Journal of Engineering Physics and Thermophysics, Vol. 78, No. 6, 2005

HEAT CONDUCTION AND HEAT EXCHANGE IN TECHNOLOGICAL PROCESSES

MODELING OF THERMAL PROCESSES IN LASER SINTERING OF REACTIVE POWDER COMPOSITIONS

L. P. Kholpanov,[a] **S. E. Zakiev,**[a]
and I. V. Shishkovskii[b]

UDC 621.7:537.5(043.3) + 621.785(043.3)

A two-dimensional mathematical model describing a combination of the processes of self-propagating high-temperature synthesis and selective laser sintering of powder compositions (it is controlled by the laser-radiation energy) has been proposed. The model makes it possible to evaluate the correspondence of the geometric characteristics of the system to the values of the velocities of a moving laser spot at which the layer poured completely reacts in the vicinity of the spot.

Introduction. Selective laser sintering (SLS) is one of the most developed (commercially) procedures of realization of the technology of fast prototyping. The SLS process represents the creation, layer by layer, of material copies of three-dimensional objects using spatially selective laser action on the surface of a freely poured powder composition [1]. A distinguishing feature of the SLS method is the possibility of creating functional composite products, not just their physical models, directly.

In our opinion, the development of the SLS method can be the most promising when the SLS process is combined with the well-known process of self-propagating high-temperature synthesis (SHS) [2]. Three-dimensional products created due to the SHS reaction in this case can possess a set of physicomechanical properties that cannot be obtained by other methods. We have shown experimentally the possibility of realizing a controlled SHS combustion reaction in a diffusion regime to form intermetallide and piezo- and ferroelectric phases in the systems Ni–Ti, Ni–Al, Ti–Al [3–5], $Pb(Zr_xTi_{1-x})O_3$, $Li_{0.5}Fe_{2.5-x}Cr_xO_4$, and $BaFe_{12x}Cr_xO_{19}$ [6, 7]. We note that the combination of the SHS and SLS processes is difficult to control. The beginning of the SHS reaction can "anticipate" the process of sintering itself or can "lag" behind it; also, we have the combustion (incomplete burning) of the starting components. The prime objective of laser sintering is precision selection of laser-action regimes in which both processes — SHS and SLS — would be in dynamic equilibrium. Therefore, the large number of controlling parameters in the above processes makes the problem of theoretical modeling topical.

The SLS of multicomponent powder compositions is traditionally associated with the process of liquid-phase sintering; this process is well known in powder metallurgy. We note that, even in a one-component powder medium, we always have a variation in the particle size and the early melting of the finely divided part of the fraction is actually analogous to liquid-phase sintering. We know of numerous attempts at modeling the SLS process by the finite-element method and within the framework of the semiclassical approach in the literature [8–10].

The present work seeks to construct and investigate a two-dimensional model theoretical description of the SLS of such SHS layers. It should be emphasized that, unlike the SHS macrokinetics, our interest was predominantly with the conditions of preservation of the controllability of the process in question due to the corresponding modifications of the laser-source parameters (the power and rate of scanning of the laser action, the spot diameter) rather than the special properties of reaching quasistationary model regimes (their stability, self-propagation velocity, etc.) [11].

---

[a] Institute of Problems of Chemical Physics, Russian Academy of Sciences, 18, Institutskii Prospekt, Chernogolovka, 142432, Noginsk District, Moscow Region, Russia; email: kholp@icp.ac.ru and zakiev@ism.ac.ru; [b] Samara Branch of the P. N. Lebedev Physical Institute, Russian Academy of Sciences, Samara, Russia; email: shiv@fian.smr.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 78, No. 6, pp. 42–48, November–December, 2005. Original article submitted December 8, 2004.

Formulation of the Model. We consider the motion (in a strictly prescribed direction and with a constant velocity $V_{\text{l.s}}$) of a laser source in a spot of power P and constant diameter $d_{\text{l.s}}$ over the surface of a reactive two-component powder mixture (for example, Ni–Ti, Ti–Al, or Ni–Al). Next, special emphasis will be placed on the thermal dynamics of the phenomenon in question and its controllability by the measured energy of the laser source in SLS, which is complicated by the heat release caused by chemical transformations. To simplify the formal part of the model we assume that the density, heat capacity, and thermal conductivity of the mixture remain constant throughout the entire SLS process. To determine their values we have used the following approximation:

$$A = \frac{\rho}{\nu_1 \rho_1 + (1 - \nu_1)\, \rho_2} (\nu_1 A_1 + (1 - \nu_1)\, A_2) + \frac{\nu_1 \rho_1 + (1 - \nu_1)\, \rho_2 - \rho}{\nu_1 \rho_1 + (1 - \nu_1)\, \rho_2} A_{\text{a}} .$$

Mathematically, the model is formulated in the two-dimensional half-space $\Pi(x) \times \Pi^{+}(y) = (-\infty, \infty) \times (0, +\infty)$; the positive direction of the Ox axis coincides with the direction of the velocity of motion of the laser source; the Oy axis is directed deep into the powder mixture:

$$c\rho \frac{\partial T}{\partial t} = \lambda \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) + Q_{\text{l.s}} + Q_{\text{h}} , \quad (x, y) \in \text{Ï} \times \text{Ï}^{+} , \tag{1}$$

$$\frac{\partial \eta}{\partial t} = (1 - \eta)\, k_0 \exp \left(- \frac{E}{RT} \right) . \tag{2}$$

The initial and boundary conditions are as follows:

$$\left. \frac{\partial T}{\partial y} \right|_{y=0} = 0 , \quad T\,(t, x = +\infty) = T_0 , \quad \left. \frac{\partial T}{\partial x} \right|_{x \to \pm\infty} = 0 , \tag{3}$$

$$T\,(0, x, y) = T_0 , \quad \eta\,(0, x, y) = 0 . \tag{4}$$

According to the available experimental data [12, 13], for the powder systems of interest, heat release from the laser source occurs in a volume, decreasing with distance from the surface in depth (i.e., in the positive direction of the Oy axis) by the exponential law:

$$Q_{\text{l.s}}\,(t, x, y) = Q_{\text{m}} \exp \left(-4 \left(\frac{x - V_{\text{l.s}} t}{d_{\text{l.s}}} \right)^2 \right) \exp \left(- \frac{y}{\alpha_{\text{l.s}}} \right) , \tag{5}$$

where the maximum density of the laser-action power at the center is calculated from the formula

$$Q_{\text{m}} = \frac{4P}{\pi \alpha_{\text{l.s}} d_{\text{l.s}}^2} .$$

The heat release due to the chemical transformations will be described in accordance with the approach [14] well known in macrokinetics by introduction of the dimensionless conversion η taking on values from the segment [0, 1] and satisfying Eq. (2) as

$$Q_{\text{h}} = Q_{\text{r}} \rho \frac{\partial \eta}{\partial t} .$$

For an SHS reaction one usually selects spatial parameters of the systems such that heat transfer to the ambient medium turns out to be insignificant for them. Under these conditions, the temperature T_{r} at which we have chemical transformation in the thermal-wave front (i.e., most of the system's transformation) is essentially one of the basic parameters determined experimentally and making it possible to find the values of k_0 and E in formula (2) for a specific system. It is precisely at the temperature T_r that the reaction heat Q_r is determined. A characteristic feature of the process in question is the fact that, depending on the width of the sintered reacting layer and on other SLS factors, the characteristic transformation temperature T_r can noticeably differ from the corresponding quantity for an SHS reaction. The quantity $1/\Delta_t$, where Δ_t is the characteristic time of complete reaction of the system's volume element at the temperature T_r, rather than the preexponent k_0 will, possibly, be more convenient in this situation. Therefore, it seems expedient to introduce the parameters

$$\Delta_r = \frac{RT_r}{E}, \quad \Delta_t = \frac{\exp(1/\Delta_r)}{k_0}$$

and to transform (2) to the form

$$\frac{\partial \eta}{\partial t} = \frac{1-\eta}{\Delta_t} \exp\left(\frac{T - T_r}{\Delta_r T}\right). \tag{6}$$

It is noteworthy that an analog of the quantity Δ_r in SHS theory is the parameter β, which, for example, has an order of 10^{-2} or lower for reactions with a "narrow combustion zone." We tie the coordinate system to the center of the laser-source spot. We introduce a new variable $z = x - V_{l.s}t$. Then the system of equations (1) and (6) takes the form

$$c\rho \frac{\partial T}{\partial t} - c\rho V_{l.s} \frac{\partial T}{\partial z} = \lambda \left(\frac{\partial^2 T}{\partial z^2} + \frac{\partial^2 T}{\partial y^2}\right) + Q_m \exp\left(-\left(2\frac{z}{d_{l.s}}\right)^2\right) \exp\left(-\frac{y}{\alpha_{l.s}}\right) + Q_r \rho \frac{\partial \eta}{\partial t} - Q_r \rho V_{l.s} \frac{\partial \eta}{\partial z}, \tag{7}$$

$$\frac{\partial \eta}{\partial t} - V_{l.s} \frac{\partial \eta}{\partial z} = \frac{(1-\eta)\exp\left(\frac{(T - T_r)}{\Delta_r T}\right)}{\Delta_t}.$$

Using the dimensionless variables

$$\tau = \frac{t}{\Delta t}, \quad \xi = \frac{z}{\Delta x}, \quad \zeta = \frac{z}{\Delta y}, \quad \theta = \frac{T - T_r}{T_r}, \quad \theta_0 = \frac{T_0 - T_r}{T_r},$$

$$v_{l.s} = \frac{V_{l.s}}{(\Delta x/\Delta t)}, \quad q_m = \frac{Q_m \Delta_t}{c\rho T_r} = \frac{4P\Delta_t}{\pi \alpha_{l.s} d_{l.s}^2 c\rho T_r},$$

$$q_r = \frac{Q_r}{cT_r}, \quad d_{l.s} \Rightarrow \frac{d_{l.s}}{\Delta x}, \quad \alpha_{l.s} \Rightarrow \frac{\alpha_{l.s}}{\Delta y},$$

where $\Delta t = \Delta_t$ and $\Delta x = \Delta y = \sqrt{\frac{\lambda \Delta_t}{c\rho}}$, we write system (7) as

$$\frac{\partial \theta}{\partial \tau} - v_{l.s} \frac{\partial \theta}{\partial \xi} = \frac{\partial^2 \theta}{\partial \xi^2} + \frac{\partial^2 \theta}{\partial \zeta^2} + q_m \exp\left(-\left(2\frac{\xi}{d_{l.s}}\right)^2\right) \exp\left(-\frac{\zeta}{\alpha_{l.s}}\right) + q_r (1-\eta) \exp\left(\frac{\theta}{\Delta_r(\theta+1)}\right),$$

$$\frac{\partial \eta}{\partial \tau} - v_{l.s} \frac{\partial \eta}{\partial \xi} = (1-\eta) \exp\left(\frac{\theta}{\Delta_r(\theta+1)}\right) \tag{8}$$

with initial and boundary conditions

$$\left.\frac{\partial\theta}{\partial\zeta}\right|_{\zeta=0} = 0\,,\quad \theta\,(\tau, \xi, +\infty) = \theta_0\,,\quad \left.\frac{\partial\theta}{\partial\xi}\right|_{\xi\to\pm\infty} = 0\,, \tag{9}$$

$$\theta\,(0, \xi, \zeta) = \theta_0\,,\quad \eta\,(0, \xi, \zeta) = 0\,. \tag{10}$$

Numerical Analysis. The system of equations (8) was solved based on difference schemes by the well-known method of variable directions with the use of the marching method. The computational procedure was constructed at each $(n + 1)$th time step as follows:

1. First, relying on the conversion distribution η^n computed earlier at the nth step, we found a new conversion distribution η^{n+1} using the difference representation of the second equation of system (8). We used the conditions

$$\Delta\eta = \eta^{n+1} - \eta^n\,,\quad 0 \le \eta^{n+1} \le 1\,.$$

2. Once η^{n+1} had been determined by the marching method, we found the solution of the first equation of system (8). For this purpose we represented it in the form

$$\frac{\partial\theta}{\partial\tau} = L_\xi + L_\zeta + Q\,, \tag{11}$$

where L_ξ and L_ζ are the operators in the directions ξ and ζ and Q is the source term determined by the temperature and conversion distributions obtained earlier. We took the following values of the parameters: $q_m = 198$, $q_r = 0.45$, $d_{l.s} = 0.03$, $\alpha_{l.s} = 5$, and $\Delta_r = 0.1$.

Discussion of the Results. One basic feature of an analysis of the model proposed lies in investigating the problem on the interrelation between the velocity of the laser source and the thickness of the layer of a completely reacted chemically active mixture (charge) immediately behind the laser spot just passed. From the practical viewpoint, this is the problem on the thickness of the layer poured for SLS. Here, we should recognize, first of all, two limiting cases:

I. The laser-source velocity is too low. There can be two variants:

1. The mixture layer is quite thin, and (or) we have a strong heat removal from the system (for example, the mixture lies on a cold massive substrate). Then the thermal wave of chemical transformation will have a complex unstable character. It will constantly keep ahead of the laser source but will stop after a short time interval and will wait for its arrival, since it is incapable of self-propagating without additional external heat. Part of the transformation will occur in its front, whereas the other part will occur directly in the laser-source spot. The heat from the laser source, which is pumped into the mixture already heated, will heat the system to such an extent that we will have melting of the layer instead of sintering; this melting will break the scheme of structure formation and shaping of an SLS product. Although in this case we are dealing only with a partial loss of control of the SLS process, nonetheless, the extremely unfavorable arising conditions of formation of the product make such a regime unacceptable for the SLS technology. From the formal viewpoint, model description of this situation involves corresponding variations in the construction of the model, but since the situation was of no practical interest we did not carry out its model description.

2. Quite a thick mixture layer. Then the heat released during the reaction of the SHS mixture is so large that it gives rise to the self-propagating high-temperature thermal transformation wave well studied in macrokinetics. The laser source here is only its initiator and rapidly lags behind it. This is the case of total incompatibility of SHS and SLS, where control of the process using the laser source is totally lost. Such a regime is qualitatively describable within the framework of this model in which an infinitely wide layer is considered. As is seen in Fig. 1a and b, after a short interval of time of switching on the laser, the SHS process becomes totally uncontrolled: the SHS wave acts in accordance with the macrokinetics of SHS, and the laser source is only a means of igniting the SHS mixture and next pumps additional heat to the system already reacted.

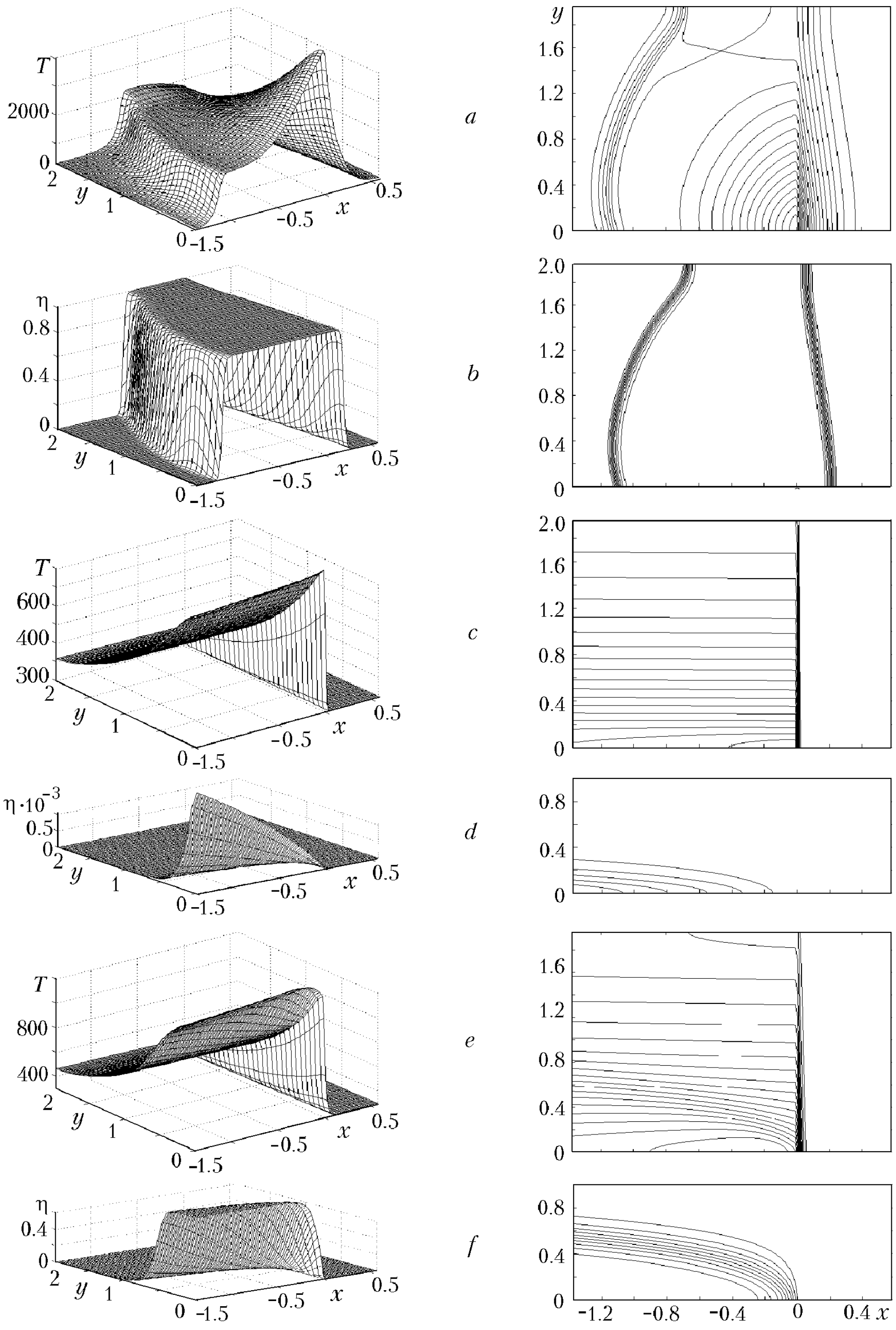

Fig. 1. Fields (on the left) and level lines (on the right) of temperature (a, c, and e) and conversion (b, d, and f) at $v_{\text{l.s}} = 0.76$ (a and b), 12 (c and d), and 5 (e and f).

II. High laser-source velocities. In this case, the SLS process also becomes uncontrolled, since even a thin mixture layer in the vicinity of a moving laser source has no time to completely react, which leads to one of two variants of evolution of the situation in the future (Fig. 1c and d). If the heat in the system is sufficient for continuation of SHS reaction in the absence of a laser source, the course of the reaction is totally uncontrolled again; otherwise, it rapidly decays and the mixture turns out to be partially unreacted.

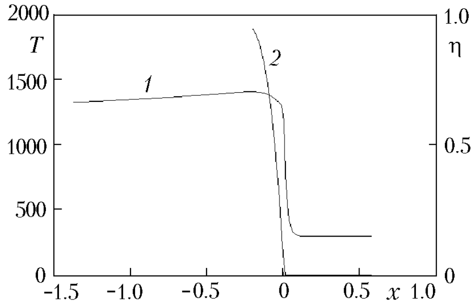

Fig. 2. Plots of temperature $T(x, 0)$ (1) and conversion $\eta(x, 0)$ (2) at $v_{\mathrm{l.s}} = 5$.

The model proposed makes it possible to evaluate the geometric characteristics and the correspondence of the value of the laser-source velocity, at which the layer poured completely reacts in the vicinity of a moving laser source, to them. This regime is shown in Fig. 1e and f. These figures also give the steady-state solution of system (8) and (9) in the vicinity of the center of the laser source; the solution is existent after a period of time sufficient for the system's point at which the laser source has begun its motion to leave the observed vicinity of the laser spot.

The form of the isolines of temperature (see Fig. 1e) for the steady-state solution of system (8) and (9) and $T(x, 0)$ and $\eta(x, 0)$ presented in Fig. 2 make it possible to evaluate the velocity $V_{\mathrm{l.s}}$ and to formulate the problem on conversion at $y \equiv 0$:

$$-V_{\mathrm{l.s}}\frac{d\eta}{dx} = \frac{(1-\eta)\exp\left(\dfrac{(T^* - T_{\mathrm{r}})}{\Delta_{\mathrm{r}} T^*}\right)}{\Delta_t}, \quad x \in [-\infty, 0]\,; \quad \eta(0) = 0\,,$$

or, changing the direction of the Ox axis, we obtain

$$V_{\mathrm{l.s}}\frac{d\eta}{dx} = \frac{(1-\eta)\exp\left(\dfrac{(T^* - T_{\mathrm{r}})}{\Delta_{\mathrm{r}} T^*}\right)}{\Delta_t}, \quad x \in [0, \infty]\,; \quad \eta(0) = 0\,. \tag{12}$$

In Eq. (12), the function η changes from 0 to 1 at the same temperature T^*, which fairly well describes the situation shown in Fig. 2. The solution of this equation has the form

$$\eta(x) = 1 - \exp\left[\left(\frac{x}{V_{\mathrm{l.s}}\Delta_t}\right)\exp\left(\frac{T^* - T_{\mathrm{r}}}{\Delta_{\mathrm{r}} T^*}\right)\right]. \tag{13}$$

To evaluate $V_{\mathrm{l.s}}$ using (13) we must indicate a certain value of $\eta < 1$, for example, $\eta = 0.9$, assuming that the reaction at it has already occurred in the main; next we must determine the length of a portion at whose end the temperature becomes a constant. In what follows, we denote this value as η^*. The width of the temperature hump in Fig. 2, which begins after a sharp rise in the temperature near zero, will be denoted by x_{r} and will be called the reaction-zone width. Therefore, we have

$$V_{\mathrm{l.s}} = \frac{x_{\mathrm{r}}}{\Delta_t}\frac{\exp\left(\dfrac{T^* - T_{\mathrm{r}}}{\Delta_{\mathrm{r}} T^*}\right)}{\ln\left(\dfrac{1}{1-\eta^*}\right)}\,. \tag{14}$$

In solving system (8) and (9) with boundary conditions (10) (the parameters of the system are $\Delta_t = 0.5$ sec, $\Delta_r = 0.1$, $T_r = 1000$ K, and $T^* = 1400$ K), we have taken the value of the velocity $V_r = 0.02$ m/sec. It is in good agreement with the velocity $V_{l.s} = 0.019$ m/sec calculated from formula (14) for $x_r = 1.25$ mm. The value of x_r has been taken based on Fig. 2.

Conclusions. We have proposed a two-dimensional model describing a combination of the processes of SHS and SLS that is controlled by the motion of a laser spot. We have considered two heat sources: the source due to the heating of the system by laser radiation and that of release in chemical transformation of reactive powder compositions. Numerical investigation of the model using the method of variable directions made it possible to differentiate the most characteristic regimes. Using this model, one can evaluate the correspondence of the geometric characteristics of the system to the values of the laser-radiation velocities at which the layer poured completely reacts in the vicinity of a moving laser spot. We have proposed a formula for evaluation of the optimum velocity of motion of the laser spot for a wide class of reactive powder systems. The results of the present work are in good agreement with the experimental data obtained earlier [6, 7].

This work was carried out with support from the Russian Foundation for Basic Research (grant No. 04-03-96500-r2004 Volga Region_a No. 05-03-32254).

NOTATION

A_1, A_2, and A_a, generalized thermophysical constants (density, heat capacity, and thermal conductivity); c, heat capacity of the mixture, J/(kg·K); $d_{l.s}$, diameter of the laser-source spot, m; E, activation energy of the chemical reaction of combustion, J/mole; k_0, preexponent, 1/sec; P, power of the laser action, W; Q_m, maximum power density at the center of the laser-source spot, J/(m^3·sec); $Q_{l.s}$, energy of the laser heat source, J/(m^3·sec); Q_h, heat-source energy determined by chemical transformations, J/(m^3·sec); Q_r, reaction heat, J/kg; R, universal gas constant, J/(kg·K); T, temperature of the mixture, K; T_r, temperature of the reaction, K; T_0, initial temperature of the mixture, K; t, time coordinate, sec; $V_{l.s}$, rate of scanning of the laser source, m/sec; x, space coordinate (the Ox axis is collinear to the direction of the laser-source velocity), m; y, space coordinate (the Oy axis is perpendicular to the plane of motion of the laser source), m; $\alpha_{l.s}$, penetration depth of the laser source, 1/m; Δ_r, relative thermal width of the reaction; Δ_t, characteristic time of reaction of the volume element, sec; η, conversion of the chemical reaction; λ, thermal conductivity of the mixture, J/(m·sec·K); ν_1, specific fraction of the first component in the starting mixture; ρ, density of the mixture, kg/m^3. Subscripts: a, air; l.s, laser source; 0, initial; h, heat source; r, reaction; m, maximum.

REFERENCES

1. V. V. Bagrov, N. A. Klimov, S. V. Nefedov, A. L. Petrov, V. I. Shcherbakov, and I. V. Shishkovskii, Program-device system on selective laser sintering, *Izv. Nauch. Tsentra Ross. Akad. Nauk*, **5**, No. 1 (9), 55–64 (2003).
2. I. V. Shishkovskii, A. G. Makarenko, and A. L. Petrov, Studying the conditions of SHS of intermetallides in selective laser sintering of a powder composition, *Fiz. Goreniya Vzryva*, **35**, No. 2, 59–64 (1999).
3. I. V. Shishkovskii, D. M. Gureev, and A. L. Petrov, Formation of biocompatible intermetallide phases in laser sintering of powder SHS compositions, *Izv. Ross. Akad. Nauk*, *Ser. Fizicheskaya*, **63**, No. 10, 2077–2081 (1999).
4. A. V. Kamashev, A. S. Panin, A. L. Petrov, and I. V. Shishkovskii, Use of a laser source for synthesis of intermetallides in the system Ni–Al, *Pis'ma Zh. Tekh. Fiz.*, **27**, Issue 12, 28–33 (2001).
5. Yu. G. Morozov, S. A. Nefedov, A. S. Panin, A. L. Petrov, and I. V. Shishkovskii, Studying the conditions of selective laser sintering in the powder system Al–Ti, *Izv. Ross. Akad. Nauk*, *Ser. Fizicheskaya*, **66**, No. 8, 1156–1158 (2002).
6. D. M. Gureev, R. V. Ruzhechko, and I. V. Shishkovskii, Studying the conditions of selective laser sintering of ceramic powder materials of the lead zirconate-titanate system, *Pis'ma Zh. Tekh. Fiz.*, **26**, Issue 6, 84–89 (2000).

7. I. V. Shishkovskii, M. V. Kuznetsov, and Yu. G. Morozov, Manufacture of bulk products based on barium hexaferrite with addition of chromium by combining the processes of SHS and SLS, *Steklo Keram.*, **60**, No. 6, 14–18 (2003).
8. K. Dai and L. Shaw, Thermal and mechanical finite element modeling of laser forming from metal and ceramic powders, *Acta Materialia*, **52**, 69–80 (2004).
9. G. B. M. Cervera and G. Lombera, Numerical prediction of temperature and density distributions in selective laser sintering processes, *Rapid Prototyping J.*, **5**, No. 1, 21–26 (1999).
10. Y. Zhang, A. Faghri, C. M. Buckley, and T. L. Bergman, Three-dimensional sintering of two-component metal powders with stationary and moving laser beams, *J. Heat Transfer*, *Trans. ASME*, **122**, No. 2, 150–158 (2000).
11. S. E. Zakiev and L. G. Shkadinskii, Thermal effect of high-frequency radiation on the front of high-temperature synthesis, *Khim. Fiz.*, **17**, No. 10, 112–120 (1998).
12. A. M. Ivanova, S. P. Kotova, N. L. Kupriyanov, E. Yu. Tarasova, and I. V. Shishkovskii, Physical principles of the process of selective laser sintering of metal-polymer powder compositions, *Kvantovaya Élektron.*, **28**, No. 5, 433–438 (1998).
13. I. V. Shishkovsky, Thermal field analysis under SLS of metal-polymer powder compositions, *Proc. SPIE*, **4**, 446–449 (2002).
14. A. G. Merzhanov, History and new developments in SHS, *Ceram. Trans.*, **56**, 3–25 (1995).