Numerical modeling of the nucleation of crystallization centers during the modification of the surface layer of a metal using laser heating

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Abstract. Laser surface treatment using nanoscale particles of refractory compounds is a promising way to improve the operational characteristics of machine parts. Nanoscale particles increase the number of crystallization centers in the melt that occurs on the metal surface when exposed to a laser beam and, thereby, improve the dispersion and uniformity of the crystalline grains and the quality of the surface processed. The mathematical model used in the work allows one to describe the processes of nucleation and crystallization in the melt, the kinetics of the solid phase growth. Steady-state processes of heating, phase transition, heat transfer in the melt, nucleation, and growth of the solid phase are considered. The distribution of the temperature field, the size of the crystallization zone, and the number of crystallization centers in the molten metal are estimated.

1. Introduction

A promising way to improve the operational properties of machine parts is laser processing of their surfaces with the melt modification by nanosized particles of refractory compounds (carbides, nitrides, carbonitrides, etc.) [1, 2]. This allows of increasing the number of crystallization centers, and the resulting high dispersion and uniformity of the crystalline grains contribute to improving the quality of the treated surfaces [3–6].

In this paper, using numerical simulation, we consider the nucleation of crystallization centers in molten metal of a moving substrate when its surface is exposed to laser radiation and contains modifying nanosized particles. A mathematical model is formulated that describes the thermodynamic processes in the metal, including heterogeneous nucleation and crystallization of the primary phase of the melt, which allows one to determine the kinetics of the solid phase growth. Steady-state processes are considered, including heating, phase transition and heat transfer in the molten metal, nucleation and growth of the solid phase. Based on the results of numerical experiments, the distribution of the temperature field, the size of the crystallization zone, and the number of crystallization centers that have arisen in the molten metal of the substrate are estimated.

2. Mathematical model

The effect of a laser beam with focal spot of radius $r_0$ and flux power density described by a Gaussian distribution on a moving substrate of mild steel is considered. The process scheme is illustrated in figure 1.
The plate moves with constant speed $V$ along the $x$ axis, therefore, the processes occurring in it under the influence of laser radiation energy (heating and melting followed by solidification of the metal) are considered in the quasi-stationary approximation. The phase transition occurs at melting temperature $T_l$ of the substrate material. The surface of the substrate is covered by a layer of modifying nanosized particles of a refractory compound. A part of the particles is assumed to penetrate from the surface of the melt and get uniformly distributed throughout the volume, contributing to the emergence of crystallization centers [4-6]. After moving the plate from the area affected by the laser beam energy, due to heat removal into unheated material and heat exchange with the environment, the melt cools and crystallizes. To protect the metal from oxidation, the surface of the processed plate is blown with an inert gas. The boundaries $x_g$, $y_g$, $z_g$ of the region under consideration are chosen in such a way that their position does not affect the processes under study.

To simplify the problem, we assume that the thermophysical characteristics of liquid, solid, and two-phase media are the same and do not depend on temperature. Mass content $M_p$ of the particles penetrating into the melt is small ($M_p \leq 0.05\%$), the particles are cubic with edge $l_p$ much smaller than the characteristic size of the liquid pool, therefore, the influence of inclusions on the physical parameters of the melt can be neglected. Metal melting is considered in the approximation of the Stefan problem: it is assumed that under the considered heating conditions, the small values of convective velocities in the melt determine the flat shape of the free surface of the liquid.

The processes of heat transfer, melting and crystallization of the metal in plate are described in the quasi-stationary case by equation in Cartesian coordinate system

$$c_p \rho V \frac{\partial T}{\partial x} = \lambda \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + \kappa \rho V \frac{\partial f_s}{\partial x}$$

where $T$ is the temperature; $\rho$ is the density of the plate material; $c_p$ is the specific heat; $\lambda$ is the coefficient of thermal conductivity; $\kappa$ is the specific heat of fusion; $f_s$ is fraction of solid phase in the material ($0 \leq f_s \leq 1$).

We assume that the central point of the laser action spot of radius $r_0$ is located at point $(x_0, 0, 0)$. On the surface $z = 0$ of the plate, the boundary conditions

$$\lambda (\partial T / \partial z) = q(x, y) + (\alpha_k + \alpha_r)(T - T_g)$$

Here, $T_g$ is the temperature of the protecting gas, $\alpha_r = \varepsilon \sigma_0 \left( T^4 + T_s^4 \right) (T + T_s)$ is coefficient of the radiative heat transfer, $\varepsilon$ is the reduced degree of blackness, $\sigma_0$ is the Stefan-Boltzmann constant, $\alpha_k$ is the convective heat transfer coefficient.
is power density of the laser beam with $q_0$ being its maximum value.

On the plane $y = 0$, $0 \leq x \leq x_g$, $0 \leq z \leq z_g$, the symmetry condition is used. The conditions at the remaining borders are as follows:

$$\lambda(\partial T / \partial x) = 0, \ x = 0, \ x = x_g; \ \lambda(\partial T / \partial y) = 0, \ y = 0; \ \lambda(\partial T / \partial z) = 0, \ z = z_g$$

Fraction $f_i$ of the solid phase is calculated according to the model proposed in [7, 8]:

$$f_i(x, y, z) = 1 - \exp \left\{ -\frac{1}{V} \int_{x_0} I(\xi, y, z) \left[ 1 - f_i(\xi, y, z) \right] d\xi \right\}, \quad V(\xi) = \frac{4\pi}{3} \left( R_e + \frac{K_e}{V} \int_\xi \Delta T d\xi \right)^3$$

where $I(x, y, z)$ is the nucleation rate:

$$I = \frac{M_p \rho \sigma^2 D_0}{50 \rho_f \rho_p \sigma^2 \Delta \rho_c^2} R_e^4 \sin^2 \theta (1 - \cos \theta) \exp \left[ -\frac{E + \Delta G^*}{k_B T} \right]$$

$1 - f_i(x, y, z)$ is fraction of the liquid phase; $V(x, y, z)$ is the volume of growing grain; $M_p$ is the amount of nanopowder, % by mass; $\rho$ is the metal density; $D_0$ is pre-exponent in the Arrhenius law; $\rho_p$ is the nanopowder density; $l_p$ is the edge size of the cubic seed; $l_0$ is the melt atom diameter; $l_0$ is the interatomic distance of the seed material; $R_e = R_0 (1 - \delta / R_0)$ is the critical radius of the solid phase nucleus, $R_0 = 2\sigma^{1/2} T_0 / (\kappa \rho X_0)$ is the initial value of the nanoseed effective radius; $\Delta T_0 = T_0 - T$, $T_0$ is the initial liquidus temperature; $\delta$ is the Tolman parameter; $\theta$ is the contact angle of wettability of the particle surface; $E$ is the activation energy of diffusion of the alloying component; $k_B$ is the Boltzmann constant; $\Delta G^*$ is the free energy of formation of the critical solid phase nucleus on a flat substrate, defined by expression

$$\Delta G^* = \frac{\pi}{3} \sigma_{12}^\infty R_0^2 \left[ 1 - \frac{6\delta}{R_0} \right] (1 - \cos \theta)^{(2 + \cos \theta)}$$

$\Delta T = T_A - \beta C_0 (1 - f_j)$ is local supercooling of the melt ($T_0 = T - \beta C_0$); $\sigma_{12}^\infty$ is surface tension at the nucleus—melt interface; $k$ is the coefficient of the alloying component distribution in the alloy; $K_c$ is the constant of growth of the crystalline grain nucleus; $x_i$ is coordinate on the melt–two-phase-zone surface, where the alloy temperature is equal to the equilibrium temperature $T_i$. The number of crystals formed in a unit volume of the solidified metal is calculated by formula

$$N = \frac{1}{V} \int_{x_0} I(\xi, y, z) \left[ 1 - f_i(\xi, y, z) \right] d\xi$$

3. Simulation results

Numerical studies were carried out with the following parameters [6, 9-11]: $r_0 = 0.001$ m, $x_0 = 0.006$ m, $x_g = 0.024$ m, $y_g = 0.012$ m, $z_g = 0.008$ m; $V = 0.005–0.025$ m/s; $T_0 = 300$ K; $q_0 = (2.5–4.0) \times 10^8$ W/m$^2$; $\sigma_0 = 5.7 \times 10^6$ W/(m$^2$ K)$^2$; $\alpha_k = 100$ W/(m$^2$ K); $\rho = 7065$ kg/m$^3$, $c_p = 787$ J/(kg K), $\lambda = 27$ W/(m K), $\kappa = 2.77 \times 10^5$ J/kg K, $T_d = 1775$ K, $C_0 = 0.49\%$ mass, $k = 0.4$, $\beta_0 = 91.7$ K/\%, $K_c = 3.5 \times 10^8$
\( \sigma_{12}^0 = 0.44 \text{ J/m}^2, \ \theta = 5–15^\circ, \ D_0 = 1.4 \cdot 10^{-7} \text{ m}^2/\text{s}, \ E = 9.6 \cdot 10^{-20} \text{ J}, \ \delta = 1.53 \cdot 10^{-11} \text{ m}, \ M_p = 0.03\%, \ 
\rho_p = 5440 \text{ kg/m}^3 \text{ (TiN)}, \ l_a = 2.86 \cdot 10^{-10} \text{ m}, \ l_c = 8.23 \cdot 10^{-10} \text{ m}, \ l_p = 8 \cdot 10^{-8} \text{ m}. \)

**Figure 2.** Temperature distribution in the volume and on the plate surface at:

(a) \( V = 0.015 \text{ m/s}, \ q_0 = 2.5 \cdot 10^8 \text{ W/m}^2; \) (b) \( V = 0.020 \text{ m/s}, \ q_0 = 3.5 \cdot 10^8 \text{ W/m}^2. \)

Figure 2 shows the temperature distribution inside and on the surface of the plate. Figure 2a illustrates the temperature distribution on the upper surface and plane of symmetry. Figure 2b, illustrating surface heating, shows the irregular temperature distribution due to heat generation in the two-phase crystallization zone. Only the part of the computational domain including the crystallization zone is shown.

**Figure 3.** Dependence of nucleation rate \( I \) on temperature \( T/T_0 \) at wetting angles:

\( \theta = 10^\circ \) (a) and \( \theta = 5^\circ \) (b).
Figure 3 illustrates the dependence of nucleation rate \( I \) on dimensionless temperature \( T = T/T_{l0} \) and various values of the wettability angle \( \theta \). From the results obtained, it follows that with the emergence of supercooling, the formation of nuclei of the metal crystals begins. With an increase in supercooling, the nucleation rate increases, however, after reaching a certain maximum value, it begins to decrease and subsequently stops completely. At lower values of \( \theta \), the nuclei arise earlier, the rate of their appearance is higher and, it can be said, is explosive. Small values of \( \theta \) are of the greatest interest for research, because they are more consistent with the values of supercooling at which crystallization occurs.

![Figure 3](image)

**Figure 3.** The dependence of nucleation rate \( I \) on dimensionless temperature \( T = T/T_{l0} \) and various values of the wettability angle \( \theta \).

Figure 4 illustrates the number \( N \) of nuclei formed at the boundary of the two-phase zone at the time of complete solidification of the melt and the patterns of their distribution inside the two-phase zone at speed \( V = 0.015 \) m/s and wettability angle \( \theta = 10^\circ \). A decrease in the number of nuclei (figure 4a), as well as in the rate of their nucleation, is observed inside the two-phase zone during solidification of the melt with the distance from the line of symmetry at \( y = 0 \) (figure 4b). This can be explained by a decrease in the melt overheating in the region of influence of the laser beam energy with increasing distance from the axis of symmetry of the system and due to an increase in the heat removal to the unheated material in the \( y \) direction. We can conclude that there are various conditions for nucleation.

Based on the results of computational experiments, it was determined that a change in velocity \( V \) affects the size and shape of the crystallization zone, but does not significantly affect the number of nuclei formed.

### 4. Conclusion
A model and an algorithm for its implementation are proposed, which allow one to study the processes of nucleation of crystallization centers when modifying the surface layer of a metal substrate using laser energy. The process of crystallization centers nucleation in the molten surface layer of the metal, in particular, the influence of the wettability angle of the surface of nanosized particles, is studied. The temperature fields, the sizes of the crystallization zone of the substrate, depending on the speed of its movement, as well as the distribution of the number of crystallization nuclei in the hardening and hardened metal, depending on the wettability angle of the surface of nanoscale inoculators, are determined. The study contributes to the understanding of the processes of laser surface modification of steel, which triples the microhardness of the modified layer and eliminates structural defects such as cracks and porosity [4].
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