

Brief Review of Kinetic Regularities of Ti_xC_y -Ti Composites Synthesis

A.G. Knyazeva^{1,2} and E.N. Korosteleva^{1,2}

¹Institute of Strength Physics and Materials Science, Akademicheskii pr., 2/4, Tomsk, 634055, Russia

²Tomsk Polytechnic University, Lenin Av., 30, Tomsk, 634050, Russia

Received: July 07, 2020

Abstract. The main approaches to the synthesis of titanium carbide-based composites used in numerous studies during the last five decades are reviewed in order to generalize and analyze the correctness of phenomenological ideas to explain the physical processes that can occur during the interaction of titanium and carbon. The main theoretical approaches to the modeling of the synthesis process developed mainly in the field of combustion and explosion are described. These are models of solid-phase combustion, models with separation of reaction cells, and models of mechanics of heterogeneous media. Both advantages and disadvantages of the used approaches and models are analyzed, indicating those essential parameters which should be taken into account for a more adequate interpretation of the synthesis results. None of the known approaches can be used to predict the phase composition and structure when the synthesis conditions change.

1. INTRODUCTION

Titanium carbide and composites containing it as strengthening particles find wide application in industry [1-6]. This is due to the fact that titanium carbide TiC, along with HfC, ZrC, and WC has a high melting point and high wear resistance as well as thermal stability. Since the preferential properties of carbides are realized only in multiphase composites, the problems of carbide formation directly (in situ) in complex heterogeneous systems remain relevant.

Methods of titanium carbide synthesis have been known for a long time [3], are very diverse and are regularly developing [6-14]. In the generalized case several types of titanium carbide synthesis can be distinguished. One of them is based on chemical reactions of reduction in gas medium or dissolution-deposition in melts [3,9, 12-20].

In particular, a well known method of producing titanium carbide powders by reduction of TiO_2 under thermochemical reaction conditions [15], where the total reaction can be presented as



In practice, carburization of titanium oxide is carried out at high temperature ~ 2000 °C, which can be referred to a significant disadvantage of this method.

The mechanism of formation of single crystals of titanium carbide by dissolution of Ti and C in liquid calcium and subsequent crystallization of TiC particles from the melt is a modification of the solution method of producing single crystals of carbides of transition metals, conducted in melts of magnesium, aluminum, iron, cobalt and nickel [20]. The group of thermochemical methods also includes obtaining titanium carbide by sol-gel method [16-19], but such processes are complicated and multistage [19]. Among the variety of used chemical compounds of titanium, titanium tetrachloride and its hydride are widely used as precursors for carbide production besides titanium oxides. For example, a two-step method of titanium carbide production from aluminum subchloride, titanium tetrachloride and carbon is known [21], magnesothermic reactions of

Corresponding author: A.G. Knyazeva, e-mail: anna-knyazeva@mail.ru

titanium carbide synthesis involving titanium dioxide are also used [22-24].

Another group of methods for producing titanium carbide is based on classical metallurgical processes of powder technologies. This group includes traditional technologies of sintering of pure titanium and carbon components, high-temperature synthesis under conditions of combustion and thermal explosion, using hybrid (combined) technologies of thermal force and electrophysical effects (hot isostatic pressing, radiant heating, electrospark sintering, high frequency current heating, etc.) [25-42]. In most cases of using methods of this group, the standard reaction is realized:



But using pure titanium as a feedstock is not always economically feasible.

A special direction was the development of technologies for obtaining titanium carbide using DC arc discharge plasma [42]. But a common disadvantage of plasma chemical methods is the complexity of the hardware design and high expenditure of electrical energy required to maintain chemical transformations in the plasma, as well as the use of hydrogen [43-47].

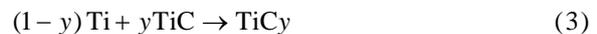
The continuing interest to titanium carbides is also due to a number of its structural features that have been discovered and investigated recently. In particular, materials based on non-stoichiometric titanium carbide (species $\text{Ti}_3\text{C}_2\text{T}_x$), which have an extremely high melting point (up to 3260 °C), high hardness, high electrical conductivity, and excellent chemical and thermal stability, are of considerable interest [48-53]. They are two-dimensional inorganic compounds consisting of layers of several carbide molecules. Each layer is coated with negatively charged atoms such as oxygen, nitrogen or fluorine. Solid-phase processes are used to produce titanium carbide in this form, in which the reaction occurs between metals (or metal oxides) and elemental carbon at high temperatures of 1500 to 2300 K. The high temperature of the solid-phase reaction accelerates the diffusion of carbon into the metal oxide or metal, which accelerates the reaction, controlled by diffusion. Nanoscale structures based on titanium carbide [4,51,52] have great potential in the production of lightweight materials and can be used for microwave absorption, electromagnetic shielding, and energy conversion and in the field of chemical catalysis. Composites containing titanium carbide and two-dimensional structures based on it are of interest from the point of view of applicability in mechanical engineering and aerospace industry, as well as in 3D-technologies [48,51-52].

The purpose of the brief review is to analyze the available ideas about the kinetics of formation of com-

posites based on titanium carbide in self-supported modes and the applicability of the available theoretical approaches to predicting the appearance of nonequilibrium phases and the choice of synthesis modes of composites.

2. EXPERIMENTAL STUDY

Since the Ti-C system has been studied for quite a long time, a wealth of experimental material has been accumulated that describes not only the physical and chemical criteria for obtaining carbides in a wide range of their homogeneity, but also the structural-phase state features of a large set of non-stoichiometric carbides. If we consider the classical methods of powder metallurgy [29,35-39,54] of obtaining a Ti-TiC metal matrix composite, the procedure is reduced to milling, mixing and subsequent heat treatment, possibly in combination with extrusion at 900 °C. The authors [54] distinguish different stages, whose kinetics include dissolution of the smallest particles, saturation of the matrix with carbon, change in stoichiometry of TiC carbide from the initial composition of $\text{TiC}_{0.96}$ to the equilibrium composition ($\text{TiC}_{0.57}$). The change in carbide composition causes an increase in both the total mass fraction of particles and their diameter. This, in turn, promotes contact between individual particles in the most reinforced areas and leads to an increase in the growth rate of the particles. The authors describe the change in particle composition by the reaction



and do not identify phases of the types Ti_2C , TiC_2 , Ti_3C_2 as independent structures in the carbide composition.

Another possible way to obtain composites based on titanium with inclusions of strengthening particles can be based on the methods of self-propagating high-temperature synthesis (SHS) [55-57] or combustion synthesis. Examples of combustion synthesis of composites of the TiC/Ti type, as well as with TiC inclusions in a matrix of complex composition can be found in [30,58]. However, due to the nonequilibrium nature of the synthesis process itself and the presence of a wide area of homogeneity in the Ti-C system state diagrams [19,59], it is impossible to predict the composition of the synthesis product based only on thermodynamic calculations, as evidenced by the data [30,60]. Therefore, the preparation of Ti_xC_y -Ti composites by combustion synthesis requires a relatively high excess of Ti, based on the use of elemental powders. However, since the excess titanium acts as a heat sink (plays the role of an inert filler) during the reaction, the mixture may not be capable to self-propagating combustion under these

conditions [30]. To overcome the limitations of thermodynamics and/or kinetics, several activation methods based on thermal [61], electrical [62], mechanical [63,64], and chemical [65,66] stimuli have been proposed in the literature. In particular, the use of chemical promoters to enhance the reactivity of different systems has been investigated in the SHS literature. For the case of carbide synthesis, it is shown that the most effective choice of active self-propagating reactions in low-exothermal systems, as well as for systems whose activation is complicated by the presence of passive films on the reagents, is the use of individual additives/promoters, for example, halogenide-bearing organic polymers, alkali metal halides and nitrates [66]. In [66], self-propagating high-temperature synthesis (SHS) of titanium carbide (TiC-Ti) composites from elemental powders in the presence of gas accelerants (i.e., Teflon) is studied. In particular, the dual role played by the polymer, i.e. as a reaction promoter and as a carburizing agent, was investigated. The polymer is directly involved in the carburizing process of titanium and leads to an increase in combustion temperature and rate. The authors showed that if the carbon to titanium ratio (C/Ti) is properly changed, Ti_xC_y -Ti composites containing Ti-metal in the range of 0-25 wt.% can be prepared. As a rule, the kinetics and mechanism of phase formation are not discussed in detail in such studies.

In general, as a model system for self-propagating high-temperature synthesis (SHS), the Ti/C system has been and remains the subject of numerous studies [67-80]. Practically the first work where the titanium-carbon system is considered as gas-free was [70]. Scientific publications contain data both on the solid-phase mechanism of synthesis in this SHS system and on the mechanism in which capillary spreading plays a significant role [71,81-84]. Thus, it was shown in [81] that the combustion of mixtures of titanium and soot involves capillary spreading of the metal in the pores that are formed between refractory particles. Formed titanium carbide inhibits further reaction. The products have areas with a deficiency of one component and an excess of the other, because the finite rate of spreading only partially improves the mixing of the components. The smaller the particle size, the smaller the effect of capillary spreading [82]. The authors [71] suggest that the interaction of titanium with carbon in the combustion wave may be accompanied by the formation of a carbide phase of variable composition and carbon solution in liquid titanium. Comparing the results for mixtures of stoichiometric and nonstoichiometric compositions (calculated to form TiC_1 and $TiC_{0.5}$), the authors concluded that in the first case the leading stage is the carbidization of titanium, while in the second one the dissolution stage

of carbon in titanium with lower activation energy. The study of the explosion of mixtures of Ti and Zr with graphite under controlled conditions of electric current heating [85] also leads to the conclusion about the leading role of liquid-phase processes, namely the process of spreading of liquid metal through the pores of the soot coating. In the monograph [56], a detailed analysis of transport and spreading mechanisms within the reaction cell also states that the process of melt spreading in the combustion wave is accompanied by a heterogeneous chemical reaction of solid product formation, and these processes are intrinsically connected with each other.

As noted by the authors [86], when initiated by a laser with a wavelength of 1.06 μm , a liquid melt bath is formed first in such systems, and only then the reactions start. The transition from the solid-phase mechanism (whose rate is limited by diffusion through the solid product layer) to the liquid-phase mechanism (diffusion during dissolution of carbon in liquid titanium is determinative) is possible both with changes in the ratio of initial components, particle sizes, and during combustion. In [87], the difficulties in identifying the stages of product formation in the SHS wave, related to the fundamental features of reactions involving solids, are discussed. Based on the analysis of synchrotron radiation data, the authors believe that the leading stage is the formation of primary products in the refractory reagent layer, and that spreading cannot be directly observed. In [88], high-speed filming revealed the intensification of the process due to the release of residual gases in the synthesis wave and established that the reaction region consists of hot spots localized near the fusible reagent particles. The formation of spots is associated by the authors with the phenomenon of capillary spreading in the heating zone.

The concentration distribution in the combustion wave of the Ti-C system was studied in [89]. The beginning of a wide reaction zone on the basis of microscopic studies is selected the place where melting and spreading of titanium particles is observed. Increasing the size of the particles leads to more incomplete transformation and expansion of the reaction zone. In general, under nonequilibrium conditions, which take place in the SHS wave, synthesis can be accompanied by the formation of Ti_2C , Ti_3C_2 , etc. phases that are absent in the equilibrium state diagram [59,90,91]. However, detailed studies [92,93] suggest that there is a possibility of stabilization of nonequilibrium phases. In [94,95] it is emphasized that in the phase diagram in the range of TiC carbide there are still phases Ti_6C_5 , Ti_3C_2 , and Ti_2C , which can be synthesized experimentally. And first-principles calculations indicate that the Ti_2C , Ti_3C_2 , Ti_4C_3 , Ti_5C_4 , and

Table 1. Phase composition in SHS products for different initial compositions, lattice parameter a for titanium carbide TiC_x and the value of the stoichiometric coefficient X calculated from the lattice parameter..

Calculated phase composition	Determined phase composition, vol.%		Lattice parameter a , nm	Stoichiometric coefficient X , [99]
	TiC_x	Ti		
TiC+30 vol.%Ti	100	-	0.4320	0.69
TiC+40 vol.%Ti	95.5	4.5	0.4310	0.58
TiC+50 vol.%Ti	93.5	6.5	0.4302	0.50
TiC+60 vol.%Ti	75.4	24.6	0.4299	<0.50

Ti_6C_5 phases are stable at high pressures. The presence of these phases in the synthesis products, along with TiC, is often identified as non-stoichiometric titanium carbide TC_x [96,97] with a noticeable deviation from the equiatomic compound (Table 1).

Interest in the Ti-C system in recent years is associated with the possibility of obtaining ordered structures like Ti_2C in mixtures Ti-0.5C, with the possibility of accelerating reactions in granular mixtures and obtaining titanium carbonitride during combustion in a downflow of gas [98,99]. In contrast to powder systems, in which convective transport associated with the melt flow of a fusible component under the action of capillary forces and gas pressure plays a major role [100,101], no melt layer is formed during combustion of pellet mixtures. In general, assumptions about the possibility of the synthesis of nonequilibrium phases in the combustion wave have been suggested in the literature for a long time [56, 102] and references in [56] to earlier publications, but convincing experimental evidence has not yet been obtained. The situation has not been significantly clarified in [103] either.

3. THEORETICAL CONCEPTS

In spite of the fact that there are quite a lot of methods of titanium carbide synthesis and modifications of the methods appear every year, only in the field of combustion and explosion along with active experimental studies of the mechanism of product formation in this system, a big role is given to mathematical modeling. However, even here there is still no unified point of view on the need to take into account in the models those or other physical phenomena.

Classical thermal models [104-106], which have wandered from one review or monograph to another, are based on the assumption of a narrow chemical reaction zone and a thermal reaction mechanism. The simplest stationary model involves the heat conduction equation written in the coordinate system associated with the combustion front moving with velocity U_b (which must be found in the course of solving the problem).

$$\frac{d}{dx} \left(\lambda \frac{dT}{dx} \right) - U_b c_p \rho \frac{dT}{dx} + \Phi = 0. \quad (4)$$

The conditions correspond to the fact that the reagents are on the left and the reaction products are on the right:

$$x \rightarrow -\infty : T = T_0; \quad x \rightarrow +\infty : T = T_b, \quad (5)$$

where

$$T_b = T_{ad} = T_0 + \frac{Q}{c_p \rho} \quad (6)$$

adiabatic combustion temperature. It is assumed that the rate of the chemical reaction depends on the temperature according to the Arrhenius law

$$\Phi = QW(T) = Qk_0 \exp\left(-\frac{E_a}{RT}\right).$$

When taking into account the level of completeness of the reaction, the kinetics equation, also written in the coordinate system associated with the front,

$$U_b \frac{d\eta}{dx} = k_0 W(T) \varphi(\eta), \quad (7)$$

and additional conditions

$$x \rightarrow -\infty : \eta = 0; \quad x \rightarrow +\infty : \eta = 1. \quad (8)$$

are added to (4).

The function Φ also changes:

$$\Phi = Q\varphi(\eta)W(T) = Qk_0 \varphi(\eta) \exp\left(-\frac{E_a}{RT}\right).$$

Analytical estimates of the front velocity based on the stationary model have been made by various authors [106-109]. For

$$\varphi(\eta) = (1 - \eta)^n,$$

the approximate estimate has the form

$$U_b^2 = \sigma_n \frac{\lambda}{Q} \cdot \frac{RT_b^2}{E_a} k_0 \left(-\frac{E_a}{RT_b} \right), \quad (9)$$

where

$$\sigma_n = 2 \left[\Gamma \left(\frac{n}{2} + 1 \right) \right]^{(1-\frac{n}{2})} \left(\frac{n}{2e} \right)^{\frac{n^2}{4}},$$

where

$$\Gamma(z) = \int_0^{\infty} e^{-t} t^{(z-1)} dt$$

is the Gamma function.

In [110], the gasless combustion mechanism was studied using the $Al+Fe_2O_3$ thermite system as an example. The stoichiometric mixture was diluted with the final product. In this case, the calculated combustion temperature (2450 K) was lower than the boiling point of the most volatile component, and the gas phase was not formed. Analysis of the temperature dependence of the combustion rate showed that the leading reaction proceeds at temperatures close to the maximum. In this case, diffusion is not the limiting stage, and the combustion process is described by the simplest thermal theory. The Ti-C system also satisfies the combustion conditions for the gas-free compositions, as suggested by [70]. However, in contrast to the thermite mixture, where the reaction is predominantly in the liquid phase, only titanium melts in the mixture of titanium powders with carbon. In direct contact with carbon, titanium carbide is formed, which can become a barrier to the further course of the reaction. This leads to the need to consider the stages of the physical-chemical process associated with diffusion through the reaction product layer.

In [111], the expansion of the reaction zone under stratified combustion conditions is associated with the braking of the reaction by the refractory product layer, using the logarithmic law as an example. For systems with solid-phase products, the authors conventionally distinguish three zones in the combustion front: a heating zone, a spreading zone, where the reaction rate is high, and an afterburning zone. In general, finding the type of function is associated with great difficulties; the kinetic regularities for two limiting cases are most clear. (1) The melting temperature of the reactants is much lower than the combustion temperature, and the solubility in the liquid phase is unlimited. The rate of heat release for such processes is determined by the usual laws of kinetics of homogeneous liquid-phase reactions. (2) The reaction product and reactants (or at least one of the reactants) do not melt. Chemical interaction is carried out by diffusion of the reactants through the

layer of formed product, which separates the reactants and inhibits further course of the reaction. There is no complete mixing of the reactants, and the reaction is essentially heterogeneous. The type of the kinetic function in such systems is determined by the mechanism of reagent transfer and the structure of the growing layer of products [112]:

$$\varphi(\eta) = e^{-m\eta} \eta^{-p}, \quad (10)$$

where m and p are retardation parameters.

The influence of the type of the kinetic function on the characteristics of reaction initiation in gas-free compositions was studied in [113]. The author [114] reduces the role of changes in the interaction surface of the melt with a solid particle during the accumulation of a solid product to a change in the type of the kinetic function and further analyzes again the former problem (4), (5), (7), (8). Thermal explosion in a system with a parabolic interaction law [115,116] also has peculiarities in comparison with classical representations. However, such models have not been applied to the real conditions of bulk synthesis of titanium carbide.

Models of the form [117-119] can also be used to describe the synthesis of Ti-C mixtures with excess titanium if the excess titanium is considered as an inert diluent and the transformations of the form (3) leading to the formation of non-stoichiometric carbide are not taken into account.

Directly taking into account the slowest physical stage-the diffusion of a reactant through a refractory product layer-is associated with the appearance of combustion models with the isolation of the so-called reaction cell [72,120-123]. In formulating the problems, it is emphasized that, due to the low rates of mutual transport of reactants and products, the mixing stage is defining, which must be taken into account in the model in some form. In [120], a repeating element in a layered system with layers perpendicular to the surface is distinguished as a cell. It is assumed that a phase of variable composition is formed at the contact of the layers. Heat release in the reaction occurs when a new phase is formed. The authors find a parabolic law of new phase layer growth for a particular quasi-stationary regime. In [121], it is assumed that a heterogeneous material can be imagined as solid particles of one component uniformly distributed among the particles of the other component. In the heating zone, the particles of one kind melt first; the melt spreads evenly around the refractory particles. The product of the reaction is liquid. To determine the concentrations of reactants and product, a diffusion problem is solved in cells in a spherical coordinate system. Up to melting temperature both diffusion

and reaction are neglected. The total heat release in reactions is written in the form

$$\Phi = 4\pi N Q_i M_i \nu_i k_0 \exp\left(-\frac{E_a}{RT}\right) \int_0^{R_0} Y_1^{n_1} Y_2^{n_2} r^2 dr, \quad (11)$$

where N is the number of cells per unit volume of the mixture,

$$N = \left[\frac{4}{3}\pi R_0^3\right]^{-1},$$

$Q_i M_i \nu_i$ - are the heat release, molar mass and stoichiometric coefficient for each component Y_1, Y_2 ; it is assumed that $Q_1 M_1 \nu_1 = Q_2 M_2 \nu_2$; n_1, n_2 - are the orders of the reactions for each component. Based on the analysis of the model, the authors distinguish between kinetic and diffusion combustion modes.

In [123], the problem for the reaction cell is solved at each point of the macroscopic sample. In each element of the heterogeneous structure of the spherical shape of the SHS composition, the processes of diffusion and reaction of reagents occur at the temperature corresponding to the points of the macroscopic sample. There is no spatial distribution of temperature along the radius in the reaction cell. In each cell a diffusion problem is solved for two reactants Y_1 and Y_2 , which are spent to form one reaction product. The reactants are separated at the initial time and then a diffusion interface appears. The mutual diffusion coefficient and reaction rate in the cell depend on temperature according to Arrhenius law. The average over the volume of the cell the rate of chemical reaction is defined as:

$$W(T(x, t)) = \frac{1}{R_0} \int_0^{R_0} Y_1 Y_2 k_0 \exp\left(-\frac{E_a}{RT(x, t)}\right) r^2 dr.$$

Heat release $QW(x, t)$ depending on time and coordinate x and time t is used in the heat conduction equation, which is essentially little different from (11). The authors solve the nonstationary problem by setting the temperature at the boundary equal to the adiabatic combustion temperature; both stationary and oscillatory combustion modes are obtained. The models have not been applied to the analysis of specific systems.

In [69,82], when describing combustion in the Ta-C and Ti-C systems, a large metal particle of a given radius R_0 is located in the center of the reaction cell, which is surrounded by particles of a second smaller component with an effective radius r_{eff} . To take into account the phenomenon of capillary spreading in [82] the degree of filling S of the pores with the melt after reaching the melting temperature T_m by the fusible component is analyzed. It is assumed that the pore size decreases due

to the growth of the solid product layer, and the reaction cell size is determined by the number of fusible particles in the volume unit (12), where R_0 serves instead of R_{eff} . Then

$$S = \frac{l}{R_{eff} - R_0},$$

where l is the path travelled by the metal through the capillaries of the cell. Assuming that there is a reaction diffusion mechanism with coefficient $D(T)$, leading to a parabolic law of product layer growth, for the level of filling S the authors obtain the equation

$$U_b \frac{dS}{dx} = \frac{\sigma r_{eff} (1-Z)^{2k}}{4\mu (R_{eff} - R_0)^2 S},$$

where μ - is the viscosity; σ - is the surface tension coefficient, $Z = \delta/r_{eff}$ - is the relative thickness of the growing layer of the product,

$$U_b \frac{dZ}{dx} = \frac{SD(T)}{Z^4 r_{eff}^{n+1}}.$$

The boundary conditions are formulated by the authors at the melting point temperature $x=0$ and in the product region, where the final level of pore filling and $Z=1$ are given. The heat release function is given as

$$\Phi = \frac{4}{3}\pi N m (R_{eff}^3 - R_0^3) U_b Q \begin{cases} \frac{dS}{dx}, \varepsilon \ll 1; \\ \frac{dZ}{dx}, \varepsilon \gg 1, \end{cases}$$

where m is the porosity;

$$\varepsilon = \frac{\sigma r_{eff}^3}{2\mu (R_{eff} - R_0)^2 D(T)}$$

is the ratio of the spreading time to the reaction time.

As a result, it is possible to distinguish a kinetic regime, in which the combustion rate depends exponentially on the combustion temperatures and does not depend on the particle size, and a capillary regime with complete and incomplete transformation of reagents into reaction products.

The effect of reactions at the reagent interfaces was studied in [124] using a model heterogeneous system [120], consisting of ordered layers of initial reagents, at the boundary between which a single chemical compound is formed. The reaction cell included a repeating element. The reaction rates at the mobile interfaces were determined by Arrhenius law. The reactions led to an additional inhibition of the reaction front, which is as-

sumed to be an additional cause of incomplete transformation in SHS processes.

The diffusion problem for the reaction cell in [72] is formulated on the basis of the state diagram of the Ti-C system; the cell size is determined by the size of carbon particles and its content in the initial mixture; the formation of titanium carbide and carbon solution in titanium is taken into account. The authors believe that a spherical cell can be replaced by a flat one; two processes - dissolution of carbon in titanium and growth of carbide phase - occur simultaneously in the cell. The interaction starts after titanium melting. The problem for the reaction cell includes diffusion equations of the form:

$$U_b \frac{\partial C}{\partial x} = D_k(T) \frac{\partial^2 C}{\partial r^2},$$

$k = 1$ in the layer of titanium carbide, $r_1(x) \leq r \leq r_2(x)$; $k = 2$ in the solution of carbon in titanium, $r_2(x) \leq r \leq R_0$. In the automodel problem, the variable x plays the role of both time and coordinate. The initial state of the cell corresponds to the initial size of carbon particles, which are surrounded by titanium melt. The boundary conditions have the form:

$$\begin{aligned} r = r_1(x) : C = C_1; (1 - C_1)U_b \frac{dr_1}{dx} &= D_1(T) \frac{\partial C}{\partial r} \\ r = r_2(x) - 0 : r = r_2(x) - 0 : C = C_2; \\ r = r_2(x) + 0 : C = C_p; \\ (C_2 - C_p)U_b \frac{dr_2}{dx} &= -D_1(T) \frac{\partial C}{\partial r} \Big|_{r_2-0} + D_2(T) \frac{\partial C}{\partial r} \Big|_{r_2+0}; \\ r = R_0 : \frac{\partial C}{\partial r} &= 0. \end{aligned}$$

The heat release rate in (4) is determined by the fluxes of carbon deep into the carbide and into the liquid solution and has the form

$$\Phi = -Q_1 \rho U_b \frac{dr_1}{dx} + (Q_2 - Q_1) \rho U_b \frac{dr_2}{dx} \int_{r_2}^{R_0} C(r) dr, \quad (13)$$

where Q_1 and Q_2 - are the heat effects of carbide phases formation and carbon dissolution in liquids. The phase diagram lines corresponding to the existence of the carbide phase and solution are approximated by suitable dependences. Based on the model, the authors carried out a detailed study of the carbide formation modes and the structure of the combustion wave. The reaction zone, as a rule, turns out to be wide. It was found that stoichiometric carbide is formed during the interaction with excess carbon, and the excess carbon acts as an inert additive. The maximum combustion rate corresponds to

the stoichiometric composition, the lack of carbon leads to both a decrease in temperature and a decrease in the combustion rate. The results obtained are in agreement with the experiment. Similarly to [72], a combustion model for the Ti-C system was constructed based on the state diagram and data on the thermodynamic properties of individual substances, phases, and solutions in [125,126]. However, detailed consideration of the enthalpy balance as a function of temperature has not led to qualitatively new effects and does not add information on the reaction zone structure.

This approach has been used to model the combustion and explosion processes of other systems, including those with the formation of several phases [127-137]. A more complex microstructural model of the reaction cell is discussed in [138]. Structural variants of possible reaction cells for different systems are reflected in [56]. However, the vast majority of the variants are accompanied only by a general discussion.

Different variants of titanium carbide formation in the combustion wave based on diffusion-kinetic models are discussed in [139-142]. In [141], for example, the model of synthesis with isolation of a reaction cell of spherical geometry is considered for two scenarios: (1) growth of a solid carbide layer on the surface of solid (at $T < T_m(\text{Ti})$) or liquid (at $T > T_m(\text{Ti})$) titanium, and (2) growth of a solid titanium layer on a carbon particle if titanium melts and diffuses in the SHS wave due to rapid heating. The rate of product growth is controlled by diffusion through the solid carbide layer. For both scenarios, the Stefan problem is formulated and solved. The transition from one scenario to the other is actually done manually based on the solution of the macrolevel problem.

Peculiarities of structural transformations in a combustion wave [78,88,89] are also reflected in works [143-145] based on models of mechanics of heterogeneous media and including continuity and energy equations (in the form of thermal conductivity equations) for refractory and fusible components. The chemical reaction itself is described within the framework of the formal kinetic law. Within the stochastic model [146], the probability of transformation is introduced and perturbations are continuously generated, which makes it possible to transition from one transformation mode to another. This allows transient processes to be studied. A review of one- and two-dimensional discrete combustion models can be found in [147]. The authors of [148] also claim to describe the structural transformations in the combustion wave of the Ti-C system. However, the article does not contain the results of structural modeling.

None of the mentioned works can predict the specific phase composition of the products.

Table 2. Formally-kinetic parameters, data from [154].

No.	Reaction	z_{i0} [mole/(cm ³ s)]	E_a [Joule/mole] at melting temperature	Reaction heat Q^* [Joule/mole]
1	$Ti_2C \rightarrow Ti + TiC$	0.103×10^{16}	130400	63900
2	$Ti_3C_2 \rightarrow TiC + Ti_2C$	0.359×10^{15}	104235	163280
3	$Ti + C \rightarrow TiC$	0.157×10^{14}	66667	184100
4	$2Ti + C \rightarrow Ti_2C$	0.987×10^{11}	172401	120600
5	$TiC + Ti_2C \rightarrow Ti_3C$	0.120×10^{13}	104235	-163280
6	$Ti + TiC \rightarrow Ti_2C$	0.421×10^{12}	132845	-63900
7	$Ti + C + Ti_2C \rightarrow Ti_3C_2$	0.281×10^{12}	143766	20820
8	$Ti + 2C \rightarrow TiC_2$	0.732×10^{13}	53859	236070
9	$TiC_2 + Ti \rightarrow 2TiC$	0.204×10^{14}	58624	132930
10	$Ti_3C_2 \rightarrow Ti + 2C$	0.230×10^{16}	151852	-236070
11	$Ti_2C \rightarrow TiC + C$	0.268×10^{14}	51717	-51570
12	$Ti_3C_2 \rightarrow 2TiC + Ti$	1.775×10^{16}	209990	227580

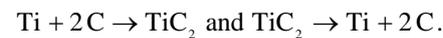
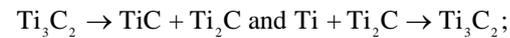
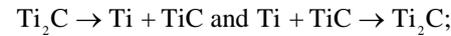
4. DETAILED SCHEMES OF CHEMICAL REACTIONS

In [149], a system of principally possible reactions in the Ti-C system is written down. The set of reactions is not complete. Based on known approaches using thermodynamic data, the same work gives an estimate of the formal-kinetic parameters. While the thermal effects of the reactions are quite expected, the activation energies and pre-exponents can be considered only as a first approximation corresponding to ideal conditions when the accompanying physical processes (wetting, diffusion, melting, and crystallization) have no effect on the kinetics, which, of course, cannot be realized. Therefore, such data (presented in Table 2) require correction based on comparison with experimental data. For example, considering that the rate of reactions involving solids can be controlled by diffusion, we must accept for solid-phase stages $E_a^* = (E_a + E_D)/2$, where E_D is the diffusion activation energy, or use the approach of [112] and introduce kinetic laws reflecting the reaction mechanism at the microlevel.

The purpose of [150] was to analyze the changes in the Ti-C system and to develop an algorithm for the numerical implementation of the kinetic models used for different variants of the kinetic schemes and different compositions of the initial mixtures at a given temperature corresponding to the initiation conditions. For the variants chosen in the paper, it was found that the most stable compounds under equilibrium synthesis conditions (at a given constant temperature) are two carbides, TiC and TiC_2 , which can be identified as Ti_xC_y . The final composition at long computation times for different given temperatures is different. Restriction of the synthesis time and synthesis under unsteady temperature condi-

tions can lead to a more complex composition. The conditions for obtaining a nonequilibrium composition (when the temperature changes) require a separate study.

Three groups of reversible reactions can be distinguished in Table 2, which in the full model for nonequilibrium synthesis conditions will play an important role in the formation of the final product composition. These are



As an example, let us consider a model of fusion in volume. We assume that the pressing is heated by thermal irradiation, homogeneously on all sides of the sample; the sintered sample is small compared to the thickness of the thermal boundary layer that can be formed during heating. Consequently, the heat balance equation is enough to describe the temperature dynamics:

$$Vc\rho \frac{dT}{dt} = VW_{ch} + \sigma\varepsilon S (T_w^4 - T^4),$$

where V – is the specimen volume; S – is area of its surface; σ – is Stephan-Boltzmann constant; ε – is the blachness level; T_w – is the temperature of vacuum chamber walls, changing with a which varies according to a given law.

Summary chemical heat release W_{ch} can be presented in the form

$$W_{ch} = \sum_{i=1}^n Q_i \varphi_i,$$

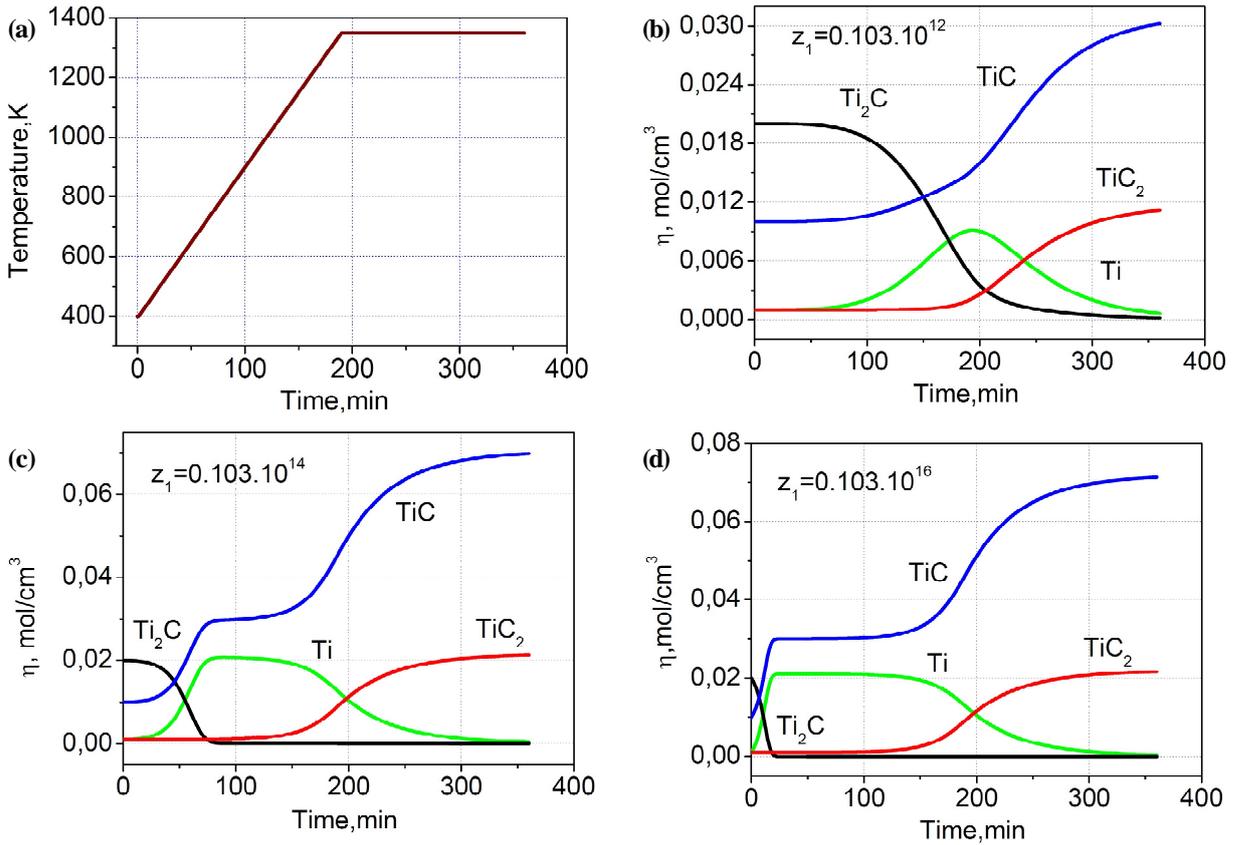


Fig. 1. Temperature (a) and phase concentration evolution (b,c,d) during the sintering.

where Q_i - is the heat of the i^{th} reaction, J/mol, ϕ_i - is the rate of i^{th} reaction; n - is the number of reactions.

The rates of chemical reactions depend on temperature according to the Arrhenius law, and on the concentrations of components according to the law of acting masses. To take into account the possible retardation of reactions by a layer of refractory products, we introduce retardation parameters, which in general are different for different reactions. Then, relations for reaction rates will take the form:

$$\phi_i = z_i(T) \prod_{\text{reagents}} y_k^{v_k} \exp(-m_i Y_i),$$

where v_{ki} - is the stoichiometric coefficient of k -component in i -reaction; Y_i and m_i - are refractory product concentration and retardation parameter for reaction i ;

$$z_i(T) = z_{i0} \exp\left(-\frac{E_i}{RT}\right),$$

$y_k = \rho_k/\rho_s$ are mass concentrations of components, $\rho_k = \eta_k M_k / z_{i0}$ - the pre-exponential factors;

$$\rho_s = \sum_{(i)} \rho_i;$$

η_k - are molar concentrations; M_k - are molar masses of components. The components are renumbered in the following order

(1) - Ti, (2) - C, (3) - TiC, (4) - Ti_2C , (5) - TiC_2 , (6) - Ti_3C_2 .

The balance equations for the components are as follows

$$\rho \frac{d y_k}{d t} = \omega_k,$$

where

$$\omega_k = M_k \sum_{i=1}^r v_{ki} \phi_i,$$

r - is reaction number.

The plasticizer removal stage and melting are not analyzed in the simplest model. The problem is solved numerically. Varying the heating conditions, the initial composition of the powder composition, the initial temperature, we obtain different product compositions. Since the method [149] gives estimates of pre-exponential factors for an ideal mixture (actually for mixing the reactants at the molecular or atomic level), a corrective multiplier, identical for all reactions, was introduced into the macromodel to account for non-ideality. This factor makes it possible to adjust the time of the sintering process in a numerical experiment with the data obtained in a laboratory experiment. In this case the qualitative characteristics of the process do not change. A change in the numerical values of the z_i constants leads to a change

in the proportions between the different phases both in the sintering process and at the end of the observation. However, in any case, the titanium present at the initial moment of time and the titanium appearing in the intermediate stages of the decomposition of nonequilibrium phases pass into carbide phases.

In the calculation, which is illustrated in Fig. 1, it was assumed that the reaction mixture has an initial temperature of 400 K. Initial composition of the specimen, mol/cm³: $\eta_{10}=0.001$; $\eta_{20}=0.0001$; $\eta_{30}=0.01$; $\eta_{40}=0.02$; $\eta_{50}=0.001$; $\eta_{60}=0.045$.

The dynamics of the temperature T_w is shown in Fig. 1a. After the heating stage, the sintering stage begins at a given temperature. The main changes in the composition (decomposition of Ti₂C with release of titanium) are observed even during the heating stage. During the isothermal stage a slow accumulation of TiC₂ and TiC carbides occurs. At a given set of parameters, the concentration of Ti₃C₂ practically does not change; reactions 1, 3, 6, 8, 9 make the main contribution to the dynamics of the process. The role of the inverse reaction (1) can be clearly seen in Figs. 1b, 1c, and 1d. of the reactive sintering product, which correspond to different values of z_1 . The larger z_1 , the faster Ti₂C disappears, the earlier the concentration of free titanium increases and the larger share of the reaction products is occupied by TiC₂.

Additional studies are required to clarify the kinetic parameters.

5. CONCLUSION

A selective review of the currently known scientific publications considering the kinetic regularities of synthesis of titanium carbide and Ti_xC_y-Ti composites on the basis of experimental data, theoretical approaches, and proposed models allows us to draw the following conclusions:

- (1) The approach to modeling the synthesis of composites by combustion with separation of reaction cells can be considered as a simplified understanding of multilevel modeling. However, this approach should be modified by applying a rigorous mathematical justification for the transitions between the levels of description. Intervening in the process by replacing some cells with others when given conditions are met is, generally speaking, not justified in most cases because it pre-determines the path of the process.
- (2) The phase field method could find its application in model building on micro level. But for real systems this approach is not yet applicable due to the lack of the necessary thermodynamic data.
- (3) An approach based on the mechanics of heterogeneous media would be promising. However, the model [151] has not been continued, and publications [152-

154] and others do not pay attention to the kinetics of chemical reactions. So, research in this area is far from being completed.

Thus, in spite of numerous publications covering the problems of synthesis by combustion of composites of system Ti - C, a number of questions remain unanswered, associated with an adequate interpretation of the whole complex of physical and chemical phenomena occurring during the realization of this process.

ACKNOWLEDGEMENTS

This work was supported by the Russian Science Foundation, grant № 17-19-01425-II.

REFERENCES

- [1] Sefiu Abolaji Rasaki, Bingxue Zhang, Kousika Anbalgam, Tiju Thomas and Minghui Yang, *Synthesis and application of nano-structured metal nitrides and carbides: A review*, Progress in Solid State Chemistry, 2018, vol. 50, pp. 1–15. <https://doi.org/10.1016/j.progsolidstchem.2018.05.001>
- [2] W. Lengauer, *Transition metal carbides, nitrides, and carbonitrides*, In: *Handbook of ceramic hard materials* ed. by R. Riedel (Weinheim: Wiley-VCH Verlag GmbH, 2000), pp. 238–241.
- [3] S.S. Kiparisov, Yu. V. Levinsky and A.P. Petrov, *Titanium carbide (production, properties, application)* (M.: Metallurgiya, 1987), In Russian.
- [4] B.-X. Dong, F. Qiu, Q. Li, S.-L. Shu, H.-Y. Yang, Q.-C. Jiang, *The Synthesis, Structure, Morphology Characterizations and Evolution Mechanisms of Nanosized Titanium Carbides and Their Further Applications (Review)*, *Nanomaterials*, 2019, vol. 9 no. 8, art. <https://doi.org/10.3390/nano9081152>
- [5] H.O. Pierson, *Handbook of Refractory Carbides* (Noyes Publication, Estwood, New Jersey, USA, 1996).
- [6] C.J. Quinn and D.L. Kohlstedt, *Reactive processing of titanium carbide with titanium. Part I Liquid-phase sintering*, *Journal of Materials Science*, 1984, vol. 19, pp. 1229-1241. <https://doi.org/10.1007/BF01120033>
- [7] I.L. Shabalin, M.V. Luñhka and L.I. Shabalin, *Vacuum SHS in systems with group IV transition metals for production of ceramic compositions*, *Physics and Chemistry of Solid State*, 2007, vol. 8, no. 1, pp. 159-175. <http://page.if.ua/uploads/pcss/vol8/0801-23.pdf>
- [8] S.P. Bogdanov, *Synthesis of titanium carbide in the presence of iodine*, *Novye Ogneupory*, 2015,

- vol. 10, pp. 57-62, In Russian. <https://newogneup.elpub.ru/jour/article/view/151/153>
- [9] A.V. Kasimtsev and V.V. Zhigunov, *The mechanism and kinetics of producing single-crystal powders of titanium carbide via a hydride-calcium method*, Russian Journal of Non-Ferrous Metals, 2008, vol. 49, pp. 471-477. <https://doi.org/10.3103/S1067821208060072>
- [10] Yu.L. Krutsky, E.A. Lozhkina, E.A. Maksimovsky, I.A. Balagansky, M.V. Popov, O.V. Netskin, A.G. Tyurin and T.S. Kvashina, *Application of nanofibrous carbon for obtaining finely dispersed titanium carbide*, Science Bulletin of the Novosibirsk State Technical University, 2017, vol. 64, no. 4, pp. 179-191. <https://doi.org/10.17212/1814-1196-2017-4-179-191>
- [11] S. Dyjak, M. Norek, M. Polański, S. Cudziło and J. Bystrzycki, *A simple method of synthesis and surface purification of titanium carbide powder*, Int. Journal of Refractory Metals and Hard Materials, 2013, vol. 38, pp. 87-91. <https://doi.org/10.1016/j.ijrmhm.2013.01.004>
- [12] H. Shin and J.-H. Eun, *Titanium Carbide Nanocrystals Synthesized from a Metatitanic Acid-Sucrose Precursor via a Carbothermal Reduction*, Journal of Nanomaterials, 2015, vol. 2015, Article ID 469121-11. <http://dx.doi.org/10.1155/2015/469121>
- [13] Y.-J. Kim, H. Chung and S.-J.L. Kang, *In situ formation of titanium carbide in titanium powder compacts by gas-solid reaction*, Composites Part A Applied Science and Manufacturing, 2001, vol 32, no. 5 pp. 731-738. [https://doi.org/10.1016/S1359-835X\(99\)00092-5](https://doi.org/10.1016/S1359-835X(99)00092-5)
- [14] C. Zhang, Z. Guo, F. Yang, H. Wang, Y. Shao and B. Lu, *In situ formation of low interstitials Ti-TiC composites by gas-solid reaction*, Journal of Alloys and Compounds, 2018, vol. 769, pp. 37-44. <https://doi.org/10.1016/j.jallcom.2018.07.344>
- [15] R. Koc and J.S. Folmer, *Carbothermal synthesis of titanium carbide using ultrafine titanium powders*, Journal of materials science, 1997, vol. 32, pp. 3101-3111. <https://doi.org/10.1023/A:1018634214088>
- [16] Y. Leconte, H. Maskrot, L. Combemale, N. Herlin-Boime and C. Reynaud, *Application of the laser pyrolysis to the synthesis of SiC, TiC and ZrC pre-ceramics nanopowders*, Journal of Analytical and Applied Pyrolysis, 2007, vol. 79, no. 1-2, pp. 465-470. <https://doi.org/10.1016/j.jaap.2006.11.009>
- [17] H. Lin, B. Tao, J. Xiong and Q. Li, *Using a cobalt activator to synthesize titanium carbide nanopowders*, International Journal of Refractory Metals & Hard Materials, 2013, vol. 41, pp. 363-365. <https://dx.doi.org/10.1016/j.ijrmhm.2013.05.010>
- [18] V. Raman, S.R. Dhakate and P.D. Sahare, *Synthesis of titanium carbide whiskers (TiCW) through sol-gel process from rayon fibers*, Journal of materials science letters, 2000, vol. 19, pp. 1897-1898. <https://doi.org/10.1023/A:1006782526946>
- [19] *Properties, production, and application of refractory compounds: reference book*, ed. by T.Ya. Kosolapova (Moscow, Metallurgiya, 1986), In Russian.
- [20] V.E. Popov and V.N. Gurin, *Carbides and alloys based on them* (Kiev, Naukova Dumka, 1976), In Russian.
- [21] R.A. Zakirov and O.G. Parfenov, *A Method of Titanium Carbide Production*, Patent Ru 2495826, 27.05.2012. <http://www.freepatent.ru/images/patents/493/2495826/patent-2495826.pdf>
- [22] H.I. Won, H. Nersisyan, C.W. Won and H.H. Lee, *Simple synthesis of nano-sized refractory metal carbides by combustion process*, Journal of Materials Science, 2011, vol. 46, pp. 6000-6006. <https://doi.org/10.1007/s10853-011-5562-0>
- [23] R. Ebrahimi-Kahrizangi, M. Alimardani and O. Torabi, *Investigation on mechanochemical behavior of the TiO₂-Mg-C system reactive mixtures in the synthesis of titanium carbide*, International Journal of Refractory Metals and Hard Materials, 2015, vol. 52, pp. 90-97. <https://doi.org/10.1016/j.ijrmhm.2015.05.008>
- [24] S.V. Aleksandrovsky, D.V. Li and V.M. Sizyakov, *Production of titanium carbide nanopowders by magnesium-thermic reduction of chloride mixture*, Russian Journal of Non-Ferrous Metals, 2004, vol. 5, pp. 60-65.
- [25] V.A. Drozdenko et al., *A Method for Titanium Carbide Production and the Installation for it*, Patent RU 2038296, 27.06.1995. <http://www.freepatent.ru/patents/2038296>
- [26] A.G. Merzhanov et al., *A Method for Titanium Carbide Production*, Patent RU 1570225, 20.10.2003. <https://patentimages.storage.googleapis.com/76/4c/95/de2542e606b2ee/RU2495826C1.pdf>
- [27] S.V. Alexandrovsky et al., *A Method for Titanium Carbide Production*, Patent RU 2066700, 20.09.1996. <http://www.freepatent.ru/patents/2066700>
- [28] S.V. Alexandrovsky et al., *A Method for Titanium Carbide Production*, Patent RU 2175988, 27/04/2000. <http://www.freepatent.ru/patents/2175988>

- [29] B. Winkler, E.A. Juarez-Arellano, A. Friedrich, L. Bayarjargal, J. Yan and S.M Clark, *Reaction of titanium with carbon in a laser heated diamond anvil cell and reevaluation of a proposed pressure-induced structural phase transition of TiC*, Journal of Alloys and Compounds, 2009, vol. 478, no. 1-2, pp. 392-397. <https://doi.org/10.1016/j.jallcom.2008.11.020>
- [30] M. Kobashi, D. Ichioka and N. Kanetake, *Combustion Synthesis of Porous TiC/Ti Composite by a Self-Propagating Mode*, Materials, 2010, vol. 3, vol. 7, pp. 3939-3947. <https://doi.org/10.3390/ma3073939>
- [31] E. Ghasali, M.S. Ali Nezhad and S. Ghazvinian, *Preparation of Ti-based laminated composites through spark plasma sintering with different carbon sources as the bonding layer*, Ceramics International, 2019, vol. 45, no. 11, pp. 14045-14057. <https://doi.org/10.1016/j.ceramint.2019.04.104>
- [32] K. Vasanthakumar, S. Ghosh, N.T.B.N. Koundinya, S. Ramaprabhu and S.R. Bakshi, *Synthesis and mechanical properties of TiC_x and Ti(C,N) reinforced Titanium matrix in situ composites by reactive spark plasma sintering*, Materials Science and Engineering: A, 2019, vol. 759, pp. 30-39. <https://doi.org/10.1016/j.msea.2019.05.021>
- [33] W.H. Lee, J.G. Seong, Y.H. Yoon, C.H. Jeong, C.J. Van Tyne, H.G. Lee and S.Y. Chang, *Synthesis of TiC reinforced Ti matrix composites by spark plasma sintering and electric discharge sintering: A comparative assessment of microstructural and mechanical properties*, Ceramics International Part A, 2019, vol. 45, no. 7, pp. 8108-8114. <https://doi.org/10.1016/j.ceramint.2019.01.062>
- [34] Y. Tan, L. Xu, Z. Xu, T. Ali, Z. Ma, X. Cheng and H. Cai, *Effects of Ti foil thickness on microstructures and mechanical properties of in situ synthesized micro-laminated TiC/Ti composites*, Materials Science and Engineering: A, 2019, vol. 767, art. 138296. <https://doi.org/10.1016/j.msea.2019.138296>
- [35] L. Liu, B. Wang, X. Li, Q. He, L. Xu, X. Cao, C. Meng, W. Zhu and Y. Wang, *Liquid phase assisted high pressure sintering of dense TiCnanoceramics*, Ceramics International, 2018, vol. 44, no. 15, pp. 17972-17977. <https://doi.org/10.1016/j.ceramint.2018.06.274>
- [36] F. Sun, L. Huang, R. Zhang, S. Wang, S. Jiang, Y. Sun, Q. An, Y. Jiao and L. Geng, *In-situ synthesis and superhigh modulus of network structured TiC/Ti composites based on diamond-Ti system*, Journal of Alloys and Compounds, 2020, vol. 834, art. 155248. <https://doi.org/10.1016/j.jallcom.2020.155248>
- [37] P.J. Teja, S.R. Shial, D. Chaira and M. Masanta, *Development and characterization of Ti-TiC composites by powder metallurgy route using recycled machined Ti chips*, Materials Today: Proceedings, 2020, vol. 26, Part 2, pp. 3292-3296. <https://doi.org/10.1016/j.matpr.2020.02.467>
- [38] X. Zhang, F. Song, Z. Wei, W. Yang and Z. Dai, *Microstructural and mechanical characterization of in-situ TiC/Ti titanium matrix composites fabricated by graphene/Ti sintering reaction*, Materials Science and Engineering: A, 2017, vol. 705, pp. 153-159; <https://doi.org/10.1016/j.msea.2017.08.079>
- [39] C. Yu, P. Cao and M. I. Jones, *Titanium Powder Sintering in a Graphite Furnace and Mechanical Properties of Sintered Parts*, Metals, 2017, vol. 7, no. 2, art. 67. <https://doi.org/10.3390/met7020067>
- [40] H. Abderrazak, F. Schoenstein, M. Abdellaoui and N. Jouini, *Spark plasma sintering consolidation of nanostructured TiC prepared by mechanical alloying*, International Journal of Refractory Metals and Hard Materials, 2011, vol. 29, no. 2, pp. 170-176. <https://doi.org/10.1016/j.ijrmhm.2010.10.003>
- [41] M.B. Rahaei, R. Yazdanirad, A. Kazemzadeh and T. Ebadzadeh, *Mechanochemical synthesis of nanoTiC powder by mechanical milling of titanium and graphite powders*, Powder Technology, 2012, vol. 217, pp. 369-376. <https://doi.org/10.1016/j.powtec.2011.10.050>
- [42] A. Ya. Pak, T. Yu. Yakich, G. Ya. Mamontov, M. A. Rudmin & Yu. Z. Vasil'eva, *Obtaining Titanium Carbide in an Atmospheric Electric Discharge Plasma*, Tech. Phys, 2020, vol. 65, pp. 771-776. <https://doi.org/10.1134/S1063784220050205>
- [43] E. Neuenschwander, *Herstellung und charakterisierung von ultrafeinen Karbiden, Nitriden und Metallen*, Journal of the Less-Common Metals, 1966, vol. 11, no. 5, pp. 365-375. [https://doi.org/10.1016/0022-5088\(66\)90069-5](https://doi.org/10.1016/0022-5088(66)90069-5)
- [44] S.A. Panfilov, V.F. Rezvykh and Yu.V. Tsvetkov, *Influence of geometrical and consumed parameters on the TiC plasma-chemical synthesis process for titanium tetrachloride reprocessing*, Fizika i chimiya obrabotki materialov, 1979, vol. 2, pp. 21-27, In Russian.
- [45] V.F. Rezvykh, S.A. Panfilov and V.V. Khaidaro, *Influence of feedstock input conditions on titanium carbide synthesis process*, (in Russian), Fizika i chimiya obrabotki materialov, 1983, vol. 2, pp. 58-61, In Russian.

- [46] A.T. Ibragimov, R.I. Kalmazov and Yu.V. Tsvetkov, *Physical and chemical properties of highly dispersed titanium carbide*, Fizika i chimiya obrabotki materialov, 1985, vol.5, pp. 84-89, In Russian.
- [47] V.A. Dostovalov et al., An Approach to form a TiC-based wear-resistant coating, Patent RU 2424352, 23.03.2009, <http://www.freepatent.ru/patents/2424352>
- [48] J. Theerthagiri, G. Durai, K. Karuppasamy, P. Arunachalam, V. Elakkiyad, P. Kuppasami, T. Maiyalagan and H.-S.Kim, *Recent advances in 2-D nanostructured metal nitrides, carbides, and phosphides electrodes for electrochemical supercapacitors – A brief review*, Journal of Industrial and Engineering Chemistry, 2018, vol. 67, pp. 12–27. <https://doi.org/10.1016/j.jiec.2018.06.038>
- [49] K. Rajavel, S. Luo, Y. Wan, X. Yu, Y. Hu, P. Zhu, R. Sun and Ch. Wong, *2D $Ti_3C_2T_x$ MXene/polyvinylidene fluoride (PVDF) nanocomposites for attenuation of electromagnetic radiation with excellent heat dissipation*, Composites Part A, 2020, vol. 129, art. 105693. <https://doi.org/10.1016/j.compositesa.2019.105693>
- [50] S. Mazhar, A. Ali Qarni, Y. Ul Haq., Z. Haq. Ul and Imran Murtaza, *Promising PVC/MXene based flexible thin film nanocomposites with excellent dielectric, thermal and mechanical properties*, Ceramics International, 2020, vol. 46, pp. 12593–12605. <https://doi.org/10.1016/j.ceramint.2020.02.023>
- [51] L. Verger, Ch. Xu, V. Natu, Hui-Ming Cheng, W. Ren and M.W. Barsoum, *Overview of the synthesis of MXenes and other ultrathin 2D transition metal carbides and nitrides*, Current Opinion in Solid State and Materials Science, 2019, vol. 23, no. 3, pp. 149-163. <https://doi.org/10.1016/j.cossms.2019.02.001>
- [52] R.M. Ronchi, J.T. Arantes and S.F. Santos, *Synthesis, structure, properties and applications of MXenes: Current status and perspectives*, Ceramics International, 2019, vol. 45, no. 15, pp. 18167-18188. <https://doi.org/10.1016/j.ceramint.2019.06.114>
- [53] A. Pazniak, P. Bazhin, N. Shplis, E. Kolesnikov, I. Shchetinin, A. Komissarov, J. Polcak, A. Stolin and D. Kuznetsov, *$Ti_3C_2T_x$ MXene characterization produced from SHS-ground Ti_3AlC_2* , Materials and Design, 2019, vol. 183, art. 108143. <https://doi.org/10.1016/j.matdes.2019.108143>
- [54] Roger Jérôme, Gardiola Bruno, Andrieux Jérôme, Viala Jean-Claude and Dezellus Olivier, *Synthesis of Ti matrix composites reinforced with TiC particles: thermodynamic equilibrium and change in microstructure*, Journal of Materials Science, 2017, vol.52, pp. 4129–4141. <https://doi.org/10.1007/s10853-016-0677-y>
- [55] A.G. Merzhanov and A.S. Mukasyan, *Solid flame combustion* (Éöscow, Torus Press, 2007), In Russian.
- [56] A.S. Rogachev and A.S. Mukasyan, *Combustion for material synthesis: introduction to structural macro kinetics* (Éöscow, Fizmatlit, 2013), In Russian.
- [57] Guanghua Liu, Jiangtao Li and Kexin Chen, *Combustion synthesis of refractory and hard materials: A review*, Int. Journal of Refractory Metals and Hard Materials, 2013. vol. 39, pp. 90-102. <https://doi.org/10.1016/j.jirmhm.2012.09.002>
- [58] A.S. Rogachev, S.G. Vadchenko, N.A. Kochetov, D. Yu. Kovalev, I.D. Kovalev, A.S. Shchukin, A.N. Gryadunov, F. Baras and O. Politano, *Combustion synthesis of TiC-based ceramic-metal composites with high entropy alloy binder*, Journal of the European Ceramic Society, 2020, vol. 40, no. 7, pp. 2527-2532. <https://doi.org/10.1016/j.jeurceramsoc.2019.11.059>
- [59] T.B. Massalski, *Binary Phase Diagrams* (American Society for Metals, Metals Park, OH, USA, 1986).
- [60] M.G. Krinitcyn, G.A. Pribytkov and E.N. Korosteleva, *Structure of Sintered Ti – TiC Materials*, Applied Mechanics and Materials, 2014, vol. 682, pp. 127-131. <https://doi.org/10.4028/www.scientific.net/AMM.682.127>
- [61] C.R. Kachelmyer, J-P. Lebrat, A. Varma and P.J. McGinn, In: *Heat Transfer in Fire and Combustion Synthesis* ed, by B. Farouk, M.P. Pinar Menguc, R. Viskanta, C. Presser and S. Chellaiah (ASME, New York, 1993), pp. 271–276.
- [62] Z.A. Munir, W. Lai and K.H. Ewald, *Field-assisted combustion synthesis*, 08.03.1993. <https://patents.google.com/patent/US5380409A/en?qoq=+%5c380%2c409>
- [63] V. Gauthier, C. Josse, F. Bernard, E. Gaffet and J.P. Larpin, *Synthesis of niobium aluminides using mechanically activated self-propagating high-temperature synthesis and mechanically activated annealing process*, Mater. Sci. Eng. A, 1999, vol. 265, no. 1-2, pp. 117-128. [https://doi.org/10.1016/s0921-5093\(98\)01141-1](https://doi.org/10.1016/s0921-5093(98)01141-1)
- [64] M. A.Korchagin and D. V. Dudina, *Application of self-propagating high-temperature synthesis and mechanical activation for obtaining nanocomposites*, Combustion, Explosion, and

- Shock Waves, 2007, vol. 43, no. 2, pp. 176-187. <https://doi.org/10.1007/s10573-007-0024-3>
- [65] L.S. Abovyan, H.H. Nersisyan, S.L. Kharatyan, R. Orrù, R. Saiu, G. Cao and D. Zedda, *Synthesis of alumina–silicon carbide composites by chemically activated self-propagating reactions*, *Ceram. Int.*, 2001, vol. 27, no. 2, pp. 163-169. [https://doi.org/10.1016/s0272-8842\(00\)00057-2](https://doi.org/10.1016/s0272-8842(00)00057-2)
- [66] Roberta Licheri, Roberto Orrù and Giacomo Cao, *Chemically-activated combustion synthesis of TiC–Ti composites*, *Materials Science and Engineering A*, 2004, vol. 367, no. 1-2, pp. 185–197. <https://doi.org/10.1016/j.msea.2003.10.238>
- [67] S.L. Kharatyan and H.H. Nersisyan, *Combustion synthesis of silicon carbide in Conditions of Oxidative Activation*, *Int. J. SHS*, 1994, vol. 3, no. 1, pp. 17-25.
- [68] H.H. Nersisyan and S.L. Kharatyan, *Combustion of carbide systems under conditions of chemical stimulation*, *Int. J. SHS*, 1995, vol. 4 no. 2, pp. 159-170. https://www.researchgate.net/profile/Suren_Kharatyan/publication/271700503_Combustion_of_carbide_systems_under_conditions_of_chemical_stimulation/links/54cf647b0cf298d656635610/Combustion-of-carbide-systems-under-conditions-of-chemical-stimulation.pdf
- [69] A. P. Aldushin, S. G. Kasparyan and K. G. Shkadinskii, *Exothermal reaction front propagation in condensed mixtures forming two-phase products*, In: *Combustion and Explosion*, ed. by L. N. Stesik (Moscow, Nauka, 1977), pp. 207-212, In Russian.
- [70] A.G. Merzhanov and I.P. Borovinskaya, *Self-propagating high temperature synthesis of refractory inorganic compounds*, *Dokl. Akad. Nauk. SSSR*, 1972, vol. 204, no. 2, pp. 366-369.
- [71] A.I. Kirdyashkin, Yu.M. Maksimov and E.A. Nekrasov, *Titanium-carbon interaction mechanism in a combustion wave*, *Combustion, Explosion, and Shock Waves*, 1981, vol. 17, no. 4, pp. 377-379. <https://doi.org/10.1007/bf00761204>
- [72] E. A. Nekrasov, V. K. Smolyakov and Yu. M. Maksimov, *Adiabatic heating in the titanium-carbon system*, *Combustion, Explosion, and Shock Waves*, 1981, vol. 17, no. 3, pp. 305-311. <https://doi.org/10.1007/bf00751306>
- [73] J.B. Holt and Z.A. Munir, *Combustion synthesis of titanium carbide: Theory and experiment*, *J. Mater. Sci.*, 1986, vol. 21, no. 1, pp. 251-259. <https://doi.org/10.1007/bf01144729>
- [74] J.P. Lebrat and A. Varma, *Self-propagating reactions in finite pellets: Synthesis of titanium carbide*, *AIChE J.*, 1993, vol. 39, no. 10, pp. 1732-1734. <https://doi.org/10.1002/aic.690391019>
- [75] D. Vrel, J. M. Lihmann and P. Tobaly, *Contribution of solid-state diffusion to the formation of titanium carbide by combustion synthesis*, *J. Mater. Synth. Proc.*, 1994, vol. 2, pp. 179-187.
- [76] K. Mishra, S. Das, R.P. Goel and P. Ramachandrarao, *Self-propagating high temperature synthesis (SHS) of titanium carbide*, *J. Mater. Sci. Lett.*, 1997, vol. 16, no. 12, pp. 965-967. <https://doi.org/10.4028/www.scientific.net/KEM.395.15>
- [77] A.S. Rogachev, A.S. Mukasyan and A. G. Merzhanov, *Structural transitions during gasless combustion of titanium–boron mixtures*, *Dokl. Phys. Chem.*, 1987, vol. 297, no. 6. pp. 240–1243.
- [78] A.G. Merzhanov, A.S. Rogachev, A.S. Mukasyan and B.M. Khusid, *Macrokinetics of structural transformation during the gasless combustion of a titanium and carbon powder mixture*, *Combustion, Explosion, and Shock Waves*, 1990, vol. 26, no. 1, pp. 92-102. <https://doi.org/10.1007/bf00742281>
- [79] B.S. Septyarskii, R.A. Kochetkov and T.G. Lisina, *Coflow combustion in granulated Ti + xC mixtures: boundary conditions for convection-driven wave propagation*, *International Journal of Self-Propagating High-Temperature Synthesis*, 2019, vol. 28, no. 3, pp. 183–186. <https://doi.org/10.3103/S1061386219030129>
- [80] B.S. Septyarskii, R.A. Kochetkov and T.G. Lisina, *Convective combustion of a Ti + 0.5C granulated mixture. Domain of existence and fundamental phenomena*, *Combustion, Explosion, and Shock Waves*, 2019, vol. 55, no. 3, pp. 295-299. <https://doi.org/10.1134/s0010508219030079>
- [81] V.M. Shkiro and I.P. Borovinskaya, *Capillary flow of liquid metal during combustion of titanium mixtures with carbon*, *Combustion, Explosion, and Shock Waves*, 1976, vol. 12, no. 6, pp. 828-831. <https://doi.org/10.1007/bf00740761>
- [82] E.A. Nekrasov, Yu.M. Maksimov, M.Kh. Ziatdinov and A.S. Steinberg, *Effect of capillary spreading on combustion-wave propagation in gas-free system*, *Combustion, Explosion, and Shock Waves*, 1978, vol. 14, no. 5, pp. 575-581. <https://doi.org/10.1007/bf00789713>
- [83] A.I. Kirdyashkin, Yu.M. Maksimov and E.A. Nekrasov, *Effect of mass forces on combustion of heterogeneous systems with condensed combustion products*, *Combustion, Explosion,*

- and Shock Waves, 1986, vol. 22, no. 1, pp. 20-23. <https://doi.org/10.1007/bf00750700>
- [84] A.I. Kirdyashkin, Yu.M. Maksimov and A.G. Merzhanov, *Effects of capillary flow on combustion in a gas-free system*, Combustion, Explosion, and Shock Waves, 1981, vol. 17, no. 6, pp. 591-595. <https://doi.org/10.1007/bf00784246>
- [85] S.G. Vadchenko, Yu.M. Grigor'ev and A.G. Merzhanov, *Investigation of the mechanism of the ignition and combustion of the systems Ti + C, Zr + C by an electrothermographic method*, Combustion, Explosion, and Shock Waves, 1976, vol. 12, no. 5, pp. 606-612. <https://doi.org/10.1007/bf00743162>
- [86] I.I. Korotkevich, G.V. Khil'chenko, G.P. Polunina and L.M. Vidavskii, *Initiation of self-propagating high-temperature synthesis reactions by pulsed laser radiation*, Combustion, Explosion, and Shock Waves, 1981, vol. 17, no. 5, pp. 545-540. <https://doi.org/10.1007/bf00798141>
- [87] V.V. Aleksandrov and M.A. Korchagin, *Mechanism and macrokinetics of reactions accompanying the combustion of SHS systems*, Combustion, Explosion, and Shock Waves, 1987, vol. 23, no. 5, pp. 55-63. <https://doi.org/10.1007/bf00756537>
- [88] E.A. Levashov, Yu.V. Bogatov and A.A. Milovidov, *Macrokinetics and mechanism of the SVS-process in systems on a titanium-carbon base*, Combustion, Explosion, and Shock Waves, 1991, vol. 27, no. 1, pp. 88-93. <https://doi.org/10.1007/bf00785363>
- [89] V.M. Shkiro, V.N. Doroshin and I.P. Borovinskaya, *Concentration structure of the combustion wave in the titanium-carbon system*, Combustion, Explosion, and Shock Waves, 1980, vol. 16, no. 4, pp. 370-374. <https://doi.org/10.1007/bf00742981>
- [90] T.Ya. Velikanova, *Carbon-Titanium*, In: *Phase diagrams of double metallic systems*, ed. by N.P. Lyakishev, (Moscow, Mashinostroenie, 1996), vol. 1, pp. 769-771, In Russian.
- [91] K. Frisk, *A revised thermodynamic description of the Ti-C system*, Calphad, 2003, vol. 27, no. 4, pp. 367-373. <https://doi.org/10.1016/j.calphad.2004.01.004>
- [92] A.I. Gusev, *Phase equilibria, phases and compounds in the Ti-C system*, Russ. Chem. Rev., 2002, vol. 71, no. 6, pp. 439-463. <https://doi.org/10.1070/RC2002v071n06ABEH000721>
- [93] R.A. Andrievski, *High-melting point compounds: new approaches and new results*, Phys. Usp., 2017, vol. 60, no. 3, pp. 276-289. <https://doi.org/10.3367/UFNe.2016.09.037972>
- [94] Xiaojing Sha, Namin Xiao, Yongjun Guan and Xiaosu Yi, *A first-principles investigation on mechanical and metallic properties of titanium carbides under pressure*, Journal of Materials Science & Technology, 2018, vol. 34, no. 10, pp. 1953-1958. <https://doi.org/10.1016/j.jmst.2018.02.012>
- [95] D.A. Aksyonov, A.G. Lipnitskii and Yu.R. Kolobov, *Ab initio study of Ti-C precipitates in hcp titanium: Formation energies, elastic moduli and theoretical diffraction patterns*, Computational Materials Science, 2012, vol. 65, pp. 434-441. <https://doi.org/10.1016/j.commatsci.2012.08.014>
- [96] G.A. Pribytkov, M.G. Krinitsyn and V.V. Korzhova, *Study of products of SH synthesis in powder mixtures of titanium and carbon containing an excess of titanium*, Perspective materials, 2016, vol. 5, pp. 59-68, In Russian.
- [97] L.V. Zueva and A.I. Gusev, *Influence of non-stoichiometry and ordering on the period of the basic structure of cubic titanium carbide*, Fizika tverdogo tela, 1999, vol. 41, no. 7, pp. 1134-1141, In Russian. <https://journals.ioffe.ru/articles/viewPDF/35442>
- [98] B.S. Seplyarskii, A.G. Tarasov and R.A. Kochetkov, *Experimental investigation of combustion of a gasless pelletized mixture of Ti + 0.5C in argon and nitrogen coflows*, Combustion, Explosion, and Shock Waves, 2013, vol. 49, no. 5, pp. 555-562. <https://doi.org/10.1134/s0010508213050079>
- [99] B.S. Seplyarskii, R.A. Kochetkov and S.G. Vadchenko, *Burning of the Ti + xC (1 > x > 0.5) powder and granulated mixtures*, Combustion, Explosion, and Shock Waves, 2016, vol. 52, no. 6, pp. 51-59. <https://doi.org/10.1134/s001050821606006x>
- [100] B.S. Seplyarskii and S.G. Vadchenko, *Role of Convective Heat Transfer in Gasless Combustion by the Example of Combustion of the Ti-C System*, Doklady Physical Chemistry, 2004, vol. 398, pp. 203-207. <https://doi.org/10.1023/B:DOPC.0000041487.87644.26>
- [101] B.S. Seplyarskii, S.G. Vadchenko, S.V. Kostin and G.B. Brauer, *Combustion of Bulk Density Powder Mixtures in a Coflow of Inert Gas. 2. The Ti-C System*, International Journal of Self-Propagating High-Temperature Synthesis, 2008, vol. 17, no. 2, pp. 117-120. <https://doi.org/10.3103/s1061386208020052>
- [102] A.G. Merzhanov, *Solid flames: discoveries, concepts, and horizons of cognition*, Combust.

- Sci. Tech. , 1994, vol. 98, no. 4–6, pp. 307–336. <https://doi.org/10.1080/00102209408935417>
- [103] M.G. Krinitcyn, E.N. Korosteleva, A.G. Knyazeva and E.S. Sheremet, *Structural-phase composition of TiC/Ti composites and powders obtained by combustion of Ti–C green mixtures with a titanium excess*, High Temperature Material Processes, 2020, vol. 24, no. 3, pp. 227–238. <https://doi.org/10.1615/HighTempMatProc.2020036732>
- [104] B.V. Novozhilov, *Velocity of exothermic reaction front propagation in the condensed phase*, Dokl. Akad. Nauk. SSSR, 1961, vol. 141, no. 1, pp. 151–153, In Russian. <http://www.mathnet.ru/links/7e7f0e16f4ba827cec9bb274096dc72bdan25737.pdf>
- [105] A.G. Merzhanov, *On the role of dispersing in powder combustion*, Dokl. Akad. Nauk. SSSR, 1960, vol. 135, no. 6, pp. 1439–1441, in Russian. <http://www.mathnet.ru/links/0d49e8859b46e5a60ac089a54d29e9aadan24447.pdf>
- [106] B.I. Khaikin and A.G. Merzhanov, *Theory of thermal propagation of a chemical reaction front*, Combustion, Explosion, and Shock Waves, 1966, vol. 2, no. 3, pp. 36–46. <https://doi.org/10.1007/bf00749022>
- [107] A.G. Merzhanov, *Theory of gas-free combustion: preprint* (Chernogolovka, Russia, izd. IOCHF AN SSSR, 1973), in Russian.
- [108] V.A. Volpert, A.I. Volpert and D.S. Davtyan, *Estimates of the velocity of the combustion wave in a condensed medium: preprint* (Chernogolovka, Russia, izd. IOCHF AN SSSR, 1985), in Russian.
- [109] E.A. Nekrasov, Yu.M. Maksimov and A.P. Aldushin, *Calculation of combustion wave parameters in gas-free systems*, Dokl. Akad. Nauk. SSSR, 1980, vol. 255, no. 3, pp. 656–659.
- [110] E.I. Maksimov, A.G. Merzhanov and V.M. Shkiro, *Gasless compositions as a simple model for the combustion of nonvolatile condensed systems*, Combustion, Explosion, and Shock Waves, 1965, vol. 1, no. 4, pp. 15–18. <https://doi.org/10.1007/bf00748806>
- [111] A.P. Aldushin, A.G. Merzhanov and B.I. Khaikin, *On some peculiarities of combustion of condensed systems with refractory reaction products*, Dokl. Akad. Nauk. SSSR, 1972, vol. 204, no. 5, pp. 1139–1142.
- [112] A.P. Aldushin, T.M. Martem'yanova, A.G. Merzhanov, B.I. Khaikin and K.G. Shkadinskii, *Propagation of the front of an exothermic reaction in condensed mixtures with the interaction of the components through a layer of high-melting product*, Combustion, Explosion, and Shock Waves, 1972, vol. 8, no. 2, pp. 159–167. <https://doi.org/10.1007/bf00740444>
- [113] V.P. Stovbun, V.V. Barzykin and K.G. Shkadinskii, *Problem concerning constant heat flow ignition of heterogeneous systems with condensed products*, Combustion, Explosion, and Shock Waves, 1977, vol. 13, no. 2, pp. 121–128. <https://doi.org/10.1007/bf00754988>
- [114] G.V. Zhizhin, *Model of an Ideal Solid-Flame Combustion Wave with a Variable Chemical-Reaction Surface*, Combustion, Explosion, and Shock Waves, 2004, vol. 40, no. 1, pp. 85–91. <https://doi.org/10.1023/b:cesw.0000013671.95999.6c>
- [115] B.I. Khaikin, V.N. Bloshenko and A.G. Merzhanov, *On the ignition of metal particles*, Combustion, Explosion, and Shock Waves, 1970, vol. 6, no. 4, pp. 412–422. <https://doi.org/10.1007/BF00742774>
- [116] V.Yu. Filimonov, *Criteria for thermal stability of parabolically oxidable heterogeneous systems*, Combustion, Explosion, and Shock Waves, 2006, vol. 42, no. 3, pp. 292–294. <https://doi.org/10.1007/s10573-006-0053-3>
- [117] K.G. Shkadinskii and P.M. Krishenik, *Steady combustion front in a mixture of fuel and inert material*, Combustion, Explosion, and Shock Waves, 1985, vol. 21, no. 2, pp. 52–57. <https://doi.org/10.1007/bf01463731>
- [118] A.A. Chashchina and A.G. Knyazeva, *Regimes of Connecting Materials with the Help of Synthesis in the Solid Phase*, Chemistry for Sustainable Development, 2005, vol. 13, no. 2, pp. 343–350. <https://www.sibran.ru/upload/iblock/b3b/b3becf3ea6c0883f4bc8c519d92276f0.pdf>
- [119] A.A. Chashchina and A.G. Knyazeva, *Influence of inert filler melting on explosion of reaction mixture in a thick-walled vessel*, Combustion and plasma chemistry, 2005, vol. 1, pp. 71–80.
- [120] A.P. Aldushin and B.I. Khaikin, *Combustion of mixtures forming condensed reaction products*, Combustion, Explosion, and Shock Waves, 1974, vol. 10, no. 3, pp. 273–280. <https://doi.org/10.1007/bf01463752>
- [121] E.V. Okolovich, A.G. Merzhanov, B.I. Khaikin and K.G. Shkadinskii, *Propagation of the combustion zone in melting condensed mixtures*, Combustion, Explosion, and Shock Waves, 1977, vol. 13, no. 3, pp. 264–272. <https://doi.org/10.1007/bf00740301>

- [122] V.A. Andreev, E.A. Levashov, V.M. Mal'tsev and N.N. Khavskii, *Characteristics of capillary mass transfer in a combustion wave in multicomponent heterogeneous systems*, Combustion, Explosion, and Shock Waves, 1988, vol. 24, no. 2, pp. 189-193. <https://doi.org/10.1007/bf00749186>
- [123] D.S. Shults and A. Yu. Krainov, *Mathematical modeling of the SHS process in heterogeneous reacting powder mixtures*, Computer investigations and modeling, 2011, vol. 3, no. 2, pp. 147-153. <https://doi.org/10.20537/2076-7633-2011-3-2-147-153>
- [124] V.K. Smolyakov, E.A. Nekrasov and Yu.M. Maksimov, *Effects of boundary kinetics in stationary combustion in a gas-free system*, Combustion, Explosion, and Shock Waves, 1982, vol. 18, no. 3, pp. 312-315. <https://doi.org/10.1007/bf00783042>
- [125] A.M. Locci, A. Cincotti., F. Delogu and R. Orrù, *Combustion synthesis of metal carbides: Part I. Model development*, Journal Materials Research, 2005, vol. 20, no. 5, pp. 1257-1268. <https://doi.org/10.1557/jmr.2005.0152>
- [126] A.M. Locci, A. Cincotti, F. Delogu and R. Orrù, *Combustion synthesis of metal carbides: Part II. Numerical simulation and comparison with experimental data*, Journal Materials Research, 2005, vol. 20, no. 5, pp. 1269-1277. <https://doi.org/10.1557/jmr.2005.0153>
- [127] E.A. Nekrasov, Yu.M. Maksimov and A.P. Aldushin, *Calculation of critical thermal explosion conditions in hafnium-boron and tantalum-carbon systems using state diagrams*, Combustion, Explosion, and Shock Waves, 1980, vol. 16, no. 3, pp. 342-347. <https://doi.org/10.1007/bf00742138>
- [128] E.A. Nekrasov, Yu. M. Maksimov and A.P. Aldushin, *Parameters of combustion wave in the zirconium-aluminum system*, Combustion, Explosion, and Shock Waves, 1981, vol. 17, no. 2, pp. 140-145. <https://doi.org/10.1007/bf00770822>
- [129] A.M. Kanury, *A kinetic model for metal+nonmetal reactions*, Metall. Trans. A., 1992, vol. 23A, no 9, pp. 2349-2356. <https://doi.org/10.1007/bf02658036>
- [130] G. Cao and A. F. Varma, *A new expression for velocity of the combustion front during self-propagating high-temperature synthesis*, Combust. Sci. Technol, 1994, vol. 102, pp. 181-191. <https://doi.org/10.1080/00102209408935475>
- [131] V.K. Smolyakov, E.A. Nekrasov and Yu.M. Maksimov, *Modeling gas-free combustion with phase transitions*, Combustion, Explosion, and Shock Waves, 1984, vol. 20, no. 2, pp. 182-191. <https://doi.org/10.1007/bf00751589>
- [132] Yu.M. Maksimov, V.K. Smolyakov and E.A. Nekrasov, *Theory of combustion of multicomponent systems with condensed reaction products*, Combustion, Explosion, and Shock Waves, 1984, vol. 20, no. 5, pp. 479-476. <https://doi.org/10.1007/bf00782232>
- [133] F. Baras, D.K. Kondepudi and F. Bernard, *Combustion synthesis of $MoSi_2$ and $MoSi-Mo_5Si_3$ composites: Multilayer modeling and control of the microstructure*, J. Alloys Compounds **505** (2010) 43-53. <https://doi.org/10.1016/j.jallcom.2010.06.024>
- [134] F. Baras and D.K. Kondepudi, *A Multilayer Model for Self-Propagating High-Temperature Synthesis of Intermetallic Compounds*, J. Phys. Chem. B., 2007, vol. 111, pp. 6457-6468. <https://doi.org/10.1021/jp066776p>
- [135] O.V. Lapshin and V.E. Ovcharenko, *A mathematical model of high-temperature synthesis of nickel aluminide Ni_3Al by thermal shock of a powder mixture of pure elements*, Combustion, Explosion, and Shock Waves, 1996, vol. 32, no. 3, pp. 299-305. <https://doi.org/10.1007/bf01998460>
- [136] O.B. Kovalev and V.V. Belyaev, *Mathematical modeling of metallochemical reactions in a two-species reacting disperse mixture*, Combustion, Explosion, and Shock Waves, **2013**, vol. 49, no. 5, pp. 563-574. <https://doi.org/10.1134/s0010508213050080>
- [137] V.V. Evstigneev, V.Yu. Filimonov and K.B. Koshelev, *Mathematical model of phase-formation processes in a binary mixture of Ti and Al powders in the regime of a nonadiabatic thermal explosion*, Combustion, Explosion, and Shock Waves, 2007, vol. 43, no. 2, pp. 170-175. <https://doi.org/10.1007/s10573-007-0023-4>
- [138] N.A. Kochetov, A.S. Rogachev, A.N. Emel'yanov, E.V. Illarionova and V.M. Shkiro, *Microstructure of Heterogeneous Mixtures for Gasless Combustion*, Combustion, Explosion, and Shock Waves, 2004, vol. 40, no. 5, pp. 564-570. <https://doi.org/10.1023/b:cesw.0000041408.95421.d2>
- [139] B.B. Khina, F. Bormanek and I. Solpan, *Limits of applicability of "diffusion-controlled product growth" kinetic approach to modeling SHS*, Physica B: Condensed Matter, 2005, vol. 335, pp.

- 14-31. <https://doi.org/10.1016/j.physb.2004.09.104>
- [140] B.B. Khina, *Interaction kinetics in SHS: is the quasi-equilibrium solid-state diffusion model valid?*, International Journal of Self-Propagating High-Temperature Synthesis, 2005, vol. 14, pp. 21-31. https://www.researchgate.net/publication/235247904_Interaction_kinetics_in_SHS_is_the_quasi-equilibrium_solid-state_diffusion_model_valid
- [141] B.B. Khina, *Modeling the kinetics of non-isothermal heterogeneous interaction during combustion synthesis of advanced micro- and nanocrystalline materials*, In: Proceedings of SPIE (The International Society for Optical Engineering), 2008, art. 7377. <https://doi.org/10.1117/12.836971>
- [142] B.B. Khina, *Chemistry research and application series. Combustion synthesis of advanced materials* (Nova Science Publishers, Inc., New York, 2010).
- [143] V.K. Smolyakov, *Macrostructural transformation in gasless combustion processes*, Combustion, Explosion, and Shock Waves, 1990, vol. 26, no. 3, pp. 301-307. <https://doi.org/10.1007/bf00751368>
- [144] V.K. Smolyakov, *On the Structural mechanics of matter in the wave of self-propagating high-temperature synthesis*, Physical mesomechanics, 1999, vol. 2, no. 3, pp. 59-74. <http://www.ispms.ru/en/61/330/1195/>
- [145] V.G. Prokof'ev and V.K. Smolyakov, *Unsteady combustion regimes of gasless systems with a low-melting inert component*, Combustion, Explosion, and Shock Waves, 2002, vol. 38, no. 2, pp. 143-147. <https://doi.org/10.1023/A:1014990529587>
- [146] A.S. Astapchik, E.P. Podvoisky, I.S. Chebotko, B.M. Khusid, A.G. Merzhanov and B.B. Khina, *Stochastic model for wavelike isothermal reaction in condensed heterogeneous systems*, Phys.Rev. E, 1993, vol. 47, no. 1, pp. 319-326. <https://doi.org/10.1103/PhysRevE.47.319>
- [147] A.S. Mukasyan and A.S. Rogachev, *Discrete reaction waves: Gasless combustion of solid powder mixtures*, Progress in Energy and Combustion Science, 2008, vol. 34, pp. 377-416. <https://doi.org/10.1016/j.pecs.2007.09.002>
- [148] A.M. Locci, A. Cincotti, F. Delogu, R. Orr and G. Cao, *Advanced modelling of self-propagating high-temperature synthesis: the case of the Ti-C system*, Chemical Engineering Science, 2004, vol. 59, no. 22-23, pp. 5121-5128. <https://doi.org/10.1016/j.ces.2004.07.032>
- [149] A.G. Knyazeva and O.N. Kryukova, *Simulation of the synthesis of multiphase composites on a substrate, taking into account the staging of chemical reactions*, Applied Solid State Chemistry, 2019, vol. 2, no. 1, pp. 32-44. <https://doi.org/10.18572/2619-0141-2019-1-32-44>
- [150] V.N. Demidov and A.G. Knyazeva, *Multistage kinetics of the synthesis of Ti-Ti_xC_y composite*, Nanoscience and Technology: An International Journal, 2019, vol. 10, no. 3, pp. 195-218. <https://doi.org/10.1615/NanoSciTechnolIntJ.2019031220>
- [151] Yu. Dimitrienko, *Mathematical Modelling of Ceramic Composite Processing Based on Combustion*, Mathematical and Computer Modelling, 1995, vol. 21, no. 8, pp. 69-83. [https://doi.org/10.1016/0895-7177\(95\)00040-9](https://doi.org/10.1016/0895-7177(95)00040-9)
- [152] V.G. Prokof'ev, O.A. Borodatov and V.K. Smolyakov, *Filtration combustion of porous metallic samples in a gas diluted by an inert component*, Combustion, Explosion, and Shock Waves, 2008, vol. 44, no. 1, pp. 64-70. <https://doi.org/10.1007/s10573-008-0009-x>
- [153] V. K. Smolyakov, O. V. Lapshin and V. G. Prokof'ev, *To the Theory of Macrostructural Transformations during Gasless Combustion*, International Journal of Self-Propagating High-Temperature Synthesis, 2018, vol. 27, no. 4, pp. 201-206. <https://doi.org/10.3103/s1061386218040076>
- [154] V.G. Prokof'ev and V. K. Smolyakov, *Gasless combustion of a system of thermally coupled layers*, Combustion, Explosion, and Shock Waves, 2016, vol. 52, no. 1, pp. 62-66. <https://doi.org/10.1134/s0010508216010081>