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MATHEMATICAL MODELING OF THE NON-STATIONARY THERMAL STATE OF A COMPOSITE COATING OF CLOSE TO EQUIMOLAR COMPOSITION DURING LASER REMELTING

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ABSTRACT

Based on assumptions and limitations, a mathematical model of the non-stationary thermal state of a composite coating during laser remelting on a metal substrate to obtain an alloy of equimolar or close to equimolar composition has been developed. The model includes the boundary value problem of calculating the nonstationary thermal state of the temperature distribution in the solid, two-phase and liquid regions, considering the heat release of crystallization according to the theory of a quasi-equilibrium two-phase zone in the presence of porosity of a mixture of metal powders. Based on the mathematical model, the computer program "Composite coating thermal state" was created, which allows to determine the non-stationary temperature distribution in the formed coating and substrate, the depth of penetration of the high-entropy coating layer, to evaluate the shrinkage of the molten coating under different technological conditions: laser power, the diameter of its focal spot, as well as the speed of movement along the surface of the processed material. The created program also allows to determine the dynamics of the position of two-dimensional liquidus and solidus lines for each metal included in the mixture. Using the created program, a computer simulation of the process of unsteady heating of a mixture of three metal powders in the same mass fractions: nickel, chromium and iron was carried out. Non-stationary temperature fields in the composite coating are obtained, considering its penetration and heating of the substrate. The depth of penetration of all metals, including the most low-melting one, was determined during laser remelting on a metal substrate in the production of a high-entropy alloy. The practical significance of the developed computer model lies in its use to predict the penetration depth of a composite coating under specified technological modes of laser remelting. At the same time, its adaptation is necessary, based on experimental data on the porosity and thickness of the coating before and after melting of simple metal systems with similar thermophysical properties.

Keywords: mathematical modelling, non-stationary thermal state, laser surfacing, composite coatings, multicomponent base alloys.

INTRODUCTION

In recent decades, a new promising area has emerged in scientific research on materials – the creation and study of so-called "high-entropy materials". This area of scientific research is based on the production of materials with an equimolar or close to equimolar ratio of several components [1, 2]. Even though the first articles were published in 2004, research on the production of various highly entropic materials is developing very quickly. All new composite materials with high practically significant properties are obtained. High-entropy alloys (HEA) have attractive mechanical properties superior to those of many industrial materials, for example, such as high toughness at low temperatures or high strength at high temperatures. The possibilities of using these materials as radiation-resistant and for various biomedical applications, including coatings, are also being considered [3, 4].

Studies conducted to date have shown that new, promising effects found in high-entropy alloys can also be manifested in alloys that formally cannot be classified as high-entropy. A broader concept has emerged - multiprincipal element alloys (MPEAs), which include not only high-entropy, but also medium-entropy alloys. The main feature that allows the alloy to be attributed to this group is that more than two metals form the base of the alloy, and the amounts of metals forming the base are equal or close enough.

The processes of structure and phase formation in such alloys, the mechanisms of formation of mechanical properties and thermal stability differ significantly from alloys based on one or two elements. At the same time, such alloys have increased thermal stability of composition and structure, which is an advantage both during operation and during production. In addition, there is a tendency for their widespread use for additive manufacturing technologies or modern methods of surface engineering [5 - 7].

In this regard, MPEAs-based coating methods have been widely developed using modern laser surfacing technologies. The development of methods for obtaining such coatings from non-highly entropic alloys or mixtures of available pure metal powders remains the most in demand.

Previously, we studied the possibilities for two two-stage MPEAs coating techniques, at the first stage: in the first case, the method of cold gas dynamic spraying is used to apply powders of different metals to the surface, in the second - detonation spraying [8, 9]. In the second stage, to form a homogeneous alloy, the resulting composite coatings from dissimilar powders are remelted with a laser. Under its action, the coating is melted and further, when thermal energy is dissipated deep into the substrate, the melt solidifies and solid solutions are formed.

In the remelting technology used, the laser beam is scanned along the trajectory of parallel lines along the processed surface of the material at a given speed.

Laser remelting of the coating can be carried out with partial melting of the substrate, which leads to mixing of the composite alloy with the substrate material. In order to avoid changes in the composition of the coating, only its upper surface is most often subjected to reflow.

Thus, in the two methods of coating the substrate under consideration, the same problems arise related to the rational selection of technological modes of laser remelting during the formation of a high-entropy coating.

To determine the temperature distribution in the area of the focal spot, the formula for the one-dimensional distribution of the temperature field in a semi-infinite body in the *x* direction (deep into the processed material) is most often used [10]:

$$t(x,\ \tau) - t_0 = \frac{2 \cdot q}{\lambda} \sqrt{a\tau} \cdot ierfc\left[\frac{x}{2\sqrt{a\tau}}\right], \qquad (1)$$

where τ - time; $\alpha=\lambda/(c\rho)$, λ, c, ρ– the coefficient of thermal conductivity, thermal conductivity, specific heat capacity and density of the material, respectively; t_0- initial temperature of the material; $q=A \cdot I_0$ – heat flow under the action of a laser beam; A – absorption capacity of the material, I_0 – average intensity of incident radiation.

However, this formula was obtained for heating a homogeneous material under the action of a heat flux and does not consider the complexity of the kinetics of the laser remelting process: heat propagation through the material in horizontal directions, complex movement of the laser spot, melting, shrinkage of the composite powder material, etc.

The process of heating and melting the composite layer is quite complex and depends on a variety of technological parameters and thermophysical properties of the processed materials. The idea arose to create a mathematical model for predicting the behaviour of the processes under consideration, which allows at least qualitatively establishing how the depth of penetration of the composite depends on the power of the laser beam, its focal diameter, speed and strategy of its movement along the surface. The adaptation of the model based on experimental data will make it possible to predict the penetration depth of a powder metal or a mixture of metal powders and alloys in the coating and further predict the technological properties of the resulting coating.

The aim of the work is to develop a mathematical model and conduct computer modeling of the non-stationary thermal state of a composite coating, determine the depth of its penetration and shrinkage during laser remelting on a metal substrate to obtain an alloy of equimolar or close to equimolar composition.

EXPERIMENTAL

Suppose there is a horizontal plate with length *L* consisting of two layers (or parts) *I-II*, the first layer with height *h* is a composite material to be processed, the second is a metal substrate *H*. Let's choose a Cartesian coordinate system (Oxyz) with the origin in the upper left corner of the plate (Fig. 1).

Along the upper surface of the *I* layer of the plate along the *Oy* axis, a focal spot of a laser with a diameter of d_f moves at a speed of $W_н$. The coordinate of the center of the spot is given as $y_f(\tau) = r_f + W_H \cdot \tau$, where τ – time, $r_f = d_f / 2$ - focal spot radius.

The time of one laser pass along the length of the plate is $\tau_{k1} = (L - 2r_f)/W_H$, where $W_н$ is the speed of movement. If the step between the lines is $\delta \geq r_f$, then the laser beam will pass through the Oy axis only once and the number of passes will be p = 1 (see Fig. 1). If $\delta < r_f$, then through the line coinciding with the Oy axis, the spot of the laser beam will pass several times with a variable focal diameter and the number of passes will be $p = \text{round}\,(2.r_f / \delta) - 1$.

The laser melts a homogeneous mixture of metal powders having an initial porosity of Π_0 and a known mass composition (or mass fractions) $\varepsilon_i = m_i / m_0$, and $\sum_{i=1}^{K} \varepsilon_i = 1$, where K is the amount of metals in the mixture, m_0 is the mass of the composite material, m_i is the mass of individual metal components.

When setting the thermal problem, we assume that at the initial moment of time τ = 0, the substrate and composite material have the same temperature t_0 and at τ > 0 they begin to heat up under the action of absorbed laser radiation. When heating the surface of metal composite powders to a high temperature (T > 500°C), it is necessary to consider the thermal flux of q_{izl} radiation into the environment.

When developing the mathematical model, the following assumptions and limitations were adopted.

1. When determining the maximum penetration of the *I* layer, it is quite acceptable to solve the two-dimensional problem of the thermal state of the composite coating on the substrate with one pass along the *Oy* axis. We assume that the temperature field is nonstationary $\partial T / \partial \tau \neq 0$ and $\partial T / \partial z << \partial T / \partial y$.

2. When exposed to laser radiation on metal, the electromagnetic wave exponentially attenuates in a very thin surface skin layer (~ 10^{-5} - 10^{-6} cm), and absorption occurs on conduction electrons, and the electrons transfer part of the absorbed energy to the metal lattice. During laser processing, the depth of heat penetration into the metal is almost adjacent to its surface, and therefore the laser will be considered as a surface heat source. We also believe that the effect of laser radiation on the material is limited by the diameter of its focal spot.

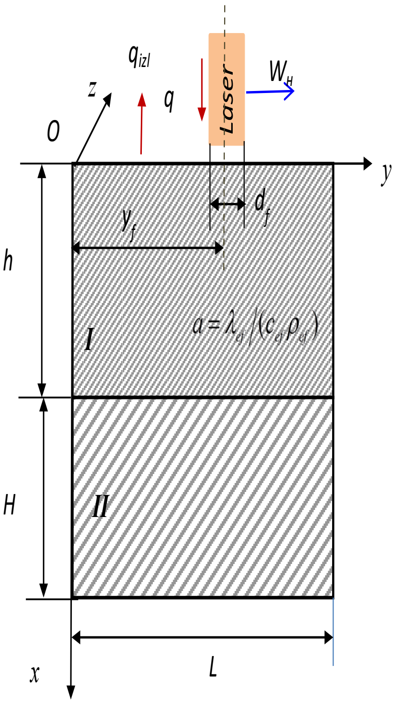

Fig. 1. Coordinate system and basic dimensions of the substrate and composite material during laser melting.

3. We believe that the thermal state in layer I is described by the energy equation considering phase transitions according to the theory of a quasi-equilibrium two-phase zone, and in layer II by the thermal conductivity equation.

4. The remeltable coating is a mixture of iron group powders and the melting heat L_p is known for each metal. For pure metals, the melting point T_p acts as the phase transition temperature, and for alloys, the liquidus temperature T_L and the solidus temperature $T_S < T_L$. For the sake of generality of the problem statement, we will assume that during the melting of pure metal, there formally exists a two-phase zone at T_S slightly less than $T_L = T_p$.

5. When processing metals with low vapor elasticity, we believe that the evaporation of metals, and hence the

removal of additional energy for their vaporization, can be neglected.

6. Assuming that $L >> d_f$, $L >> h$, $L >> H$ for the processing time of the material $\tau_k \sim L / W_H$, we will neglect the heat losses through the lower surface of the *II* layer of the plate and the side surfaces of the *I* and *II* layer.

Let's consider a two-dimensional mathematical model of the thermal state of the coating and the substrate when the laser spot moves along the coating surface. The unsteady temperature distribution in the solid, two-phase and liquid regions is described by the law of conservation of energy [11]. Taking into account the heat release of crystallization according to the theory of a quasi - equilibrium two - phase zone in the presence of porosity of a mixture of metal powders (at $\tau > 0, 0 \leq$

$$c_{ef} \cdot \rho_{ef} \cdot \frac{\partial T}{\partial \tau} - (1 - \varPi) \cdot \sum_{i=1}^{K} \left(\varepsilon_i \cdot \rho_i \cdot L_{p\,i} \frac{\partial g_i}{\partial \tau} \right) =$$

$$= \lambda_{ef} \cdot \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right), \tag{2}$$

where τ - time; $T(x, y, \tau)$ - temperature, K - the number of components in the composite coating; $g_i(T)$ - the proportion of solid phase in the coating metal; ρ_i - the density of cast metal in the coating; $\lambda_{ef}(T)$, $c_{ef}(T)$ and $\rho_{ef}(T)$ - effective coefficients of thermal conductivity, specific heat capacity and density depending on temperature, respectively; L_{pi} - melting heat of metal; $\prod = V_n / V_0$ - material porosity; V_Π - volume of effective voids; V_0 - total volume. The second term of this equation (2) determines the heat of phase transitions for individual metals from the solid state to the liquid state and vice versa.

The amount of solid phase *i* of the metal in the solidification interval will be determined by knowing the temperature of the liquidus $T_{L\,i}$ and solidus $T_{S\,i}$, respectively, for the *i* metal according to the linear law model $g_i(T) = (T_{Li} - T)/(T_{Li} - T_{Si})$, from which it is possible to obtain:

$$dg_i/\mathrm{d}T = -1/(T_{Li} - T_{Si}) \tag{3}$$

The effective density of the initial powder material, depending on the density of individual cast metals ρ_i, their mass fraction in the mixture ε_i and the porosity of the mixture *Π*, can be written as:

$$\rho_{ef}(T) = (1 - \varPi) \cdot \sum_{i-1}^{K} \varepsilon_i \cdot \rho_i(T). \tag{4}$$

Effective specific heat capacity of the initial powder material depending on the heat capacity of individual metals c_i and their mass fraction in the mixture ε_i:

$$c_{ef}(T) = \sum_{i-1}^{K} \varepsilon_i \cdot c_i(T).$$

Using substitution $\frac{\partial g_i}{\partial \tau} = \frac{\partial g_i}{\partial T} \frac{\partial T}{\partial \tau}$ and expression (2), equation (1) can be written as:

$$\rho_{ef} \cdot \frac{\partial T}{\partial \tau} \cdot \left[\sum_{i-1}^{K} \varepsilon_i \cdot c_i + \sum_{i=1}^{K} \left(\frac{L_{p\,i}}{T_{Li} - T_{Si}} \right) \right] =$$

$$= \lambda_{ef} \cdot \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right)$$

or

$$\frac{\partial T}{\partial \tau} = a_{ef}(T) \cdot \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right), \tag{5}$$

where the effective coefficient of thermal conductivity is a temperature function:

$$a_{ef}(T) = \frac{\lambda_{ef}(T)}{\rho_{ef}(T) \cdot C_{ef}(T)}; \tag{6}$$

Effective heat capacity of a metal mixture considering phase transitions:

$$C_{ef}(T) == \sum_{i=1}^{K} C_i = \sum_{i-1}^{K} \left[\varepsilon_i \cdot \left(c_i(T) + \frac{L_{p\,i}}{T_{Li} - T_{Si}} \right) \right]. \tag{7}$$

Eq. (5) uses the law of conservation of energy and is suitable for an approximate description of the entire remelted composite material, without distinguishing the boundaries of solid, two-phase and liquid zones for each metal.

The thermophysical properties of heated and molten metal entering the initial mixture, depending on temperature, are described by piecewise continuous functions:

coefficient of thermal conductivity

$$\lambda_i(T) = \begin{cases} \lambda_{\text{liq}\,i} & \text{at } T \geq T_{L\,i}; \quad g_i = 0; \\ \lambda_{\text{sol}\,i} g_i + \lambda_{\text{liq}\,i}(1 - g_i) & \text{at } T_{S\,i} < T < T_{L\,i}, \quad 0 < g_i < 1; \\ \lambda_{\text{sol}\,i} & \text{at } T \leq T_{S\,i}; \quad g_i = 1; \end{cases} \tag{8}$$

Density

$$\rho_i(T) = \begin{cases} \rho_{\text{liq}\,i}, & \text{at } T \geq T_{L\,i}; \quad g_i = 0; \\ \rho_{\text{sol}\,i} g_i + \rho_{\text{liq}\,i}(1 - g_i)\,, & \text{at } T_{S\,i} < T < T_{L\,i}, \quad 0 < g_i < 1; \\ \rho_{\text{sol}\,i}, & \text{at } T \leq T_{S\,i} \quad g_i = 1; \end{cases} \tag{9}$$

Specific heat capacity

$$C_i(T) = \varepsilon_i \cdot \begin{cases} c_{\text{liq}\,i}, & \text{at } T \geq T_{L\,i}; \quad g_i = 0; \\ c_{\text{sol}\,i} g_i + c_{\text{liq}\,i}(1 - g_i) + \frac{L_{p\,i}}{T_{Li} - T_{Si}}\,, & \text{at } T_{S\,i} < T < T_{L\,i}, \quad 0 < g_i < 1 \\ c_{\text{sol}\,i}\,, & \text{at } T \leq T_{S\,i} \quad g_i = 1, \end{cases} \tag{10}$$

where $\lambda_{\text{liq i}}$, $\lambda_{\text{sol i}}$ – thermal conductivity of liquid and solid metal; $\rho_{\text{liq i}}$, $\rho_{\text{sol i}}$ – density of liquid and solid metal ; $c_{\text{liq i}}$, $c_{\text{sol i}}$ – specific heat capacity of liquid and solid metal.

To simplify the calculation of the effective thermal conductivity coefficient, we select the equimolar composition of the coating from a mixture of iron group metal powders having fairly similar thermophysical properties, for example Fe, Cr, Ni, Co. We consider the known thermal conductivity coefficients of each metal included in the coating metal mixture λ_i, their mass fractions ε_i and the initial (initial) porosity Π. To determine the coefficient of thermal conductivity depending on the temperature of a multicomponent mixture, we use the calculation method considered in [12]. Let the composite material be an isotropic mixture of powders consisting of a binding component 0 (air) and closed inclusions of K metals. We consider that the coefficients of thermal conductivity λ_0, λ_1 , λ_2. λ_K and volume concentrations (fractions) v_0, v_1, v_2.. v_K are known ($\sum_{i=1}^{K} v_i = 1$), $v_1 = \varepsilon_i \,.\, \rho_{ef} / p_i$. Assuming that the components do not react with each other, and the metals included in the composite have similar properties, the effective thermal conductivity coefficient of the composition can be estimated as the geometric mean of the thermal conductivity of the metal and air phases [13]:

$$\lambda_{ef} = \lambda_{\text{м}}{}^{1-\Pi} \lambda_{\text{в}}{}^{\Pi}, \tag{11}$$

where $\lambda_{\text{met}} = \sum_{i=1}^{K} (\lambda_i \cdot v_i)$- average thermal conductivity of the metal phase; λ_{air}– thermal conductivity of air.

Temperature in the *II* layer of the plate (substrate) $t(x, y, \tau)$ is described by the equation of thermal conductivity without phase transitions (at $\tau > 0$, $h \leq x \leq (h+H)$, $0 \leq y \leq L$)

$$\frac{\partial t}{\partial \tau} = a_p \cdot \left(\frac{\partial^2 t}{\partial^2 x} + \frac{\partial^2 t}{\partial y^2} \right), \tag{12}$$

where $a_p = \lambda_p / (C_p \,.\, \rho_p)$ - coefficient of thermal conductivity of the substrate material; $\lambda_p(T)$, $C_p(T)$ and $\rho_p(T)$ – the coefficient of thermal conductivity, specific heat capacity and density of the substrate material depending on the temperature, respectively.

To solve differential Eq. (3) and Eq. (12), they must be supplemented with boundary conditions. At the initial moment of time, we assume that the temperature at all points of the *I* and *II* layers is the same (at $\tau = 0$) $T(x,y,0) = t(x,y,0) = t_0$.

Boundary conditions at $\tau > 0$ according to the adopted assumption (6), the thermal insulation condition on the lower, as well as on the left and right borders of the coating and substrate:

at $0 \leq y \leq L$ $$\left.\frac{\partial t}{\partial x}\right|_{x=h+H} = 0. \tag{13}$$

at $0 \leq x \leq h$ $$\left.\frac{\partial T}{\partial y}\right|_{y=0} = 0. \tag{14}$$

at $h \leq x \leq (h+H)$ $$\left.\frac{\partial t}{\partial y}\right|_{y=0} = 0. \tag{15}$$

at $0 \leq x \leq h$ $$\left.\frac{\partial T}{\partial y}\right|_{y=L} = 0. \tag{16}$$

at $h \leq x \leq (h+H)$ $$\left.\frac{\partial t}{\partial y}\right|_{y=L} = 0. \tag{17}$$

At the boundary of the I and II layers between the substrate and the powder material, we set a boundary condition of the fourth kind:

at $0 \le y \le L$ $\left.\frac{\partial T}{\partial x}\right|_{x=h} \lambda_{ef} = \lambda_p \left.\frac{\partial t}{\partial x}\right|_{x=h}$;

$$t(x,y) = T(x,y) \cdot \qquad (18)$$

There is a boundary condition of the 2nd kind on the upper surface of the plate:

at $0 \le y \le L$

$$-\lambda_{ef} \cdot \left.\frac{\partial T}{\partial x}\right|_{x=0} = q - q_{izl}(T) = q_{\Sigma}(T), \qquad (19)$$

where q - the heat flux from the laser radiation acting in the area of the arc spot; q_{izl} – the flow of thermal radiation from the heated surface into the environment.

Knowing the movement of the center of the focal spot $y_f(\tau)$ when the center of the laser spot moves along the Oy axis, it is possible to determine the coordinate of the left and right boundaries of the spot from time as $0 \le \tau \le \tau_{kL}$: $yL = y_f(\tau) - r_f$; $y_R = y_f(\tau) + r_f$.

Photons incident on the processed powder material have a Maxwell distribution, so the heat flux density in the focal spot obeys the Gauss curve $q = A \,.\, I_n \,.\, (1-\Pi) \,.\, exp(-r^2/r_f^2)$, where I_n - maximum laser power density (at $r = 0$); moreover, the average density of the heat flow $\bar{q} = P_н/(\pi \cdot r_f^2) \approx 0{,}747 \cdot I_n$.

For engineering calculations, it is possible to use a simplified dependence of the average heat flux propagating deep into the material when exposed to a laser in the focal spot area:

$$q = \frac{A \cdot P_н \cdot (1-\Pi) \cdot \eta}{\pi \cdot r_f^2}, \qquad (20)$$

where η - laser efficiency; P_H - laser power, W.

When metals are heated, they begin to radiate heat flow from the surface into the environment:

$$q_{izl}(T) = E \cdot \sigma \cdot \left[\left(\frac{T_{surf} + 273}{100} \right)^4 - \left(\frac{t_{env} + 273}{100} \right)^4 \right] \qquad (21)$$

where $\sigma = 5.7$ (W/m^2 . K^4) – Stefan Boltzmann constant; $E = 1/\left(1/\varepsilon_m + 1/\varepsilon_{env} - 1\right)$ - emissivity factor, ε_m, ε_{air} – emissivity factor of the metal surface and environment, respectively; T_{surf} and t_{env} - the temperature of the upper surface of the plate and the environment, respectively, °C.

Due to the nonlinearity of the heat conduction equations (5), (12), an accurate analytical solution of the boundary value problem (5) - (21) is impossible. The finite difference method and the coordinate splitting method were used to obtain an approximate solution using a computer. For this purpose, equations (5) and (12) were written in finite-difference form and each of them is reduced to the form of a tridiagonal matrix. Each of the obtained systems of linear algebraic equations was solved by the run-through method [14]. It should be noted that this calculation scheme is locally one-dimensional and certainly stable.

Based on the created mathematical model and calculation algorithm, the computer program "Composite coating thermal state" was created using the Matlab v. 7.11 (R2010b) development environment. It allows you to determine the non-stationary temperature field in the coating and substrate, the depth of penetration of the high-entropy coating layer.

For an example of calculation according to the proposed model, a system of three metal powders of pure nickel, chromium and iron was chosen. The initial data of thermophysical properties from temperature were taken from works and approximation equations to the melting temperature are obtained on their basis [15, 16].

Density, specific heat capacity and thermal conductivity coefficient of solid nickel, respectively:

$\rho_{t1}(t) = 8927{,}5 - 0{,}4631 \cdot t$, kg m^{-3}, .
$c_{t1}(t) = 466{,}02 + 0{,}1909 \cdot t - 6 \cdot 10^{-5} t^2$, J (kg K)$^{-1}$,
at $20 \le t \le 427$ °C
$\lambda_{t1}(t) = 93{,}864 - 0{,}1253 \cdot t + 10^{-4} t^2$,
at $427 < t < t_{m1}$ °C
$\lambda_{t1}(t) = 37{,}762 + 0{,}064 \cdot t - 3 \cdot 10^{-5} t^2$, W (m K)$^{-1}$.

Density, specific heat capacity and thermal conductivity coefficient of solid chromium, respectively:

$\rho_{t2}(t) = 7208{,}3 - 0{,}2661 \cdot t$, kg m^{-3},
$c_{t2}(t) = 449{,}42 + 0{,}175 \cdot t + 9 \cdot 10^{-5} t^2$, J (kgK)$^{-1}$,
$\lambda_{t2}(t) = 108{,}74 - 0{,}0562 \cdot t + 10^{-5} t^2$, W (m K)$^{-1}$.

Density, specific heat capacity and thermal conductivity coefficient of solid iron, respectively:

$\rho_{t3}(t) = 7885{,}2 - 0{,}3583 \cdot t$, kg m^{-3},
at $20 \le t \le 769$ °C

$$c_{t3}(t) = 490{,}43 - 0{,}2983 \cdot t + 1{,}4 \cdot 10^{-3} t^2,$$

at $769 < t \leq t_{m3}$ °C

$$c_{t3}(t) = 12192 - 28{,}655 \cdot t + 2{,}31 \cdot 10^{-2} t^2 - 6 \cdot 10^{-6} t^3 \quad \text{J (kg K)}^{-1},$$

$$\lambda_{t3}(t) = 111{,}77 - 0{,}1223 \cdot t + 4 \cdot 10^{-5} t^2, \ \text{W (m K)}^{-1}.$$

Coefficient of thermal conductivity of air depending on temperature:

$$\lambda_0 \ (t) = 2{,}54 \cdot 10^{-2} + 7 \cdot 10^{-5} t - 1{,}4 \cdot 10^{-8} t^2, \quad \text{W (m K)}^{-1}.$$

Calculation of heat capacity and thermal conductivity for solid phase steels with a carbon content from 0.05 to 0.20% (low carbon steel) can be performed according to the formulas [17]:

$$c_p(t) = 418 + 0{,}199t + 812 \cdot exp(-0{,}0099|t - 768|)$$

$$\lambda_p(t) = 62{,}99 - \frac{36{,}77}{ch\left[\frac{0{,}245(t-975)}{100}\right]}.$$

The density of low-carbon steel from temperature (Steel AISI1015):

$$\rho_p(t) = 7866 - 0{,}406 \cdot t + 9 \cdot 10^{-5} t^2.$$

Table 1 shows the thermophysical properties for the selected coating materials (nickel, chromium, iron) in the solid and liquid phases. The properties of the substrate material (low carbon steel) and air are also shown there. For coating materials for the solid phase, the average integral values of the main thermophysical properties are given in the temperature range from 20°C to the melting point of the corresponding metal.

Fig. 2 shows the calculated dependences of the effective density and effective heat capacity on temperature (below the phase transitions of 1450°C). The dependences of the thermal conductivity of individual metals (Ni, Cr, Fe) (Fig. 3a) and the effective thermal conductivity of their mixture according to formula (11) on temperature are given (Fig. 3b).

Table 1. Properties of the materials included in the coating and substrate.

№	Property	Designation	Unit	Value (1– Ni, 2 – Cr, 3 – Fe)
1	Melting point (liquidus temperature)	$t_{mi}=T_{Li}$	°C	1452; 1907; 1537
	Formal solidus temperature	T_{si}	°C	1442; 1897; 1527
2	Specific heat of melting	L_i	kJ kg^{-1}	305; 280; 270
3	Density of the solid phase (at $T<T_s$)	ρ_{ti}	kg m^{-3}	8587; 7073; 7606
4	Density of the liquid phase (at $T>T_l$)	ρ_{gi}	kg cm^{-3}	7850; 6200; 7040
5	Specific heat capacity of metals in the solid phase	c_{mi}	J kg^{-1}K^{-1}	564; 508; 690
6	Specific heat capacity of metals in the liquid phase	c_{gi}	J kg^{-1}K^{-1}	735; 961.6; 825
7	Coefficient of thermal conductivity of metals in the solid phase	λ_{mi}	W m^{-1}K^{-1}	70; 67; 48
8	Coefficient of thermal conductivity of metals in the liquid phase	λ_{gi}	W m^{-1}K^{-1}	78,5; 70,5; 39
9	Steel density	ρ_p	kg m^{-3}	7689
10	Heat capacity of steel	c_p	J kg^{-1}K^{-1}	678
11	Coefficient of thermal conductivity of steel	λ_p	W m^{-1}K^{-1}	40.9
12	Coefficient of thermal conductivity of air	λ_0	W m^{-1}K^{-1}	0.056
13	The initial porosity of a homogeneous mixture	Π	%	26
14	Mass fractions of metal powders (i=1, 2, 3)	ε_i	~	1/3

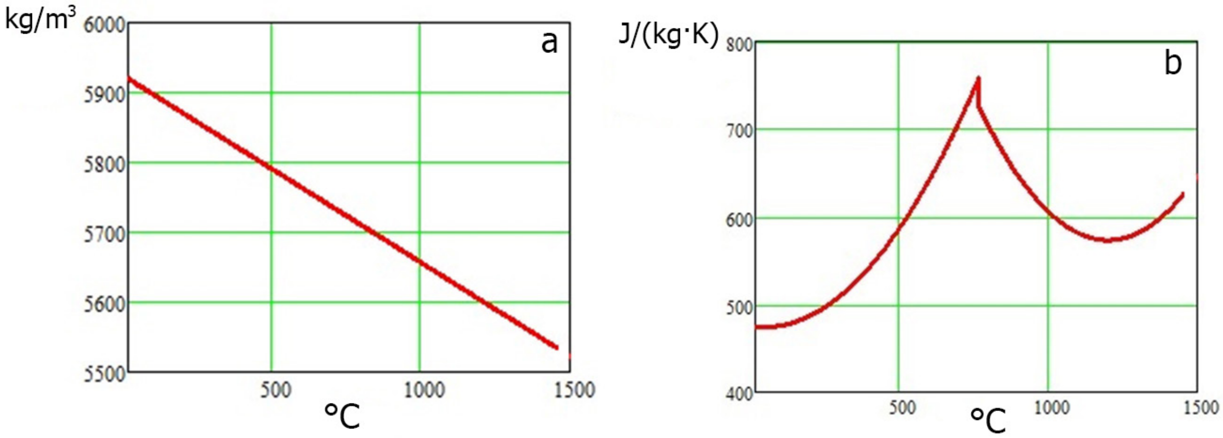

Fig. 2. Dependences of the effective density (a) and effective specific heat (b) of the powder mixture on temperature (at temperatures below melting of metals).

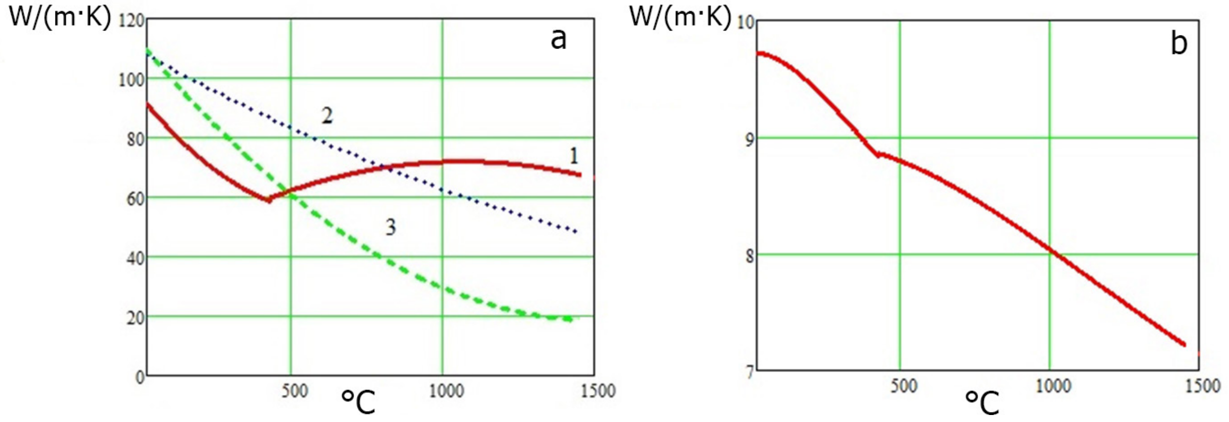

Fig. 3. Dependences of the thermal conductivity of individual metals (a) and the effective thermal conductivity of the powder mixture (b) on temperature: (1 - Ni, 2 - Cr, 3 - Fe).

RESULTS AND DISCUSSION

As an example, the process of laser remelting of a system of three metal powders of pure nickel, chromium and iron in the same mass fractions was considered. The substrate is made of low-alloy steel. A computer simulation was carried out using the "Composite coating thermal state" program with the following initial data: $h = H = 3$ mm; $L = 50$ mm; $d_f = 2$ mm; $W_н = 12.5$ mm·s^{-1}; $t_0 = 20$°C; $t_{env} = 15$°C; $A = 0.74$; $P_н = 1200$ W; $\eta = 0.6$; $П = 0.26$; $\varepsilon_m = 0{,}7$; $\varepsilon_{env} = 0.85$.

The program outputs temperature fields in tabular form in MS Excel file format, in the form of diagrams and graphs in jpg format. Under the selected remelting conditions, for a plate with a length of L = 50 mm, the beam passage time is 3.84 seconds. The average heat flux in the focal spot area is q ≈ 12.6 kW cm^{-2}. Fig. 4 shows the calculated diagrams of the temperature distribution at time τ = 1.92 s (the coordinate of the center of the focal spot is in the middle of the plate y_f=L/2=25 mm) and at the time of full passage τ = 3.84 s. At the same time, the maximum temperature in the focal spot area is about 5450°C. The penetration depth of the most low - melting metal (nickel) was approximately 0.8 mm, and the most refractory (chromium) - 0.5 mm.

The dependences of the average surface temperature of the processed powder, the average temperature of the substrate and powder boundary and the maximum temperature at a given depth on time are obtained (Fig. 5). During the entire passage of the laser beam, the average surface temperature of the powder and substrate is constantly increasing, and the maximum temperature

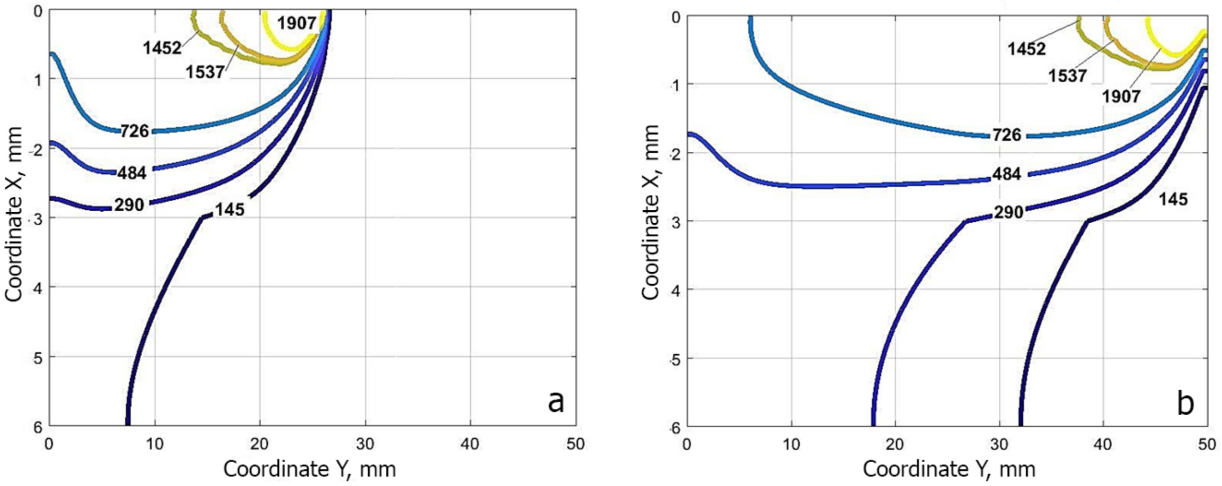

Fig. 4. Temperature distribution diagram at the time of passage of half of the plate by the laser beam 1.92 s (a) and at the time of full passage 3.84 s (b). The three isotherms with the highest temperature are the liquidus temperatures of the metals of the composition.

at a given depth from the surface of the formed coating after establishment (approximately for 0.5 - 0.8 seconds) practically does not change. At the same time, the maximum temperature of the steel substrate does not exceed 400°C.

The created program allows you to output tabular values of the temperature field at a given time in the form of an Excel spreadsheet. Based on the data obtained, Fig. 6 shows the temperature distribution in the composite coating at different depths from its surface along the length of the plate at the moment at the time when the laser beam passes half (y = 25 mm) and the entire plate (y = 50 mm).

It can be seen that the maximum temperature in the focal spot allows melting the most refractory metal, in our case it is chromium Cr, the depth of penetration of individual coating components depends on the speed and trajectory of the beam along the surface.

Knowing the temperature distribution at a given time (Fig. 4) it is possible to determine the maximum penetration depth of the x_{fus} layer, this is the distance from the coating surface, where the maximum temperature is equal to the liquidus temperature of the most fusible metal. For the depth of complete penetration of the layer, we will take the largest distance x_{all}, where a temperature equal to the liquidus temperature of the most refractory metal in the composition is observed. For our composition, $x_{fus} = 0.8$ mm, $x_{all} = 0.6$ mm. We consider that at the depth of complete penetration ($x \leq x_{all}$) all metals have formed an alloy and it is possible to estimate the shrinkage of the resulting coating after laser treatment $\Delta h = x_{all} \cdot (1 - \Pi)$ and its full thickness after laser penetration as $h = h - \Delta h$.

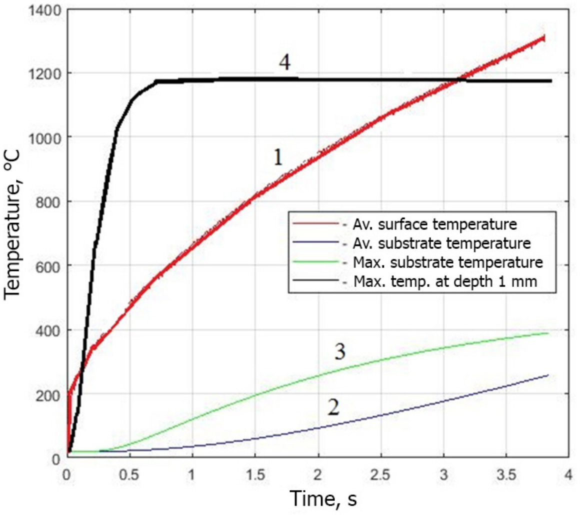

Fig. 5. Time dependence of the average surface temperature of the powder 1, average 2 and maximum (3) substrate temperature and maximum temperature at a depth of x = 1 mm (4) from the beginning of the passage to the time of 3.84 s (full passage of the laser beam).

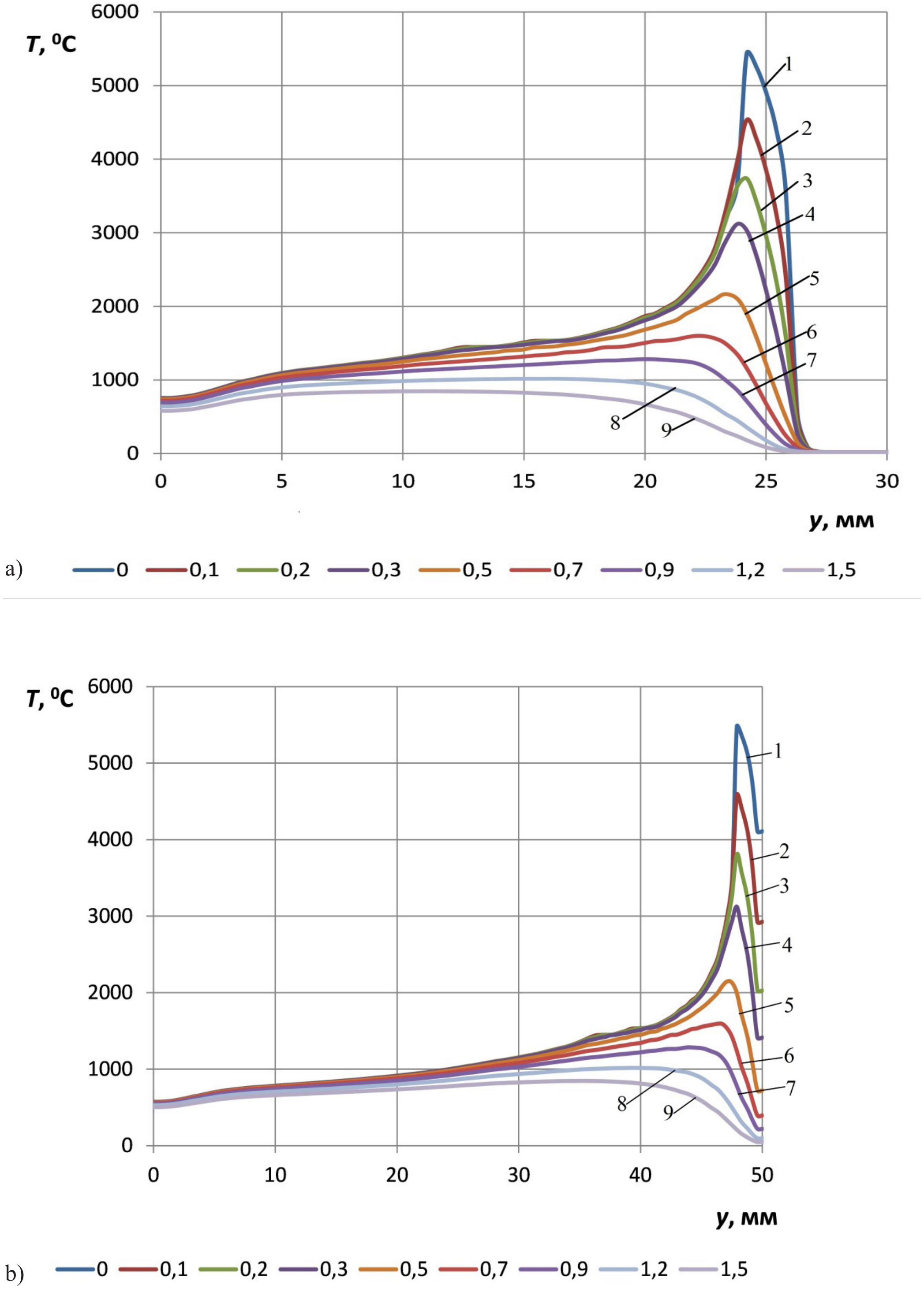

Fig. 6. The temperature in the coating along the Y coordinate at the moment when the laser beam passes through the halves (a) and all plates (b) at different depths from the surface x: 1 - 0 mm; 2 - 0.1 mm; 3 - 0.2 mm; 4 - 0.3 mm; 5 - 0.5 mm; 6 - 0.7 mm; 7 - 0.9 mm; 8 - 1.2 mm; 9 - 1.5 mm.

CONCLUSIONS

Based on the assumptions and limitations considered, a simplified mathematical model is formulated, which is a boundary value problem for calculating the non-stationary thermal state of a composite coating during its laser remelting on a metal substrate to obtain an alloy of equimolar composition. The novelty of the developed mathematical model is the proposed formulation suitable for describing the entire remeltable porous composite material, without distinguishing the boundaries of solid, two-phase and liquid zones for each metal. The computer program "Composite coating thermal state" has been created, which allows determining the dynamics of the position of two-dimensional boundary lines of a two-phase region for the liquidus and solidus of a given metal or alloy entering the mixture. The program also allows you to determine the depth of maximum and complete penetration of a layer during its laser remelting on a metal substrate of a high-entropy coating as the greatest distance where a temperature equal to the liquidus temperature of the most fusible and refractory metals in the composition is observed to obtain an alloy of equimolar or close to equimolar composition. This model uses a large amount of empirical data, so adaptation is required for its practical use. It is possible according to experimental data on changes in porosity and coating thickness before and after laser remelting of simple systems with similar thermophysical properties, for example, three elements Fe-Ni-Co, Ni-Cr-Fe, etc. The calculation of the laser remelting process of a system of three metal powders of nickel, chromium and iron in the same mass fractions is considered. Nonstationary temperature fields in the composite coating are obtained, taking into account its penetration and heating of the substrate. The depth of penetration of all metals and the most low-melting metal during laser remelting on a metal substrate to obtain a high-entropy alloy is determined. It was found that the maximum temperature at a depth of about 1 mm in the coating is set after about a certain time and then practically does not change over time. A method is proposed for calculating the penetration depth of all metals and the resulting shrinkage of the coating during laser remelting on a metal substrate to obtain a high-entropy alloy.

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REFERENCES

1. A.D. Pogrebnyak, A.A. Bagdasaryan, I.V. Yakushchenko, V.M. Beresnev, The structure and properties of high-entropy alloys and nitride coatings based on them, Russian Chemical Reviews, 83, 2014, 1027-1061. https://doi.org/10.1070/RCR4407
2. D.B. Miracle, O.N. Senkov, A critical review of high entropy alloys and related concepts, Acta Materialia, 122, 2017, 448-511. https://doi.org/10.1016/j.actamat.2016.08.081
3. M.C. Gao, J.-W. Yeh, P.K. Liaw, Y. Zhang, High-entropy alloys. Fundamentals and applications, Switzerland, Springer International Publishing, 2016. https://doi.org/10.1007/978-3-319-27013-5
4. B. Murty, J.-W. Yeh, S. Ranganathan, P. Bhattacharjee, High Entropy Alloys, Elsevier, 2019.
5. M.H. Tsai, J.W. Yeh, High-Entropy Alloys: A Critical Review, Materials Research Letters, 2, 2014,107-123. https://doi.org/10.1080/21663831.2014.912690
6. E.P. George, D. Raabe, R.O. Ritchie, High-entropy alloys, Nature Reviews Materials, 4, 2019, 515-534. https://doi.org/10.1038/s41578-019-0121-4
7. A. Ostovari Moghaddam, M.N. Samodurova, K. Pashkeev, M. Doubenskaia, A. Sova, E.A. Trofimov, A novel intermediate temperature self-lubricating CoCrCu1-xFeNix high entropy alloy fabricated by direct laser cladding, Tribology International, 156, 2021, 106857. https://doi.org/10.1016/j.triboint.2021.106857
8. A. Sova, M. Doubenskaia, E. Trofimov, M. Samodurova, Deposition of high-entropy alloy coating by cold spray combined with laser melting: Feasibility tests, Journal of Thermal Spray Technology, 31, 2022, 1112-1128. https://doi.org/10.1007/s11666-021-01300-0
9. I.S. Batraev, V.Yu. Ulianitsky, A.A. Sova, M.N. Samodurova, E.A. Trofimov, K.Yu. Pashkeev, A.G.

Malikov, D.V. Dudina, A.V. Ukhina, A feasibility study of high-entropy alloy coating deposition by detonation spraying combined with laser melting, Materials, 15, 2022, 4532. https://doi.org/10.3390/ma15134532

10. Yu.M. Klimkov, V.S. Mayorov, M.V. Khoroshev, Interaction of laser radiation with matter, Moscow, MIIGAiK, 2014, (in Russian).
11. R. Heui-Seol, Internal energy transfer theory for thermodynamic non-equilibrium, quasi-equilibrium, and equilibrium, International Journal of Heat and Mass Transfer, 78, 2014, 778-795. https://doi.org/10.1016/j.ijheatmasstransfer.2014.07.028
12. G.N. Dulnev, Yu.P. Zarichnyak, Thermal conductivity of mixtures and composite materials, Leningrad, Energy, 1974, (in Russian).
13. L.L. Vasiliev, S.A. Tanaeva, Thermophysical properties of porous materials, Minsk, Science and Technology, 1971, (in Russian).
14. V.S.V. Patankar, Numerical heat transfer and fluid flow, New York, Hemisphere Publishing Corporation, 1980. https://doi.org/10.1201/9781482234213
15. V.S. Chirkin, Thermophysical properties of nuclear engineering materials, Moscow, Atomizdat, 1968, (in Russian).
16. V.E. Zinoviev, Thermophysical properties of metals at high temperatures, Moscow, Metallurgy, 1989, (in Russian).
17. V.A. Makovsky, I.I. Lavrentik, Algorithm for controlling heating furnaces, Moscow, Metallurgy, 1974, (in Russian).