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Surface Tension Gradient as Additional Driving Force for Grain Boundary Diffusion. Equilibrium and Non-Equilibrium Cases

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Classic Fisher model of grain-boundary diffusion with leakage into bulk is generalized by consideration of the surface-tension change along the grain boundary.

Класична Фішера модель для зерномежової дифузії з відсмоктуванням в об'єм зерен узагальнено з урахуванням зміни поверхневого натягу вздовж межі зерна.

Классическая модель Фишера для зернограничной диффузии с отсосом в объём зёрен обобщена с учётом изменения поверхностного натяжения вдоль границы зерна.

Key words: diffusion, grain boundary, surface tension, chemical potential.

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1. INTRODUCTION

It is well known that diffusion flux of i -th component is governed mainly by the gradient of its chemical potential. Consequently, at constant temperature, the driving forces usually discussed are the concentration gradient in an ideal solution or thermodynamic activity gradient in non-ideal solution [1, 2]. Stress gradient is an example of additional driving force, which can change the diffusion process [3]. These forces fit for bulk and interface diffusion.

During round table discussion at the International Conference DSS-2010 [4], Prof. L. Klinger stated new idea that if grain boundaries (GB) energy is not constant for all points of the GB, its gradient provides

the additional and independent driving force for atoms motion in GB (by analogy with Marangoni effect).

Some later, L. Klinger and Eu. Rabkin [5] applied this idea to the penetrative wetting of GB's.

The main goal of this paper is to develop the model of GB diffusion taking into account the surface tension gradient as an additional driving force.

2. DESCRIPTION OF THE MODEL

Grain boundaries are the paths of fast mass transport in polycrystalline solids. Mainly, the macroscopic description of GB diffusion is based on the Fisher's model [6]. According to this model (Fig. 1), GB is a thin plate with the thickness δ ($\delta \approx 5 \cdot 10^{-9}$ m) and diffusion coefficient, which is much higher than the bulk diffusivity ($D_b \gg D_v$). The model takes into account the fast diffusion flux from the surface ($y = 0$) along GB and diffusion cleavage from GB to the bulk.

Later Gibbs [7] developed this model for the case of heterodiffusion and took into account enrichment coefficient s , which gives the relation between the GB and bulk concentrations

$$s = \frac{C_b}{C_v} \Big|_{x=\delta/2}. \quad (1)$$

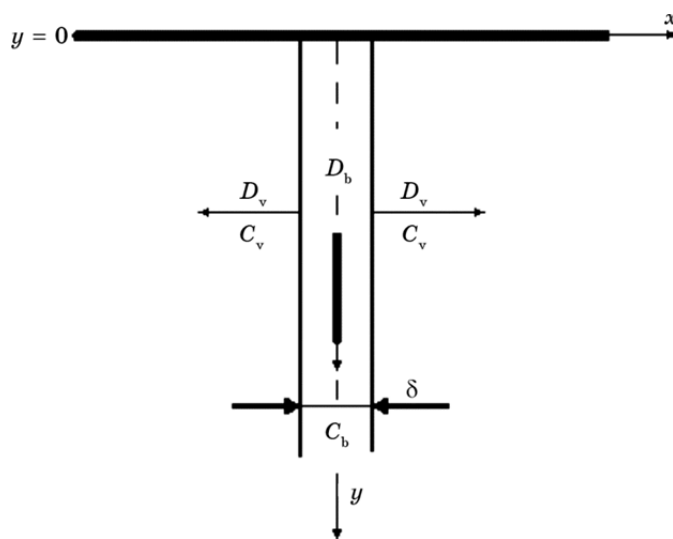


Fig. 1. Schematic description of GB diffusion model according to Fisher with condition $C_b(y, t) = C_v(x = \delta/2, y, t)$.

The simplest solution was obtained with following approximations: concentration on the surface is constant; GB concentration weakly depends on time ($\partial C_b/\partial t \approx 0$, quasi-stationary approximation); diffusion flux along y -axis in the grain bulk is neglected; segregation isotherm is linear (s does not depend on concentration).

This solution can be represented as:

$$\begin{aligned} C_b(y, t) &= C_b(0) \exp(-y/L), \\ C_v(x, y, t) &= C_b(y, t) \operatorname{erfc}\left[x/(2\sqrt{Dt})\right], \end{aligned} \quad (2)$$

where $L = (s\delta D_b[\pi t/(4D_v)]^{1/2})^{1/2}$, and Fisher's solution corresponds to $s = 1$ (self-diffusion).

It should be noted that later the exact solutions for the GB diffusion problem were obtained by Whipple [8]. Different adsorption models were used to describe the effect of segregation on GB diffusion (see, *e.g.*, [9–13]).

The important point is that if GB adsorption takes place, the surface tension γ becomes dependent on concentration. The gradient of surface tension is an additional driving force for the mass transport along the interface. To take it into account, the Fisher's model can be combined with Zhukhovitskii theory of surface phenomena [14].

According to this theory, GB chemical potential of a solute in an ideal solution can be written as

$$\mu_b = \mu^{\text{st}} + RT \ln C_b - \gamma f, \quad (3)$$

where f is the area corresponding to 1 mole of atoms, $f \approx \Omega/\delta$ (Ω is a molar volume for the solvent).

The diffusion flux along GB can be written as:

$$j_b(y, t) = -M_b \operatorname{grad} \mu_b(y, t) = -M_b \frac{\partial \mu_b}{\partial y}, \quad (4)$$

where M_b is a diffusant mobility at GB.

For complete understanding of the problem, we need to divide two different states of GB's: equilibrium and non-equilibrium.

Equilibrium State. It is well known that GB's are the non-equilibrium defects of crystals. From thermodynamic point of view, there are no conditions for equilibrium between GB and the bulk. Nevertheless, due to geometrical restrictions, it is valid to assume that GB's are in metastable equilibrium with the adjacent bulk region [15, 16]. In this case, we have to use the condition of equality of chemical potentials for each component at GB and in the bulk:

$$\mu_{ib} = \mu_{iv}, \quad (5)$$

and, consequently, the equation (4) can be rewritten for a dilute solution as

$$j_b(y, t) = -M_b \frac{\partial \mu_v}{\partial y} = -\frac{M_b RT}{C_v} \frac{\partial C_v}{\partial y}. \quad (6)$$

For the linear segregation isotherm (see Eq.(1)) with constant s , we can obtain:

$$j_b(y, t) = -\frac{M_b RT}{C_b} \frac{\partial C_b}{\partial y} = -D_b \frac{\partial C_b}{\partial y}. \quad (7)$$

Here, the relation $D_b = MRT/C_b = \text{const}$ was used.

Thus, the same equations, as in Fisher–Gibbs model, will be retained, neglecting dependence of γ on C_b [17].

Non-Equilibrium State. Let us assume now that GB chemical potential for the diffusant is not equal to its value in the bulk. On the other hand, we will keep the condition of equality of chemical potentials for the matrix element at GB and in adjacent bulk.

The GB concentration change with time can be described as

$$\begin{aligned} \frac{\partial C_b}{\partial t} = -\text{div} j_b(y, t) - \frac{2}{\delta} D j_x \Big|_{x=\frac{\delta}{2}} = -\text{div} \left\{ -\frac{M_b RT}{C_b} \frac{\partial C_b}{\partial y} + M_b f \frac{\partial \gamma}{\partial y} \right\} - \\ - \frac{2}{\delta} D j_x \Big|_{x=\frac{\delta}{2}} = D_b \text{div} \left\{ \frac{\partial C_b}{\partial y} - \frac{C_b f}{RT} \frac{\partial \gamma}{\partial y} \right\} - \frac{2}{\delta} D j_x \Big|_{x=\frac{\delta}{2}}. \end{aligned} \quad (8)$$

For demonstration of this effect, the approximations indicated above are kept.

The assumption of equality of chemical potential of solvent at GB and in the bulk, according [14], leads to the following concentration dependence of GB surface tension:

$$\gamma = \gamma_1 + (RT/f) \ln(a_{1b}/a_1), \quad (9)$$

where γ and γ_1 are the GB surface tensions of the solution with given concentration of solute (C_v) and of pure solvent, a_1 and a_{1b} are the thermodynamic activities of the solvent in the bulk and in GB. With the use of ideal dilute solution approximation ($a_i = X_i$) and assumption that Eq. (1) is still valid, we arrive to

$$\ln(a_{1b}/a_1) \approx \ln X_{1b} - \ln X_1 = \ln(1 - X_b) - \ln(1 - X) \approx -X_b + X = -(X_b - X_b/s).$$

The expression (9) can be rewritten as

$$\gamma = \gamma_1 - X_b (RT/f)(s - 1)/s \quad (10)$$

or, taking into account that $f \approx \Omega/\delta$ and $C = X/\Omega$,

$$\gamma = \gamma_1 - C_b \delta RT(s - 1)/s. \tag{11}$$

Using the substitution:

$$\frac{\partial \gamma}{\partial y} = \frac{\partial \gamma}{\partial C_b} \frac{\partial C_b}{\partial y} = -\left(\frac{s - 1}{s}\right) \delta RT \frac{\partial C_b}{\partial y} \tag{12}$$

and the solution for bulk diffusion along x -axis from the constant source, one can obtain:

$$\begin{aligned} \frac{\partial C_b}{\partial t} &= D_b \frac{\partial}{\partial y} \left\{ \frac{\partial C_b}{\partial y} + \frac{C_b f}{RT} \left(\frac{s - 1}{s}\right) \delta RT \frac{\partial C_b}{\partial y} \right\} - \frac{2\sqrt{D}}{\delta\sqrt{\pi t}} C_v(x \approx 0) = \\ &= D_b \left\{ \frac{\partial^2 C_b}{\partial y^2} + \frac{\partial}{\partial y} \left(C_b \Omega \left(\frac{s - 1}{s}\right) \frac{\partial C_b}{\partial y} \right) \right\} - \frac{2D}{\delta\sqrt{\pi t}} C_v(x \approx 0). \end{aligned}$$

For the quasi-stationary regime, we finally get the following equation:

$$\left\{ \frac{\partial^2 C_b}{\partial y^2} + \frac{\partial}{\partial y} \left(C_b \Omega \left(\frac{s - 1}{s}\right) \frac{\partial C_b}{\partial y} \right) \right\} - \frac{2\sqrt{D} C_b}{s\delta D_b \sqrt{\pi t}} = 0 \tag{13}$$

or

$$(1 + AC_b) \frac{\partial^2 C_b}{\partial y^2} + A \left(\frac{\partial C_b}{\partial y}\right)^2 - \frac{C_b}{L^2} = 0, \tag{14}$$

where $A = \Omega(s - 1)/s$, and $L^2 = s\delta D_b [\pi t/(4D)]^{1/2}$, or

$$\frac{\partial^2 C_b}{\partial y^2} + \frac{A}{(1 + AC_b)} \left(\frac{\partial C_b}{\partial y}\right)^2 - \frac{C_b}{(1 + AC_b)L^2} = 0. \tag{15}$$

3. RESULTS OF CALCULATIONS

Solution of this equation with boundary condition $C_b(y = 0) = C_{b0} = \text{const}$ and $C_b(y = \infty) = 0$ can be written as an integral:

$$y = -\int_{C_{b0}}^{C_b} \frac{L(1 + A\xi)}{\xi(1 + 2A\xi/3)^{1/2}} d\xi. \tag{16}$$

It is easy to see that, if $A = 0$ ($s = 1$), we get Fisher's solution. To illustrate this solution, the diffusion parameters were taken suitable to Cu self-diffusion [18]. For bulk diffusion, $D = 10^{-5} e^{-196800/(RT)}$ m²/sec. For grain boundary diffusion, $\delta D_b = 1,2 \cdot 10^{-15} e^{-85700/(RT)}$ m²/sec. In Figure

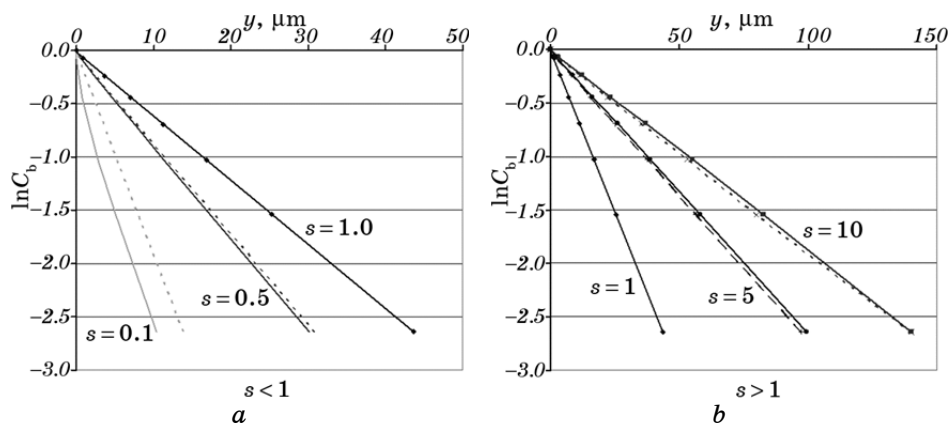


Fig. 2. Calculated GB-concentration profile for 100 h of annealing at 600°C ($D_b = 1.4 \cdot 10^{-7}$ and $D_v = 1.8 \cdot 10^{-12}$ cm²/s) for different s values (dashed lines correspond to the Gibbs solution).

2, the GB-concentration profiles for different s values in comparison with Gibbs' solution are shown.

The results of calculation show that: GB surface tension gradient, as an additional driving force for GB diffusion, alters the GB diffusion profile; the concentration profile in this case is not linear in semi-logarithmic coordinates; the effect of GB surface tension gradient is the most important in the case of negative segregation, while for the $s > 1$, it is negligible.

One can see that effective Fisher length L (y value, corresponding to $\ln(C_b/C_{b0}) = -1$) decreases with decreasing of s . Note that the less is the value of s , the less is L . Consequently, the concentration gradient and the gradient of surface tension increase. That is the reason why the additional force connected with surface tension gradient is important for negative adsorption only ($s < 1$).

4. APPLICATION TO THE Fe GB DIFFUSION IN Cu

In study of Fe diffusion in Cu [19], very strange result was obtained. With the use of the microprobe analysis, it was shown that in a wide temperature range (550–800°C) the difference between concentration profiles near and far from GB is very small. The authors could not explain that. It should be noted that the temperature range 550–600°C corresponds to regime «B» of GB diffusion [20], if annealing time is about 100 h. Let us take as approximation that GB diffusion coefficient of Fe is not very different in comparison with Cu GB diffusion coefficient (both the atomic size and the bulk diffusion coefficient are almost the same) and use the model described above. To compare the

penetration depth, we can compare the depth (y^*), at which the concentration in e^2 times smaller in comparison with surface concentration ($\ln(C^0/C)=2$). In the bulk for 100 h, $y^*=17\ \mu\text{m}$, and, in GB if $s=1$, $y^*=35\ \mu\text{m}$ (Fig. 2). Depending on s value, the depths will be as follow: $y^*(s=0.1)=7\ \mu\text{m}$, $y^*(s=0.5)=20\ \mu\text{m}$.

Unfortunately, we do not know the segregation factor for this system, but according to surface tension measurements: $\gamma^{\text{surface}}(1200\ \text{K})=1.8\ \text{J/m}^2$ for pure Cu and $\gamma^{\text{surface}}(1200\ \text{K})=1.9\ \text{J/m}^2$ for Cu-0.72 at.% Fe [21]. Using the estimation $\gamma^{\text{GB}}=\gamma^{\text{surface}}/3$, the enrichment coefficient can be calculated from Eq. (10) ($\Omega=7.13\cdot 10^{-6}\ \text{m}^3/\text{mole}$):

$$s = 1 + \frac{s\Omega(\gamma_1 - \gamma)}{3X_b RT\delta} = 1 + \frac{\Omega(\gamma_1 - \gamma)}{3XRT\delta} =$$

$$= 1 + \frac{7.13 \cdot (1.8 - 1.9) \cdot 10^{-6}}{3 \cdot 0.72 \cdot 10^{-2} \cdot 8.31 \cdot 1220 \cdot 5 \cdot 10^{-9}} = 1 - 0,67 = 0,33.$$

Of course, it is very roughly estimated value. However, the tendency can be clearly seen. If the segregation factor is less than 0.5, the estimated in Fisher's model penetration depth along GB is less than bulk diffusion depth.

Finally, we can conclude that GB surface tension gradient acts as an additional driving force and it must be taken into account in the case of negative adsorption ($s < 1$).

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