

# Simulation of the synthesis of multiphase composites on a substrate, taking into account the staging of chemical reactions

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*When constructing models of technological processes for the synthesis of materials with regard to the staging of chemical reactions, problems in searching for or calculating the formal-kinetic parameters of chemical reactions arise. For non-equilibrium conditions, such data are usually not available. This paper describes the stages of chemical reactions in the Ti-C, Ti-B, Ti-Si, Ti-C-Al systems that can occur under non-equilibrium conditions for the synthesis of composites on a substrate, and estimates of the formal kinetic parameters of the reactions are given. A model of controlled synthesis of a multiphase composite on a substrate, taking into account the evolution of properties and staging of the transformation, is presented. An example of the calculation illustrates the capabilities of the model. The results obtained are consistent and provide detailed information on the mutual influence of various physicochemical processes under unsteady conditions, and also predict a change in the phase composition with a change in the synthesis conditions.*

**Keywords:** *Composite synthesis, thermal cycles, kinetics, thermodynamics, modeling*

## 1. Introduction

Metal matrix composites attract much attention in various fields, due to their high physicochemical and operational properties. Methods for obtaining them are very diverse. Among them, there are such methods as melt impregnation of porous frameworks of powders; mechanical mixing of discrete particles with metal melts; processes based on controlled chemical reactions of high-temperature synthesis in a matrix melt, etc. The main problem in obtaining composite alloys in traditional technologies is the need to ensure the physicochemical compatibility of the matrix and the reinforcing phase. The preparation of composite alloys is accompanied by interfacial interaction processes: mutual diffusion and chemical reactions. A necessary condition for the formation of strong adhesive bonds at interphase boundaries is the wettability of particles with a melt, which is improved by various methods: due to the introduction of active additives; coating the particles with hydrophilic properties; use of ultrasound, etc. Along with wettability, an important role is played by the uniform distribution of particles in the volume of the alloy and the finished product, which is difficult to achieve due to the difference

in particle size and the difference in the physical properties of the particles and the matrix. These and other problems inevitably manifest themselves in modern additive technologies - the creation of multilayer coatings and three-dimensional products from mixtures of metal powders [1] or mixtures of metal and nonmetal powders. The problems can be solved by using composite powders in additive technologies, obtained, for example, by methods of self-propagating high-temperature synthesis (SHS) [2]. During the synthesis by combustion or in the mode of a dynamic thermal explosion, a non-equilibrium phase composition is obtained, as a rule, so that chemical and structural transformations continue under conditions of selective laser or electron beam fusion.

In electron-beam and laser technologies there are various options for organizing the process for surface modification and synthesis of metal-based composite coatings. In some of them, a powder layer is preliminarily applied to the substrate, and then treatment with a moving energy source is performed [3]. In other technologies, the modifying powder or material of the future coating is fed into the molten bath formed by an electron or laser beam [4]. In turn, the powders can be a mixture of

№ of reaction	Reaction	Heat, Q, (J·mol <sup>-1</sup> )	k <sub>0</sub> , s <sup>-1</sup>	E <sub>a</sub> (J·mol <sup>-1</sup> )
1	Ti+2B=TiB <sub>2</sub>	315900	0.381·10 <sup>14</sup>	77096
2	Ti+B=TiB	160000	0.115·10 <sup>15</sup>	24962
3	TiB+B=TiB <sub>2</sub>	155900	0.466·10 <sup>14</sup>	71153
4	2TiB+TiB <sub>2</sub> =Ti <sub>3</sub> B <sub>4</sub>	-125610	0.254·10 <sup>10</sup>	247233

**Table 1.** Formal kinetic parameters of reactions in the Ti-B system

powders of individual components, but they can also be composite powders of a non-equilibrium phase composition, depending on the preparation conditions. In any case, the technological process of controlled synthesis of a composite on a substrate is accompanied by various physicochemical transformations, the kinetics of which is not obvious.

Experimental study of non-equilibrium processes for the synthesis of composites faces the difficulty of interpreting the results obtained and the impossibility of direct measurements in dynamics (with the exception of temperature). However, the staging of chemical reactions largely causes the structure of the future composite; the limiting stages depend on the synthesis conditions, the properties and structure of the composite change continuously, there are possible accompanying phenomena of different physical nature, etc. In such situations, mathematical modeling is attracted.

In turn, when modeling the technological processes of synthesizing new materials with regard to the physicochemical stages, the problem of finding or estimating formal-kinetic parameters and the dependence of the effective thermophysical properties on the composition arises. However, the description of the detailed kinetics of chemical reactions involving solids is a serious problem.

In macrokinetics [5], two main approaches are common. The first is based on the formal

description of the transformation kinetics for the total reaction. The kinetic function can take into account the inhibition of the reaction layer of the product using the parameters of inhibition, which depend on the type of substances entering into the reaction [6, 7]. The second approach uses the concept of a reaction cell, the sequence of stages in which is set in accordance with the equilibrium state diagram [8, 9].

In the present work (a) the stages of chemical reactions in the Ti-C, Ti-B, Ti-Si, Ti-C-Al systems, which can occur under non-equilibrium conditions for the synthesis of composites on a substrate are described; (b) estimates of the formal-kinetic parameters of the reactions are given; (c) a model of controlled synthesis of a multiphase composite on a substrate, taking into account the evolution of properties and staging of the transformation, is presented; and (d) an example of calculation illustrating the capabilities of the model is described. A general approach to the construction of such models is described in [10].

## 2. The object of study

The object of the study is titanium based composites with inclusions of borides, carbides and silicides, as well as composites based on the same systems with aluminum additives. When organizing the synthesis process in the thermal explosion mode

**Table 2.** Formal kinetic parameters of reactions in the Ti-Si system

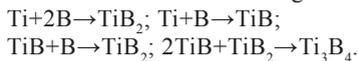
№ of reaction	Reaction	Heat, Q, (J·mol <sup>-1</sup> )	k <sub>0</sub> , s <sup>-1</sup>	E <sub>a</sub> (J·mol <sup>-1</sup> )
1	Ti+Si=TiSi	129700	0.363·10 <sup>14</sup>	16145
2	Ti+2Si=TiSi <sub>2</sub>	133900	0.146·10 <sup>14</sup>	26935
3	TiSi <sub>2</sub> +Ti=2TiSi	122500	0.573·10 <sup>14</sup>	79065
4	3Ti+Si=Ti <sub>3</sub> Si	330000	0.342·10 <sup>15</sup>	29169
5	2Ti+TiSi=Ti <sub>3</sub> Si	200300	0.638·10 <sup>15</sup>	36644
6	5Ti+3Si=Ti <sub>5</sub> Si <sub>3</sub>	579500	0.374·10 <sup>15</sup>	40187
7	5Ti+4Si=Ti <sub>5</sub> Si <sub>4</sub>	697770	0.583·10 <sup>12</sup>	115997
8	Ti <sub>5</sub> Si <sub>3</sub> +4Ti=3Ti <sub>3</sub> Si	410500	0.235·10 <sup>16</sup>	52343
9	2TiSi+Ti <sub>3</sub> Si=Ti <sub>5</sub> Si <sub>3</sub>	-9900	0.287·10 <sup>15</sup>	35115
10	3Ti <sub>5</sub> Si <sub>4</sub> +5Ti=4Ti <sub>5</sub> Si <sub>3</sub>	224270	0.546·10 <sup>23</sup>	415753
11	4TiSi+Ti=Ti <sub>5</sub> Si <sub>4</sub>	178970	0.705·10 <sup>13</sup>	70557

**Table 3.** Formal kinetic parameters of reactions in the Ti-C system

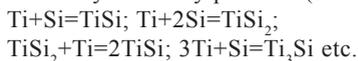
№ of reaction	Reaction	Heat, Q, (J·mol <sup>-1</sup> )	k0, s <sup>-1</sup>	Ea (J·mol <sup>-1</sup> )
1	Ti <sub>2</sub> C=Ti+TiC	63900	0.103·10 <sup>16</sup>	130400
2	Ti <sub>3</sub> C <sub>2</sub> =TiC+Ti <sub>2</sub> C	163280	0.359·10 <sup>15</sup>	104235
3	Ti+C=TiC	184100	0.157·10 <sup>14</sup>	66667
4	2Ti+C=Ti <sub>2</sub> C	120600	0.978·10 <sup>11</sup>	172401
5	TiC+Ti <sub>2</sub> C=Ti <sub>3</sub> C <sub>2</sub>	-163280	0.12·10 <sup>13</sup>	104235
6	Ti+TiC=Ti <sub>2</sub> C	-63900	0.421·10 <sup>12</sup>	132845
7	Ti+C+Ti <sub>2</sub> C=Ti <sub>3</sub> C <sub>2</sub>	20820	0.281·10 <sup>12</sup>	143766
8	Ti+2C=TiC <sub>2</sub>	236070	0.732·10 <sup>13</sup>	53859
9	TiC <sub>2</sub> +Ti=2TiC	132930	0.204·10 <sup>14</sup>	58624
10	TiC <sub>2</sub> =Ti+2C	-236070	0.23·10 <sup>16</sup>	151852
11	TiC <sub>2</sub> =TiC+C	-51570	0.268·10 <sup>14</sup>	51717
12	Ti <sub>3</sub> C <sub>2</sub> =2TiC+Ti	227580	1.775·10 <sup>16</sup>	209990

or in the combustion mode, it is expected that Ti-TiC Ti-TiB<sub>2</sub> and Ti-Ti<sub>3</sub>Si<sub>3</sub> composites are formed from the nonstoichiometric mixture. However, the composition of composites turns out to be more complex [11], and the subsequent use of composite powders in technologies of selective laser and electron beam fusion requires special study. The nonequilibrium composition of the powders undergoes subsequent changes in the conditions of unsteady and non-uniform heating.

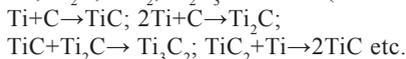
In accordance with the equilibrium state diagrams of binary systems, TiB, Ti<sub>3</sub>B<sub>4</sub>, TiB<sub>2</sub> and Ti<sub>2</sub>B<sub>3</sub> can exist in the Ti-B system. Information about the properties of the Ti<sub>2</sub>B<sub>3</sub> is negligible. The formation of the first three is possible, for example, in accordance with the following reactions (Table 1)



In the Ti-Si system [12], at least twelve stages are thermodynamically possible (Table 2):



The Ti-C system is the most complex in the kinetic relation. Here at least 12 reactions are potentially possible, as a result of which such phases as TiC, Ti<sub>2</sub>C, TiC<sub>2</sub>, Ti<sub>2</sub>C<sub>3</sub> can form (Table 3):



On standard equilibrium state diagrams, a mixture of different carbides is displayed as Ti<sub>x</sub>C<sub>y</sub> carbide, appearing in a wide area of homogeneity. Compounds of TiC<sub>2</sub>, Ti<sub>2</sub>C<sub>3</sub> type belong to the so-called maxenes, the unique structure of which is related to the structure of graphenes and leads to

special properties that determine the use of these phases in microelectronics, electrochemistry, catalysis, in the development of energy storage methods, etc. [13-17]. All the above equilibrium and non-equilibrium phases can be formed during the synthesis of composites both in traditional SHS technologies and in conditions of controlled synthesis on a substrate.

The proposed reaction schemes include both direct and reverse stages. Considering them as elementary stages, for reaction rates we can use the law of mass action and the Arrhenius law:

$$(1) \quad \varphi_i = k_{0i} \exp\left(-\frac{E_{ai}}{RT}\right) \prod_{(k)} y_k^{v_{ki}}$$

where  $k_{0i}$  are the pre-exponents, 1/s;  $R$  - is universal gas constant;  $T$  - is temperature, K;  $E_{ai}$  - are activation energies of reactions, J/mol;  $i$  - is reaction number;  $v_{ki}$  - are the stoichiometric coefficients of the reactants with the number  $k$  in the  $i$  reaction;  $y_k$  - are the relative molar concentrations of the components. For many of the above reactions, experimental data on formal-kinetic parameters are missing. And if they can be found, they can be used only for those conditions in which they are defined. The data of different authors differ significantly. The calculations carried out with the help of different thermodynamic packages also differ. In the present work, as in [18], we use a rather simple approach, based on chemical thermodynamics and standard tables of the thermodynamic properties of substances to estimate the formal-kinetic parameters of the reactions.

### 3. Calculation of formal-kinetic parameters

#### 3.1. Parameters of elementary stages

The approach described in [19–21] and classical chemical thermodynamics allow one to estimate the constants of reaction rates  $k_{0i}$ , activation energy  $E_{ai}$ , and heat of reactions  $Q_i$ . So, in accordance with the theory of the activated complex, the reaction constant can be calculated by the formula

$$(2) \quad k_{0i} = e \cdot \left[ \frac{RT}{N_A h} \right] \cdot \exp \left[ \frac{\Delta S_r^0}{R} \right]$$

where  $N_A$  is the Avogadro number, ( $N_A = 6,022 \times 10^{23}$ );  $h$  is Planck's constant, ( $h = 6,626176 \times 10^{-34}$ );  $\Delta S_{\text{reac}}^0$  - is the entropy of the reaction,  $T$  is the melting point of the compound. For each of the reactions we have

$$(3) \quad S_r^0 = \sum_{\text{products}} \nu_{ki} S_{f,k} - \sum_{\text{reagents}} \nu_{kj} S_{f,k}$$

where  $S_{f,k}$  - are the entropies of the formation of components. From reference data [21–30], it is possible to determine the values of the entropies of formation for a part of the discharged compounds. The rest is required to calculate. Of the known methods for calculating entropy, the Eastman formula [31, 32] is the most convenient and accurate:

(4)

$$S_{f,k} = S_{298}^0 = R \left( \frac{3}{2} \ln M_a + \ln V_a - \frac{3}{2} \ln T_m \right) + a$$

where  $M_a$  - is the average atomic weight, (i.e., molecular weight divided by the number of atoms in the molecule);  $V_a$  - is the average atomic volume, i.e. average atomic mass of a compound, related to its density;  $T_m$  - is the melting point of the compound, K;  $a$  - is a constant equal to 52.3 J/(K×mol)

In the literature [31, 33, 34] there are many empirical and semi-empirical methods for determining the entropy of formation of compounds: methods based on the additivity of the entropy of the constituent phases, and comparative methods. Some of the formulas are given in table 4.

Other formulas [31] require knowledge of the coefficients, the determination of which is often not possible (for example, the methods of M.Kh. Karapetiyants and VA Kireev).

The activation energy of each reaction can be found from the formula [19]

$$(5) \quad E_{ai} = T_m (S_r + R)$$

which is actually a reflection of the law of conservation of energy.

The enthalpies of the reactions  $\Delta H_{ri}$  are calculated by the formulas:

$$(6) \quad \Delta H_{r,i} = \sum_{\text{products}} \nu_{ki} H_{f,k} - \sum_{\text{reagents}} \nu_{kj} H_{f,k}$$

where are the enthalpies of formation.

The heat of formation (enthalpy) for pure substances is obviously taken to be zero. Enthalpies and entropies of formation of compounds, found from the literature [21-30, 33, 34], as well as heat capacity, melting temperature, molar masses are given in Table 5.

Table 4. Basic formulas for calculating the entropy of formation of compounds

The author of the method	Formula for calculating entropy $S_{298}^0$	Calculation error
Latimer	$S_{298}^0 = 1.5R (\ln A_k + y \ln A_a) - 0.94 (1+y)$ , where $A_k, A_a$ - are the atomic weights of cation, anion	15-50 % (abs.)
Hertz	$S_{298}^0 = k (M/C_{p,298})^{1/3}$ , $k=1033$ $M$ - is the molecular weight of the compound	20 %
Kelly	$C_{p,298}$ - is the standard heat capacity of the compound $S_{298}^0 = 1.5R x \ln A_k + 1.5R (C_{p,298}/(6-x) \ln A_a) + (x+y)S_0$ $S_{298}^0 = xS_A + yS_B - U_{298} / (k_1 U_{298} + k_2)$	4-15 % (abs.)
Yazimirsky	$S_A, S_B$ - are the entropy of the gaseous cation and anion under standard conditions, $U_{298}$ - is lattice energy	5 % (abs.)
Kaufman	$S_{298}^0 = S_k (\Theta_A / 298) + 10^{-4} U_k (\Theta_A / 298) + S_k (\Theta_B / 298) + 10^{-4} U_k (\Theta_B / 298)$ $S_k, U_k$ - are oscillatory entropy and energy according to Debye, $\Theta_A, \Theta_B$ - are «Partial» characteristic temperatures of components A and B	5-10 % (abs.)

Table 5. Physical and thermodynamic properties of phases

Phase	Tm (K)	P (g·cm-3)	Cp (J·mol-1·K-1)	M (g·mol-1)	S° <sub>298</sub> (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	-ΔH <sub>298</sub> (kJ·mol <sup>-1</sup> )
TiB	2463	4.56	29.722	58.721	34.727	160.247
Ti <sub>3</sub> B <sub>4</sub>	2412	4.59	-	186.845	-	-510.29
TiB <sub>2</sub>	3498	4.52	44.145	69.489	28.493	-315.9 -323.9
TiSi	2393	4.21	27.753	75.984	49	-129.7
TiSi <sub>2</sub>	1773	4.04	53.96	104.088	61.1	-133.9
Ti <sub>3</sub> Si	1443	4.31	-	171.784	-	-330
Ti <sub>5</sub> Si <sub>3</sub>	2403	4.32	139.979	325.752	218	-579.5
Ti <sub>5</sub> Si <sub>4</sub>	2193	4.26	-	351.836	-	-584
TiC	3530	4.93	33.64	59.89	24.24	-184.5
Ti <sub>2</sub> C		4.46	-	107.8	22.43	-120.6
TiC <sub>2</sub>		4.7	-	71.9	23.01	-384
Ti <sub>3</sub> C <sub>2</sub>		2.71	-	167.7	27.86	-236.07

Note that if the latter formula (6) fully complies with the thermodynamic laws, then the calculation by formula (5) is very approximate, since it does not take into account the contributions of other related processes. Quantum chemistry for such complex systems is still powerless, and the experimental determination of the activation energies of reactions sometimes encounters insurmountable difficulties, due to the mutual influence of processes of different physical and chemical nature.

### 3.2. Features of reactions involving solids

So, the above estimates of formal-kinetic parameters are correct for ideal conditions when the reactants are mixed at the molecular level. In a real situation, this is far from the case. An important and even limiting stage of reactions involving solids is diffusion, which affects the magnitude of formal-kinetic parameters for total reactions determined experimentally [30]. Hindered diffusion through the solid layer of the reaction product leads to a significant change in its rate and expansion of the reaction zone [36]. Other features of the reaction involving solids are associated with the presence of structural defects, internal surfaces and impurities that affect the rate and mechanism of reactions, etc. [37]. Therefore, the numerical values of the pre-exponential factors cannot be considered true. The relations of these constants to each other can be considered more or less correct. To take into account the factors unaccounted for in (1), when recording the kinetic laws for reaction rates, we introduce

the deceleration parameters  $S$ ,  $p$  and the correction factor  $z$ , which makes it possible to coordinate the calculated characteristic synthesis time with the observed experimentally

(7)

$$\varphi_i = zk_{oi} \frac{1}{(Y_0 + Y)^p} \exp(-SY) \exp\left(-\frac{E_{ai}}{RT}\right) \prod_{(k)} y_k^{v_k}$$

where  $Y$  – is the total concentration of refractory phases.

Modern thermodynamic packages, a brief overview of which in relation to condensed phases is presented in [38, 39], allows calculating the equilibrium composition of multiphase multicomponent systems for isothermal conditions, calculating the equilibrium composition of products and the adiabatic temperature for high-temperature synthesis, as well as building equilibrium phase diagrams for binary and more complex systems. However, for non-equilibrium conditions with high gradients and rates of temperature change, thermodynamic modeling can only give a rough preliminary estimate. Based on the use of thermodynamics, the modern phase field method has other disadvantages associated with the need to select a large number of parameters, which reduces all efforts to a simple description of the observed effects [40]. An attempt to describe the conditions for the formation of structures of composites based on thermodynamics with allowance for the energy of internal surfaces was made by author of [41]. However, without studying the kinetics of phase

**Table 6.** Formal kinetic parameters of reactions involving Al

Nº of reaction	Reaction	Heat, Q, (J·mol <sup>-1</sup> )	k0, s <sup>-1</sup>	E <sub>a</sub> (J·mol <sup>-1</sup> ) (calculated)
1	Ti+Al=TiAl	75312	0.112·10 <sup>15</sup>	15977
2	3Ti+Al=Ti <sub>3</sub> Al	98324	0.826·10 <sup>12</sup>	56354
3	Ti+3Al=TiAl <sub>3</sub>	146440	0.861·10 <sup>14</sup>	15325
4	TiAl+2Ti=Ti <sub>3</sub> Al	23012	0.108·10 <sup>13</sup>	57404
5	TiAl+2Al=TiAl <sub>3</sub>	71128	0.743·10 <sup>14</sup>	16182
6	2Ti+TiAl <sub>3</sub> =3TiAl	79496	1.512·10 <sup>14</sup>	20391
7	TiAl <sub>3</sub> =TiAl+2Al	-71128	1.148·10 <sup>14</sup>	16182
8	TiC+Al+Ti=Ti <sub>2</sub> AlC	73860	1.459·10 <sup>14</sup>	20183
9	TiC+2Al+3Ti+C=2Ti <sub>2</sub> AlC	333220	0.711·10 <sup>17</sup>	117930
10	TiC+TiAl=Ti <sub>2</sub> AlC	-1452	1.324·10 <sup>14</sup>	18740
11	2Ti+C+Al=Ti <sub>2</sub> AlC	258300	0.34·10 <sup>14</sup>	34267
12	Ti <sub>2</sub> AlC=Ti <sub>2</sub> C+Al	-137760	0.168·10 <sup>13</sup>	81773
13	2TiC+TiAl <sub>3</sub> =TiAlC <sub>2</sub> +2Al	-82570	0.0612·10 <sup>11</sup>	217407
14	3Ti+Al+2C=Ti <sub>3</sub> AlC <sub>2</sub>	432870	0.118·10 <sup>11</sup>	204398
15	2TiC+TiAl <sub>3</sub> =Ti <sub>3</sub> AlC <sub>2</sub>	-11442	0.0498·10 <sup>11</sup>	221483
16	Ti <sub>2</sub> AlC+TiC=Ti <sub>3</sub> AlC <sub>2</sub>	-9900	0.0413·10 <sup>11</sup>	225185
17	Ti <sub>3</sub> AlC <sub>2</sub> =Ti <sub>2</sub> AlC+TiC	9900	0.457·10 <sup>19</sup>	225185
18	2Ti <sub>2</sub> AlC=Ti <sub>3</sub> AlC <sub>2</sub> +TiAl	-8538	0.027·10 <sup>11</sup>	183071
19	3Ti+Al+C=Ti <sub>2</sub> AlC	277570	4.622·10 <sup>11</sup>	99334
20	Ti <sub>2</sub> C+TiAl=Ti <sub>3</sub> AlC	81658	0.886·10 <sup>14</sup>	18340

formation processes, such an approach is hardly applicable for non-equilibrium conditions.

### 3.3. Ti-Al-C system

The chemical reaction system becomes more complex, when aluminium is added to the mixture. There is a potential for the formation of intermetallic phases. Triple compounds appear. For example, in the Ti-C-Al system, reactions leading to the formation of TiAl, TiAl<sub>3</sub>, Ti<sub>2</sub>AlC, Ti<sub>3</sub>AlC<sub>2</sub>, etc. (Tables 6 and 7) are added to the reactions listed in Table 3. The main reason for the growing interest in MAX phases is the unusual combination of their properties, as well as the corresponding carbides (nitrides, silicides) MAX phases have high mechanical properties, heat and electrical conductivity, resistance to chemical

influences and have a low coefficient of thermal expansion [42]. These properties lead to a search for the possibilities of obtaining and/or using MAX phases in 3D technologies [43]; to search for ways to control the relative content of MAX phases in SHS conditions [44-46]

Table 6 contains the possible stages of chemical reactions involving MAX phases [47-49] and some of the reactions of formation of intermetallic compounds in the Ti-Al system.

## 4. Model of controlled synthesis of a composite on a substrate

### 4.1. Basic equations

When formulating a mathematical model of sintering with a laser or electron beam, we

**Table 7.** Physical and thermodynamic properties of MAX phases and intermetallic compounds [27,29,50-53]

Phase	T <sub>m</sub> (K)	ρ (g·cm <sup>-3</sup> )	C <sub>p</sub> (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	M (g·mol <sup>-1</sup> )	S <sub>298</sub> <sup>o</sup> (J·mol <sup>-1</sup> ·K <sup>-1</sup> )	-ΔH <sub>298</sub> (kJ·mol <sup>-1</sup> )
TiAl	1753	3.82	49.239	73.981	52.3	-75.31
TiAl <sub>3</sub>	1613	3.36	98.885 90.499	127.943	92.38	-146.44
Ti <sub>3</sub> Al	1313	4.42		167.981	78.094	-98.324
Ti <sub>2</sub> AlC	1898	4.11	81	134.7155	78.1	-258.36
Ti <sub>3</sub> AlC <sub>2</sub>	2373	4.2	125.4	194.605	15.759	-432.87
Ti <sub>2</sub> AlC	1853	4.24	-	182.5825	73.146	-277.57

assume that the powder used for layer-by-layer growing of the product is a composite of a given complex composition depending on the production conditions, or a mixture of powders. Based on the simulation, it is necessary to select the technological conditions that ensure uniform sintering and the predicted amount of shrinkage [54, 55]. Below we will demonstrate the model of the electron-beam sintering process for the technology with a pre-applied powder layer. Note that when growing products of small sizes, the process is essentially non-stationary, therefore, it is required to explicitly set the mode of beam movement and energy distribution in the beam:

$$(8) \quad q_e(x, y, z, t) = q_0 \exp\left[-\frac{(x - V_x t)^2 + (y - V_y t)^2}{R_0^2}\right]$$

where the components of the rate vector  $V_x$  and  $V_y$  determine the scanning mode (the trajectory of the electron beam), the parameter  $R_0$  is the effective radius of the beam, and the value of  $q_0$  depends on the  $R_0$  current in the beam and the voltage. Additionally, in the numerical implementation of several passes, new parameters  $h_{ox}$ ,  $h_{oy}$  appear, which determine the scanning steps along the axes of the Cartesian coordinate system.

For a thermally thin plate or a thin coating and a thin surface layer of the substrate (the thickness of the layers should be less than the characteristic thermal scale), as in [56-58], we neglect the temperature distribution over depth. We do not analyze the hydrodynamics of the melt clearly, but we believe that the kinetic parameters in the law of porosity change and the degree of shrinkage depend on hydrodynamics. Then the thermal part of the problem will include the two-dimensional heat equation

$$(9) \quad h_1 U \frac{\partial T}{\partial t} + c_2 \rho_2 h_2 \left[ u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right] = h_1 \left[ \frac{\partial}{\partial x} \left( W \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( W \frac{\partial T}{\partial y} \right) \right] - \sigma \varepsilon_0 (T^4 - T_0^4) + q_e(x, y, t) + W_{ch} - \alpha_{eff} (T - T_0)$$

where

$$W = \lambda_1 + \lambda_2(\theta) \frac{h_2}{h_1}$$

is equivalent thermal conductivity,

$$U = c_1 \rho_1 + c_2 \rho_2 \frac{h_2}{h_1} (1 - \theta)$$

is equivalent heat capacity

$$u = \frac{\lambda_2}{c_2 \rho_2} \frac{1}{h_2} \frac{\partial h_2}{\partial x} \quad v = \frac{\lambda_2}{c_2 \rho_2} \frac{1}{h_2} \frac{\partial h_2}{\partial y}$$

are convective rates appearing due to changes in layer thickness [59];  $\lambda_i$ ,  $c_i$ ,  $\rho_i$  and  $h_i$  - are thermal conductivity, heat capacity, density, and thickness of the substrate (base material)  $i = 1$  and powder layer  $i = 2$ . The third term in (9) describes the fourth heat loss from the surface according to the Stefan-Boltzmann law; fourth - external heating;  $W_{ch}$  represents the total chemical heat release, and the last term shows the effective heat loss to the depth of the substrate with the coefficient  $\alpha_{eff}$  (if the substrate has a considerable thickness).

A change in the porosity  $\theta$  leads to a change in the thermophysical properties and shrinkage of the powder layer. The heat capacity of the filled particles  $c_2 \rho_2$  is calculated according to the mixture rule, depending on the fraction of the phases. The thermal conductivity of the powder layer depends on the porosity of the law

$$\lambda_2(\theta) = \lambda_{m2} \exp\left(-\frac{1.5\theta}{1-\theta}\right)$$

where  $\lambda_{m2}$  - is the thermal conductivity, also calculated by the rule of the mixture. The law of change in porosity (as a thermally activated process) is written in the form:

$$(10) \quad \frac{d\theta}{dt} = -z_0 \exp(-E/RT) \theta(\theta_0 - \theta)$$

where  $z_0$ ,  $E$  - are parameters that depend on the dynamics of various physical processes at the micro level, which are not explicitly taken into account in the model.

The thickness of the powder layer varies according to the law:

$$(11) \quad \frac{dh_2}{dt} = k_p \varphi(\theta),$$

where

$$\varphi(\theta) = d_p \frac{(1 - \theta_0)}{(1 - \theta)}$$

$d_p$  - is the average particle diameter of the powder,  $\theta_0$  - is the bulk porosity.

The system of kinetic equations for the components involved in the reactions is:

$$(12) \quad \frac{dy_k}{dt} = \omega_k, \quad k = 1, 2, \dots, n$$

where

$$\omega_k = \sum_{i=1}^r v_{ki} \varphi_i, \quad k = 1, 2, \dots, n$$

Close the task boundary and initial conditions:

$$(13) \quad x=0, H_x: \lambda \frac{\partial T}{\partial x} = 0; \quad y=0, H_y: \lambda \frac{\partial T}{\partial y} = 0;$$

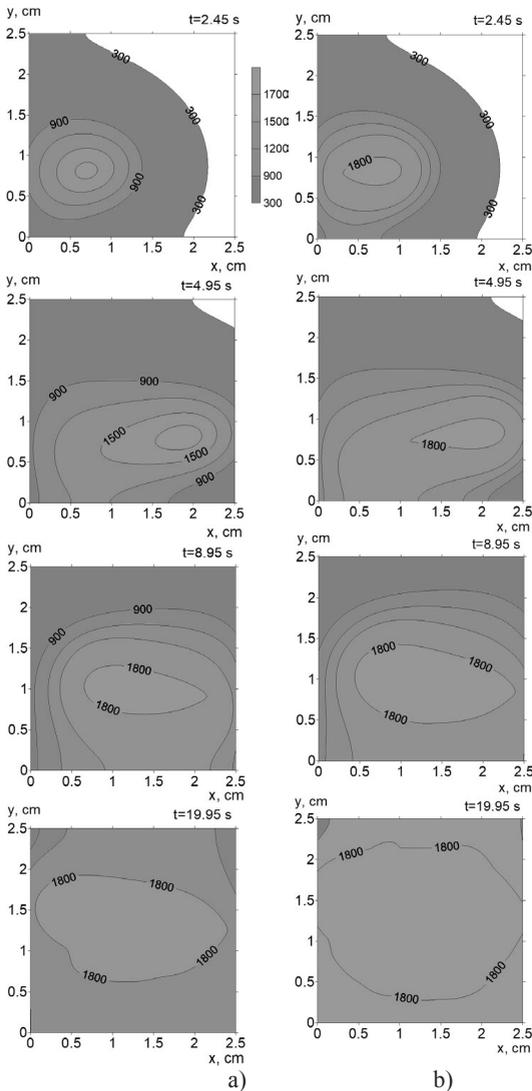
(14)

$$t=0: \quad T(x, y, 0) = T_0, \quad h_2 = 0, \quad \theta = \theta_0$$

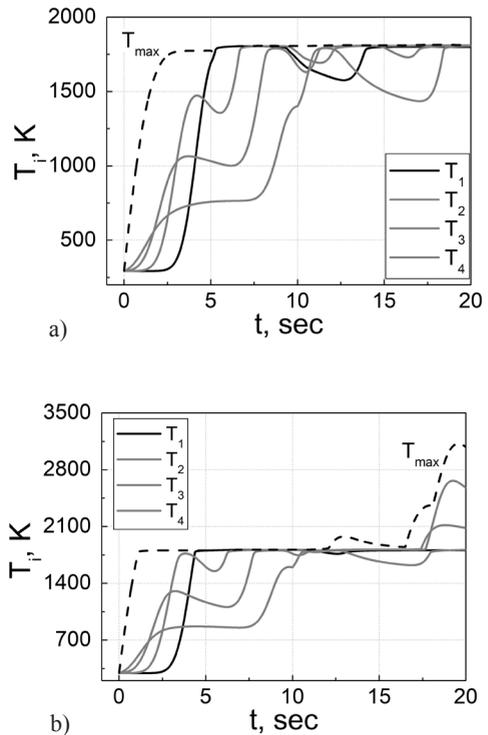
Numerical implementation of such models is carried out using implicit difference schemes, coordinate splitting and the sweep method for the heat equation, and any suitable method for solving systems of kinetic equations.

## 4.2. Calculation example

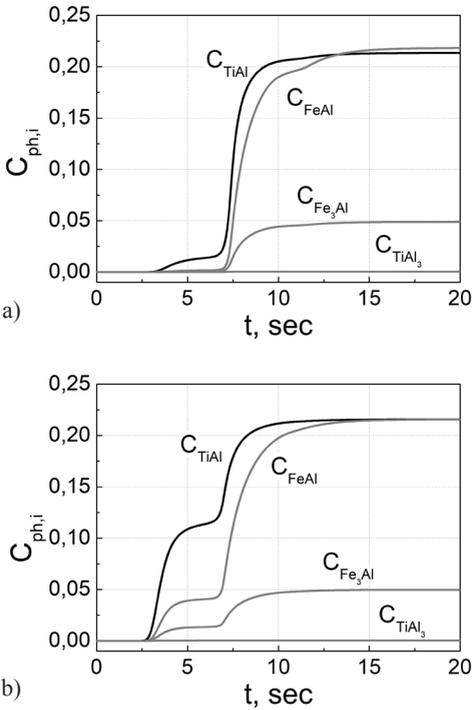
As an example, let us dwell on the system of Ti and Al, which attracts increased attention of researchers. The metal matrix composites obtained on their basis have a high level of physicomaterial



**Figure 1.** Inhomogeneous temperature field in the process of electron beam fusion for different densities of electron beam flux moving with rate  $V = 0.5$  cm/s. a)  $q_0 = 0.9 \cdot 10^5$  W/cm<sup>2</sup>; б)  $q_0 = 1.35 \cdot 10^5$  W/cm<sup>2</sup>



**Figure 2.** Thermal cycles. Temperature curves correspond to the coordinates 1- ( $x = 2.125, y = 0.875$ ), 2- ( $x = 1.5, y = 1.125$ ), 3- ( $x = 1, y = 1.375$ ), T4 = ( $x = 0.5, y = 1.625$ ). a)  $q_0 = 0.9 \cdot 10^5$  W/cm<sup>2</sup>; б)  $q_0 = 1.35 \cdot 10^5$  W/cm<sup>2</sup>

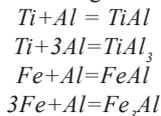


**Figure 3.** The evolution of mass concentrations of the formed compounds in time for different values of electron beam energy flux densities:

a)  $q_0 = 0.9 \cdot 10^5 \text{ W/cm}^2$ ; b)  $q_0 = 1.35 \cdot 10^5 \text{ W/cm}^2$

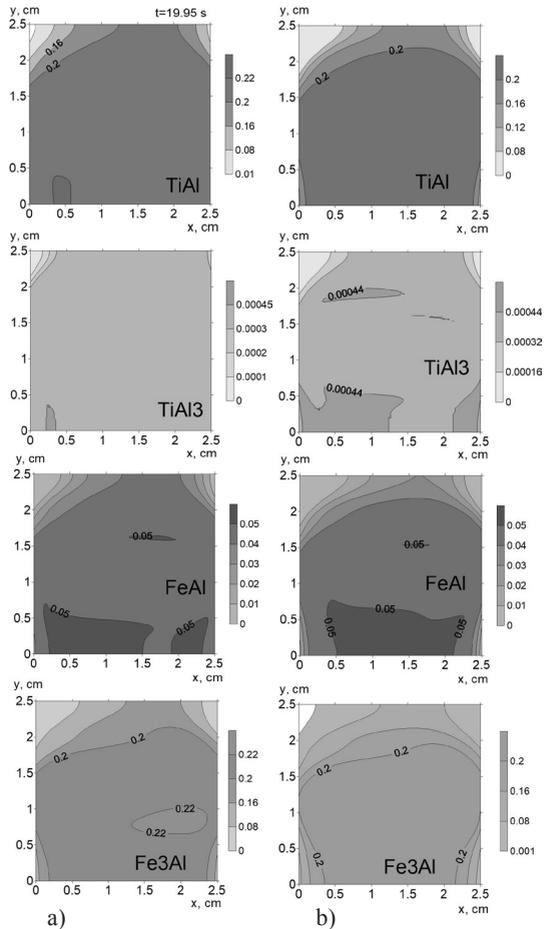
and operational properties, which leads to the expansion of the temperature and force intervals of operation of the corresponding products [60]. Significant progress has been made in the preparation of modifying ligatures and composite alloys of the Al-Ti, Al-Ti-B, Al-Ti-C systems [61]. The possibilities of synthesizing intermetallic composites of the Al-Ti system under the conditions of modern 3D laser technologies are discussed, for example, in [62–64]. However, when using the energy of the electron beam, there are features associated with other conditions of heat transfer.

During the deposition of the first layer or heat treatment of a previously applied surface layer, the interaction of Ti and Al with the substrate is possible. Considering that it is made of iron, we will additionally consider the stages

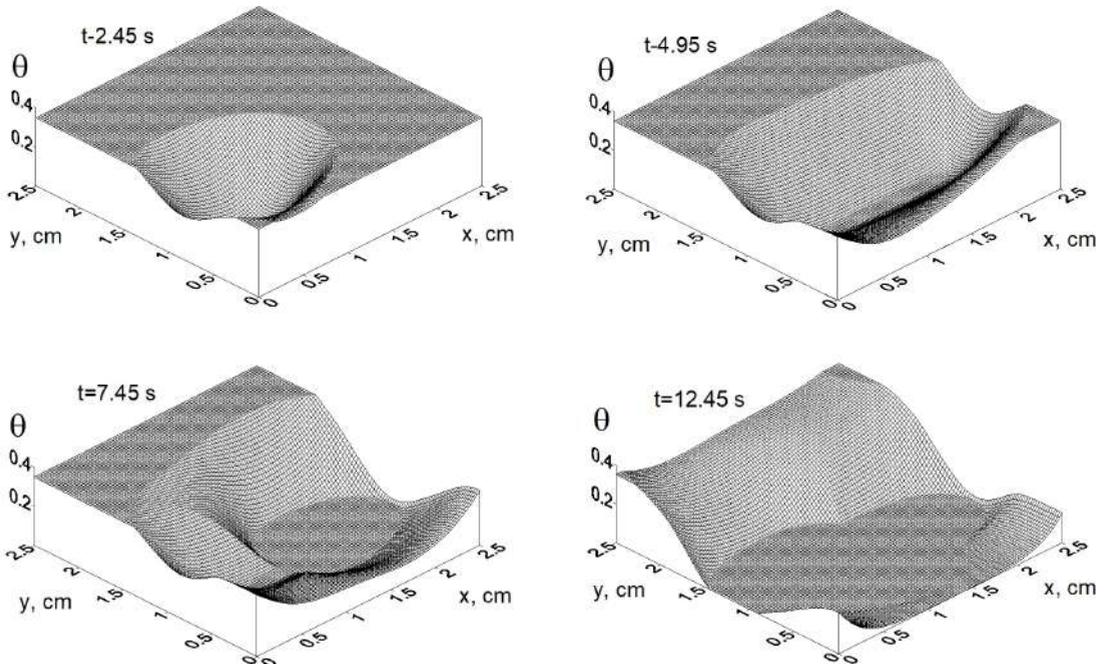


At the initial time, the molar concentrations of the components are  $y_{Ti} = 0.0354 \text{ mol/cm}^3$ ,  $y_{Al} = 0.0625 \text{ mol/cm}^3$ ,  $y_{Fe} = 0.141 \text{ mol/cm}^3$ . This corresponds to the mass content of Ti and Al - 50/50. In the calculations it is assumed:  $q_0 = 0.9 \cdot 10^5 \text{ J/cm}^2$ ,  $v_x = 1$ ;  $v_x = 0 \text{ cm/s}$ ;  $a = 0.1 \text{ cm}$ ,  $a_p = 0.05$ ,  $z_0 = 2.5 \cdot 10^4 \text{ 1/s}$ ;  $E = 85000 \text{ J/mol}$ .

Fig. 1-5 demonstrate the non-stationary picture of the process and the heterogeneous nature of the synthesis. The beginning of the movement of the beam starts at a point with coordinates ( $x=0$ ,  $y=0.875$ ) cm. The next three passes start from points - ( $x=2.5$ ,  $y=1.125$ ), ( $x=0$ ,  $y=1.375$ ), the fourth and ( $x=2.5$ ,  $y=1.625$ ), respectively. Only the area adjacent to the area of the beam is heated to a temperature sufficient to melt and accelerate chemical reactions (Fig. 1). The stationary form



**Figure 4.** The final phase composition of the surface layer at the time of the end of the fourth passage a)  $q_0 = 0.9 \cdot 10^5 \text{ W/cm}^2$ ; b)  $q_0 = 1.35 \cdot 10^5 \text{ W/cm}^2$



**Figure 5.** The evolution of porosity in the process of surface treatment with an electron beam.  
 $V = 0,5 \text{ cm/s}$ ,  $q_0 = 0.9 \cdot 10^5 \text{ W/cm}^2$ ;

of the molten bath and the heat-affected zone are not established, which does not allow stationary models commonly used in the literature to be used to analyze such processes.

Thermal cycles depend both on the distance between passes, the rate of the beam, the flux density, and the size of the workpiece. At  $q_0 = 0.9 \cdot 10^5 \text{ W/cm}^2$  the maximum temperature (dotted line in Fig. 2, a, b), reached on the surface is close to the melting point. On the curves  $T(t)$ , plotted at different points of the sample, there is a plateau corresponding to the melting point. As observed in the experiment, melting in separate parts can occur repeatedly. With an increase in the flux density up to  $q_0 = 1.35 \cdot 10^5 \text{ W/cm}^2$  (Fig. 2b), considerable overheating is possible, associated not only with the accumulation of heat in the process of heating by the electron beam, but also as a result of chemical heat release.

Heterogeneous phase composition is a consequence of non-uniform heating. Different dynamics of phase accumulation correspond to different processing conditions (different values of flux density). For example, at  $q_0 = 0.9 \cdot 10^5 \text{ W/cm}^2$  the acceleration of reactions in the center of the plate starts with  $t \sim 6.5\text{-}7 \text{ sec}$  (Fig. 3,a), and then there is a slow completion of the reactions, then at  $q_0$

$= 1.35 \cdot 10^5 \text{ W/cm}^2$  the acceleration of the reactions is observed twice (Fig. 3,b). However, the resulting phase composition in the center of the sample turns out to be the same.

The curves correspond to a point with coordinates  $(x=1.125, y=1.125)$

In other parts of the sample, the composition is different. After four passes, the heterogeneous phase composition is shown in Fig.4. In the considered variant of the model and under the specified treatment conditions, the surface layer consists mainly of two phases TiAl and Fe<sub>3</sub>Al. Other phases are formed in significantly smaller quantities. It is likely to expect that the reactions may end in the process of slow cooling, and the heterogeneity of the composition may disappear. However, due to the inhibition of the reactions by the layer of the formed product, the complete transformations in the system are not observed.

Inhomogeneous porosity is associated with the non-uniform nature of the process (Fig. 5), which, in turn, affects the absorption of beam energy, the process of heat conduction and the dynamics of phase formation. In the related model, the role of all factors is interrelated, which leads to non-trivial non-linear laws.

## 5. Conclusion

Thus, the paper presents possible chemical reactions in the Ti-C, Ti-B, Ti-Si, Ti-C-Al systems and provides approximate estimates of formal-kinetic parameters for these reactions. The presented set of stages is not complete, and the reaction parameters need to be clarified. However, in the absence of experimental data for most stages, the obtained numerical values can be used to simulate the synthesis of multiphase materials under non-equilibrium conditions. This is demonstrated by the example of a model of controlled synthesis of a multiphase composite on a substrate, which takes into account the evolution of properties and the staging of the transformation. The results obtained are consistent and provide detailed information on the mutual influence of various physicochemical processes in non-stationary conditions.

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