# Grain Boundary Diffusion with Simultaneous Chemical Interaction in Grain Boundary

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The new model is developed, taking into account the simultaneous grain boundary diffusion (within the Fisher–Gibbs approximation) and chemical interaction, which leads to the $AB$-type molecules' formation in a binary system. The evaluation of 'reaction' effect on the rate of the whole process is made.

Розглянуто нову модель, що враховує дифузію вздовж меж зерен (в рамках апроксимації Фішера–Ґіббса) одночасно з хімічною взаємодією, яка веде до утворення молекул типу $AB$ у бінарних системах. Зроблено оцінку впливу «реакції» на швидкість процесу в цілому.

Рассмотрена новая модель, которая учитывает диффузию по границам зёрен (в рамках аппроксимации Фишера–Гиббса) одновременно с химическим взаимодействием, ведущим к образованию молекул типа $AB$ в бинарных системах. Сделана оценка влияния «реакции» на скорость процесса в целом.

**Key words:** grain boundaries, diffusion, Fisher's model, kinetics, chemical compound.

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## 1. INTRODUCTION

Usual description of grain boundary diffusion (GBD) is based on Fisher's model [1]—model of advancing diffusion in grain boundary (GB) with leakage to grain bulk. Various methods of diffusant concentration field calculation were applied: for selfdiffusion and heterodiffusion, taking into account a segregation [2, 3] and formation of atomic

complexes in GB [4–6], for various temperature conditions [7] and various structural types of GBs [8].

It may seem strange, but the model describing influence of chemical processes in grain boundary, which bind a part of diffusing atoms, on the rate of their moving in GB was not developed. Though the experimental fact of GBD delay due to precipitation of nanoparticles in grain boundary is well-known, it is usually connected with the idea that fine particles, which are formed in GB, reduce the section of boundary and diffusive flux.

The purpose of this work is to develop the Fisher's model of GBD taking into account simultaneous chemical interaction of solute and solvent atoms in GB. Situations of such kind—parallel carrying out of two processes with participation of the same atoms—are well-known in heterogeneous kinetics [9].

## 2. MODEL

Let us consider a bicrystal in a dilute binary solution $A[B]$ ($A$ is matrix atom, $B$ is diffusing impurity). There are three processes in GB at the same time: two correspond to Fisher's model (advanced diffusion of atoms in GB and leakage to the bulk) and the third, connected with chemical interaction and formation the molecule of $A_m B_n$ type. Further, we will restrict our consideration to the simplest case of $AB$.

For description of the first two processes, we use Fisher's model: GB is located normally to external surface, the substance $B$ moves from a surface where its concentration $c_s = \text{const}$, along grain boundary (on $y$-axis), with diffusion coefficient $D_b$, and leaks from GB into volume (along $x$-axis) with coefficient $D << D_b$ (see Fig. 1). Let us keep all assumptions of Fisher's model corresponding to the $B$-regime according to Harrison [7]: width of GB is $\delta << (Dt)^{1/2}$, where $t$ is the time of diffusion annealing. We will neglect direct diffusion from the surface to the bulk.

Let us describe a process of formation of $AB$ molecule in GB as a chemical reaction:

$$A + B \xrightarrow{\ k\ } AB. \tag{1}$$

According to the theory of simple collisions [9], the reaction rate can be described as:

$$w = -\frac{dc_b}{dt} = k' c_b(A) c_b(B), \tag{2}$$

where $c_b(A)$ and $c_b(B)$ are the concentrations of solvent ($A$) and solute ($B$) in grain boundary, and $k$ is the constant of the process rate (1). In a
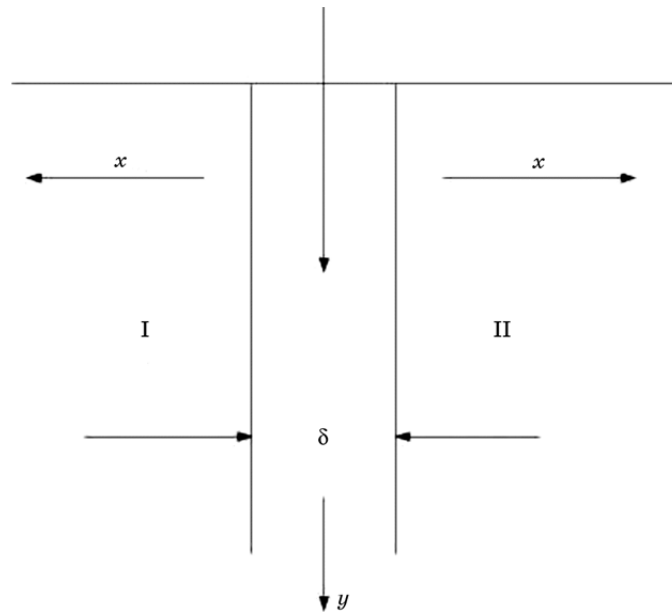
**Fig. 1.** Diffusion of $B$ in GB with leakage to the bulk, $\delta$ is the GB thickness.

bulk, we neglect formation of $AB$ compound. As $c_b(A) = \text{const}$, it is possible to write:

$$w = kc_b(B), \qquad (3)$$

where $k = k'c_b(A)$ instead of (2).

Taking into account reaction (3), Fisher's equations will look like:

$$\frac{\partial c(x,y,t)}{\partial t} = D\frac{\partial^2 c(x,y,t)}{\partial x^2}, \qquad (4)$$

$$\frac{\partial c_b(y,t)}{\partial t} = D_b \frac{\partial^2 c_b(y,t)}{\partial y^2} + \frac{2}{s\delta} D \frac{\partial c(x,y,t)}{\partial x}\bigg|_{x=\pm\frac{\delta}{2}} - kc_b, \qquad (5)$$

where $c$ is the concentration of the element $B$ in a grain bulk.

The third term of sum in the right part of equation (5) describes reduction of concentration of diffusing element in GB due to the binding of part of $B$ atoms—this is a new element of the model. The second term of the sum, as well as at Fisher's model, describes leakage of $B$ atoms from GB to the bulk, $s$ is a segregation factor

$$s = \frac{c_b}{c}\bigg|_{x=\pm\delta/2}. \qquad (6)$$

## 3. RESULTS AND DISCUSSION

Solving equation (4), substituting $\left.\dfrac{\partial c}{\partial x}\right|_{x=0}$ , and, according to the Fisher's quasi-stationary condition, assuming $\dfrac{\partial c_b}{\partial t} = 0$ , we obtain

$$\frac{d^2 c_b}{dy^2} - \left( \frac{k}{D_b} + \frac{2\sqrt{D}}{s\delta D_b \sqrt{\pi t}} \right) c_b = 0 \qquad (7)$$

instead of Eq. (5).

Equation (7) differs from the usual Fisher's one by the term $k/D_b$, which describes contribution of chemical interaction in GBD. The solution of Eq. (7) looks like

$$c_b = c_s \exp\left( -\frac{y}{L} \right), \qquad (8)$$

where

$$L = \frac{L_k L_D}{\left( L_k^2 + L_D^2 \right)^{1/2}}, \qquad (9)$$

$$L_k^2 = D_b / k \qquad (10)$$

and

$$L_D^2 = \frac{s\delta D_b \sqrt{\pi t}}{2\sqrt{D}}. \qquad (11)$$

In these equations, $L_D$ is diffusion length or distance on which concentration of diffusing substance decreases in $e$ times owing to GBD and leakage, and $L_k$ is kinetic length. Concentration decreases due to formation of chemical compound $AB$. Linear dependence of $\ln c_b$ remains, but, as $L_k^2 + L_D^2 > L_D^2$, diffusion at GB is slowed down.

The grain boundary concentration decreases due to the chemical reaction in GB (kinetic braking factor, $f_k$), and to the leakage from GB to the bulk (diffusion braking factor, $f_d$). Both factors

$$f_d = \frac{\sqrt{Dt}}{s\delta}, \quad f_k = kt \qquad (12)$$

slow down GBD.

The ratio of kinetic braking factor $f_k$ to diffusion factor $f_d$ is the following:

$$\frac{f_{\mathrm{k}}}{f_{\mathrm{d}}} = \frac{kt}{\dfrac{\sqrt{Dt}}{s\delta}} = \frac{s\delta k\sqrt{t}}{\sqrt{D}},$$  (13)

*i.e.* the ratio of dimensionless time of chemical reaction to dimensionless path of bulk diffusion. From the equation **(13)**, we can see that this ratio is proportional to $k$, $s$, $(t)^{1/2}$ and inversely depends on $(D)^{1/2}$. As for the temperature dependence, it looks like

$$\frac{f_{\mathrm{k}}}{f_{\mathrm{d}}} = \frac{s_0\delta k_0\sqrt{t}}{\sqrt{D_0}}\exp\left(-\frac{E_{\mathrm{s}} + E_{\mathrm{k}} - \dfrac{1}{2}E_{\mathrm{d}}}{RT}\right)$$  (14)

with the effective activation energy of GBD

$$E_{\mathrm{eff}} = E_{\mathrm{s}} + E_{\mathrm{k}} - \frac{1}{2}E_{\mathrm{d}},$$  (15)

where $E_{\mathrm{s}}$ is the energy of segregation ($E_{\mathrm{s}} < 0$), $E_{\mathrm{k}}$ and $E_{\mathrm{d}}$ are the activation energies of chemical reaction and of bulk diffusion.

Usually, $E_{\mathrm{k}} > E_{\mathrm{d}}$, the more so $E_{\mathrm{k}} > \dfrac{1}{2}E_{\mathrm{d}}$, and even though $E_{\mathrm{s}} < 0$, $E_{\mathrm{eff}} > 0$, and the ratio $\dfrac{f_{\mathrm{k}}}{f_{\mathrm{d}}}$ increases with temperature.

## 4. CONCLUSIONS

Many factors can slow down GBD flux and eliminate or decrease accelerated GBD. In this paper, we showed that one of such factors has kinetic nature. The chemical reaction decreases GB flux and GB concentration. The kinetic braking effect is proportional to the reaction rate constant.

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