CONCENTRATION DISTRIBUTION IN CONTACT MELTING
IN THE FIELD OF A TEMPERATURE GRADIENT

P. F. Zil'berman, P. A. Savintsev,
and R. M. Gazaryan

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Mutual diffusion in the contact melting of ionic crystals in a temperature
gradient field is analyzed.

Technological processes associated with mutual diffusion of ions in contact melting may often occur in an inhomogeneous temperature field. It is important here to know what influence the operating factor has on the ion distribution in the diffusion zone. It is known that the electrical fields lead to pronounced change in the kinetics of contact melting in ionic crystals [1-3] and, taking account that electrical, thermal, and mass transfer are closely interconnected in this process, changes may also be expected when a temperature-gradient field is imposed.

To solve this problem, contact melting in nonsteady diffusion conditions [4, 5] when a temperature gradient is applied in the experimental region is analyzed and the numerical results obtained are compared with the experimental results for the given system. If convection in the melt is neglected, which holds for the conditions under analysis, the temperature and concentration distributions in the given zone may be described by differential equations on the basis of the mass and energy conservation laws [6]

$$\frac{\partial T}{\partial t} = \operatorname{div}(\lambda \operatorname{grad} T + D'' \operatorname{grad} c), \tag{1}$$

$$\frac{\partial c}{\partial t} = \operatorname{div}(D' \operatorname{grad} T + D \operatorname{grad} c). \tag{2}$$

Using the fusibility diagram of the system here, as in [7], the boundary and initial conditions may be written in the form

$$D \frac{\partial c'}{\partial x} = c(z_{i-1,1}, t)v; \quad D \frac{\partial c}{\partial x} = c(z_{i,2}, t)v; \tag{3}$$

$$T(z_{i-1,1}, t) = T_1(t); \quad T(z_{i,2}, t) = T_2(t); \tag{4}$$

$$c(x, 0) = ac_0(x); \quad T(x, 0) = bT_0(x), \tag{5}$$

where $z_{i-1} \leq x \leq z_i$; $c(z_{i-1,1}, t)$ and $c(z_{i,2}, t)$ are determined from the fusibility diagram of the system; $z_{i-1,1} = K_{i-1,1}\sqrt{t}$, $z_{i,2} = K_{i,2}\sqrt{t}$ are the coordinates of the left-hand and right-hand interphase boundaries; $v = dz/dt$, $i = 1, \ldots, n$.

Equations (1) and (2) and the conditions in Eqs. (3)-(5) give the formulation of the problem for each position of the boundary determined by the index i. Calculation of the concentration distribution entails simultaneous solution of Eqs. (1) and (2). First, the temperature distribution is determined from Eq. (1); the term D'' grad c may be neglected here, in view of the smallness of D'', and, substituting the resulting temperature field into Eq. (2), the desired concentration distribution is determined for a definite temperature gradient in the melt and time of the experiment. Since nonsteady diffusional conditions are characterized by a parabolic law of liquid-phase growth [4], the temperature gradient acting on the melt at a given time will change. The change in temperature gradient, in turn, will change the limiting concentrations and hence also the concentration profile in the liquid

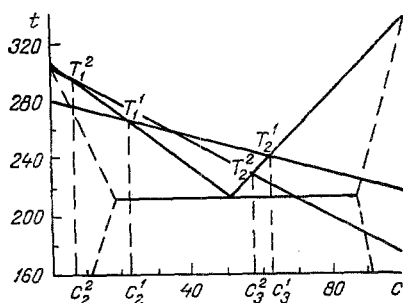Fig. 1   Fig. 2

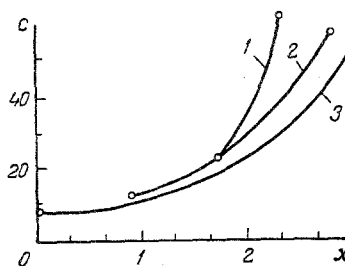Fig. 1. Fusibility diagram of the system $KNO_3 - NaNO_3$ on which a temperature gradient is imposed; c, mol.% KNO_3; t, °C.

Fig. 2. Concentration distribution of ions in the contact zone: 1) time of experiment t = 600 sec; 2) 1800; 3) 3000; x, mm.

diffusion zone. Therefore, finding the concentration distribution of the elements in the diffusion zone at each moment of the time entails knowing the relation between the temperature and the concentration of the elements at the phase boundaries. Since equilibrium is established at the crystal—melt phase boundaries at each moment of time, the limiting concentrations of elements there may be determined using the state diagram of the system. Thus, in Fig. 1 it is shown that the temperatures T_1^1 and T_2^1 correspond to the concentrations c_2^1 and c_3^1 and the temperatures T_1^2 and T_2^2 to the limiting concentrations c_2^2 and c_3^2. Analogous constructions may be performed for other temperature gradients. This problem may be solved by numerical methods. These methods were used earlier in analyzing the concentration distribution in the contact melting of ionic crystals [7, 8]. The initial equations are approximated by a balance method at the points of a shifted grid [9]. As a result of all the successive transformations, a finite-difference analog of the problem to be solved is obtained. The resulting difference scheme is realized by the fitting method; the concentration dependence of the elements in the contact zone for the give time step is obtained here. Higher accuracy in the calculations is obtained using the iterative method. Each time step is accompanied by movement of the boundary points over the spatial grid; the new position of the boundary then establishes new boundary conditions calculated from the fusibility diagram. Then the temperature field is again calculated from the heat-conduction equation and the concentration profile from the thermodiffusion equation. The calculation continues until one of the boundaries reaches the end of the sample. Programs are written in FORTRAN, and calculations are performed on an EC 10-35 computer. A sample (length 0.001 m) of the system $KNO_3 - NaNO_3$ with an initial gradient over the solid phase of 100 deg/cm is chosen for analysis. When liquid phase appears, temperatures $T_1 = 543°K$ and $T_2 = 513°K$ and concentrations $c_2 = 24$ mol.% and $c_3 = 62.2$ mol.% are established at the phase boundaries. Since the mutual diffusion coefficient in the melt is of the order of $D = 10^{-5}$ cm^2/sec, and the Soret coefficient $s_T = D'/D = 10^{-3}-10^{-5}$ deg^{-1}, the thermodiffusion coefficient of the ions is in the range $D' = 10^{-8}-10^{-10}$ cm^2/sec·deg. It is evident from Fig. 2 that the concentration distribution of the ions in the contact zone is complex in character. The profile is distinguished by clear nonlinearity and depends on the time of the experiment to a considerable extent. This distribution is evidently explained by the change in velocity of the phase boundaries and hence in concentration at the phase boundaries and near them. The reduction in temperature at one boundary of the sample is accompanied in the given case by a decrease in the velocity of this boundary and the concentration there, and the temperature increase at the other boundary by increase in the velocity of the phase boundary and the corresponding concentration. This behavior of the concentration at the boundaries also leads to enrichment of one part of the sample, and impoverishment of another, by the diffusing ions. Change in the initial temperature gradient over the sample is also accompanied by change in the concentration distribution: the larger the gradient, the larger the experimental and theoretical enrichment and impoverishment of regions of the sample by the ions.

NOTATION

T, temperature; t, time; λ, thermal conductivity; D', D", D, thermodiffusion coefficient, Dufour coefficient, and diffusion coefficient; c, ionic concentration; K_i, coefficient taking account of the velocity of the phase boundaries; $z_{i,k}$, coordinates of points of the shifted grid; v, rate of contact melting.

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STEFAN PROBLEM IN THE THEORETICAL MODEL OF THE THERMAL INTERACTION
BETWEEN A MOLTEN HEAT-LIBERATING MATERIAL AND FINITE WALLS

G. N. Vlasichev, G. B. Usynin,
and Yu. I. Anoshkin

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An approximate analytical solution of the one-dimensional Stefan problem is obtained for a single finite wall with constant heat fluxes at the boundaries. The conjugate problem for a system of molten heat-liberating material with two walls is solved by the finite-difference method.

In investigating the safe operating conditions of fast reactors, it is necessary to analyze the thermal interaction between the molten heat-liberating fuel and the casing walls of the malfunctioning and neighboring heat-liberating piles. Since this interaction is accompanied by melting of the casing wall and motion of its front, the analysis involves solving the problem of phase transition, called the Stefan problem. Accurate analytical solutions of the phase-transition problem are only known for individual cases of a semiinfinite media [1, 2]. An approximate analytical solution of the one-dimensional Stefan problem may be obtained for a single wall of finite thickness with constant heat fluxes at the boundaries ($q_{s1} > q_{s2}$). The solution is found by an integral balance method using the Lebenson method.

Integrating the one-dimensional heat-conduction equation

$$c(x,\ t) \frac{\partial T(x,\ t)}{\partial t} - \frac{\partial}{\partial x} \lambda(x,\ t) \frac{\partial T(x,\ t)}{\partial x} \qquad (1)$$

within the limits of the liquid and solid phases of the wall, and using the Stefan condition

$$-\lambda_l \frac{\partial T}{\partial x}\bigg|_{x=y(t)-0} + \lambda_s \frac{\partial T}{\partial x}\bigg|_{x=y(t)+0} = R_m \frac{\partial y(t)}{\partial t}\ , \qquad (2)$$

it is found that

$$R_m \frac{\partial y(t)}{\partial t} = q_{s1} - q_{s2} - c_l \int_{X_1(t)}^{y(t)} \frac{\partial T(x,\ t)}{\partial t}\, \partial x - c_s \int_{y(t)}^{\delta} \frac{\partial T(x,\ t)}{\partial t}\, \partial x. \qquad (3)$$

Taking account of the downward runoff of the molten wall material under its own weight, it is assumed that the coordinate of the molten-layer boundary is determined by the expression $X_1(t) = by(t)$, where b is some constant ($0 \le b \le 1$).