SINGULARITIES IN DETERMINATION OF THE DIFFUSION COEFFICIENTS
OF COMPONENTS IN MELTS OF $\text{Al}_{11}\text{Bi}_3\text{V}$ SYSTEMS

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A critical analysis is performed of the mathematical expressions used to compute the diffusion coefficients of components on the basis of data on the growth rate or dissolution of crystals of $\text{Al}_{11}\text{Bi}_3\text{V}$ compounds. It is shown that neglect of high-order terms of the series that are the solution of the mass transport differential equations will result in substantial errors during processing of the experimental results. To simplify the computations and eliminate mathematical inaccuracy, it is proposed to use the analytic solution of the diffusion mass transport equations in the approximation of a semi-infinite medium. The diffusion coefficient of arsenic in liquid indium in the 550-750°C temperature range is computed on the basis of experimental results on the rate of InAs dissolution in an unsaturated In-As melt by using the method proposed.

A number of studies [1-3] have been devoted to methods of determining the diffusion coefficients of components in binary $\text{Al}_{11}\text{Bi}_3\text{V}$ melts. However, the information from different authors is quite contradictory and requires a critical approach. For instance, values of the diffusion coefficients of arsenic in gallium, cited for the 900-1100 K temperature range, differ by almost two orders of magnitude [3]. A similar spread can be explained by both the methodological errors of the experiment and the substantial inaccuracies in processing the experimental data.

An analysis is made in this paper of the possible mathematical inaccuracies in determining the diffusion coefficients of components by the growth rate or the dissolution of crystals under isothermal conditions.

In order to eliminate possible errors as well as to simplify the mathematical treatment of the experimental data, the utilization is proposed of the analytic solutions of the diffusion mass transfer equations for the case of a semi-infinite medium. The method proposed for treatment of the experimental data is realized in determining the diffusion coefficient for arsenic in liquid medium in a 550-750°C temperature range.

In the absence of convection, the diffusion delivery of a crystallizable substance to a growth surface is described by the following equation:

$$\frac{\partial x}{\partial t} = D \frac{\partial^2 x}{\partial z^2},$$

where $x$ is the concentration of the dissolved component in the liquid phase, $D$ is the diffusion coefficient, $t$ is the time, and $z$ is the coordinate along the normal to the interphasal boundary. The following boundary and initial conditions

\[ x(0, t) = x_0; \quad x(z, 0) = x_{in}; \quad \frac{\partial x(L, t)}{\partial z} = 0, \]  

(2) are satisfied for isothermal dissolution or growth, where \( L \) is the height of the melt, \( x_0 \) is the equilibrium concentration of the dissolved component on the interphasal boundary determined from the phase equilibrium condition, and \( x_{in} \) is the initial concentration of the dissolved component. It is assumed that the diffusion coefficient is independent of the concentration while the change in melt volume caused by displacement of the interphasal boundary is negligibly small as compared with the initial value. The solution of this boundary-value problem is the following expression for the concentration profile of the component in the liquid phase [4]

\[
x(z, t) = (x_{in} - x_0) \frac{4}{\pi} \left( \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[ -\frac{(2n+1)^2 \pi^2 Dt}{4L^2} \right] \right) \times \sin \left( \frac{(2n+1) \pi z}{2L} \right) + x_0.
\]

(3)

The quantity of substance (component) \( Q \) that has gone over into the liquid phase during isothermal contact can be found either by integrating the component distribution profile with respect to the coordinate after subtraction of its initial content, or by integrating the diffusion flux \( J \) through the interphasal boundary with respect to the time:

\[
Q = \int_0^L [x(z, t) - x_{in}] dz = \int_0^t J dt.
\]

(4)

where \( J = -D \frac{\partial x(0, t)}{\partial z} \). We note that there are no other reasons, either physical or mathematical, to prefer either of the methods of solution although other viewpoints [3] also exist on this account. For any approach, the identical final result can be obtained:

\[
Q = (x_0 - x_{in}) L \frac{8 \pi}{\pi^2} \left( \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} - \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \right) \times \exp \left[ -\frac{(2n+1)^2 \pi^2 Dt}{4L^2} \right].
\]

(5)

If we limit ourselves to the first terms of the series and set \( x_{in} = 0 \), which corresponds to the case of substrate dissolution in the melt of the metallic component, then we arrive at the following result:

\[
x(t) = \frac{Q}{L} = x_0 \frac{8}{\pi^2} \left[ 1 - \exp \left( -\frac{\pi^2 Dt}{4L^2} \right) \right].
\]

(6)

It is easy to see that as \( t \to \infty \) the mean concentration of the dissolved component in the liquid phase becomes \( (8/\pi^2)x_0 \); i.e., the equilibrium concentration corresponding to the liquidus of the system is not achieved, and this contradicts the physical meaning. Consequently, computation of the diffusion coefficient by means of the formula

\[
D = -\frac{4L^2 \ln \left( 1 - \frac{\pi^2 x(t)}{8x_0} \right)}{\pi^2 t}
\]

(7)
yields results known to be inaccurate, or even absurd, for large \( t \). Such a methodological error was admitted in determining the mutual diffusion coefficients of components in the melts In-As and Ga-As [5, 6].

The systematic error can be eliminated if higher-order terms are taken into account for the first series in (5). It is known that \( \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} = \frac{\pi^2}{8} \) [7]. Taking account of this circumstance, the main concentration of substance in the liquid phase during epitaxy from the melt is described by the expression [8]

\[
x(t) = x_0 \left[ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[ -\frac{(2n+1)^2 \pi^2 Dt}{4L^2} \right] \right].
\]

(8)

Neglecting terms of the series with \( n > 0 \), we obtain an analytic expression for the diffusion coefficient