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ORDER PARAMETER AND KINETICS OF NON-EQUILIBRIUM PHASE TRANSITION STIMULATED BY THE IMPACT OF VOLUMETRIC HEAT SOURCE

E. E. Slyadnikov[1,3] **and I. Yu. Turchanovskii**[2,3]

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The authors formulated an understanding of the order parameter and built a kinetic model for the non-equilibrium first-order "solid body – liquid" phase transition stimulated by the impact of the volumetric heat source. Analytical solutions for kinetic equations were found, and it was demonstrated that depending on the phase transition rate "surface" and "bulk" melting mechanisms are implemented.

Key words: non-equilibrium phase transition, heat source, kinetic equations.

INTRODUCTION

As it is known, slow change in temperature of a structural unstable system leads to various equilibrium phase transitions, for instance magnetic, ferroelectric ones etc. [1]. It is common practice to describe spontaneous transformations of this type with one low-frequency and long-wavelength mode, the intensity of which is set by the order parameter [2]. It is possible, when intensity of heat impact is small, as far as the system has time to relax into the equilibrium state. When power of the heat source is large, the system does not have time to return to the equilibrium state and can move so far away from it that the transition process itself becomes non-equilibrium, non-linear. Such kinetic transformation is observed, for instance, on the surface of materials subjected to the heat impact of nanosecond electron-ray beams [3]. Unlike the equilibrium phase transition, description of kinetic transformation requires identifying several hydrodynamic modes and is developed in synergetics [4].

The classical approach to modelling a non-equilibrium first-order phase transition [5, 6] includes tracing the phase interface that separates the new phase from the initial one. This requires solving the Stefan problem with a free phase interface, position and shape of which are part of the solution. This model does not take into account the effect of such a factor as finite width of the interface, inside which initial and growing phases coexist and the transformation process unfolds.

Continuum models of the phase field [7], describing the process of relaxation in non-equilibrium condensed medium as a change in spatially non-uniform field of the order parameter characterizing the system deviation from the equilibrium state, take into account the finite width of the phase interface. They take into account the interrelation between order parameter decrease in each point of the medium and absorption of heat that self-consistently reduces the phase transition rate. However, they do not take into account the thermodynamic fluctuations of the order parameter, fluctuations of the potential relief of the atoms of the medium that play a crucial role in the vicinity of the critical phase transition point.

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[1]National Research Tomsk State University, Tomsk, Russia, e-mail: nadiet@mail.ru; [2]National Research Tomsk Polytechnic University, Tomsk, Russia, e-mail: tur@hcei.tsc.ru; [3]Institute of Computational Technologies, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 9, pp. 125–133, September 2016. Original article submitted March 31, 2016; revision submitted June 21, 2016.

Publications [8, 9] suggest a kinetic model of the first-order "solid body – liquid" phase transition, stimulated by the impact of a volumetric heat source, taking into account both the finite width of the phase interface and the random processes of fluctuations of the potential relief of the atoms of the medium in the vicinity of the critical phase transformation point. Phenomenological parameters of the model were evaluated; typical regularities of temperature and order parameter on time were obtained; kinetic equations were numerically solved for transition of unstable copper microvolume from the solid to the liquid phase.

The goal of the present paper is to formulate an understanding of the order parameter and carry out an analytical study of the kinetic model of non-equilibrium first-order phase transition stimulated by a volumetric heat source, as well as to identify the melting mechanisms depending on the phase transition rate.

1. ORDER PARAMETER AND KINETIC MODEL OF THE MELTING TRANSITION

Under the impact of intense nanosecond energy sources on the material surface, area with enhanced heat energy output (volumetric heat source) is formed deep inside the irradiated sample [3]. In the case of high surface density of energy and small pulse time of ionizing radiation, the process of substance heating is accompanied with phase transitions under non-equilibrium conditions [4]. Phenomenon of non-equilibrium transformation of one phase of the medium into another, stimulated by the impact of a heat source, is characterized by continuous distributed influx of energy from the outside and its dissipation. So material in the zone affected by a heat source is a dissipative structural unstable medium [9]. Owing to the fact that the energy flow from source to thermostat flows in the area of phase transformation through every physically small volume of the structural unstable medium, this microvolume is thrown off the heat equilibrium and acquires the ability to be bistable.

Bistable microvolume of the structural unstable medium has two stable fixed states (low-temperature and high-temperature phases) and can stay in each of them for an unlimited period of time. External heat impact can lead to transitions from one fixed state to another. In order to trigger the non-equilibrium transition, power of the heat impact needs to exceed the threshold level.

All thermodynamic theories of structural phase transitions rely on the idea [2] that the process of relaxation in the non-equilibrium medium can be described as change in spatially non-uniform field of the order parameter characterizing the system deviation from the equilibrium state. Moreover, change in the order parameter is accompanied with change in the medium symmetry, i.e. order parameter is a measure of deviation of atomic configuration in a less symmetrical phase from atomic configuration in a more symmetrical phase, measure of change in the short-range order of atoms. For instance, "crystal – melt" transformation is a transition from periodic symmetry of the crystal to complete symmetry of the liquid phase.

It is known that the structure of liquid can be called "quasi-crystalline" for the melted metal near the transition temperature, because it reveals a certain degree of the short-range order of the same type as in the corresponding crystal. In that case, one can judge about the degree of the short-range order based on the average distribution of atoms around each of them. Obviously, this relative distribution should not depend on the choice of a central atom and should have spherical symmetry in relation to it. It can be characterized by some function of density distribution $\rho(r)$, equal to the average number of atoms per volume unit at the distance r from the central atom. By definition, product $4\pi r^2\rho(r)dr = g(r)dr$ determines the average number of atoms located at the distance of r to $r+dr$ from the central atom.

Atoms located at the same distance from the central atom form its coordination sphere. Numbers of coordination spheres go up, the farther they are from the central atom. For an ideal crystal, binary function of density distribution can be presented as a sum for individual coordination spheres. Position of atoms in a crystal can be described by setting a digital number of distances r_s and coordination numbers n_s ($s = 1, 2, 3, \ldots$), in practice by two vectors $(r_1, r_2, \ldots, r_s)$, $(n_1, n_2, \ldots, n_s)$. The melt is characterized by atoms of the first coordination sphere being located at a certain (as in the crystal) distance r_1. And starting from the second sphere, they are described not by a single distance from the central selected atom, but by a set of close distances, i.e. each sphere turns out to be "blurred". Such blur increases, as the numbers of spheres go up. That is why when r increases, Gaussian functions start overlapping more and more, finally forming the constant “background” ρ = const corresponding to the average atom concentration in the crystal.

Analyzing behavior of the binary function of density distribution in various structural states of a substance, one can make a conclusion that for unequivocal description of structural state of the medium undergoing transformation, one needs to introduce the following quantitative parameters of the structure: coordination numbers, equilibrium interatomic distance, root mean displacement of atoms and, finally, radius of correlation of particle positions (i.e. radius of coordination sphere on which particle concentration equals average atom concentration in the medium).

Obviously, phase transition occupies a certain spatial volume. Describing the phase state in the course of melting, one needs to construct a certain functional dependence that will, in a continuous manner, describe the change of structure in all three volumes (crystal, liquid, and phase transition volume). Lev Landau in [2] introduced one characteristic value called the order parameter, in order to provide high-quality description of the phase transition accompanied with change in the structural state of the medium. This value changes from one in the solid phase to zero in the liquid phase. It is known from the experiment that for medium in the liquid state correlations in particle positions disappear completely on the sixth coordination sphere.

As for the order parameter η describing crystal – liquid transition, we suggest taking the value equal to the sum of squared differences of particle concentrations on the coordination sphere and average atom concentration in the crystal at temperature T starting from the sixth coordination sphere. This value needs to be normalized by the same sum at the absolute zero. In that case, at the absolute zero, the order parameter η is equal to one, and after melting transition it will turn into zero.

Following [2], let us present the thermodynamic potential of the structural unstable medium in the non-equilibrium state F as a function of temperature T and order parameter η. One should note that while temperature can be set arbitrarily, equilibrium value of the order parameter η_0 should stem from condition that value F is minimal at the set temperature in the zero external field. Breakdown for thermodynamic potential $F(T,\eta)$ of non-uniform unidimensional system, experiencing non-equilibrium first-order transition and located in the random field linked to the order parameter, looks as [9]

$$F(\eta)=\int dx\{[\eta^4(x,t)/4-\eta^3(x,t)(1/2-\Theta)+\eta^2(x,t)/4]+\psi(x,t)\eta(x,t)+(D/2\alpha)(\partial\eta/\partial x)^2\}\,, \tag{1}$$

$$<\psi(x,t)>=0\,,\ <\psi(x,t)\psi(x',t')>=S\delta(x-x')\delta(t-t')\,. \tag{2}$$

Axis x is chosen along the direction of electron beam propagation. Here $\psi(x,t)$ – random internal field (noise) emerging as a result of fluctuations of the potential relief of the atoms of the medium, $\Theta=\Theta(T(x),q))$ – non-equilibrium parameter of the medium, q – volumetric density of the heat source energy, T_c – equilibrium temperature of initial and final phases, S – noise intensity, $<......>$ – averaging over random field configurations, D – mobility index of the order parameter. For instance, under equilibrium transition conditions, when $q\to 0$, i.e. transition proceeds infinitely slowly, $\Theta=[(T-T_{\mathrm{c}})/T_{\mathrm{c}}]$, where T – temperature of the medium overheating in relation to T_{c}. Under non-equilibrium transition conditions, when q is finite, i.e. transition proceeds infinitely quickly, non-equilibrium parameter is determined by the rate of energy change in the elementary volume, in other words – by the sum of heat flow through the surface of elementary volume and volumetric density of the heat source energy. That is why $\Theta=\Theta(\partial T/\partial x,q))$, where $\partial T/\partial x$ – temperature gradient. At $\Theta=0$ the medium described by thermodynamic potential (2) has two stable states $\eta_{01}(0)=0$, $\eta_{03}(0)=1$ and one unstable state $\eta_{02}(0)=1/2$, but at $\Theta_*=1/2$ the medium has only one physical stable state $\eta_{01}(1/2)=0$. Averaged (1) over random configurations of potential relief fluctuations of the atoms of the medium at first approximation can be put as $<\psi(x,t)>=0$.

Fixed states of the medium η_{0i} for $i=1,\ 2,\ 3$ can be determined from condition

$$f(\eta_{0i})=\partial F(\eta)/\partial\eta=\{\eta^3{}_{0i}-3(1/2-\Theta)\eta^2{}_{0i}+(1/2)\eta_{0i}\}=0\,, \tag{3}$$

$$\eta_{01}(\Theta)=0\,,\ \eta_{02}(\Theta)=(1/2)+3\Theta\,,\ \eta_{03}(\Theta)=1-6\Theta\ \text{ for }\ \Theta<<1/2\,. \tag{4}$$

Hence, values $F(T,\eta)$ in these fixed states are equal to

$$F(T,\eta_{01})=0\,,\ F(T,\eta_{02})=(1/64)+(1/8)\Theta\,,\ F(T,\eta_{03})=\Theta\,. \tag{5}$$

According to [2], regression of the order parameter fluctuations in the non-uniform medium to the non-equilibrium is described by the Landau–Khalatnikov equation

$$\partial\eta/\partial t=-\partial F(\eta)/\partial\eta=-\alpha(\eta-\eta_{01})(\eta-\eta_{02})(\eta-\eta_{03})+D\partial^2\eta/\partial x^2\,, \tag{6}$$

$$-\infty<x<+\infty\,,\ t>0\,,\ \eta(-\infty,t)=1\,,\ \eta(+\infty,t)=0\,,\ \eta(x,0)=1\,, \tag{7}$$

where α – positive coefficient that has dimensionality (1/s) and is proportionate to frequency of the atoms fluctuations of the medium. In order to take into account the processes of heat propagation in the unidimensional medium accompanied with emission (absorption) of heat, equation of the order parameter relaxation (6) needs to be supplemented with a heat transfer equation

$$c\rho\partial T/\partial t=\lambda\partial^2 T/\partial x^2+q(t)f(x)-L\rho\partial\eta/\partial t\,, \tag{8}$$

$$\lambda\partial T(-\infty,t)/\partial x=0\,,\ \lambda\partial T(+\infty,t)/\partial x=0\,,\ T(x,0)=T_{\mathrm{c}}\,. \tag{9}$$

Here x – spatial coordinate chosen along the direction of electron beam propagation, t – time, T – temperature, λ – heat conductivity factor, J/(m·s·K), ρ – material density, kg/m^3, c – specific heat capacity of material, J/(kg·K), q – volume density of the heat source power, J/(m^3·s), L – latent heat of phase transition, J/kg. $q(t)=q\cdot H(t)$, $H(t)=1$ at $0<t<t_{\mathrm{im}}$, $H(t)=0$ at $t<0$ и $t>t_{\mathrm{im}}$, t_{im} – duration of the heat source impact, $q=W/(t_{\mathrm{im}}\cdot 2\sigma)$, where W – surface density of the heat source energy, J/m^2, σ – half-width of the Gaussian function $f(x)$. Thermophysical properties of the medium were taken as independent from temperature and identical in solid and liquid phases.

System of equations (6)–(9) allows for solutions of the running front type, propagating at the constant rate v [5], provided that the heat source is switched off after the start of melting. Physically, the sense of this condition is clear: the state of system in front of the running front does not change with time, i.e. substance identical in terms of composition, temperature and other physical properties feeds into the transformation front the entire time. If the heat source is not switched off, properties of the medium in front of the running front change with time and propagation of transformation will occur with variable distributions of temperature, order parameter and rate $v(t)$. Let us suppose that transformation in the initial substance proceeds sufficiently slowly, then the front will slowly, in a quasi-fixed manner, change its rate of propagation, at each moment of time adjusting to the physical properties of the substance fed to the transformation front at that moment. Thus, propagation of the front goes through the substance undergoing transformation, in which order parameter and temperature slowly change in space.

Let us search for wave solutions for system (6)–(9); in the case of wave propagation at variable rate $v(t)$ there is a transition in the crystal: from low-temperature phase with order parameter $\eta_{03}=1$ to high-temperature phase with order parameter $\eta_{01}=0$. For that purpose, let us move to the system of coordinates associated with the transformation wave front propagating from right to left:

$$z=x+\int v(t)dt\,,\ t=t\,. \tag{10}$$

Argument $z=x+\int v(t)dt$ generalizes the customary wave combination $z=x+vt$ for the case of variable transformation propagation rate $v(t)$. Independent impact of time is the second argument in (10), it is associated with the fact that temperature distribution in the wave propagating with variable transformation rate $v(t)$ also changes with the change in substance state before the front.

Taking into account (10), the system of equations (6)–(9) will look as follows:

$$c\rho\partial T/\partial t + c\rho v\partial T/\partial z = \lambda\partial^2 T/\partial z^2 + q - L\rho\partial\eta/\partial t - L\rho v\partial\eta/\partial z\,, \tag{11}$$

$$-\infty < z < +\infty\,,\ t > 0\,,\ \lambda\partial T(-\infty,t)/\partial z = 0\,,\ \lambda\partial T(+\infty,t)/\partial z = 0\,,\ T(z,0) = T_{\mathrm{c}}\,, \tag{12}$$

$$\partial\eta/\partial t + v\partial\eta/\partial z = -\alpha(\eta-\eta_{01})(\eta-\eta_{02})(\eta-\eta_{03}) + D\partial^2\eta/\partial x^2\,, \tag{13}$$

$$-\infty < z < +\infty\,,\ t > 0\,,\ \eta(-\infty,t) = 1\,,\ \eta(+\infty,t) = 0\,,\ \eta(z,0) = 1\,. \tag{14}$$

2. SOLVING ORDER PARAMETER RELAXATION AND THERMAL CONDUCTIVITY EQUATIONS

2.1. Solving the order parameter relaxation equation

It is difficult to solve system (11)–(14) analytically. However, one can see from (11)–(14) that volumetric source is only in the equation for temperature, so order parameter distribution does not depend on time and only depends on self-simulated variable *z*. That is why we shall first study kinetics of the non-equilibrium transition in the structural unstable medium using only the evolution equation for the order parameter (13). As for non-equilibrium parameter Θ, we shall consider it an external parameter to be calculated later when solving equation (11). The main solution for equation (13) under condition $\partial\eta/\partial t = 0$ is a switching wave [5]; during its propagation in the crystal, transition occurs from low-temperature phase with order parameter $\eta_{03} = 1$ to high-temperature phase with order parameter $\eta_{01} = 0$. Rate of the switching wave equals

$$\nu = (2D\alpha)^{1/2}(\eta_{01} + \eta_{03} - 2\eta_{02}) = -12(2D\alpha)^{1/2}\Theta\,. \tag{15}$$

The minus sign is due to the fact that the wave propagates from right to left. One can see from (15) that the switching wave rate is proportionate to the value of non-equilibrium parameter $\Theta = \Theta(\partial T/\partial x, q))$, squared root of transformation rate α and mobility index of the order parameter. Stemming from the physical sense of the problem, value Θ is limited ($\Theta \le 1/2$), so the switching wave propagation rate is also limited and has a maximum $\nu^* = -6(2D\alpha)^{1/2}$, which is determined only by properties of the medium.

If the wave rate ν is small, then the profile of this wave $\eta = \eta(z)$, $z = x + \nu t$ differs little from the profile of the resting interface boundary at $\nu = 0$ that has a view

$$\eta(z) = (1/2)[1 - \mathrm{th}(z/l)]\,,\ l = (2D/\alpha)^{1/2}\,. \tag{16}$$

Here parameter l plays the role of the switching wave front width.

One can see from (13) that fixed uniform states with order parameter η_{03} and η_{01} are always stable in relation to small non-uniform fluctuations of the order parameter. However, when there is a local order parameter source (crystal surface, grain boundary), emergence of a large (critical) order parameter fluctuation is possible, which can lead to formation of the switching wave front and transition from metastable state η_{03} to stable state η_{01} (see Fig. 1). I.e. the Stefan (surface) melting mechanism is implemented.

However, in the case of critical level of intensity and heat source impact depth, local absolutely unstable areas of the crystal emerge in the sample volume (areas of overheating maximums) in relation to infinitely small new phase fluctuations. I.e. a different, non-Stefan, bulk mechanism of non-equilibrium transformation is implemented.

Values α, D are phenomenological model parameters that can be assessed using their physical sense and interconnection with thermophysical parameters of the medium, with characteristics of volumetric heat source of phase transformation t_{ft}, temperature conductivity coefficient a:

$$t_{\mathrm{ft}} = [L\rho / q] = [L\rho / (W / t_{\mathrm{imp}}\sigma)] \, , \; a = \lambda / c\rho \, , \; \alpha >> (1/t_{\mathrm{ft}}) \, , \; D << a \, . \tag{17}$$

Inserting characteristic thermophysical parameters for copper in the solid phase $c = 0.385$ J/(g·K), $\rho = 8.36$ g/cm^3, L = 213 J/g, T_{c} = 1358 K, λ = 4 J/(s·cm·K), and for the heat source – volumetric power density $q = 4.06 \cdot 10^{11}$ J/(cm^3·s) (for the electron beam $W = 2$ J/cm^2, $\sigma = 10^{-4}$ cm, $t_{\mathrm{imp}} = 7 \cdot 10^{-8}$ s), from (17) we shall obtain $t_{\mathrm{ft}} = 4.4 \cdot 10^{-9}$ s, $\alpha = 10^{11}$ s^{-1}, $a = 0.7$ cm^2/s, $D = 10^{-3}$ cm^2/s.

Obtained estimates of parameters α, D allow determining the maximal rate v^* and width of the switching wave front l:

$$v^* \cong 840 \text{ m/s}, \; l = (2D/\alpha)^{1/2} \cong 1.4 \cdot 10^{-9} \text{ m}. \tag{18}$$

Hence the switching wave rate can change from zero to 840 m/s, and width of the phase transformation front is small in terms of order parameter and equals four interatomic distances. In order to calculate the switching wave front rate, one needs to estimate the value of non-equilibrium parameter $\Theta = \Theta(\partial T / \partial x, q))$, for that purpose we shall self-consistently solve the thermoconductivity equation (11), (12).

2.2. Solving the thermal conductivity equation

Estimates show that thermal conductivity factor is much higher in a solid body than mobility index of the order parameter D ($a = \lambda / c\rho >> D$). That is why width of the transformation wave front in terms of order parameter will be much smaller than the temperature front width, hence it can be sent to zero when solving the thermal conductivity equation. Then in point $z = 0$ temperature $T(0,t) = T_{\mathrm{c}}$, $\eta(-0,t) = 1$, $\eta(0,t) = 1/2$, $\eta(+0,t) = 0$, hence $\partial T(0,t)/\partial t = 0$, $\partial \eta(0,t)/\partial t = 0$, $\partial \eta(0,t)/\partial z = \infty = \delta(z)$, as far as $\int_{+0}^{-0} dz(\partial \eta(z,t)/\partial z) = \eta(-0,t) - \eta(+0,t) = 1$. Taking into account the latter properties, system (11)–(14) will look as follows:

$$c\rho \partial T / \partial t + c\rho v \partial T / \partial z = \lambda \partial^2 T / \partial z^2 + q - L\rho v \delta(z) \, , \tag{19}$$

$$-\infty < z < +\infty \, , \; t > 0 \, , \; \lambda \partial T(-\infty,t)/\partial z = 0 \, , \; \lambda \partial T(+\infty,t)/\partial z = 0 \, , \; T(z,0) = T_{\mathrm{c}} \, , \; T(0,t) = T_{\mathrm{c}} \, , \tag{20}$$

$$\eta(z,t) = 1 \text{ for } -\infty < z < -0 \, , \; \eta(0,t) = 1/2 \, , \; \eta(z,t) = 0 \text{ for } +0 < z < +\infty \, . \tag{21}$$

It is known [6] that system (19)–(21) is equivalent to the Stefan problem

$$c\rho \partial T / \partial t + c\rho v \partial T / \partial z = \lambda \partial^2 T / \partial z^2 + q \, , \tag{22}$$

$$-\infty < z < +\infty \, , \; t > 0 \, , \; \lambda \partial T(-\infty,t)/\partial z = 0 \, , \; \lambda \partial T(+\infty,t)/\partial z = 0 \, , \; T(z,0) = T_{\mathrm{c}} \, , \; T(0,t) = T_{\mathrm{c}} \, , \tag{23}$$

$$L\rho v = -\lambda \partial T(-0,t)/\partial z + \lambda \partial T(+0,t)/\partial z + q\sigma \, , \tag{24}$$

where v – movement rate of the phase transformation boundary. Let us solve system (22)–(24) behind the transformation front that moves from right to left along axis z:

$$c\rho\partial T/\partial t + c\rho v\partial T/\partial z = \lambda\partial^2 T/\partial z^2 + q\,,\ 0 < z < +\infty\,,\ t > 0\,, \tag{25}$$

$$T(0,t) = T_{\mathrm{c}}\,,\ \lambda\partial T(+\infty,t)/\partial z = 0\,,\ T(z,0) = T_{\mathrm{c}}\,, \tag{26}$$

$$L\rho v = -\lambda\partial T(-0,t)/\partial z + \lambda\partial T(+0,t)/\partial z + q\sigma\,. \tag{27}$$

For that purpose, let us move on to dimensionless variables

$$t = t/t_r\,,\ z = z/z_r\,,\ T = T/T_c\,,\ v = v/v_r\,,\ a = a/a_r\,,\ \omega = q/\omega_r\,, \tag{28}$$

where t_r, z_r, T_{c}, $v_r = z_r/t_r$, $a = \lambda/c\rho$, $a_r = z_r^2/t_r$, $\omega_r = c\rho T_c/t_r$ – values characteristic for the process of non-equilibrium phase transformation. Obviously, we can determine the characteristic time t_r as time of phase transformation $t_{\mathrm{ft}} = L\rho/q$, and characteristic length z_r as depth of radiation penetration σ. Then system (25)–(27) will look as follows:

$$\partial T/\partial t + v\partial T/\partial z = a\partial^2 T/\partial z^2 + \omega\,,\ 0 < z < +\infty\,,\ t > 0\,, \tag{29}$$

$$T(0,t) = 1\,,\ \lambda\partial T(+\infty,t)/\partial z = 0\,,\ T(z,0) = 1\,, \tag{30}$$

$$v = (cT_{\mathrm{c}}/L)[-a\partial T(-0,t)/\partial z + a\partial T(+0,t)/\partial z + \omega]\,. \tag{31}$$

Solving system (29)–(31) using the Laplace transform at $0 < z < +\infty$, we obtain

$$T(z,t) = 1 + \omega\left\{t - 1/2\left[\int_0^t d\tau\left(\operatorname{erfc}\left[\left(z/2\sqrt{a\tau}\right) - \sqrt{v^2\tau/4a}\right] + \exp(vz/a)\operatorname{erfc}\left[\left(z/2\sqrt{a\tau}\right) + \sqrt{v^2\tau/4a}\right]\right)\right]\right\},$$

$$\partial T(+0,t)/\partial z = \omega\left[-(v/2a)t + \left(2/\sqrt{\pi a}\right)\exp(-v^2/4a)t^{1/2} + \left(v^2/6a\sqrt{\pi a}\right)\exp(-v^2/4a)t^{3/2}\right]. \tag{32}$$

One can solve system (22)–(24) in analogous way in front of the transformation front that is moving from right to left along axis *z*, when $-\infty < z < 0$:

$$T(z,t) = 1 + \omega\left\{t - 1/2\left[\int_0^t d\tau\left(\operatorname{erfc}\left[\left(-z/2\sqrt{a\tau}\right) + \sqrt{v^2\tau/4a}\right] + \exp(vz/a)\operatorname{erfc}\left[\left(-z/2\sqrt{a\tau}\right) - \sqrt{v^2\tau/4a}\right]\right)\right]\right\},$$

$$\partial T(-0,t)/\partial z = -\omega\left[(v/2a)t + \left(2/\sqrt{\pi a}\right)\exp(-v^2/4a)t^{1/2} + \left(v^2/6a\sqrt{\pi a}\right)\exp(-v^2/4a)t^{3/2}\right]. \tag{33}$$

Inserting (32), (33) into (31), we obtain the non-linear equation for movement rate of the phase transformation boundary

$$v = (cT_{\mathrm{c}}/L)\omega\left[1 + 4\sqrt{a/\pi}\exp(-v^2/4a)t^{1/2} + \left(v^2/3\sqrt{\pi a}\right)\exp(-v^2/4a)t^{3/2}\right]. \tag{34}$$

In limit $t \ll 1$, $(cT_{\mathrm{c}}/L)\omega = 1$ dimensionless rate of the phase transformation boundary equals

$$v = \left[1 + 4\sqrt{a/\pi}\,t^{1/2} + \left(1/\left(3\sqrt{\pi a}\right)\right)t^{3/2}\right]. \tag{35}$$

Correspondingly, dimensional rate of the phase transformation front is equal to

$$v(t) = v_0\left[1 + 4\sqrt{a/\pi}\,t^{1/2} + \left(1/\left(3\sqrt{\pi a}\right)\right)t^{3/2}\right],\ v_0 = (\sigma \cdot q / L \cdot \rho)\,. \tag{36}$$

One can see from (34), (35) that in the beginning of the transition period, rate of the phase transformation boundary assumes a value v_0 that equals the ratio of product of depth and bulk density of the source power and the product of melting heat and medium density. One can see that the front rate is non-uniform, it increases first in proportion to the square root of time (as far as dimensionless temperature conductivity is $a >> 1$), but then it becomes limited. The latter result enables us to equate expression for rates (15) and (36) in the limit $t << 1$

$$\nu(t) = 12(2D\alpha)^{1/2}\,\Theta(t) = v_0\left[1 + 4\sqrt{a/\pi}\,t^{1/2} + \left(1/\left(3\sqrt{\pi a}\right)\right)t^{3/2}\right] \tag{37}$$

and self-consistently calculate the dimensionless parameter of the medium non-equilibrium

$$\Theta(q,t) = \Theta_0\left[1 + 4\sqrt{a/\pi}\,t^{1/2} + \left(1/\left(3\sqrt{\pi a}\right)\right)t^{3/2}\right],\ \Theta_0(q) = (\sigma \cdot q / L \cdot \rho)/12(2D\alpha)^{1/2}\,. \tag{38}$$

Therefore, there is a solution for system (11)–(14) representing the interconnected system of two fronts of order parameter and temperature propagating in space at a non-uniform rate (with acceleration first and then at a limited rate) that describes the process of non-equilibrium melting phase transition process.

3. DISCUSSION OF RESULTS AND CONCLUSIONS

Studying the binary function of atom distribution in the melting phase transition, one can conclude that for unequivocal description of structural state of the medium the following quantitative structure parameters need to be determined: coordination numbers, equilibrium interatomic distance, root mean displacement of atoms and, finally, distance at which correlations in particle positions disappear (i.e. particle concentration on the coordination sphere equals average atom concentration in the crystal). It is known from the experiment that for the medium in liquid state correlations in particle position disappear completely on the sixth coordination sphere. As for the order parameter η describing "crystal – liquid" transition, we take the value equal to the sum of squared differences of particle concentrations on the coordination sphere and average concentration of atoms in the crystal at temperature *T*, starting from the sixth coordination sphere that needs to be normalized by the same sum at the absolute zero. In that case, at the absolute zero, the order parameter η equals one, and after melting transition it turns to zero.

Analysis of the kinetic model study results allows making a conclusion that the process of melting phase transition stimulated by a volumetric heat source occurs under non-equilibrium conditions of significant local overheating of the volume. It can be accompanied with formation of the locally unstable state of the microcrystal and proceed according to two mechanisms: surface and bulk.

At small heating rates, the melting process is described as a system of two fronts of the order parameter (Fig. 1) and temperature propagating in space at a non-uniform rate (first with acceleration in proportion to root of time, and then at a limited rate). Crystal is in metastable state; it is stable in relation to small fluctuations. If a large critical fluctuation of the new phase emerges on its free side surface, melting starts that propagates to its center in the form of a wave switching from metastable state to stable liquid state. I.e. the "surface" mechanism of the phase transition is implemented. If there is a grain boundary in the crystal, melting starts from the free surface and on the grain boundary practically at the same time. Melting front consists of four atomic layers, and rate of melt front propagation is not constant for the "surface" mechanism (for instance, at volumetric density of the source q = $4.06 \cdot 10^{11}$ J/(cm^3·s) it is 24 m/s), while its value is proportionate to the source intensity, but limited by physical properties of the medium (less than 840 m/s).

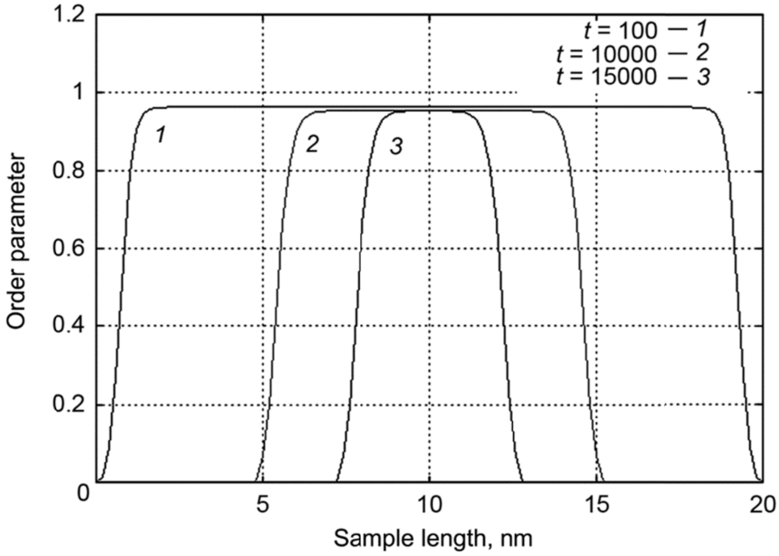

Fig. 1. Dependence of order parameter η(*x*) on a coordinate for various moments of time *t* in the range $0 < t < t_{\text{ft}}$ with interval $(4.4/20000)\cdot 10^{-9}$ s (propagation of the switching wave): curve *1* – $0.005t_{\text{ft}}$, curve *2* – $0.5t_{\text{ft}}$, curve *3* – $0.75t_{\text{ft}}$.

If the system heating proceeds quickly, local areas of the crystal overheating emerge in the sample bulk (up to 200 K), where value of the non-equilibrium parameter becomes equal to the critical value $\Theta_* = 1/2$. At the critical level of non-equilibrium parameter (intensity and depth of the source impact), absolutely unstable areas emerge inside the crystal (crystal becomes locally unstable) in relation to infinitely small new phase fluctuations. As a result, transformation occurs quickly throughout the entire volume, and fronts of the order parameter and temperature emerging on the free surface and volume quickly run and merge. At very high heating rates, transformation in the initial substance occurs quickly throughout the entire volume, and emerging fronts have no time to move by a visible distance in the medium. I.e. another mechanism is implemented – the "bulk" mechanism of the non-equilibrium transformation.

Therefore, research shows that the kinetic model describes the process of non-equilibrium phase transition of melting stimulated by the impact of a volumetric heat source.

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