



Modeling of Thermal Processes at Forming a Composite Coating of plastering with SHS-reagents

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Abstract Thermal processes at forming a composite titanium carbide basis coating are investigated in work. The mathematical model of thermal processes at influence by a plasma impulse on the plaster containing SHS-reagents with initiation of the self-propagating high temperature synthesis is developed. Boundary value problem was solved by finite volume method in two-dimensional statement with use of iterative processes. A series of numerical experiments on studying of behavior of initial charge at various processing of a sample is carried out. It is shown that a character of SHS significantly depends on the power of a plasma stream, a distance of processing, heating of a substrate, etc.

Keywords: Thermal processes, SHS-reagents, numerical modeling, finite volume method, composite coating.

1. Introduction

Management of surface properties of details by application of protective coatings plays important role in increase in their service life and increase of operational durability of modern machines and mechanisms. Large number of works in domestic and foreign literature is devoted to technology of application of the strengthening coatings (for example, [3], [9], [17]). Effective process forming of the wear-resistance materials and coatings containing solid inclusions (for example, titanium carbides), is the self-propagating high-temperature synthesis (SHS) [11].

The main differences of temperature mode SHS in burning wave are as follows:

- high speeds of heating which cannot be implemented when using other processes take place;
- burning temperature in wave of SHS can reach 4000 K. Obtaining such temperatures in furnaces demands the high-end equipment with use of expensive heaters and thermal insulations from special materials. Besides, it requires big energy costs (power of furnaces of 10-15 kw is necessary for receiving even rather low temperatures about 1700°C). High temperature of burning in SHS - wave creates conditions for increase of process efficiency;
- heating of the environment happens equally on mass (unlike external heating) due to chemical reaction heat.

Application of SHS is usually connected with additional processing of initial materials [1], [6], [10]. In particular, crushing is required as the initial product has to represent mass with certain dispersion. SHS fall within the realms of kinds of burning processes, has the thermal nature basis of which is reaction of exothermic interaction of two or several chemical elements (reaction proceeds in the mode of the directed burning). After local initiation the interaction of reagents is carried

out in fine layer and propagates on all system due to heat transfer from hot products in reaction zone to cold initial substance. Series of methods of initiation of SHS is applied, and the choice of one of them is defined only by practical conveniences and does not influence on properties of the final product. It is experimentally established that SHS applies to difficult initiated burning processes.

At high-energy source effect on sample there is initiation of burning [13]. In thermal process it is possible to allocate three zones conditionally: preheating; reaction zone where burning with big allocation of heat energy on support of burning reaction is carried out; cooling zone. In models of microheterogeneous burning it is supposed that distribution of its front takes place two stages: fast burning of the local area or elementary reactionary cell and relatively long stage of preliminary heating of the following cell, i.e. ignition delay stage. According to this theory, one area initiates another, i.e. the burning mechanism in system is relay [2].

Let's note that for systems with high heat of reaction to which refers composition Ti+C, burning speed poorly depends on the sample size even at very small values (less than 1 cm in the diameter) as the heat generation rate in reaction zone considerably exceeds the level of heatlosses (fast-burning systems).

At the same time for many SHS-systems (slowburning) in which the heat generation rate is insufficiently high, heatlosses start affecting at the sample sizes about 1 cm that lead to reduction of burning rate, non-afterburning and even attenuation of process.

Noted features demand more detailed description of thermal processes for coatings applying technologies using SHS-reagents.

Modeling Bases of processes of thermal spraying of coatings are stated in [4]. The researches and technology development executed for the last decades in the field of SHS have laid the foundation of modern and perspective scientific and technical area which have own structure, the directions of researches and applications. Purposeful search of new SHS-systems, studying of the mechanism and regularity of their burning and conditions of synthesis are perspective of development of the SHS method and development of new effective technology processes.

Actuality of creation of mathematical model and its research it is caused also by need of the analysis of considerable number of experimental data, part from which will not be coordinated among themselves.

The purpose of work is development of mathematical model of the self-propagating high-temperature synthesis at forming composition coatings of the plastering containing powder mix of pure elements of titanium and carbon in stoichiometrical ratio, inert filling agent as nichrome powder with provision for possible melting of components and chemical kinetics of reaction.

The offered model was used for optimization of SHS-process at forming composite coatings NiCr/FeCr+TiC.

2. Formulation of the problem

2.1. Technology Bases of Coating Formation of the plastering containing SHS-reagents

For applying a coating use powder mass with a certain dispersion of particles. For implementation of technology a preparation of charge of Ni80Cr20 or FeCr30 and SHS-reagents (titanium and carbon) with preliminary mechanical activation of components is provided. For applying initial layer of components as plastering on a surface of a substrate use binding substance on a nitrocellulose basis (zapon lacquer). The binding substance allows to receive a layer of initial reagents and to displace intensive oxidation of the titanium in area of the increased temperatures. The organic connective allows to carry out also drying of a plastering with simultaneous preliminary heating of a sample. Then the plastering is processed an impulse of plasma and create the high-concentrated energy stream for initiation of heating and interaction of SHS-reagents with heat allocation. Thus the solid refractory titanium carbide distributed in Ni80Cr20/FeCr30 or in others binding agents are synthesized, the liquid phase is formed, and the coating on a substrate is formed. For consolidation, crushing of structure and receiving non-equilibrium amorphous phases of the increased durability the coating is processed by impulses of plasma and carry out its layer-wise fusion on all thickness additionally.

At impact of the high-concentrated energy stream on a sample there is a burning initiation. Burning speed and temperature of reaction depend on a number of parameters: thermodynamic (heat of formation of the final products of synthesis, thermal capacity of products of reaction, initial temperature of process, composition of initial mix); physical (heat conductivity of initial mix, sample density, external pressure of gas, form and size of particles of powders, existence of external influences); technological (uniformity of agitation of components of mix, extent of activation of powders); chemical (degree of moisture content of powders, concentration in them the adsorbed impurity and the dissolved gases).

Impulses of a plasma stream received by gas-discharge quasistationary accelerator of a type magnetoplasma compressor (MPC). The first impulse has to initiate exothermic reaction in system "titanium-carbon" without destruction of a plastering, the subsequent its – layer-wise fuse sinter formed on a substrate (Figure 1) [5].

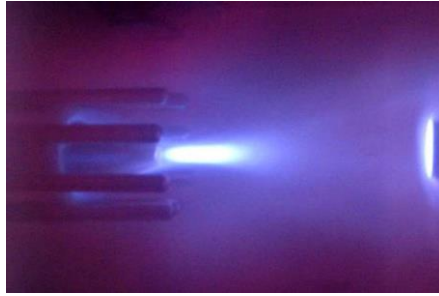


Figure 1. Impulse - plasma processing of a plastering for formation of a coating

Duration, power of impulses and distance of processing get out in such a way that conditions to start exothermic reaction in the nearby to a surface particles of microcomposite "titanium-carbon" and possibility of initiation of burning in the nearby reactionary cells were provided.

Characteristic appearance of samples before and past impact on a plastering by optimized impulse of plasma is shown in Figure 2. Pictures are executed on a stereomicroscope "Technival" by "Carl Zeiss Jena" (Germany).

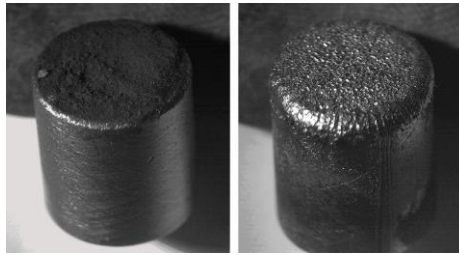


Figure 2. Characteristic appearance of samples before processing of a plastering and after influence by the optimized plasma impulse

2.2. Mathematical Model of Thermal Processes

Let's consider the thermal processes arising in a sample under the influence of an impulse of a plasma stream with provision for possibility of burning of powdery mixes of the titanium and carbon with the mass content of components 80% Ti and 20% C that corresponds to the equation of reaction $Ti+C$. One refractory product TiC is result of this irreversible single-stage reaction of solid reagents.

We will describe thermal processes in a coating-substrate in two-dimensional cartesian reference system.

At developing thermal model we will assume that as particles with reactionary components we have a particle-"microcomposite" of the same structure, but with rather big reactionary surface.

Power of a thermal source has to provide heating of system in such a way that it was capable to burn, i.e. was rather exothermal.

2.2.1. Computation domain

As the studied model domain in the cartesian reference system we will choose a sample in the form of a rectangle with sizes 10x10 mm on which top part the plastering with thick 0.6 mm is evenly applied (see Figure 3). From a plastering, perpendicular to a sample the high-concentrated thermal stream of a plasma stream falls, on other boundaries of domain there is a heat exchange to environment.

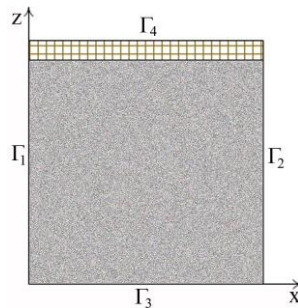


Figure 3. Computation domain

We will carry out the description of processes proceeding from fundamental laws of mechanics of the continuous environment. As the coating is composite structure, we will agree that in the continuous environment, for example, from ni-chrome, particles—"microcomposites" of structure Ti+C are evenly distributed.

2.2.2. Main Equations

We will describe heat distribution in a sample by the equation of balance of energy in the cartesian reference system at the assumption of isotropy of the environment

$$\rho \frac{\partial H}{\partial t} = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial z} \left(\lambda \frac{\partial T}{\partial z} \right) + Q, \quad \text{for } t > 0, \quad (1)$$

where H – specific enthalpy, $\rho = \rho(T)$ – density, $T = T(x, z, t)$ – temperature at point (x, z) at the moment of time t , $\lambda = \lambda(T)$ – heat conduction of material, Q – thermal effect from reaction for reactionary cells, for other cells $Q = 0$.

Let's copy a specific enthalpy with provision for melting of components as

$$H = H(T) = \begin{cases} H(T_o) + cT, & T < T_m, \\ H(T_m - 0) + L_m + \delta(T - T_m), & T > T_m, \end{cases}$$

where $H(T_o)$ – initial enthalpy, c – thermal capacity of unit of volume, T_m – material melting temperature, L_m – hidden specific heat of melting of material, δ – Delta function of Dirac. Value L_m defines the minimum energy necessary for transition of unit of mass of substance from a solid state in liquid at a material melting temperature.

Let's enter effective coefficient of a thermal capacity of materials with provision for heat of melting as $c^{eff} = c + L_m \delta(T - T_m)$, where $c = c(T)$.

For composite material heat-physical coefficients it is calculated according to the rule of mix taking into account a mass fractions of the materials Ti, C and TiC

As an initial condition at $t = 0$ we will consider the known reference temperature T_0 or initial energy H_0

$$T(x, z, 0) = T_0 \quad \text{or} \quad H(x, z, 0) = H_0. \quad (2)$$

2.2.3. Chemical reaction

Characteristic of exothermic reactions is the structure and properties of the final product substantially depend on reaction course conditions, in particular on the mass content of components, their power state, porosity, etc.

Also information on reaction rates and characteristic temperatures have great importance. For receiving a qualitative product it is necessary to know how each factor influences on course of reaction and distribution of the burning front. Therefore, for computation experiments by developed model it is necessary to make also a series of the technological experiments confirming the used parameters and bonds.

Let's consider in reactionary cells reaction of burning of the two-component Ti+C system forming a refractory product TiC in irreversible single-stage reaction, i.e. we will consider reaction types



Let $W = d\eta / dt$ – rate of chemical conversion, where η – the depth of conversion of the reagent in the reaction cell. Obviously $0 \leq \eta \leq 1$.

In [7] regularities of burning of mixes of the fine-dispersed titanium particles at diameter in the order of 1 mm with carbon are experimentally studied and the mechanism of interaction of the titanium with carbon in a burning wave is described. According to [7] from the analysis of the state diagram, in a wave of burning the carbide phase of variable structure and solution of carbon in the liquid titanium can be formed. Then, interaction of the titanium with carbon in a burning wave can be presented in the form of two stages: 1) formation of a carbide layer of variable structure, 2) dissolution of carbon in the liquid titanium.

As the kinetic equations are fair only for homogeneous reactions, and reagent can be in a liquid phase, it is necessary to consider two types of chemical reaction: for a solid and liquid phase [15]. In [8] for the mix Ti and C it is established that the leading stage of transformation proceeds on a zero order.

Therefore for the description of kinetics of chemical reaction we will consider the kinetic equations of a zero order with a constant of the chemical reaction given by the Arrhenius law

$$W = k_1(T) f_1(\eta) = k_{0,1} \exp(-E_{a,1}/(RT)) f_1(\eta) \quad \text{for } T < T_{m,Ti}, \quad (4)$$

$$W = k_2(T) f_2(\eta) = k_{0,2} \exp(-E_{a,2}/(RT)) f_2(\eta) \quad \text{for } T \geq T_{m,Ti}, \quad (5)$$

where $k_{0,1}$, $k_{0,2}$ – pre-exponentials coefficients (c^{-1}), $E_{a,1}$, $E_{a,2}$ – energy of activation before and after melting of

reagent Ti, $T_{m,Ti}$ – temperature of melting of reagent Ti; $f_i(\eta) = 1$ if $\eta \leq 1$, and otherwise $f_i(\eta) = 0$ if $\eta > 1$.

The assignment of different constants of chemical reactions $k_1(T)$ and $k_2(T)$ in (3), (4) allows take into account the change of response rate with the appearance of the liquid phase.

As an initial condition for (4), (5) we will consider system in which reagents did not react, i.e. we will put

$$\eta(x, z, 0) = 0. \quad (6)$$

We will calculate thermal effect from formation of a product in reactionary cells by formula

$$Q = \tilde{Q}\rho \frac{\partial \eta}{\partial t}, \quad (7)$$

where \tilde{Q} – specific heat of reaction, $d\eta/dt$ – part of the reacted component.

2.2.4. Boundary Conditions

On lateral (Γ_1 and Γ_2) and lower (Γ_3) boundaries of domain we consider boundary conditions of heat transfer with environment which temperature is constant (see Figure 4)

$$\lambda \frac{\partial T}{\partial x} \Big|_{x=0} = \alpha_{T,1}(T - T_{1,out}), \quad -\lambda \frac{\partial T}{\partial x} \Big|_{x=L_x} = \alpha_{T,2}(T - T_{2,out}), \quad (8)$$

$$\lambda \frac{\partial T}{\partial z} \Big|_{z=0} = \alpha_{T,3}(T - T_{3,out}), \quad (9)$$

where $T_{l,out}$ – environment-temperature on the corresponding boundary of domain, $\alpha_{T,l}$ – heat transfer coefficients on boundaries.

On the upper bound of sample from plasma stream we will consider the law of heat transfer in the form of boundary conditions of heat transfer with radiation

$$-\lambda \frac{\partial T}{\partial z} \Big|_{z=L_z} = \alpha_{T,4}(T - T_{str}) + \beta\varepsilon(T^4 - T_{str}^4), \quad (10)$$

where β – Stefan-Boltzmann constant, ε – degree of blackness of the surface, $T_{str} = T_{str}(x)$ – temperature of plasma stream on domain boundary.

The heat flow from plasma stream has axisymmetric form and Gaussian distribution of temperature from axis of plasma stream. According to data [4], temperatures on the section of axis of traditional plasma stream at different distances from nozzle are presented on Figure 4.

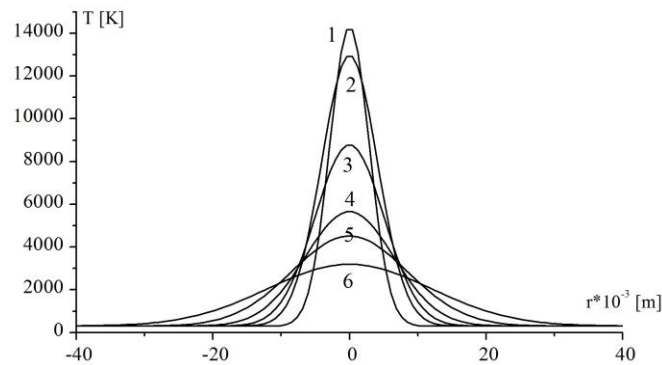


Figure 4. Distribution of temperature of stream on axis section at distance from nozzle:
1) 0.0 m; 2) 0.02 m; 3) 0.05 m; 4) 0.08 m; 5) 0.10 m; 6) 0.15 m

At shutdown of impulse considered boundary conditions

$$-\lambda \frac{\partial T}{\partial z} \Big|_{z=L_z} = \alpha_{T,4}(T - T_{4,out}), \quad (10a)$$

where $T_{4,out}$ – ambient temperature after shutdown of impulse, $\alpha_{T,4}$ – heat exchange coefficient with environment.

Equations system (1), (4), (5) with boundary (8) - (10) and initial conditions (2), (6) and auxiliary ratios make the mathematical model describing heating and burning of heterogeneous system with SHS-reagents as "microcomposites" at the influence of impulse of plasma stream.

The given equations system are solved concerning temperature and the degree of reagent conversion in cells with "microcomposite".

2.3. Numerical method

For research of thermal condition of model with broad range of materials with significantly different heat-physical properties and at different method of temperature processing of surface of model the most effective instrument of research in addition to experimental methods is numerical modeling. For creation of numerical method we will use method of finite volume method (FVM). Let's carry out discretization of grid domain.

2.3.1. Grid domain

Domain of calculation D (e.g. Figure 3) in cartesian coordinate system x, z connected with the considered model, we will divide into rectangular cells $\omega_{i,k} = [x_i, x_{i+1}] \times [z_k, z_{k+1}]$ so that $D = \bigcup_{i,k} \omega_{i,k}$. We will carry out numbering of cells on indexes of coordinates of the left bottom corner of cell.

We will make initial splitting into cells according to structure of plastering of coating. Let's choose the scheme of laying of particles—"microcomposites" with SHS reagents in matrix. The plastering fragment from one of schemes of laying of particles—"microcomposites" in binding matrix of nichrome is presented on Figure 5.

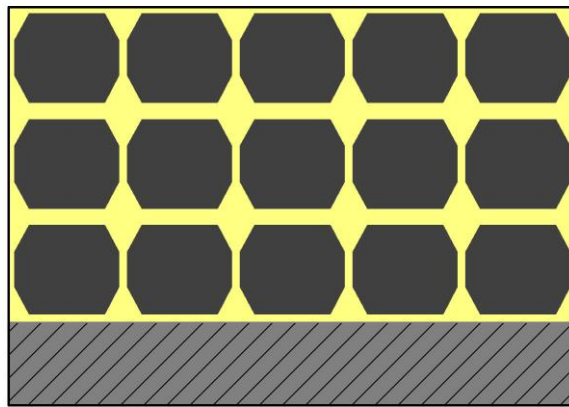


Figure 5. Geometrical model of fragment of plastering of the coating containing 15 particles—"microcomposites"

Contact between "microcomposites" is carried out through layer of inert binding material. Representation of plastering in the form of the structured environment is represented to more perspective for the description of thermal processes in coating in view burning of SHS-reagents as considers features of structure and local changes of heat conductivity in initial plastering.

As reactionary cells considerably exceed by the layer sizes between them, for numerical method they divide into smaller which by the sizes will be commensurable with inert particles of matrix. The number of splittings varies depending on the sizes of "microcomposites".

The considered model system of grid cells represents two-dimensional structure of the interacting particles located in cells of grid domain.

Each cell is characterized by temperature average on the volume of cell

$$T_{i,k} = T(x_{i+1/2}, z_{k+1/2}) \approx \frac{1}{V_{i,k}} \int_{x_i}^{x_{i+1}} \int_{z_k}^{z_{k+1}} T \, dx \, dz$$

and certain heat-physical properties, such as heat conductivity, heat capacity, density, i.e. corresponding properties of material of this cell which define heat exchange with the next cells. Therefore the condition of reactionary cell $\langle i, k \rangle$ at any moment is unambiguously set by two parameters – the cell average on volume temperature and depth of transformation $\eta_{ik} = 1 - m_{ik} / m_{0,ik}$, where m_{ik} and $m_{0,ik}$ respectively the current and initial mass of fuel in reactionary cell. At any moment we set condition of inert cells $\langle i, k \rangle$ only temperature T_{ik} .

The considered model rather general and includes such processes as the accounting of various mechanisms of reac-

tion which are more effective and adequate at modeling thermal processes after mechanical activation of components. Mechanical activation provides additional energy of particles—"microcomposites", a big surface of contact between reagents that often provides course of reaction on a solid-phase sign. As the main emphasis in work is placed on modeling of thermal processes with SHS-reagents without mechanic activation, at numerical modeling we will stop on process of burning on the liquid-phase mechanism.

2.3.2. Difference scheme

On the grid domain differential problem (1)-(10) we approximate a by FVM. For this purpose we will integrate the equation (1) on the volume of an internal cell $\omega_{i,k}$

$$\int_{x_i}^{x_{i+1}} \int_{z_k}^{z_{k+1}} c\rho \frac{\partial T}{\partial t} dx dz = \int_{x_i}^{x_{i+1}} \int_{z_k}^{z_{k+1}} \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) dx dz + \int_{x_i}^{x_{i+1}} \int_{z_k}^{z_{k+1}} \frac{\partial}{\partial z} \left(\lambda \frac{\partial T}{\partial z} \right) dx dz + \int_{x_i}^{x_{i+1}} \int_{z_k}^{z_{k+1}} Q dx dz.$$

The FVM discretization the previous equation yields the implicit differential scheme type

$$c_{i,k} \rho_{i,k} \frac{T_{i,k} - \tilde{T}_{i,k}}{\Delta t} = \frac{1}{\Delta x_i} \left(\lambda_{(i+1,k+1/2)} \frac{T_{i+1,k} - T_{i,k}}{0.5(\Delta x_{i+1} + \Delta x_i)} - \lambda_{(i,k+1/2)} \frac{T_{i,k} - T_{i-1,k}}{0.5(\Delta x_i + \Delta x_{i-1})} \right) + \frac{1}{\Delta z_k} \left(\lambda_{(i+1/2,k+1)} \frac{T_{i,k+1} - T_{i,k}}{0.5(\Delta z_k + \Delta z_{k+1})} - \lambda_{(i+1/2,k)} \frac{T_{i,k} - T_{i,k-1}}{0.5(\Delta z_k + \Delta z_{k-1})} \right) + Q_{i,k}, \quad \omega_{i,k} \in D, \quad (11)$$

where $T_{i,k}$ – temperature average on cell volume; $\tilde{T}_{i,k}$ and $\tilde{\eta}_{i,k}$ – respectively temperature and depth of transformation in reactionary cell on the previous temporary layer; sizes $\lambda_{(i,k+1/2)}$ and etc. – approximate values of thermal conductivity on the corresponding boundary of cell; $c_{i,k}$, $\rho_{i,k}$ – approximate values of coefficient of specific heat capacity and density in cell; $Q_{i,k}$ – thermal effect of reaction for cells with SHS-reagents; Δx_i , Δz_k – cell size in the coordinate directions, Δt – step on time.

For calculation of coefficient of thermal conductivity on boundaries of cell we will use the following approximations

$$\lambda_{(i,k+1/2)} = \frac{2\lambda(T_{i,k})\lambda(T_{i-1,k})}{\lambda(T_{i,k}) + \lambda(T_{i-1,k})}, \quad \lambda_{(i+1/2,k+1)} = \frac{2\lambda(T_{i,k})\lambda(T_{i,k+1})}{\lambda(T_{i,k}) + \lambda(T_{i,k+1})} \text{ and etc.,}$$

which provide the second order of approximation on space.

The thermal effect of cell $Q_{i,k}$ depends on type of the considered cells and is defined for reactionary cells as

$$Q_{ik} = \begin{cases} \rho_{ik} \tilde{Q} \frac{\eta_{ik} - \tilde{\eta}_{ik}}{\Delta t}, & \text{for } \eta_{ik} < 1, \\ 0, & \text{for } \eta_{ik} \geq 1, \end{cases} \quad (12)$$

where \tilde{Q} – thermal effect of reaction of burning.

We approximate the equation of chemical reaction for reactionary cells the implicit scheme depending on reaction type. At the made assumptions concerning reaction type, the equation of kinetics will look

$$\frac{\eta_{ik} - \tilde{\eta}_{ik}}{\Delta t} = k_{0,2} \exp\left(-\frac{E_{a,2}}{RT_{ik}}\right) f_2(\eta_{ik}), \quad T_{ik} \geq T_{m,Ti}, \quad (13)$$

where $k_{0,2}$, $E_{a,2}$ – ‘pre-exponential coefficient’ (s^{-1}) in the Arrhenius law and activation energy in fluid phase of reagent, $T_{m,Ti}$ – melting temperature T_i ; $f_2(\eta_{ik}) = 1$ if $\eta_{ik} \leq 1$, i.e. not all substance has reacted, and otherwise $f_2(\eta_{ik}) = 0$, i.e. all substance has reacted.

The equation (11) is nonlinear regarding the unknown temperatures $T_{i,k}$, $T_{i\pm 1,k}$, $T_{i,k\pm 1}$.

For boundary cells and grid nodes on boundary of domain the corresponding approximating implicit equations built taking into account the main equation on boundary of domain and boundary conditions that provided the second order of accuracy on space. For boundary angular cells, approximation was carried out taking into account the corresponding adjacent boundary conditions.

The differential scheme (11), (13) with the grid equations for boundary conditions approximates initial problem (1), (2), (4) - (10) with order $O((\Delta x_{\max})^2 + \Delta t)$.

As a result we received nonlinear system concerning temperatures $T_{i,k}$ and depth of transformation $\eta_{i,k}$ (for reactionary cells).

The implicit differential scheme more difficult in the decision in comparison with explicit algorithms, but its choice is

justified as it is steady and does not demand additional ratios on grid steps unlike the explicit scheme. For the considered problem grid steps are rather small because of accounting of structure of "microcomposites" in coating. Besides, explicit schemes, owing to the high gradients of temperature arising in coating at processing by plasma impulse and also owing to reaction, would demand for stability of method even smaller steps for the decision.

The nonlinear system decided by economic iterative method with use change of the directions on iterations and by Thomas's algorithm in the current direction. As zero approach took values from the previous temporary layer.

In the absence of reference datas on coefficients in reaction, in particular on $k_{0,2}$ and etc., it is possible to offer easier way of the decision.

Let's make some assumption. As at creation of grid of particle-"microcomposites" with reagents broke into some grid cells, for example, on 10, 20 or other, it is possible to assume that if temperature of cell has reached reagent melting temperature, in this cell synthesis of product takes place on the mechanism with participation of fluid phase Ti with reaction initiation temperature corresponding to melting temperature T_i . Effect high speed of burning and the smallness of the particles it is possible to take that it has completely reacted, i.e. $\eta_{ik} = 1$. For example, at division of particle-"microcomposite" into 10 grid cells and at achievement only in one of them of melting temperature, it is possible to consider that the grid cell has completely reacted, then for real particle-"microcomposite" extent of conversion will make 0.1 and etc.

Temperature of burning is one of the most important characteristics of the heterogeneous condensed systems. The knowledge it allows to establish a phase condition of products of combustion. Temperature of burning is defined from the equation of the law of energy conservation for the considered system. At some assumptions the adiabatic temperature of burning which is the top assessment of temperature of burning, can be calculated rather simply.

Thermodynamic calculation of adiabatic temperature of SHS for one reaction (3) can be carried out at the following assumptions: burning happens at constant pressure, and reaction proceeds completely (with extent of transformation $\eta = 1$). Then heat of reaction at the reference temperature T_0 ($T_0 \geq 278 \text{ K}$) is spent for a warming up to T_{ad} and possible melting of products.

We will find the adiabatic temperature of burning by enthalpy method. For the characteristic of materials we will enter some characteristic or "critical" temperature points indicating behavior of material at change of temperature, in particular, these include temperatures of phase transitions of products of burning reaction. According to an enthalpy method we will carry out finding of adiabatic temperature of burning to some stages:

- according to the equation of reaction ordering of critical temperatures on their increase on a numerical axis of temperatures is made, i.e. boundaries of intervals of temperature in which we will find an enthalpy are defined;
- we find thermal effect of reaction according to Hesse's law;
- we find change of an enthalpy of products of combustion in each temperature interval and we compare the received value to thermal effect of reaction; if the calculated value of change of an enthalpy exceeds thermal effect of reaction, we consider that the temperature interval contains the required temperature of burning.

Proceeding from thermodynamic characteristics of a product of reaction TiC the critical temperature is temperature 3413 K – temperature of phase transition of solid – liquid, temperature of boiling 4573 K – temperature of phase transition of liquid – gaz and thermal effect of formation from elements of reaction of interaction of the titanium with carbon is equal $\Delta H_{298}^0 = 231,57 \text{ [kJ/mol]}$. According to an enthalpy method, comparing an enthalpy of system at different temperatures and comparing it with heat of reaction, it is approximate, for example, by an iterative method, we will find the adiabatic temperature of burning: $T_{ad} \approx 3100 \text{ K}$.

Comparison of melting temperatures for the components in the reaction cell with adiabatic combustion temperature indicates that during reaction can only melt one of the initial reagents.

2.3.4. The specifics of the software implementation of the algorithm

As cells of domain differ in heat-physical properties, for software implementation of numerical method, marking of cells depending on material (Table 1) containing in them is carried out.

Table 1. Marking of cells depending on the material containing in them

Type of cell	Material in cell
1	Cell with material of substrate
2	Cell with the inert material binding matrix (nichrome Ni80Cr20)
3	Cell-"microcomposite" containing SHS-reagents (Ti+C);
4	Cell containing product of reaction TiC

At the solution of problem in full statement, considering that the adiabatic temperature of reaction is higher melting temperatures of the most low-melting reagent (titanium), it is necessary to distinguish by reaction capacity of reactionary cells containing reagents titanium and carbon. In this case, at developing of software marking of cells according to type of its reaction capacity is entered:

- reactive cells containing reagents titanium and carbon reacting on the mechanism with participation of liquid phase the temperature of initiation of reaction corresponds to melting temperature of more low-melting reagent;
- reactive cells containing reagents titanium and carbon which burning happens on the solid-phase diffusion mechanism;
- inert cells: containing initial blend, for example, the nichrome or completely reacted cells containing SHS-product TiC.

3. Numerical modeling

During computing experiments duration and power of an impulse, a processing distance, a ratio of binding material (nichrome) and SHS-reagents, the coating thickness, initial temperature of a coating and sample varied. For the analysis of efficiency and adequacy of model a series of the modes with various input parameters calculated.

The results of modeling for two modes of processing differing in the initial temperature of a sample are given below. Advantage of the second mode is shown as for the first mode at lower initial temperature of a sample at identical other parameters attenuation of chain reaction of burning happens even before shutdown of an impulse, and part of reactionary components remain not reacted.

3.1. Parameters of Model

3.1.1. Characteristics of the Used Materials

As initial materials for preparation of blend used nichrome powder (fractions ~ 50 microns) and as SHS-reagents - mix of powder of titanium (fraction ~ 50 microns) and carbon in the form of soot PM-15 (size of particles 2-5 μ m) in stoichiometrical ratio 4:1. Mass percentage of binding element (nichrome) varied in limits 40–50%.

For receiving coatings on end faces of steel samples applied with brush (thin layer \leq 1mm) suspension from initial components of blend in zapon-lacquer. The last is necessary for gluing of blend from SHS-reagents to substrate, and also for reduction of probability of oxidation of powders. The applied suspension was dried not less thirty minutes. Drying of sample carried out with simultaneous heating of substrate. It provided partial evaporation of zapon-lacquer as a result thickness of plastering became less. As a result, thickness of the received plastering is 0.6 mm.

With the purpose to reduce energy outflow from substrate used preliminary heating of sample (initial condition) for the first mode to 500 K, for the second mode to 800 K.

3.1.2. Grid Domain

Proceeding from percentage of binding element and reactionary blend, sizes of fractions of powder and soot, disk of "microcomposite" with SHS-reagents has the sizes on x and y 63 microns, on height (thickness) z – 31.5 microns and average distance (layer) between disks – 2.3 microns. The developed model of powder system (in the section plane (x, z)), including 153 (on x) \times 19 (on z) particles with SHS-reagents in the form of particles–"microcomposites" in coating, was used for modeling of thermal processes.

Considering the size of reactionary "microcomposites" and following the algorithm of creation of grid cells described above in item 2.3.2 it is enough to divide cells–"microcomposites" into five parts on x direction and into two – on z.

3.1.3. Input Parameters

Each of the modes is characterized by the following input datas.

Proceeding from temperature data of impulse of plasma stream [4] and considering expected temperatures of burning, we will choose distance of plasma stream. Curves 5 and 6 (Figure 4) answer necessary temperatures that corresponds to distance of processing of order \approx 10-12 cm. For modeling we use as external temperature from impulse the data corresponding to curve 6. Pulse width is 200 μ s.

As the external temperature of gas from other sides we will accept 300 K.

Heat-transfer coefficient on side and lower boundaries was $\alpha_{T,1} = \alpha_{T,2} = \alpha_{T,3} = 10 \text{ W/m}^2\cdot\text{K}$, from impulse was $\alpha_{T,4} = 10^6 \div 10^7 \text{ W/m}^2\cdot\text{K}$.

The thermal effect of reaction of burning is accepted $Q=251.2 \text{ kJ/mol}$.

We take thermal constants of substances from the reference book [16].

3.2. Results of Modeling

As the sizes of "microcomposites" are very small concerning the sizes of rated domain, we will show results of modeling on fragments in Figures 6–11.

Temperature of the central fragment of coating in different instants: $t=4\mu\text{s}$, $7\mu\text{s}$, $13\mu\text{s}$ at processing of sample by impulse is provided in Figures 6–8. At the left temperature for the first mode, at the right for the second is shown.

The temperature scale for all experiments is identical and given in Figure 9.

Burning of upper "microcomposites" begins through $2\mu\text{s}$ for both modes and through $4\mu\text{s}$ the temperature field in the middle of coating has the similar appearance shown in Figure 6.

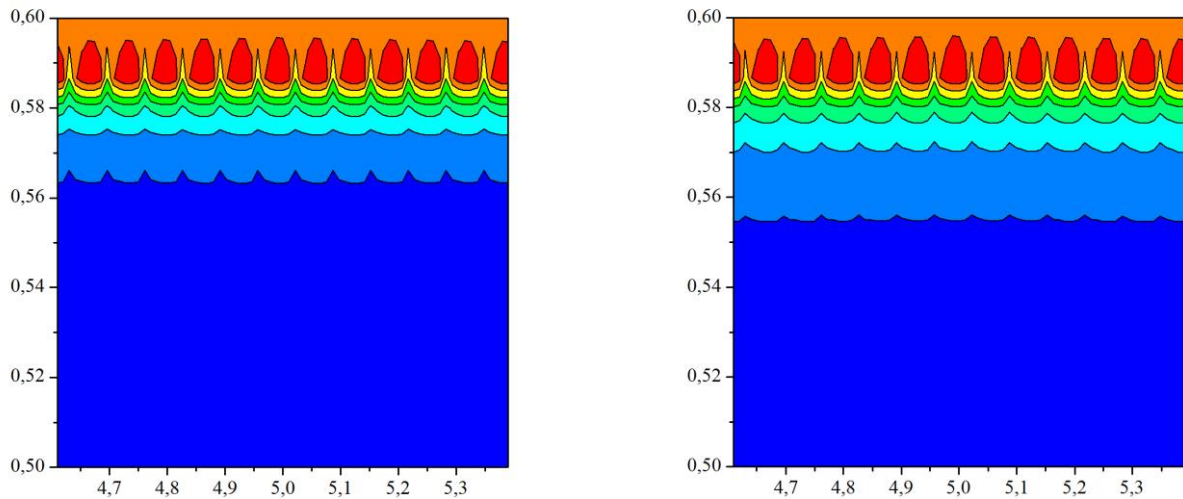


Figure 6. Temperatures in coating fragment for two modes (mode 1 at the left) through $4\mu\text{s}$

Further heating by impulse leads to temperature shown in Figure 7. It is visible that for the first mode of heat energy still it is not enough for reaction of the following row of "microcomposites", there is only heating of plastering while for the second mode in the following row of "microcomposites" burning reaction has begun.

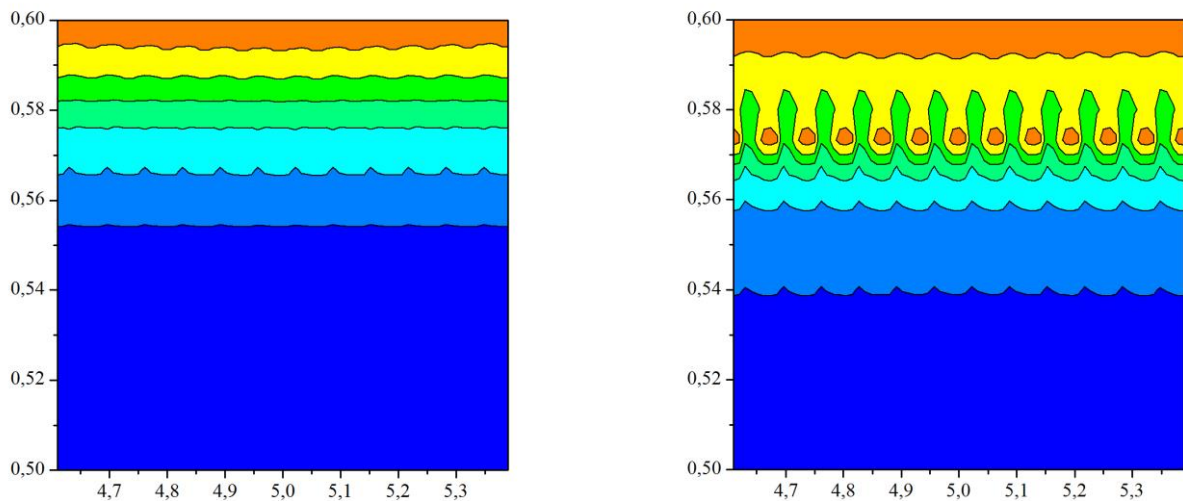


Figure 7. Temperatures in coating fragment for two modes (mode 1 at the left) through $7\mu\text{s}$

Continuation of heating in case of the first mode is characterized by uneven reaction of the separate "microcomposites" located closer to the center of plastering where the heat flux is higher. In the field of plastering boundaries burning does not happen even in upper row of "microcomposites". It is obvious that heat energy has not enough that reaction has begun in following lower on height "microcomposites" while for the second mode the following "microcomposites" on depth reacts with formation of titanium carbide.

View of temperature field of the top part of plastering through $13\mu\text{s}$ is shown in Figure 8.

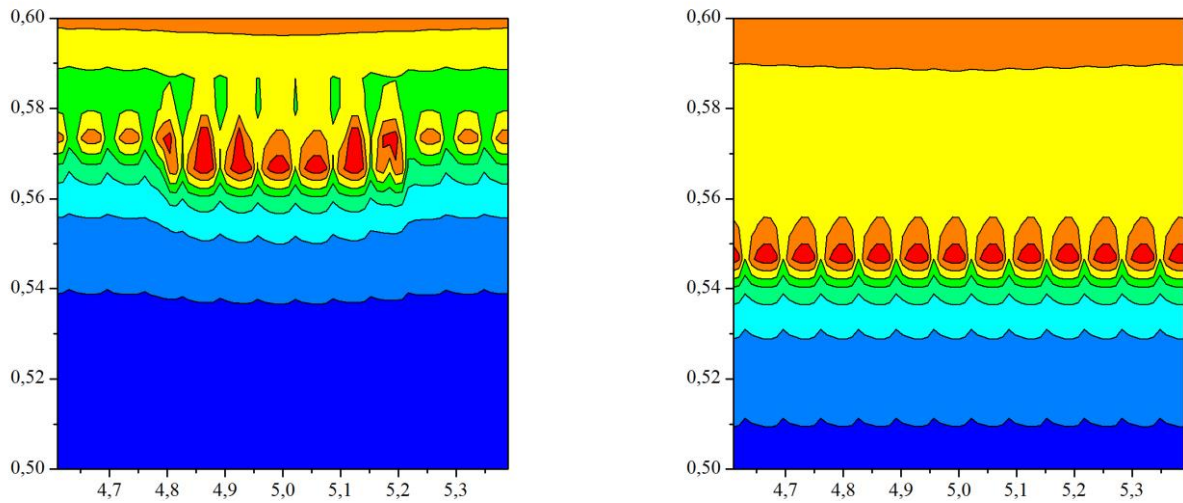


Figure 8. Temperatures in coating fragment for two modes (mode 1 at the left) through $13 \mu s$

The temperature field of half in the top part of plastering for this instant for two modes is presented in Figure 9.

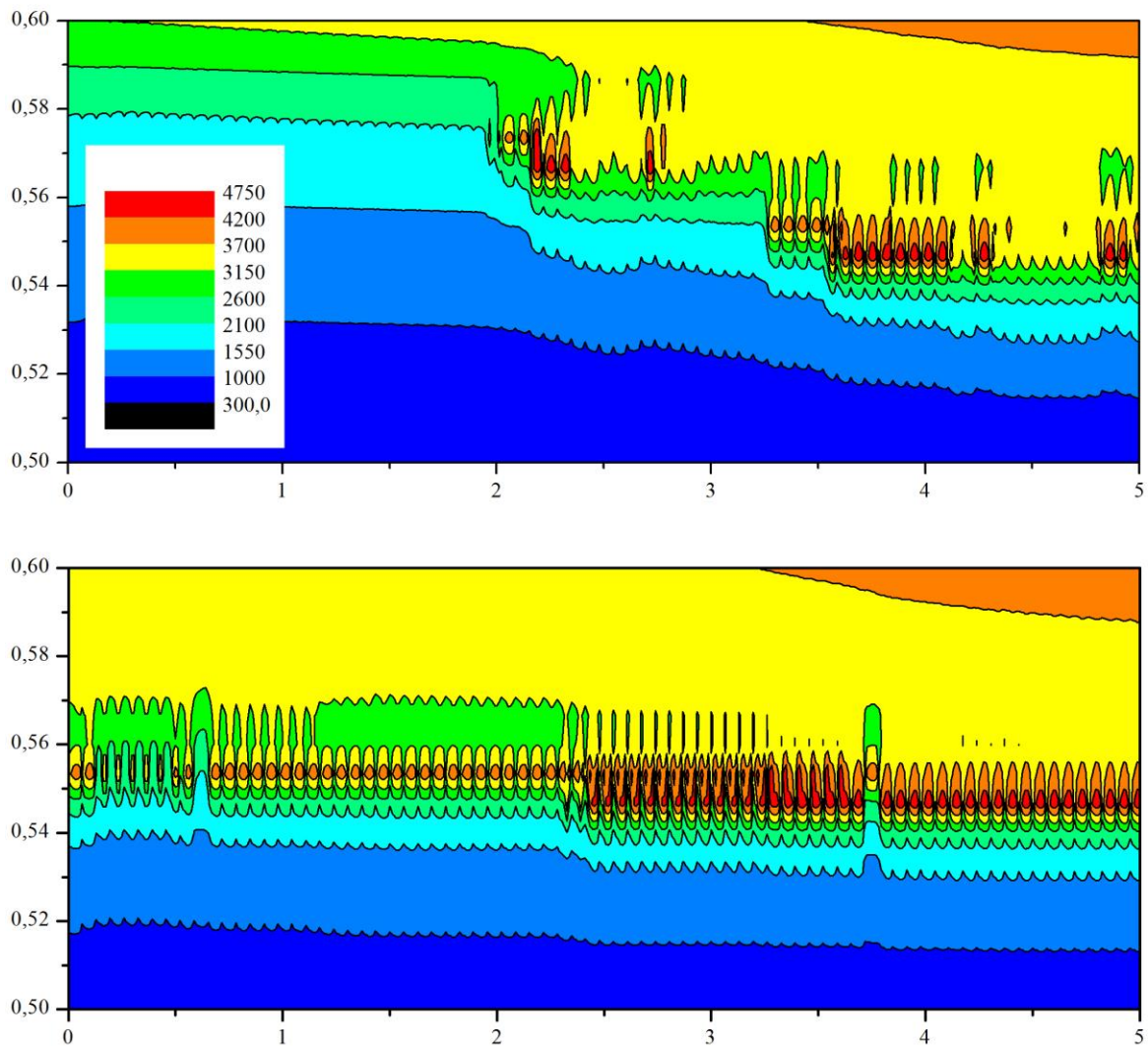


Figure 9. Temperature in the top part of a plastering through $13 \mu s$

Numerical experiment shows (Figure 9) that for the first mode the area of heating is uneven, ignition of "microcomposites" happens mainly in the central part of coating (upper drawing) whereas for the second mode burning happens on all area.

It is obvious that the qualitative coating can be received on the basis of parameters of the second mode with its final specification experimentally.

Therefore we will include below only results of modeling on the second mode.

At $t = 200 \mu\text{s}$ the impulse is disconnected.

At the time of shutdown of impulse for the second mode 3 upper (on height) "microcomposite" have reacted (left Figure 10).

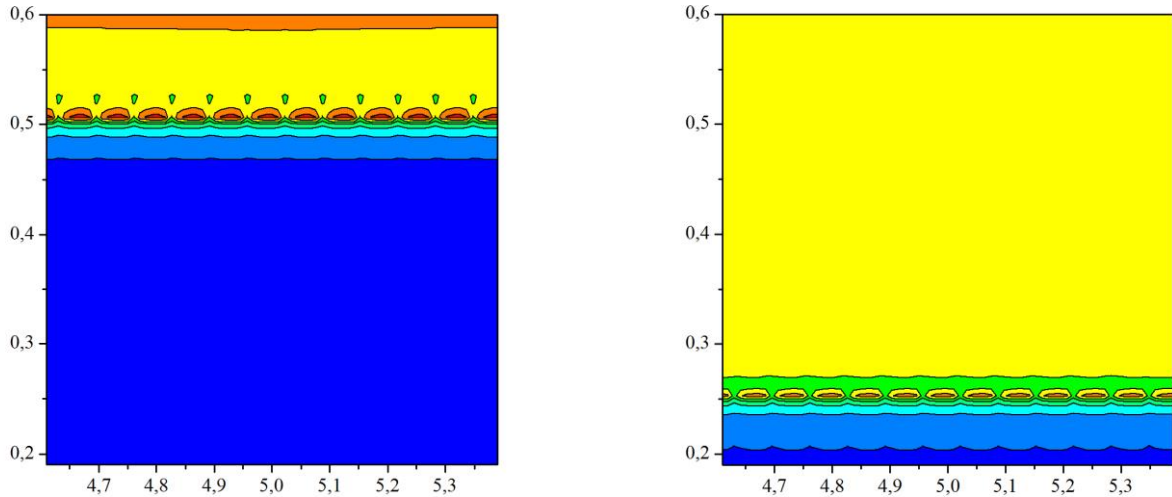


Figure 10. Dynamics of temperature (mode 2) after processing of sample one impulse (at the left) and through $600 \mu\text{s}$ after shutdown of impulse (on the right)

Obviously (the right Figure 10) that process of synthesis goes steadily in the self-propagating mode after shutdown of impulse and leads to ignition of deeper layers of "microcomposites".

Dynamics of temperature in particles-"microcomposites" of the central column of plastering ($x=5\text{mm}$) (numbering begins from first "microcomposite" from substrate) confirms that through $700 \mu\text{s}$ after shutdown of impulse (t^*) all "microcomposites" on height have reacted (Figure 11).

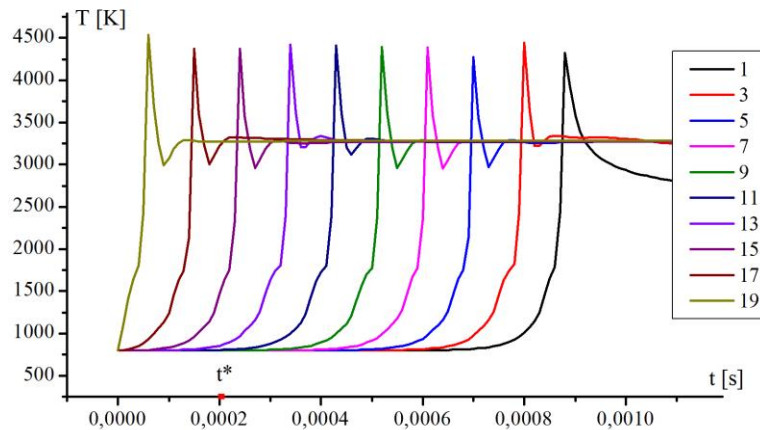


Figure 11. Dynamics of temperature in particles-"microcomposites"

Apparently from Figure 11 the relay mode of burning is observed at which there is fast burning of reactionary "microcomposites" (temperature peaks over 3100 K) and rather slow stage of ignition of the following cell. After all "microcomposites" have reacted, temperature in coating is leveled, and it slowly cools down by heat transfer. The sample is ready to further processing.

The given numerical experiment shows that for the chosen parameters of process of pulse duration of the order of $200 \mu\text{s}$ it is enough for forming of coating with titanium carbide grains.

Further processing of sample is reduced to alternation of impulse and its delay. The quantity and duration of such cycles of processing are defined by creation of conditions for receiving uniform sinter on substrate. The mathematical model in this case is provided only by the equation of heat balance (1) with boundary conditions (7) - (9). As area cells we have cells with material of substrate, binding matrix (nichrome) and cells with microcomposite TiC.

4. Conclusion

On the example of calculations it is shown that receiving of composition coating with the hardening phase of titanium carbide from initial blend in the form of plastering at high-temperature processing decides by heat transfer between "microcomposites" of reactionary mix and neutral binding metal matrix and their energy initial state. Accounting of real structure of "microcomposites" in binding matrix provides more correct description of pattern of heat transfer, shows more exact evolution of temperature in coating that allows to select better the modes of processing of plastering with SHS-reagents for forming of wear-resistance coating.

The offered model can be used for forecasting of the mechanoactivated SHS (MASHS) [14]. Process MASHS divides into two stages: at the first stage the reactionary blend is processed, for example, in planetary mills and then is used as the making plastering of coating; the second stage is SHS. In the process of mechanical activation there is significant increase in contact surface between reagents and there is additional energy. Besides, as have shown researches [12], near reagents boundary at the microlevel the thin boundary layers can be formed with the implemented crystallites in which reagents mix up without forming of oxidic connections which most often are diffusion barriers to course of chemical reactions. The specified mechanical activation processes substantially promote course of solid-phase reactions. Therefore at modeling of thermal processes for the mechanoactivated mix it is necessary to consider kinetics of chemical reactions (4), (5) and the additional energy received by reagents at mechanical activation.

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