MATHEMATICAL MODELING OF HEAT AND MASS TRANSFER IN IRREGULAR FREEZING OF ALLOYS

N. I. Nikitenko and Yu. N. Kol'chik

UDC 536.24

A mechanism of formation of structural heterogeneities in crystallization of alloys is considered. A mathematical model of heat and mass transfer in irregular freezing of alloys, a calculation algorithm, and some results of numerical calculations are given.

Establishing the interrelationship between the processes of heat and mass transfer and formation of the alloy crystalline structure is of practical importance since it offers the possibility to purposefully vary the structural properties and quality of material by controling the relevant external conditions of heat and mass transfer.

In order to explain the heterogeneity of the microstructure of materials and the substantial nonuniformity of impurity distribution in the alloy, it is usually assumed [1] that the process of freezing involves two elemental processes: crystal nucleation in the bulk of a melt and growth of the crystals from these nuclei until they collide with other growing crystals. However, numerous experimental data testify that with relatively small supercoolings of the melt we observe very rapid growth of crystals [2]. This allows us to conclude [2] that nuclear growth of crystals does not play a substantial part since the rate of this process is extremely small. The validity of the above conclusion is also confirmed by the following.

Crystal nucleation in the bulk of a supercooled melt and their subsequent growth must inevitably lead to formation of closed areas, restricted by crystal surfaces, which are filled with a liquid metal. Its freezing, by virtue of different densities of metal in the liquid and solid states, must be accompanied by origination of shrink holes, distributed throughout the entire bulk. This is not verified by experimental data. Removal of relatively large phase transition heat from the crystals growing inside the melt is possible with considerable temperature gradients. In the bulk of the melt, however, these gradients are usually small.

The present work deals with the mechanism of formation of structural heterogeneities due to the irregular growth of crystals on the frozen metal surface. A mathematical model of the process of heat and mass transfer in irregular freezing of alloys, a calculation algorithm, and some results of numerical experiments are given.

The irregular, or discontinuous, character of alloy crystallization is caused by the following condition. The process of freezing starts and resumes, given some supercooling of the alloy $\Delta T = T_L - T$, where T is the temperature at the phase boundary and T_L is the equilibrium temperature of phase transition. The process of crystallization discontinues each time, when the melt is superheated, i.e., when the temperature at the phase boundary T will exceed the temperature T_L. According to this, the process of freezing the alloy may be represented in the following manner. At the initial time, as a result of heat removal through the external boundaries of the ingot, a decrease in the alloy temperature occurs. When the temperature at the boundary of the ingot $t_b(\tau)$ attains the value at which $T_L - t_b \geq \Delta T$, crystallization of the alloy starts. At the boundary of freezing there is a jump in the impurity concentration, say carbon, determined by the distribution coefficient $k = C_s/C_L < 1$, where C_s and C_L are the impurity concentrations in the solid and liquid phases of the alloy in the vicinity of the phase boundary. Due to this circumstance, as well as to the smallness of the diffusion coefficient of the impurity in the alloy, the impurity concentration ahead of the freezing front grows with crystallization, which leads to a drop in the temperature T_L.

At the instant when T_L becomes lower than the temperature T at the phase boundary, the period of freezing the alloy stops and the period of cooling starts. It is characterized by the fact that, owing to diffusion, the impurity concentration in front of the phase boundary decreases and correspondingly the temperature T_L elevates. At the moment when the condition $T_L - T \geq \Delta T$ is satisfied, the period of cooling starts. Thus, freezing of the ingot is characterized by alternating the periods of

---

Institute of Technical Thermal Physics, Academy of Sciences of the Ukraine, Kiev. Translated from Inzhenerno-fizicheskii Zhurnal, Vol. 63, No. 6, pp. 752-759, December, 1992. Original article submitted September 24, 1991.

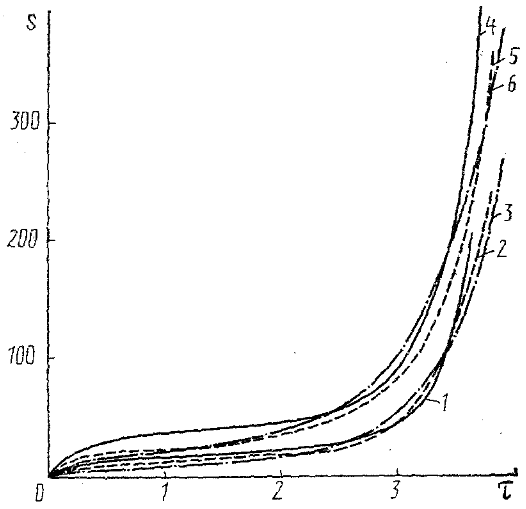

Fig. 1. Number of periods of freezing (cooling) vs time at different values of the diffusion coefficients in the liquid phase D_L and of the limiting supercooling of the melt ΔT: 1) $D_L = 0.5 \times 10^{-6}$, $\Delta T = 0.5$; 2) 0.1×10^{-5} and 0.5; 3) 0.5×10^{-5} and 0.5; 4) 0.5×10^{-6} and 0.25; 5) 0.1×10^{-5} and 0.25; 6) 0.5×10^{-5} and 0.25. s, sec^{-1} ; τ, sec.

cooling and freezing. It is obvious that each period of freezing is related to the origination and formation of new crystals. The thickness of the hard metal layer formed over one period of freezing determines the size of the crystals originating in the process.

We will give a mathematical model and a calculation algorithm for the process of irregular freezing of a sufficiently long cylindrical ingot of the two-component alloy. Let us assume that the influence of convection on the temperature and impurity concentration fields may be neglected. The functions of temperature $t(r, \tau)$ and impurity concentration $C(r, \tau)$ at the interior points of the liquid ($0 < r < z$) and solid ($z < r < R$) phases satisfy the equations of heat conduction and diffusion

$$c\rho \frac{\partial t}{\partial \tau} = \frac{1}{r} \frac{\partial}{\partial r} \left(r\lambda \frac{\partial t}{\partial r} \right), \quad 0 < r < z, \; z < r < R; \tag{1}$$

$$\frac{\partial C}{\partial \tau} = \frac{1}{r} \frac{\partial}{\partial r} \left(rD \frac{\partial C}{\partial r} \right), \quad 0 < r < z, \; z < r < R. \tag{2}$$

For the initial instant $\tau = 0$ we prescribe the temperature $t(0, r)$ and impurity concentration $C(0, r)$ fields and the coordinate of the phase boundary $z(0)$

$$t(0, r) = t_0(r), \quad C(0, r) = C_0(r), \quad z(0) = z_0. \tag{3}$$

If the process of crystallization does not commence at the initial instant, then $z(0) = R$. On the cylinder axis ($r = 0$) we have the symmetry condition

$$\frac{\partial t(0, \tau)}{\partial r} = \frac{\partial C(0, \tau)}{\partial r} = 0. \tag{4}$$

On the outer surface of the cylinder we have conditions of heat transfer of the third kind and of the absence of mass exchange

$$\lambda \frac{\partial t(R, \tau)}{\partial r} = \alpha_c [t(R, \tau) - t_c], \quad \frac{\partial C(R, \tau)}{\partial r} = 0. \tag{5}$$

The conditions of heat and mass transfer at the phase boundary (r = z) are of alternative character due to the alternation of the periods of freezing $\tau_f' < \tau < \tau_f''$ and cooling $\tau_c' < \tau < \tau_c''$ of the alloy. The condition for the onset of freezing at the instant $\tau = \tau_f$ at the boundary z satisfies the inequality

$$T_L - T(\tau_f') \geqslant \Delta T. \tag{6}$$

To determine the temperature at the phase boundary in the period of freezing $\tau_f' < \tau < \tau_f''$ with supercooling of the melt, we consider a thermal state of the elemental metal liquid layer z < r < z + dz in the vicinity of a moving boundary. Let v be the velocity of movement of the phase boundary along the normal, then in the time $d\tau$ = dz/v the element under consideration completely freezes. If the overall heat lost by the elemental layer in the time $d\tau$ is the heat of phase transition, then from the equation of energy balance for this element

$$-\lambda(z) \frac{\partial t(z, \tau)}{\partial r} + \lambda(z + dz) \frac{\partial t(z + dz, \tau)}{\partial r} = c\rho \frac{\partial t(z + dz/2, \tau)}{\partial \tau} - \rho q \frac{dz}{d\tau}$$

it follows that the heat transfer at the phase boundary in the period of freezing is determined by the Stefan condition, and the partial derivative of temperature with respect to time at the phase boundary is $\partial t(z, t)/\partial \tau = 0$. Let us assume that the temperature function at the time τ in the liquid phase in the vicinity of the moving boundary r = z is sufficiently smooth, then $t(z + dr, \tau + d\tau) = T(z, \tau) + dr(\partial t(z, \tau)/\partial r) + d\tau(\partial t(z, \tau)/\partial \tau)$. Since $\partial t(z, \tau)/\partial \tau = 0$, then from the last relation it follows that

$$\frac{dT(z, \tau)}{d\tau} = v \frac{\partial t(z, \tau)}{\partial r}.$$

In accordance with the given calculations the conditions of heat and mass transfer at the boundary r = z in the period of freezing $\tau_f' < \tau < \tau_f''$ may be written in the following way:

$$\lambda(z - 0) \frac{\partial t(z - 0, \tau)}{\partial r} - \lambda(z + 0) \frac{\partial t(z + 0, \tau)}{\partial r} = \rho q \frac{dz}{d\tau}; \tag{7}$$

$$t(z - 0, \tau) = t(z + 0, \tau) = T(z, \tau), \quad \frac{dT(z, \tau)}{d\tau} = \frac{dz}{d\tau} \frac{\partial t(z, \tau)}{\partial r}; \tag{8}$$

$$D(z - 0) \frac{\partial C(z - 0, \tau)}{\partial r} - D(z + 0) \frac{\partial C(z + 0, \tau)}{\partial r} = \frac{dz}{d\tau} [C(z + 0, \tau) - C(z - 0, \tau)]; \tag{9}$$

$$C(z - 0, \tau) = kC(z + 0, \tau), \quad k < 1; \tag{10}$$

$$T_L(z, \tau) = T_A - pC(z - 0, \tau). \tag{11}$$

The mass conservation equation in the vicinity of the phase boundary (9) may be replaced by the equivalent one

$$\int_0^L C(r, \tau) 2\pi r dr - \int_0^L C(r, 0) 2\pi r dr = 0. \tag{12}$$

The last equation can be obtained by integrating (2) with respect to r and τ, taking account of the conditions of heat and mass transfer on the boundary surfaces.

The condition of completion at the instant $\tau = \tau_f''$ of the freezing period is the occurrence of superheating in reference to the phase transition temperature

$$T_L(z, \tau_f'') \leqslant T(z, \tau_f''). \tag{13}$$

In the period of cooling $\tau_c' < \tau < \tau_c''$ at boundary $r = z$ there are the boundary conditions of the fourth kind

$$\lambda(z-0)\frac{\partial t(z-0, \tau)}{\partial r} = \lambda(z+0)\frac{\partial t(z+0, \tau)}{\partial r},$$
$$t(z-0, \tau) = t(z+0, \tau) = T(z, \tau).$$

The temperature $T(z, \tau)$ in this period decreases while the temperature T_L elevates. The condition of completion of the cooling period and onset of the freezing period at the moment $\tau = \tau_c'' = \tau_f'$ is fulfillment of inequality (6).

For the numerical realization of the formulated problem use is made of a combined difference method with explicit identification of phase boundaries [3] and a three-layer explicit difference schema [4,5]. Calculation of the grid functions t_i^n, C_i^n, z^n, approximating the functions $t(r, \tau)$, $C(r, \tau)$, $z(\tau)$ on the difference grid $r_i = ih$, $i = 0, 1, \ldots, I+1$, $h = R/I$; $\tau_n = \tau_{n-1} + l_n$, $n = 0, 1, \ldots, l_n > 0$, $\tau_0 = 0$, is performed in the following order. From the initial conditions (4) we determine

$$t_i^0 = t_0(r_i), \quad C_i^0 = C_0(r_i), \quad z^0 = z_0. \tag{14}$$

The values of t_i^{n+1} and C_i^{n+1} at the interior nodal points of the region, which are removed from the boundary $r = z$ for a distance not smaller than the space layout step h, are found from the three-layer explicit difference equations. For Eq. (1) this schema is written as follows:

$$(1+\Theta_n)\frac{t_i^{n+1}-t_i^n}{l_{n+1}} - \Theta_n\frac{t_i^n - t_i^{n-1}}{l_n} = \frac{1}{2c\rho h^2 r_i} \times$$
$$\times\, [(\lambda_{i+1}r_{i+1} + \lambda_i r_i)(t_{i+1}^n - t_i^n) - (\lambda_i r_i + \lambda_{i-1}r_{i-1})(t_i^n - t_{i-1}^n)]; \tag{15}$$
$$\Theta_n \geqslant 0, \ n = 2, 3, \ldots; \ \Theta_1 = 0;$$
$$i = 1, 2, \ldots, m_n - 2, m_n + 1, m_n + 2, \ldots, I.$$

The stability condition $\Theta_n \geq l_n\lambda(c\rho h^2) - 0.5$, $\Theta_n \geq 0$, and Eqs. (15), just as for the case of implicit schemas, do not practically impose limitations on the grid steps h and l.

At the nodal point $i = 0$ the values of t_i^{n+1} and C_i^{n+1} are determined from a linear difference equation of heat conduction written according to the symmetry conditions (4). For the function t_i^{n+1} it has the form

$$\frac{t_0^{n+1} - t_0^n}{l_{n+1}} = \frac{2}{c\rho\bar{h}^2}(\bar{\lambda} + \lambda_0)(\bar{t}^{n+1} - t_0^{n+1}). \tag{16}$$

Here $\bar{h} = h$, $\bar{t} = t_1$, $\bar{\lambda} = \lambda_1$ for $z > h$ and $\bar{h} = z$, $\bar{t} = T$, $\bar{\lambda} = \lambda(T-0)$ for $z < h$. To determine t_{I+1}^{n+1} and C_{I+1}^{n+1} at the nodal point beyond the contour we employ the difference approximations of the conditions (5)

$$\lambda_I \frac{t_{I+1}^{n+1} - t_{I-1}^{n+1}}{2h} = \alpha_C(t_I^{n+1} - t_C^{n+1}), \quad \frac{C_{I+1}^{n+1} - C_{I-1}^{n+1}}{2h} = 0. \tag{17}$$

In the period of cooling $\tau_c' < \tau < \tau_c''$ the position of the phase boundary remains unchanged, i.e., $z^{n+1} = z^n$. In the period of freezing $\tau_f' < \tau < \tau_f''$ the value of z^{n+1} is determined from the explicit difference equation which approximates (7)

$$\rho q\frac{z^{n+1} - z^n}{l_{n+1}} = \lambda_{z-0}\frac{t_m^n - T^n}{\Delta^n} - \lambda_{z+0}\frac{T^n - t_{m-1}^n}{h - \Delta^n} = Q_z^n. \tag{18}$$

Here Δ^n is the distance from the freezing front z^n to the nearest nodal point $i = m$ in the direction of the axis r, $0 < \Delta^n = r_m - z^n < h$. The temperature T^{n+1} at the phase boundary in the process of phase transition of the alloy from the liquid state to the solid one is found from the difference approximation of the conditions (8):

$$T^{n+1} = T^n + (z^{n+1} - z^n)\frac{t^n_{m-1} - T^n}{h - \Delta^n}. \tag{19}$$

The temperatures t_m^{n+1} and t_{m-1}^{n+1} at the nodal points, adjacent to the moving boundary, are determined from the implicit difference approximations of the heat conduction equation

$$\begin{aligned}\frac{t^{n+1}_m - t^n_m}{l_{n+1}} &= \frac{1}{r_m(h + \Delta^{n+1})c_m\rho_m}\Big[(\lambda_{m+1}r_{m+1} + \lambda_m r_m) \times \\ &\times \frac{t^{n+1}_{m+1} - t^{n+1}_m}{h} - (\lambda_m r_m + \lambda_{z-0}z^{n+1})\frac{t^{n+1}_m - T^{n+1}}{\Delta^{n+1}}\Big];\end{aligned} \tag{20}$$

$$\begin{aligned}\frac{t^{n+1}_{m-1} - t^n_{m-1}}{l_{n+1}} &= \frac{1}{r_{m-1}(2h - \Delta^{n+1})c_{m-1}\rho_{m-1}}\Big[(\lambda_{z-0}z^{n+1} + \lambda_{m-1}r_{m-1}) \times \\ &\times \frac{T^{n+1} - t^{n+1}_{m-1}}{\Delta^{n+1}} - (\lambda_{m-1}r_{m-1} + \lambda_{m-2}r_{m-2})\frac{t^{n+1}_{m-1} - t^{n+1}_{m-2}}{h}\Big].\end{aligned} \tag{21}$$

Equation (21) cannot be employed for the instant τ_{n+1}, when $m_n h - z^{n+1}$ becomes larger than the step h, i.e., the front passes through the nodal point $m_n - 1$. In this case the value of $m_{n+1} = m_n - 1$ and the temperature $t_{m_n-1}^{n+1}$ are determined by interpolation

$$t^{n+1}_{m_{n+1}} = T - \frac{m_{n+1}h - z^{n+1}}{m_n h - z^{n+1}}(T - t^{n+1}_{m_n}). \tag{22}$$

Equations (20) and (21) just as (22) contain one unknown each and can be solved with respect to t_m^{n+1} and t_{m-1}^{n+1}.

Concentrations at the phase boundary C_{z+0}, C_{z-0} and at the adjacent nodal points m_n and $m_n - 1$ are determined by a joint solution of Eq. (11) and the difference approximations of Eq. (12) and the heat conduction equation for the points m_n and $m_n - 1$. Equation (12), in the absence of mass transfer at the outer boundary of the solid, is represented in the form

$$G^{n+1} - G^0 = 0. \tag{23}$$

Here G^n is the approximate expression of the integral $\int_0^L C(r, \tau_n)2\pi r dr$. In view of relation (11) the function G can be determined, for example, by the trapezoid formula in the following manner:

$$\begin{aligned}G^n = \pi h\,(&r_0C^n_0 + 2r_1C^n_1 + 2r_2C^n_2 + \ldots + 2r_{m_n-2}C^n_{m_n-2} + r_{m_n-1}C^n_{m_n-1} + \\ &+ r_{m_n}C^n_{m_n} + 2r_{m_n+1}C^n_{m_n+1} + \ldots + 2r_{I-1}C^n_{I-1} + r_IC^n_I) + \\ &+ \pi\Delta^n(r_{m_n}C^n_{m_n} + z^nkC^n_{z-0}) + \pi(h - \Delta^n)(z^nC^n_{z-0} + r_{m_n+1}C^n_{m_n+1}).\end{aligned} \tag{24}$$

The diffusion equation (2) for the nodal points m_n and $m_n - 1$ is approximated by the implicit difference equations

$$\begin{aligned}\frac{C^{n+1}_{m_n} - C^n_{m_n}}{l_{n+1}} &= \frac{1}{r_m(h + \Delta z^{n+1})}\Big[(D_{m_n+1}r_{m_n+1} + D_{m_n}r_{m_n}) \times \\ &\times \frac{C^{n+1}_{m_n+1} - C^{n+1}_{m_n}}{h} - (D_{m_n}r_{m_n} + D_{z+0}z^{n+1})\frac{C^{n+1}_{m_n} - kC^{n+1}_{z-0}}{\Delta^{n+1}}\Big];\end{aligned} \tag{25}$$

$$\frac{C^{n+1}_{m_n-1} - C^{n}_{m_n-1}}{l_{n+1}} = \frac{1}{r_{m_n-1}(2h + \Delta^{n+1})}\left[(D_{z-0}z^{n+1} + D_{m_n-1}r_{m_n-1}) \times \right.$$

$$\left. \times \frac{C^{n+1}_{z-0} - C^{n+1}_{m_n-1}}{h - \Delta^{n+1}} - (D_{m_n-1}r_{m_n-1} + D_{m_n-2}r_{m_n-2})\frac{C^{n+1}_{m_n-1} - C^{n+1}_{m_n-2}}{h}\right]. \tag{26}$$

When $m_n h - z^{n+1} > h$, $C_{m_n-1}^{n+1}$ is determined from the expression, similar to (22),

$$C^{n+1}_{m_n-1} = C^{n+1}_{m_{n+1}} = kC^{n+1}_{z-0} - \frac{m_{n+1}h - z^{n+1}}{m_n h - z^{n+1}}(kC^{n+1}_{z-0} - C^{n+1}_{m_n}). \tag{27}$$

As a result of joint solution of the system of Eqs. (24)-(26) with $m_{n+1} = m_n$ or (24), (25), and (27) with $m_{n+1} = m_n - 1$ the values of C_{z-0}^{n+1}, $C_{m_n}^{n+1}$, and $C_{m_n-1}^{n+1}$ are determined. The temperature of phase transition T_L^{n+1} is determined, according to (11), from the relation

$$T_L^{n+1} = T_A - pC^{n+1}_{z-0}. \tag{28}$$

In the period of freezing T_L may decrease, while T does not decrease. The moment of transition from freezing to cooling $\tau_f'' = \tau_c'$ lies in the interval $\tau_n < \tau < \tau_{n+1}$ if $T^n < T_L^n$ and $T^{n+1} > T_L^{n+1}$. In the period of cooling the coordinate of the front z remains unchanged. In the period of cooling a reconstruction of the temperature field in the vicinity of the phase boundary occurs due to a variation of the heat-transfer conditions at this boundary. To find the temperature T in the period of cooling, in this connection it is appropriate to take advantage of the heat balance equation for the element $z^n - (h - \Delta^n)/2 < r < z^n + \Delta^n/2$

$$\frac{1}{2}[(C^n_{m_n-1} + C^n_{z-0})(h - \Delta^n) + (C^n_{z+0} + C_{m_n})\Delta^n]\frac{T^{n+1} - T^n}{l_{n+1}}$$

$$= \left(\lambda_{z-0}\frac{t^{n+1}_m - T^{n+1}}{\Delta^n} - \lambda_{z+0}\frac{T^{n+1} - t^{n+1}_{m-1}}{h - \Delta^n}\right). \tag{29}$$

To find the values of C_{z-0}^{n+1} and C_{z+0}^{n+1}, $C_{m_n}^{n+1}$, C_{m_n-1} in the period of cooling we can employ the equations of impurity mass balance for the elements $z^n - (h - \Delta^n)/2 < r < z^n$ and $z^n < r < z^n + \Delta^n/2$

$$\frac{1}{2}(h - \Delta^n)\frac{C^{n+1}_{z-0} - C^n_{z-0}}{l_{n+1}} = D_{z-0}\frac{C^{n+1}_{z-0} - C^{n+1}_{m_n-1}}{h - \Delta^n}; \tag{30}$$

$$\frac{1}{2}\Delta^n\frac{C^{n+1}_{z+0} - C^n_{z+0}}{l_{n+1}} = D_{z+0}\frac{C^{n+1}_{m_n} - C^{n+1}_{z+0}}{\Delta^n} \tag{31}$$

in combination with Eqs. (25), (26). Equations (30) and (31) are written under the assumption that the phase boundary is impermeable for the impurity mass.

If the diffusion in the solid phase can be disregarded, then in this case $C_{z+0}^{n+1} = C_{z+0}^n$, $C_{m_n}^{n+1} = C_{m_n}^n$, and C_{z-0}^{n+1} and $C_{m_n-1}^{n+1}$ may be found from the system of equations (23), (24), and (26).

Figure 1 shows the results of calculation, characterizing a variation in the number of freezing–cooling periods s depending on time at different values of the diffusion coefficient and the limiting supercooling ΔT for a cylindrical steel ingot with $R = 0.2 \times 10^{-2}$ m, $T_0 = 1510°C$, and $C_0 = 0.1\%$. From the figure it is evident that the number of periods s is approximately inversely proportional to the supercooling ΔT.

All the curves $s = s(\tau)$ have three characteristic parts. In the first part there is a rapid growth of s, which is responsible for the presence of a fine-grained structure near the outer surface of the ingot. The second part, in which s varies slowly, corresponds to the zone of large crystals. The third time part, where the rate of variation of the function s and the impurity concentration substantially grow, fits the zone of relatively small crystals. As is well known there are precisely three main zones [1]: the outer fine-grained skin, the zone of columnar crystals, and the zone of equiaxed crystals that characterize the cast ingot structure. A qualitative agreement between the results of numerical modeling and experimental data on the structure of the cast ingot points to the goodness of fit of the mathematical model given.

REFERENCES

1. A. P. Gulyaev, Physical Metallurgy [in Russian], Moscow (1977).
2. V. T. Borisov, Theory of the Two-Phase Zone of a Metal Ingot [in Russian], Moscow (1987).
3. N. I. Nikitenko, Theory of Heat and Mass Transfer [in Russian], Kiev (1983).
4. N. I. Nikitenko and Yu. N. Nikitenko, Promst. Teplotekhn., **3**, No. 6, 7-12 (1983).
5. N. I. Nikitenko, Conjugate and Inverse Problems of Heat and Mass Transfer [in Russian], Kiev (1988).