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STATIONARY PROBLEM OF CONTACT MELTING IN THE PRESENCE OF EXTERNAL FORCES

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The solution of the one-dimensional diffusion equation in the stationary problem of contact melting in the presence of external forces has been proposed. As the external forces the influence of a nonuniform magnetic field and the influence of electrotransfer have been considered. Expressions for the concentration distribution of the components in a liquid interlayer and for the partial rates of contact melting have been obtained.

Contact melting can occur in the nonstationary diffusion mode [1–3], where the thickness of a liquid interlayer increases in proportion to the square root of the time of the process. In the stationary mode [4, 5], the liquid-interlayer thickness remains constant owing to the pressure applied to the ends of samples while the newly formed portions of the liquid are removed from the contact zone. When the thickness of the liquid interlayer attains the size of about tenths of a micrometer, the process of transition of the atoms from the solid phase to a liquid one can have an effect on the liquid phase–solid phase boundaries; then contact melting can occur in kinetic or mixed modes [6, 7].

It is of interest to consider the process of contact melting in the stationary mode in the field of external forces without taking into account the hydrodynamic flow of a liquid. The electric current flowing through the liquid interlayer and a nonuniform magnetic field can be used as the external forces. The actions of these forces will lead to an additional flow of a substance (material flow) along with the diffusion flow. Under these conditions, the one-dimensional problem of diffusion is reduced to solution of the equation

$$\tilde{D}\frac{d^2C}{dx^2} \mp v\frac{dC}{dx} = 0 \tag{1}$$

with the boundary conditions

$$C(x)\big|_{x=0} = C_2\,, \quad C(x)\big|_{x=\delta} = C_3\,. \tag{2}$$

The solution of (1) with account for (2) will be sought in the form

$$C^{\pm}(x) = A_{\pm} + B_{\pm}\exp\left(\mp\frac{vx}{\tilde{D}}\right), \tag{3}$$

where $A_{\pm}$ and $B_{\pm}$ are the constants to be determined.

Satisfying boundary conditions (2), from expression (3) we find

$$A_{\pm} = \frac{-C_3 + C_2\exp\left(\mp\frac{v\delta}{\tilde{D}}\right)}{\exp\left(\mp\frac{v\delta}{\tilde{D}}\right) - 1}\,, \quad B_{\pm} = \frac{C_3 - C_2}{\exp\left(\mp\frac{v\delta}{\tilde{D}}\right) - 1}\,. \tag{4}$$

Having substituted (4) into (3), we obtain the final expression for the concentration distribution in the liquid interlayer for two opposing directions of the external force:

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$$C^{\pm}(x) = \frac{-C_3 + C_2 \exp\left(\mp \dfrac{v\delta}{\tilde{D}}\right)}{\exp\left(\mp \dfrac{v\delta}{\tilde{D}}\right) - 1} + \frac{(C_3 - C_2)\exp\left(\mp \dfrac{vx}{\tilde{D}}\right)}{\exp\left(\mp \dfrac{v\delta}{\tilde{D}}\right) - 1} . \tag{5}$$

Expression (5) can be written in the following more convenient form:

$$C^{\pm}(x) = C_2 + \frac{(C_3 - C_2)\left[\exp\left(\mp \dfrac{vx}{\tilde{D}}\right) - 1\right]}{\exp\left(\mp \dfrac{v\delta}{\tilde{D}}\right) - 1} . \tag{6}$$

Expanding the exponents into a series and restricting ourselves to the first three terms of the expansion, we obtain

$$C^{\pm}(x) = C_2 + \frac{(C_3 - C_2)\, 2\tilde{D}}{\delta\,(2\tilde{D} \mp v\delta)}\, x \mp \frac{(C_3 - C_2)\, v}{\delta\,(2\tilde{D} \mp v\delta)}\, x^2 . \tag{7}$$

For small deviations of the contact-melting temperature from the eutectic temperature and when the exponents are less than unity in modulus (in what follows it will be shown that this condition is fulfilled rather well), the error of such an expansion does not exceed a fraction of a percent.

Expression (7) is the equation of a parabola which passes through the points (0, C_2) and (δ, C_3); the sign of curvature (convexity or concavity) is determined by the direction of the external force.

When $v \to 0$, which is equivalent to the absence of the external force, expression (5) becomes an indeterminancy of the form $\frac{0}{0}$; evaluating it according to l'Hospital's rule, we obtain

$$C(x) = C_2 + \frac{C_3 - C_2}{\delta}\, x , \tag{8}$$

which coincides with the analogous result of [4]. Precisely the same result is obtained from expression (7).

Disregarding flows into the solid phases 1 and 2, we can determine the partial rates of contact melting V_1 and V_2 from the condition of balance of the substance at the phase boundaries:

$$V_1\,(C_2 - C_0) = \frac{N_3}{N_1}\left(\tilde{D}\,\frac{dC}{dx}\right)_{x=0} , \tag{9}$$

$$V_2\,(C_5 - C_3) = \frac{N_3}{N_2}\left(\tilde{D}\,\frac{dC}{dx}\right)_{x=\delta} . \tag{10}$$

If the contact melting is carried out between solid solutions which are prepared in advance and are equilibrium at a given temperature, the concentrations C_0 and C_5 in formulas (9) and (10) take on the values of C_1 and C_4 corresponding to the equilibrium state diagram (C_i, i = 0, 1, 2, 3, 4, and 5 are the concentrations of the second component).

In the presence of the external force, the expressions for the flows at the boundaries of the phases (x = 0) and (x = δ) have the following form:

$$\left(\tilde{D}\,\frac{dC}{dx}\right)_{x=0} = \left[-\tilde{D}\,\frac{dC^{\mp}}{dx} \pm vC^{\mp}\right]_{x=0} ; \tag{11}$$

$$\left(\tilde{D}\,\frac{dC}{dx}\right)_{x=\delta} = \left[-\tilde{D}\,\frac{dC^{\mp}}{dx} \pm vC^{\mp}\right]_{x=\delta} . \tag{12}$$

Substituting (11) and (12) into (9) and (10) with account for (5), we obtain

$$V_1^{\mp} = \pm\,\frac{N_3 v\left[C_3 - C_2\exp\left(\pm\,\dfrac{v\delta}{\tilde{D}}\right)\right]}{N_1\,(C_2 - C_0)\left[1 - \exp\left(\pm\,\dfrac{v\delta}{\tilde{D}}\right)\right]} , \tag{13}$$

$$V_2^{\mp} = \pm\,\frac{N_3 v\left[C_3 - C_2\exp\left(\pm\,\dfrac{v\delta}{\tilde{D}}\right)\right]}{N_1\,(C_5 - C_3)\left[1 - \exp\left(\pm\,\dfrac{v\delta}{\tilde{D}}\right)\right]} . \tag{14}$$

When $v \to 0$ expressions (13) and (14) become indeterminancies of the form $\frac{0}{0}$; evaluating them according to l'Hospital's rule, we obtain

$$V_1^{\mp} = V_1^0 = \frac{N_3\,(C_3 - C_2)\,\tilde{D}}{N_1\,(C_2 - C_0)\,\delta} , \quad V_2^{\mp} = V_2^0 = \frac{N_3\,(C_3 - C_2)\,\tilde{D}}{N_2\,(C_5 - C_3)\,\delta} .$$

The ratio of the partial rates of contact melting is a proportion in which the initial solid phases become a melt as a result of the contact melting. It is of importance in many processes which are based on the phenomenon of contact melting. As follows from (13) and (14), this ratio remains constant

$$\frac{V_1^-}{V_2^-} = \frac{V_1^+}{V_2^+} = \frac{V_1^0}{V_2^0} = \frac{N_2\,(C_5 - C_3)}{N_1\,(C_2 - C_0)} = \text{const}$$

and does not depend on the magnitude of the external force, although the rates $V_1^{\mp}$ and $V_2^{\mp}$ themselves depend on the magnitude of the external force that is directly related to v.

Let us find the total rates of contact melting for different directions of the external force. As is seen from (13) and (14) ($V^- = V_1^- + V_2^-$ is the accelerating direction and $V^+ = V_1^+ + V_2^+$ is the decelerating direction):

$$V^{\mp} = V_1^{\mp} + V_2^{\mp} = \pm\left[\frac{N_3}{N_1\,(C_2 - C_0)} + \frac{N_3}{N_2\,(C_5 - C_3)}\right]\frac{\left[C_3 - C_2\exp\left(\pm\,\dfrac{v\delta}{\tilde{D}}\right)\right]v}{\left[1 - \exp\left(\pm\,\dfrac{v\delta}{\tilde{D}}\right)\right]} . \tag{15}$$

It is easy to show that the differences are

$$V^- - V^+ = \left[\frac{N_3}{N_1\,(C_2 - C_0)} + \frac{N_3}{N_2\,(C_5 - C_3)}\right](C_3 + C_2)\,v > 0 , \tag{16}$$

$$V_1^- - V_1^+ = \frac{N_3\,(C_3 + C_2)\,v}{N_1\,(C_2 - C_0)} > 0 , \tag{17}$$

$$V_2^- - V_2^+ = \frac{N_3\,(C_3 + C_2)\,v}{N_1\,(C_5 - C_3)} > 0\,. \tag{18}$$

It is seen that if the external force, by acting on the diffusing particles, causes an additional flow of a substance, both the total rate and the partial rate of contact melting are higher in the case where these flows coincide in direction than in the case where these flows are opposing. As follows from (16)–(18), this difference grows linearly with increase in v. It follows that, having measured this difference from the experiments conducted for different directions of the external force, one can determine the structural characteristics of liquid solutions.

The analysis of formulas (13)–(15) makes it possible to draw the following important conclusion. Since for the decelerating direction of the external force (or v) both the partial rates V_1^+ and V_2^+ and the total rate V^+ of contact melting must decrease with increase in v, for certain values of the external force and of the liquid-interlayer thickness these rates will become equal to zero. From the physical considerations it follows that this state can set in when the diffusion flow I_D becomes equal to the flow occurring owing to the external force I_v. Further increase in v in modulus can cause the rates V_1^+ and V_2^+ to change their directions. From this point on the process of crystallization begins under the action of the external force. The value of the external force (or v_0) for which such a transition occurs can roughly be evaluated from formulas (13) and (14):

$$|v_0| = \frac{\tilde{D}}{\delta}\ln\frac{C_3}{C_2} \approx \frac{\tilde{D}\,(C_3 - C_2)}{\delta C_2}\,. \tag{19}$$

All the conclusions drawn above from expressions (15)–(18) which have been obtained for the stationary mode of contact melting hold true for the nonstationary diffusion mode as well, since, as is shown in [2], the rate of contact melting in the stationary mode for a certain thickness of the liquid interlayer is equal to the instantaneous rate of contact melting in the nonstationary diffusion mode for the same thickness of the liquid interlayer.

Let us elucidate now the physical meaning of the quantity v, i.e., the rate of transfer of a substance under the action of the external force.

As is well known, the driving force causing the diffusive transfer of the substance of the ith component is the gradient of chemical potential of this component and not the gradient of concentration, as follows from the first equation of Fick.

Under the action of the force $F_i = -\partial\mu/\partial x$, the atoms acquire the ordered motion with the velocity $v_i = u_i F_i$, causing the additional flow of the ith component equal to $I_i = -C_i u_i F_i$. For ideal solutions, $\mu_i = \mu_i^0 + kT \ln C_i$. Consequently:

$$I_i = -\,C_i u_i kT\,\frac{\partial \ln C_i}{\partial x} = -\,u_i kT\,\frac{\partial C_i}{\partial x}\,. \tag{20}$$

From the comparison of (20) to the first equation of Fick, we obtain the expression

$$D_i^* = u_i kT \quad \text{or} \quad v_i = \frac{D_i^*}{kT}\,F_i\,, \tag{21}$$

which is known as the Einstein–Smoluchowski relation.

Formula (21) holds for isotopic diffusion and for diffusion in infinitely diluted solutions. In the case of real solutions where each atom is surrounded by a varying number of neighbors of different sort, one must introduce the activity a_i instead of the concentration into the expression for the chemical potential (20). Then we will have

$$\mu_i = \mu_i^0 + kT \ln a_i\,, \tag{22}$$

where $a_i = \gamma_i C_i$.

Acting in the same manner as above, for D_i and the transfer rate v_i we obtain the following expressions:

$$D_i = u_i kT \frac{\partial \ln a_i}{\partial \ln C_i} = D_i^* \frac{\partial \ln a_i}{\partial \ln C_i}, \quad v_i = \frac{D_i}{kT} F_i \frac{\partial \ln C_i}{\partial \ln a_i}. \tag{23}$$

If the solutions are similar to ideal ones in properties, then

$$v_i \approx \frac{D_i}{kT} F_i . \tag{24}$$

Let us first determine the average force F_i that acts on diffusing particles in the process of mass transfer in contact melting and is caused by the gradient of chemical potential. To evaluate this force according to formula (24) we must know the magnitude of the rate v_i. The latter could be taken to be equal to the rate of contact melting. However the rate of contact melting can vary within wide limits as a function of the temperature of the experiment, the state diagram, and the time of the process and is of little use for this purpose. In our opinion, the drift velocity of the atoms in the process of diffusion is similar to the velocity of displacement of the liquid owing to the inequality of the partial coefficients of diffusion. The magnitude of this velocity has been determined experimentally in contact melting for a number of low-melting metallic systems in [8–10] according to the well-tested procedure. The numerical value of this velocity depends slightly on the temperature and the time and is found in the interval (0.1–0.4) mm/h. Having taken the average value of $v_i \approx 0.25 \text{ mm/h} \approx 0.7 \cdot 10^{-7}$ m/sec (for $D_i \approx 10^{-9}$ m^2/sec, T = 500 K, and k = 1.38·10^{-23} J/K), from (24) we find $F_i \approx 5 \cdot 10^{-19}$ N.

Let us now evaluate F_i and v_i in the case of action of a nonuniform magnetic field on the processes of diffusion in contact melting.

In the presence of the nonuniform magnetic field, the magnitude of the external force acting on diffusing particles is equal to

$$F_i = \lambda_i \frac{dB}{dx} = \frac{\chi_i H dB}{N_{\text{À}} dx} . \tag{25}$$

Since the atoms of paramagnetic substances have nonzero magnetic moments in the nonuniform magnetic field, they acquire the additional velocity of drift in the direction of the gradient of the field. The atoms of a diamagnetic, conversely, do not have magnetic moments; however, being introduced into the magnetic field, they drift in the direction opposite to the gradient of the field. Consequently, the force F_i and the rate v_i of ordered transfer of the components are related to the magnetic properties of the diffusing particles.

Let us now evaluate the magnitude of a possible effect of transfer and the conditions under which it can occur. Since $\lambda_{\text{ef}} \approx 10^{-23}$ A·m^2, by using special pole pieces we can obtain the value of $dB/dx \approx 70$ T/m with an FL-1 laboratory electromagnet. Then from (25) we will have $F_i \approx 0.7 \cdot 10^{-21}$ N (for the sake of comparison we indicate that the value of this force is two orders of magnitude lower than the force of electrotransfer). The experiments on electrotransfer have shown that the effect of transfer can be recorded well in a time of the experiment of about 10–20 h if the drift velocity is no lower than 1·10^{-11} m/sec.

In the case of diffusion in the liquid contact interlayer in the nonuniform magnetic field, the value of this velocity is ≈0.7·10^{-10} m/sec if we take $D_i \approx 1 \cdot 10^{-9}$ m^2/sec, T = 500 K, and $F_i \approx 0.7 \cdot 10^{-21}$ N.

Thus, the effect of transfer becomes quite recordable in the experiment with a duration of 10–20 h. To study the transfer in the nonuniform magnetic field in contact melting one should select substances with large diffusion coefficient and effective magnetic moment and conduct experiments in strongly nonuniform magnetic fields. Knowledge of the effective magnetic moment of the diffusing particles of an impurity would provide valuable data on the structural state of liquid solutions.

We consider the version of contact melting between paramagnetic A and diamagnetic B with the gradient of the magnetic field along the diffusion zone. When the gradient of the field is directed from A to B the diffusion flows and the flows of the components due to the nonuniform magnetic field coincide, while in the case of the opposite direction of the gradient of the field these flows are opposing for both components. Consequently, the transfer rate in the first case must be higher than in the second case, which is in agreement with the conclusions drawn from formulas (16)–(18).

In the case of electrotransfer in liquid solutions the diffusing ions are acted upon by the force [11]

$$F_i = e_0 Z_i^* E \, . \tag{26}$$

In the approximation of free electrons, as is shown in [12],

$$Z_i^* = Z_i - nl\sigma_i \, . \tag{27}$$

The magnitude of the effective charge for the liquid solutions can be both more or less than zero, while the numerical values can change from unity to tens.

The direction of the resultant force acting on the ion is determined by the sign of the left-hand side of expression (27). If this difference is more than zero, the resultant force is directed to the cathode; if it is less than zero, the resultant force is directed to the anode. Thus, the motion of the positively charged ions of a metal to the anode becomes possible as a result of the entrainment of the ions by conduction electrons. To roughly evaluate the quantities F_i and v_i in contact melting with electrotransfer we take: $|Z_i^*| = 10$, $e_0 = 1.6 \cdot 10^{-19}$ C, $\tilde{D} = 10^{-9}$ m^2/sec, $k = 1.4 \cdot 10^{-23}$ J/K, $T = 500$ K, $j = 5 \cdot 10^5$ A/m^2, and $\gamma = 1.6 \cdot 10^{-7}$ $\Omega^{-1} \cdot \text{m}^{-1}$. Then we obtain $F_i \approx 5 \cdot 10^{-20}$ N and $v_i \approx 0.7 \cdot 10^{-8}$ m/sec.

Thus, the effect of transfer in this case can be substantially higher than in the presence of a nonuniform magnetic field.

In the case of contact melting where the diffusion flows I_D and the flows of the components due to electrotransfer I_e coincide in direction and where these flows are opposing, we have the following: if the effective charges $e_0 Z_A^* > 0$ and $e_0 Z_B^* < 0$, then in passage of the electric current from A to B the flows I_D and I_e coincide for each component and when the direction of the current is reverse these flows are opposing for both components.

Thus, in the case of contact melting with electrotransfer the conclusions drawn from formulas (16)–(18) hold true.

In summary, we note that experimentally it is much more difficult to carry out the experiments on contact melting in the stationary mode than in the nonstationary mode. This is associated with the creation of special conditions of removal of the newly formed portions of a liquid from the contact zone. However, as has been indicated above, to check the qualitative conclusions one can successfully use the instantaneous values of the kinematic characteristics of contact melting in the nonstationary mode. Taking this into account, we can state that the conclusions drawn from formulas (16)–(18) are in agreement with the experimental results obtained in [13–16] for the nonstationary process of contact melting with electrotransfer and for contact melting in a nonuniform magnetic field.

NOTATION

$\tilde{D}$, coefficient of interdiffusion; C, concentration; C_2 and C_3, liquidus concentrations; C_0 and C_5, concentrations at a distance from the interphase boundary; δ, thickness of the liquid interlayer; v, average rate of ordered transfer of the substance under the action of the external force; V_1 and V_2, partial rates of contact melting of the solid phases 1 and 2 respectively; N_1, N_2, and N_3, numbers of particles in unit volume of the solid phases 1 and 2 and of the liquid phase 3 respectively; V_1^0 and V_2^0, partial rates of contact melting in the absence of the external force; I_D, diffusion flow; I_v, flow occurring due to the external force; I_e, flow of electrotransfer; u_i, mobility of a diffusing particle; μ_i, a_i, and γ_i, chemical potential, activity, and activity coefficient of the ith component respectively; D_i and D_i^*, partial coefficient of diffusion and self-diffusion coefficient of the ith component respectively; F, external force; B and H, induction and strength of the magnetic field; λ_i and χ_i, effective magnetic moment and magnetic susceptibility of the ith component respectively; N_A, Avogadro number; e_0, absolute value of the electron charge; $e_0 Z_i$ and $e_0 Z_i^*$, self-charge and effective charge of a diffusing ion; n, concentration of free electrons; l, mean free path of the electrons; σ_i, cross sections of the scattering of electrons by a given ion; E, electric field strength; signs (+) and (–) correspond to the opposing directions of the external force.

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