On thermodynamic approach to the problem of solidification of a diluted binary melt

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An approach to the problem of mass transfer in a solidifying binary melt is considered based on the principle of the least energy dissipation. A simple example has been presented demonstrating the good prospects of that approach to the solidification problems.

Рассмотрен подход к проблеме массопереноса в затвердевающем бинарном расплаве, основанный на принципе наименьшего рассеяния энергии. На простом примере показана перспективность такого подхода к проблемам затвердевания.

It is obvious that the development of any technology of crystal growing from melt depends to a great extent on the successful solution of the mass transfer problems associated with that technology. The problem of substance transfer in a solidifying melt (referred to also as the Stephan problem or the solidification problem) possess a specific place among those problems. It is sufficient to mention that its partial solution as long as five decades before [1] made it possible to substantiate the hypothesis on the concentration overcooling of melt and thus to make a break-through in the development of the melt crystallization methods. It is just investigation results in the field of the solidification problem that would allow anticipate similar break-throughs in the technology of crystal growing from melt. The rather complicated calculation of thermal and concentration fields in problems involving mobile boundary (being the crystallization front) requires non-traditional approaches and stimulates the improvement of known methods and search for new ones [2]. So the differential problem on the impurity diffusion in a solidifying melt can be reduced to a variational one by selecting an appropriate integral functional with an un-

known integration range [3]. That approach to the solidification problem can be considered as an application of the classical calculus of variations [4]. At the same time, analysis of so obtained functional has shown [3] that its value is in proportion to energy being dissipated at the impurity diffusion in the melt that should take the minimum value according to thermodynamics laws. In this connection, it is of interest to state the problem basing ab initio not on the diffusion equation but on the integral thermodynamic principle that is the minimum energy dissipation one. This work is aimed at consideration of that approach to the mass transfer problem in a diluted binary melt under solidification.

The principle of minimum energy dissipation formulated first by Onsager for a special case of heat conduction [5] and referred to as the Onsager principle was developed further and generalized for the whole nonequilibrium thermodynamics by Gyarmati and co-workers. Those works resulted in a book [6] containing the statements forming the base for our approach. To provide an entirety to our considerations, let us start from one of general On-

sager principle formulations and finish by a specific example of its use.

For the transfer of a substance within the volume V of a medium (isotropic and homogeneous), that principle can be presented as

$$\int_V [\mathbf{J}\mathbf{X} - \Psi]_{\mathbf{J}} dV = \max, \qquad (1)$$

$$\delta\mathbf{J} = 0, \quad \delta\mathbf{X} \neq 0, \qquad (2)$$

where $\mathbf{X}$ is thermodynamic force; $\mathbf{J}$, the substance flow across a unit area caused by that force; Ψ, so-called nonequilibrium scattering potential. (Although $\mathbf{J}$ is by definition the flow density, we will refer it to as flow, for short). The variation conditions (2) mean that the functional (1) is varied with respect to forces, the flows being fixed. It is just that presentation of the principle (in terms of forces) that is used to consider the transfer problems.

Let us assume further that the medium is a melt and the substance being transferred consists of impurity particles of one and the same kind having the diffusion coefficient D and concentration C expressed as the mole fraction and depending on coordinates and on time t. The impurity concentration in the melt is assumed to be low, the resulting solution, to be diluted, and the melt density ρ, to be constant over the whole volume. If the diffusion is considered within a relatively small region of the melt (the diffusion zone), the temperature T therein can be assumed to be constant and the diffusion process itself, to be isothermal. In this case, along with the principle presentation in terms of forces, it is expedient to use its energetic expression. Then the flow $\mathbf{J}$ will be conjugated to a corresponding force $\mathbf{X} = -\nabla\mu$ where μ is chemical potential of the diluted solution. The quantity $\mathbf{J}\mathbf{X}$ equal to $T\sigma$ (where σ is entropy formation) will present the energy being dissipated as the impurity diffuses in the melt.

The specific form of the potential Ψ (that is of a specific importance in Onsager theory) depends on the functional relation between $\mathbf{J}$ and $\mathbf{X}$. In linear thermodynamics of irreversible processes being the frame of our studies, the following relations hips are valid:

$$\mathbf{J} = L\mathbf{X} = -L\nabla\mu, \qquad (3)$$

and $\Psi = L\mathbf{X}^2/2 = L(\nabla\mu)^2/2$, where L is the Onsager coefficient.

Substituting the above expressions for $\mathbf{X}$ and Ψ into (1) and changing the sign, we obtain

$$\int_V \left[\mathbf{J}\nabla\mu + \frac{1}{2}L(\nabla\mu)^2\right] dV = \min. \qquad (4)$$

Using the identity known from the vector analysis and the Gauss-Ostrogradsky theorem on divergence, we transform the extreme condition (4) into

$$\int_V \left[\frac{1}{2}L(\nabla\mu)^2 - \mu\nabla\mathbf{J}\right] dV + \int_\Omega \mu\mathbf{J}d\Omega = \min, \qquad (5)$$

where Ω is the surface confining the diffusion zone. Now let the impurity balance equation be used:

$$\rho\dot{C} + \nabla\mathbf{J} = 0 \qquad (6)$$

and present the expression (5) in the form:

$$\int_V \left[\frac{1}{2}L(\nabla\mu)^2 + \rho\mu\dot{C}\right] dV + \int_\Omega \mu\mathbf{J}d\Omega = \min, \qquad (7)$$

where, along with $\mathbf{J}$, the quantity $\dot{C}$ is not varied, according to (6). The diluted solution can be assumed to be ideal, and therefor, the following formula [7] is valid:

$$\mu(C) = \mu(C_a) + RT\ln C/C_a, \qquad (8)$$

where R is gas constant and C_a, a certain characteristic impurity concentration in the melt. For the concentration range near C_a, the expression (8) can be linearized:

$$\mu(C) = \mu(C_a) + \frac{RT}{C_a}(C - C_a). \qquad (9)$$

In this case, the coefficients L and D will be in the following correlation:

$$L = \frac{\rho C_a}{RT}D. \qquad (10)$$

Finally, making use of (3), (7), (9), and (10), we obtain a functional

$$I\{C\} = \int_V \left[\frac{1}{2}D(\nabla C)^2 + \dot{C}C\right] dV - \int_\Omega D(\nabla C)Cd\Omega. \qquad (11)$$

Our extreme problem is reduced to its minimization.

Note that in the first integral of Eq.(11), the quantity ∇C is varied while it is not in the second one. In this situation, it is im-

possible to restrict ourselves by the definitions of the variation conditions adopted in [6] as in the case, e.g., of the functional (7) where those conditions have the form $\delta \dot{C}$, $\delta \mathbf{J} = 0$, $\delta\mu \neq 0$. From here on, the quantities remaining fixed under variations will be indicated by an upper bracket.

In connection with the above situation, the local potential method [8] developed by Glensdorf and Prigogine should be mentioned. The method is based just on the dependence of a functional on two variables that are different only in that one of those is varied and the other in not. Since the division of quantities into variable and invariable is postulated in the minimum energy dissipation principle itself, it is not surprising that the Onsager theory shows certain common features with the Glensdorf and Prigogine one. The relationship between those two theories requires a special consideration and is beyond the frame of this work.

So far, nothing was said on the melt crystallization itself. To apply the functional (11) to the solidification problem, the boundary Ω is to be mobile. Under account for the fact that the approach to that problem based on the Onsager theory is considered here for the first time, the use of a specific example will be the best way. The example should be well studied to provide comparison of the result that will be drawn with those obtained using other methods.

Let us restrict ourselves by a simple planar case where the melt is crystallized at a constant speed w along the z axis; the diffusion zone is the melt layer confined by two planes $z = wt$ and $z = h + wt$; the crystallization front (CF) coinsides with the first one and its position on the z axis is set by function $\varphi(t) = wt$; $D = $ const; the impurity concentration in the $z = h + wt$ is maintained constant: $C(h + wt) = C_0$. Another boundary condition follows from the impurity balance condition at the CF:

$$DC_z(\varphi) = -(1 - k)wC(\varphi). \qquad (12)$$

In those conditions, the functional of our extreme problem takes the form

$$I\{C(z,t)\} = \int_{\varphi=wt}^{h+wt} \left(\frac{1}{2}DC_z^2 + \hat{C}_tC\right)dz + D[\hat{C}_zC]_{z=\varphi}. \qquad (13)$$

Here we use the indices for partial derivatives with respect to z and t, upper bracket to denote the invariable quantities and take into account that $[\delta C]_{z=h+wt} = 0$. It is

known [9] that the case is reduced to stationary problem by changing $z \to z - wt$. After that change and taking into account Eq.(12), we obtain

$$I\{C(z)\} = \qquad (14)$$

$$= \int_0^h \left(\frac{1}{2}DC_z^2 - w\hat{C}_zC\}\right)dz - (1 - k)w[\hat{C}C]_{z=0}.$$

Let us pass to dimensionless variables using the changes:

$$z \to \frac{D}{w}z, \quad C \to C_0C, \quad I \to wC_0^2I. \qquad (15)$$

Then the functional (14) and boundary conditions for $C(z)$ take the form:

$$I\{C(z)\} = \int_0^h (\frac{1}{2}C_z^2 - \hat{C}_zC)dz - (1 - k)[\hat{C}C]_{z=0}. \qquad (16)$$

$$C_z(0) + (1 - k)C(0) = 0, \qquad (17)$$

$$C(h) = 1. \qquad (18)$$

Thus, the problem of impurity distribution within the diffusion zone adjacent to the crystallization front is reduced to minimization of functional (16) from the function $C(z)$ meeting the boundary conditions (17) and (18) at two additional conditions: (i) quantities Ct_z and C remain fixed during the minimization procedure, and (ii) after that procedure is finished, the equalities $C_z = C_z$ and $C = C$ come into effect.

The problem formulated was solved in two ways. In the first one, the variation problem was reduced to the Euler differential equation and the exact problem solution was obtained by solving the equation. Then, using the calculus of variations direct method, approximated solution was obtained and compared to the exact one.

By varying the functional (16) taking into account the first additional condition, we obtain

$$\delta I = -\int_0^h (C_{zz} + \hat{C}_z)\delta Cdz - \qquad (19)$$

$$- \left[C_z(0) + (1 - k)\hat{C}(0)\right][\delta C]_{z=0}.$$

By virtue of the necessary extreme condition as well as due to arbitrarity of δC variation, both items in (20) should be zero. Thus, taking into account the second additional condition, we obtain

Table. Dependence of impurity concentration C on the distance z to the crystallization front as calculated under two approximations and using the exact formula. $I\{C\}$ is the corresponding functional value.

Z	0.0	0.2	0.4	0.6	0.8	1.0	$I\{C\}$
$C_{I\ approx}$	1.4615	1.3262	1.2123	1.1200	1.0492	1.0000	-0.38141
$C_{II\ approx}$	1.4622	1.3293	1.2205	1.1320	1.0598	1.0000	-0.38434
C_{exact}	1.4622	1.3296	1.2211	1.1323	1.0595	1.0000	-0.38447

$$C_{zz} + C_z = 0 . \qquad (20)$$

It can be noted that, although the factor at $[\delta C]_{z=0}$ in (19) does not provide any additional information (its zeroing results in the condition (17)), the out-of-integral item in (16) that forms the factor is a necessary additive to the integral; without it, the variation and differential problems would be non-equivalent to one another. Solving the Eq.(20) under account for (17) and (18), we obtain the exact solution of our problem [9]:

$$C_{exact} = \frac{k + (1 - k)e^{(-z)}}{k + (1 - k)e^{(-h)}} . \qquad (21)$$

It is to note that the book [6] does not contain any practical instructions on the use of numerical methods in the problems formulated basing on the principle of minimum energy dissipation, although it mentions that such methods could be used and this possibility is among the advantages of the calculus of variations. Perhaps the author [6] took for unnecessary to describe the use of the Ritz method in problems of that kind due to its simplicity. That simplicity is seen clearly from the calculation described lower.

The calculations were done for the case when $h = 1$ and $k = 0.5$. The solution in the N-th approximation was presented as a series [10]:

$$C_N = \sum_{n=0}^{N+1} \alpha_n z^n , \qquad (22)$$

where α are coefficients determined from the boundary conditions and the functional stationarity condition (16) taking into account the above-mentioned additional conditions. According to the first of the latter, a series

$$\hat{C}_N = \sum_{n=0}^{N+1} \hat{\alpha}_n z^n , \qquad (23)$$

was substituted into (16) along with (22). According to the second condition, in expressions obtained after calculation of partial derivatives of (16) with respect to independent parameters α, the coefficients $\hat{\alpha}$ were changed by α according to the equalities $\hat{\alpha}_{n} = \alpha_{n.}$ Then the coefficients α were determined using the usual scheme. The calculation results are given in the Table. The sequence of approximate solutions is seen to tend to the exact one. As it should be expected in the case of minimum, the functional values in the approximate solutions exceed its value for extreme. Thus, this work formulates for the first time the problem of impurity distribution in solidifying melt using the principle of minimum energy dissipation. The problem has been solved using variation methods, including a numerical one. The solution obtained coincides with that of the solution formulated in differential form. In this connection, to apply the minimum energy dissipation principle to the solidification problems seems to be very promising.

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Про термодинамічний підхід до проблеми твердіння розбавленого бінарного розплаву

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Розглянуто підхід до проблеми масопереносу у бінарному розплаві при його твердінні, оснований на принципі найменшого розсіяння енергії. На простому прикладі показано перспективність такого підходу до проблем твердіння.