Simulation of the physicochemical interaction of reacting components in a molten pool during laser cladding

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Abstract. The problems of constructing mathematical models of physicochemical and heat and mass transfer processes are discussed when using heterogeneous materials in an additive laser technologies that form chemical compounds under certain conditions. The results of calculations of thermocapillary convection induced by a laser in aluminum melt with admixture particles of a higher refractory nickel are presented, when the beam is scanned at a constant speed. A description of exothermic reactions in nickel particles added to the melt during laser cladding or alloying is proposed, which allows calculating the composition of intermetallic phases in the trace of the beam after cooling.

1. Introduction
At present, in the additive production of aerospace materials, intermetallic alloys for the manufacture of parts or protective coatings have been of great interest [1, 2]. Nickel aluminides (Ni₃Al, NiAl), as composite coatings with a gradient structure, have several advantages, such as heat resistance due to high melting point (1653, 1911 K), low density (7290, 5910 kg/m³), increased compressive strength and increased yield strength, etc. The particular interest is the production of aluminides of composite materials of a three-dimensional net-like structure, a grid of NiAl, and filler made of Ni₃Al. Attractive for this purpose are additive technologies of direct material deposition (DMD) and selective laser melting (SLM) of powders [1].

The elements of primitive coatings based on the binary NI-Al system (single beads, thin walls) obtained under laboratory conditions by two different SLM and DMD methods turned out to be identical in structure [2]. The local action of laser radiation initiates metallurgical processes in the molten pool, which can be accompanied by interphase and chemical interaction between the reacting metal (metal-metal) and nonmetallic (metal-non-metal) elements in solid or liquid states. The chemical composition of the resulting product depends on many parameters, the main of which are the rates of local heating and cooling. Mathematical modeling of the thermal state of the object and calculation of the phase composition (compounds of chemical elements) of final products is an actual task for forecasting the conditions for obtaining quality products. In [3-5], problems of mathematical modeling of self-propagating high-temperature synthesis (SHS) occurring in a mixture of reacting metal powders are discussed. Based on the analysis of state diagrams of binary systems, schemes for the formation and decomposition of intermetallic phases are proposed and a heterogeneous model of high-temperature synthesis of intermetallic compounds is constructed.

In this paper the processes of heat and mass transfer in the presence of a two-component mixture of reactants in a molten pool induced by laser are described. On the basis of the heterogeneous SHS model [3], a model of the physicochemical interaction between the components is proposed, using the
example of the nickel-aluminum (Ni-Al) system, which can form intermediate crystalline intermetallic phases.

The purpose of this work is to create a mathematical model that predicts the rate of exothermic reactions in particles of the more refractory components added to the melt during laser alloying and cladding, and also to calculate the composition of the products of the chemical interaction of the reacting components in the trace of the beam after cooling-down.

2. Statement of the problem

The transportation technique and the mechanism for adding nickel particles to the aluminum molten pool are not considered. The appearance of particles in the melt is determined by the coordinates of the initial position on the surface of the liquid, which are calculated using a random number generator. It is assumed that the used laser heating regimes cause small values of the convective velocities in such a way that the melt flow is considered to be laminar, and this causes a flat shape of the free surface of the liquid. The position of the surface of the phase transition, which limits the melt zone of the metal and determines the shape and dimensions of the molten pool, is calculated taking into account the microconvection of the liquid phase. A complete mathematical formulation of the problem of the motion of a liquid with a dispersed admixture in a molten pool induced by a laser on a plane substrate, figure 1, is described in detail in [6]. In the enthalpy formulation, the two-phase Stefan problem on the melting of a metal by a laser beam with a Gaussian intensity distribution is solved.

\[ I(x, y) = 2W/\pi a_b^2 \exp(-2(x^2 + y^2)/a_b^2), \]

where \( W \) is the radiation power and \( a_b \) is the beam radius.

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In describing the growth kinetics of the IPs on the contact surface of reacting metals, simplifying assumptions are accepted [5]: 1) the formation of IPs is limited by the diffusion of nickel, whose atoms move more slowly; 2) local thermodynamic equilibrium is quickly established at the interphase boundaries, the kinetics of the process being diffusion; 3) the dependence of the diffusion coefficients on the concentration is neglected; 4) the influence of interfacial surface tension is not taken into account; 5) the effects of thermoelasticity are neglected. From the point of view of the mathematical description, the appearance of each of the IPs is equally probable. Therefore, it is assumed that at the time of product formation, there is an infinitely thin diffusion layer, which consists of the interlayers of all possible IPs simultaneously. Taking into account only the regions of single-phase intermediate IPs, excluding transition two-phase regions, by analogy with [5], we will assume that the distribution of the Ni concentration in the diffusion layer is represented by a discontinuous function with discontinuities at points on the interphase boundaries, and to calculate the trajectories of these boundaries and obtain a system ODE. In the case of only one reaction: \( \text{Ni} + \text{Al} \rightarrow \text{NiAl} \), the ODEs take the form [3]:

\[ \frac{d\varepsilon}{dt} = -D_\varepsilon \left( \frac{c_1 - c_2}{1 - c_1} \right) \left( r_p - r_1 \right) \frac{r_1}{r_1}, \]

\[ \frac{dr_p}{dt} = D_p \left( \frac{c_1 - c_2}{c_2} \right) \left( r_p - r_1 \right) \frac{r_1}{r_p}, \]

where \( D_\varepsilon = D_0 \exp(-E_\varepsilon/RT_p) \) is the coefficient of diffusion of nickel in the aluminum melt, the dependence of equilibrium concentrations on temperature \( c_1(T_p) \), \( c_2(T_p) \), given from the phase diagram of state [7], \( T_p \) is the temperature of the nickel particle. Figure 2 schematically shows the changes in the concentrations of the reacting components in initial and current states.
According to Eq. (2), solid particles in the melt will be characterized by two radii, internal and external. By the difference between them, the proportion of the reaction product, NiAl, is determined. The equations of the conservation of energy (in the enthalpy form) and the equation of conservation of momentum during the motion of nickel particles along their trajectories entrained by an aluminum melt moving due to the Marangoni effect should also be added to the equations of fluid flow in the molten pool [6].

\[
\frac{d}{dt}(m_pH_p) = 4\pi r_p^2 \left[ \frac{A}{r_p} N_{u_p}(T_p - T) \right] + 4\pi r_p \left[ \frac{r_p}{dt} \frac{dr_p}{dt} \right] \frac{Q_p}{\mu_p},
\]

(3)

\[
m_p \frac{dV_p}{dt} = \frac{1}{2} \rho C_d \pi r_p^2 \left[ V_i - V_p \right] (V_i - V_p) + m_p g \left[ 1 - \frac{\rho_p}{\rho_i} \right],
\]

(4)

\[
\frac{d\xi_p}{dt} = V_p,
\]

(5)

\[
H_p = \int_{T_a}^{T_p} c_p(T) dT, \quad T_p = \begin{cases} T_{mp}, & c_{T_{mp}} \leq H_p \leq c_{T_{mp}} + H_{mp} \\ T_{mp} + (H_p - c_{T_{mp}}) c_m, & H_p > c_{T_{mp}} + H_{mp} \end{cases},
\]

(6)

\[
C_d(Re_p) = \frac{24}{Re_p} \left( 1 + 0.179 Re_p^{0.5} + 0.013 Re_p \right), \quad Re_p ^{0.5} \leq 10^3, \quad Re_p = \frac{2r_p \rho_m |V - V_p|}{\mu},
\]

(7)

\[
Nu_p = 2 + 0.459 Re_p^{0.55} Pr^{0.33}; \quad Nu_p = \left( \frac{2r_p \alpha_t}{k_m} \right) / k_m; \quad Pr = \mu c_m / k_m
\]

(8)

Here, \( \rho_p, V_p \) are the density and velocity of the aluminum melt; \( Q_p, \mu_p \) are the thermal effect of the product formation reaction and its molecular weight; \( g = (0,0,g) \), where \( g = 9.8 \text{ m/s}^2 \) is the acceleration due to gravity; \( m_p=4/3 \pi r_p^3 \rho_p \) is the particle mass; \( C_d \) is the drag coefficient; \( Nu_p \) is the Nusselt number; \( r_p \) is the particle radius; \( \rho_p \) is the particle density, \( V_p \) is the particle velocity, \( T_{mp} \) is the melting temperature of the particle material, and \( H_{mp} \) is the latent heat of melting of the particle material.

The heat flux to an individual particle, Eq. (3), includes heat exchange with the metal melt and the thermal effect of the chemical reaction of the formation of the product of the NiAl. In accordance with

![Figure 1.](image1.png) Figure 1. The scheme of a molten pool induced by laser beam, with the adjacent part of the substrate.

![Figure 2.](image2.png) Figure 2. The distribution of concentrations of reagents (Ni, Al) and product (NiAl) inside the particle: initial state (a); current state (b).
Eq. (6), the temperature of the particle is determined taking into account the effect of the melting of the particles.

At the initial time $t=t_p$, when the initial nickel particle enters the melt, the following parameters are given: 1) $r(t_p)=R_0(1-\Delta)$, $r_p(t_p)=R_0$, where $\Delta$ is the infinitesimal value, which determines the initial values of the reaction product layer in the Ni-Al system, is the initial radius of the initial nickel particles; 2) $T_p=T_0$, $H_p=c_p T_0$, $V_p=(0,0,0)$, $X_p=(x_p^0,y_p^0,0)$, where $x_p^0$, $y_p^0$ are the coordinates of the initial position of the particle, for which are calculated with the help of a random number generator.

### 3. Results of the calculations

Figure 3 shows the current streamlets of liquid aluminum and the position of the particles, as well as the temperatures of the melt and particles in the transverse (figure 3 a,b) and longitudinal (figure 3 c,d) sections of the molten pool. The beam is scanned from left to right at a speed of 1 m/min. A power is 5 kW, an absorption coefficient of the aluminum is 0.1, a laser spot radius 1 mm, a particle diameter 20 μm, a powder mass rate 0.05 g/min. The presented figures characterize a complex picture of the vortex motions of the melt and particles. Due to the Marangoni effect, the flow on the surface of the pool is first directed strictly from the center to the periphery (figure 3a) then the stream rushes inward and forms a toroidal vortex adjacent to the edge of the pool. In the depth of the pool, two symmetrical vortices are formed, in which the flow carries the particles to the surface of the pool (figure 3b) and the process is repeated. The double radii of particle are shown that characterize the linear dimensions of the NiAl layer on the surface. Table 1 shows the physical properties of materials used in calculations. The kinetics constants: $E_w=74.0$ kg/kmol, $D_0=4.8\times10^{-6}$ m$^2$/s, $Q_p=1.37\times10^3$ J/kg.

![Current streamlets and temperature in liquid aluminum with nickel particles layered with nickel aluminide: in transverse (a, b) ($z=0; 200$ μm) and longitudinal (c, d) ($y=0; 200$ μm) cross sections of the molten pool. The solid line shows the boundary of the liquid metal.](image)

For nickel particles, the influence of the weight force is noticeable. For a liquid with an aluminum density of $\rho_l=2700$ kg/m$^3$, particles with a nickel density of $\rho_p=7800$ kg/m$^3$ are heavy. Nevertheless, they are involved in the movement. The maximum velocity of $V_p=0.8-1.0$ m/s particles is achieved when they appear on the surface of the pool in its center. Here, due to the Marangoni effect, the melt velocity has a maximum value; the particles quickly leave the center, carrying to the periphery, where they accumulate. Therefore, in the central part of the track behind the beam, where the crystallization
of the aluminum melt has already occurred, the number of particles is much smaller or absent (figure 3).

**Figure 4.** Time dependences of the coordinates of three particles Nos. 1, 2, 3 along the trajectories of their motion.

**Figure 5.** Time dependence of the velocity, temperature, outer and inner diameters of the three particles Nos. 1, 2, 3 as they move.

Interest is the change in the parameters of the particles until the melt solidifies (figure 4). From the particle velocity fluctuations and the coordinate of their center of mass, it can be said that Nos. 1, 2 returned to the surface of the pool once, and No. 3 moved only in the depth of the pool. From the temperature fluctuations, it can be seen that the particles quickly heated up in a hot stream (up to a temperature of 1600 K), and then cooled, falling into cold streams (up to a temperature of 950 K).
Figure 5 shows the time variation of the particle diameters (external and internal), the difference between them characterizes the fraction of the NiAl product formed. We note that in No. 3 nickel was completely consumed, since the residence time in the melt was the greatest.

**Table 1.** Physical properties of alumina, nickel and intermetallic phase NiAl.

| Value                                | Al       | Ni       | NiAl     |
|--------------------------------------|----------|----------|----------|
| Temperature, K: melting / evaporating | 933/2743 | 1728/3186| 1911/3186|
| Heat capacity, J/(kg K): solid / liquid | 902/1127 | 596/767  | 550      |
| Thermal conductivity, W/(m K): solid / liquid | 185.5/89.3 | 42.7/35.85 | 76       |
| Specific heat melting, 10^0 J/kg     | 0.36     | 0.216 / 6.1 | 1.4     |
| Density, kg/m^3: solid / liquid      | 2514/2391 | 8908/7810 | -        |
| Viscosity, 10^{-3} Pa s              | 1.2      | 4.75     | -        |
| Surface tension, N/m                 | 0.868    | 1.713    | -        |
| Surface-tension gradient, dσ/dT: 10^{-3} N/(m K) | -0.152   | -0.364   | -        |

4. Conclusion

Some principles of constructing a model of the physicochemical processes occurring in the molten pool with the addition of finely dispersed impurities of the reacting components during the laser treatment of the surface of metals are proposed. The model is based on the use of state diagrams, which describe the equilibrium state of a metallic system, depending on the chemical composition and external conditions.

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