titanium carbide at high temperatures are not available (e.g., known is value $\sigma_{UTS}=280 \text{ MPa}$ at 1273 K [35]), we use an estimate $\sigma_{UTS}(T=T_m(\text{Ti})=1940 \text{ K}) \approx 0.5\sigma_b = 250 \text{ MPa}$ where σ_b is the bending strength, $\sigma_b \approx 500 \text{ MPa}$ at $T \approx 2000 \text{ K}$ [37]. Then from Eq. (16) we obtain $h_{cr}=0.62r_0$. As mentioned above, in this case the asymptotic solution (6)-(9) for the thickness of the primary product layer grown in non-isothermal conditions is valid.

From the foregoing it is seen that the following non-linear equation

$$h_{\text{TiC}}(\tau(t_m)) = h_{cr}, \quad t_m = (T_m(\text{Ti})-T_0)/v_T, \quad (17)$$

where t_m is the time corresponding to the attainment of $T_m(\text{Ti})$, must be solved in order to determine the heating rate, v_T , for which the critical thickness of a refractory product shell can be produced upon heating from T_0 to $T_m(\text{Ti})$.

Results and discussion

Equation (17) in which h_{TiC} is determined by Eqs. (6)-(9), the τ value is obtained from Eqs. (4),(5) and the upper integration limit in Eq. (5) is given by expression (17) was solved numerically with respect to v_T . A typical radius of titanium particles used in CS is 1-50 μm ; in calculations the r_0 value was varied within 0.5-150 μm . The interdiffusion parameters (D_0 and Q) for titanium carbide used in calculations (three data sets taken from different experimental works on chemical diffusion in TiC) are presented in Table 1. The equilibrium concentrations that appear in Eq. (7) were taken at the Ti-TiC eutectic temperature $T_{\text{eu}}=1918$ K (Fig.1): $c_{\text{Ti}}^0=0.00138$, $c_{\text{Ti}}^0=0.11$, and $c_{\text{TiC}}^0=0.5$ (mass fractions).

Table 1. Interdiffusion parameters for the TiC layer growth

No.	Q, kJ/mol	D_0 , m^2/s	Ref.
1	347.3	0.13	[35]
2	338.9	$7.78 \cdot 10^{-3}$	[36]
3	235.6	$5.0 \cdot 10^{-6}$	[35,42]

Diagram of phase formation routes

As demonstrated above, rupture of the spherical shell of a primary refractory product grown on the metal particle surface, which occurs due to melting of the unreacted core, determines the condition for a changeover of interaction pathways. Thus, the results of calculations presented in Fig.2 constitute a diagram of phase formation mechanisms in the Ti-C system in non-isothermal conditions; lines 1-3 refer to different sets of the diffusion parameters. Domain I corresponds to the diffusion-controlled growth mechanism (a slow, quasi-equilibrium route typical of diffusion annealing in weakly non-isothermal conditions). Here, a sufficiently thick shell of a primary product (in our system, TiC) is grown of the metal particle surface during heating so that after melting the metallic reactant remains inside the shell ($h_{\text{TiC}} > h_{\text{cr}}$) and further interaction (at $T > T_m$) proceeds slowly since the rate-limiting stage is still the solid-state diffusion across this layer. Thus, the models of CS employing this approach [3-5] are valid in this range of parameters (the heating rate and metal particle size). From Fig.2 it is seen that for small-sized metal particles ($r_0 \leq 0.5$ μm) the quasi-equilibrium diffusion-controlled growth of the refractory product can occur at high heating rates typical of the SHS wave, $\sim 10^4$ - 10^5 K/s.

Domain II corresponds to a fast route typical of CS where the non-equilibrium dissolution-precipitation mechanism operates to provide fast completion of the reaction. Here, the refractory product layer formed during heating from T_0 to the melting point of the metallic reactant is thin ($h_{\text{TiC}} < h_{\text{cr}}$) and cannot keep the melt inside the particle. Thus, melting of the metal core inevitably results in rupture of the primary shell and the melt comes into direct contact with the solid non-metal particles, which is a necessary condition for the dissolution-precipitation interaction route to occur. In this parametric domain, the model [32,33] is applicable.

The diagram demonstrates the difference, in terms of reaction mechanisms, between CS (domain II), where fast conversion of reactants into the products takes place, and traditional furnace synthesis (domain I) where the product formation proceeds slowly.

Application to other systems

A diagram similar to Fig.2 can be built for non-isothermal interaction in other metal-solid nonmetal systems where the CS temperature exceeds the melting point of a metal but is below that of both the non-metallic reactant and the product. Besides, the developed approach can be applied to certain metal-gas systems to explain the experimentally observed changeover of reaction mechanisms.

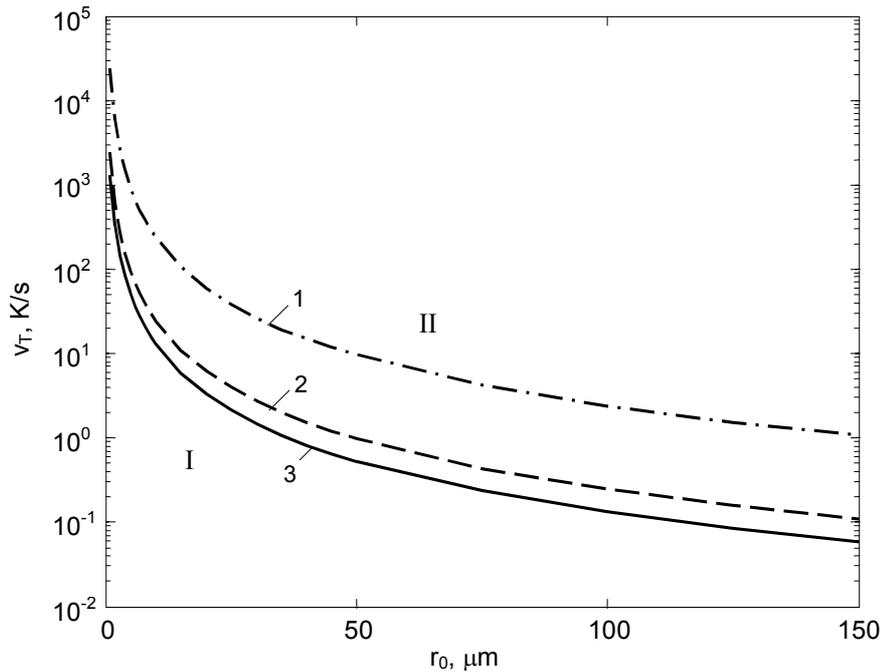


Figure 2. Diagram of interaction routes in the Ti-C system in non-isothermal conditions: I, quasi-equilibrium diffusion-controlled growth mechanism (a “slow” route, or diffusion annealing) and II, non-equilibrium dissolution-precipitation mechanism (a “fast” route typical of SHS); numbers at lines correspond to diffusion data sets in Table 1.

Earlier, a diagram of structure formation in the Ti-N system for CS in the WP mode was built taking into account the gas pressure and kinetics of nitrogen adsorption by solid titanium particles during gas flow through a porous pellet in the SHS wave front [43]. It gives a qualitative description to three experimentally observed phase formation routes: (i) solid-phase mechanism, i.e. diffusion of nitrogen into a solid titanium particle resulting in the growth of a TiN_x shell, (ii) solid-liquid phase interaction that includes rupture of the primary solid product (TiN_x), outflow of molten Ti and its interaction with gas, and (iii) liquid-phase pathway implying immediate contact of the liquid metal with nitrogen. However, the effect of heating rate in the SHS wave was not considered.

The author suggests that the approach developed in this work can be applied to the Ti-N system to build a diagram similar to that presented in Fig.2, which will permit specifying the transitions between these three mechanisms taking into account the heating rate. A combination of such a diagram with the previously published one [43] can be used for predicting the reaction route and hence microstructure of the synthesized product in the Ti-N system. However, this is a more complex problem in comparison with Eqs. (2)-(6) because the equilibrium Ti-N diagram is peritectic and contains three solid phases: $\beta\text{-Ti}$, $\alpha\text{-Ti}$ and TiN_x [44]; hence the phase layer growth via solid-state diffusion in the $\beta\text{-Ti}/\alpha\text{-Ti}/\text{TiN}_x/\text{N}_2$ system can be studied only by numerical simulation.

Besides, this approach permits interpreting the experimental results obtained by ETG in the Ti-N system [45,46]. When a titanium wire was heated in nitrogen from T_0 to a prescribed (reference) temperature $T_r < T_m(\text{Ti})$ with different heating rates v_T , at a certain v_T value ($\sim 10^5$ K/s) “outshooting” of temperature was observed due to a fast increase of the heat release rate associated with a chemical reaction. The results were explained within the classical theory of thermal explosion in terms of competition between the rates of self-heating and heat loss. The model of diffusion-controlled growth of the primary TiN layer in cylindrical symmetry was used to estimate the activation energy and preexponential factor by fitting the calculated and experimental data on the heat release rate; the following values were obtained: $Q=330$ kJ/mol, $D_0=4.8 \cdot 10^{-2}$ m²/s [45]. These parameters refer to

diffusion in phase TiN_x which is the rate-controlling stage of heat release. Then, according to Eq. (6), at reference temperature 1900 K the diffusion coefficient is: $D_{TiN}(T_r=1900\text{ K})=4.1\cdot 10^{-11}\text{ m}^2/\text{s}$. Comparing this value with available independent data on interdiffusion in titanium nitride (Table 2) clearly shows that it is overestimated by at least an order of magnitude: the upper value in Table 2 is $1.9\cdot 10^{-12}\text{ m}^2/\text{s}$. As outlined previously [31], formal fitting of the parameters appearing in the diffusion-controlled growth model to experimental data on SHS cannot give physically meaningful information about the reaction mechanism (unless it is unambiguously proved that this model is really valid for a given system in a particular range of temperature and heating rates).

Table 2. Interdiffusion parameters for TiN_x

Q, kJ/mol	$D_0, \text{m}^2/\text{s}$	$\Delta T, \text{K}$	$D_{TiN}(T_r=1900\text{ K}), \text{m}^2/\text{s}$	Ref.
276.14	$5.8\cdot 10^{-5}$	1473-1723	$1.5\cdot 10^{-12}$	[47]
376.6	$2.0\cdot 10^{-3}$	1623-1973	$8.9\cdot 10^{-14}$	[48]
218.4	$5.4\cdot 10^{-7}$	1173-1843	$5.3\cdot 10^{-13}$	[49]
304.59	$4.42\cdot 10^{-4}$	1573-1873	$1.9\cdot 10^{-12}$	[49]
286.60	$1.5\cdot 10^{-7}$	1573-1873	$2.0\cdot 10^{-15}$	[49]

In the author's view, the "overshooting" phenomenon is connected with melting of β -Ti inside the wire, local rupture of the outer TiN_x shell and direct interaction of the liquid metal with nitrogen resulting in fast crystallization of titanium nitride near the Ti/ N_2 interface, i.e. changeover of the reaction routes: from a slow, solid-state diffusion controlled mechanism to a fast one. This supposition is based on the following estimate: at $v_r=1.5\cdot 10^5\text{ K/s}$ and $T_r=1840\text{-}1900\text{ K}$, when the overshooting was observed, the heating time from T_r to $T_m(\text{Ti})=1940\text{ K}$ will be $\Delta t=0.7\text{-}0.3\text{ ms}$, correspondingly (Fig.2.b in [46]). This is smaller than the response time of the temperature controller used in experiments: 1 ms according to [45]. Hence, overheating of the wire could well take place resulting in melting of the titanium core and cracking of the primary TiN_x layer. This is supported by the presence of cracks on the wire surface in the overshooting mode (Fig.8.b in [45]).

Conclusion

The changeover of reaction routes plays an important role in non-isothermal interaction in "melting metal-solid nonmetal" or "metal-gas" systems, especially in the SHS of advanced materials where only the non-equilibrium dissolution-precipitation pathway provides fast accomplishment of heterogeneous reactions within the experimentally observed time ($\leq 1\text{ s}$). The criterion and diagram obtained in this work can be used for predicting the phase formation mechanism in the Ti-C system in substantially non-isothermal conditions, which determines the structure and hence properties of the target product. Also, the developed approach can be applied to other binary and multicomponent systems where the CS temperature or a maximal attained temperature at fast heating exceeds the melting point of a metallic reactant but is below that of a non-metal and product.

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