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NUMERICAL MODEL FOR THE EFFECT OF GRAIN BOUNDARIES ON THE TOTAL AMOUNT DIFFUSED

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Abstract—The effect of grain boundary regions on the total amount diffused during an exchange experiment has been numerically modeled. The total amount diffused increases when the grain size is decreased, and when the ratio of the grain boundary and lattice diffusion coefficients increases. Grain boundary migration increases the total amount diffused during part of the processing time. The numerical calculations have shown that when lattice diffusion distance is larger than the grain size, Hart's equation is a satisfactory approximation for calculating the apparent diffusion coefficient value.

1. INTRODUCTION

Grain boundary enhancement of diffusion in polycrystalline materials is important in a range of metallurgical situations. There have been a number of detailed reviews concerning grain boundary diffusion, e.g. by Peterson [1] on the mechanisms of grain boundary diffusion, and by Gupta et al. [2] on grain boundary diffusion in thin films. Because of this, only the literature appropriate to the present paper will be reviewed.

Harrison [3], in polycrystalline materials, defined three classes of grain boundary diffusion kinetics that depend on the relationship between the lattice diffusion distance and the grain size of the material considered. In Type A kinetics, the lattice diffusion distance is much larger than the grain size, diffusion fields at neighboring grain boundary regions overlap and each diffusing particle has entered, migrated or left a large number of grain boundaries. Based on generalized "random walk" considerations, Hart [4] demonstrated the existence of an apparent diffusion coefficient, D_{app}, during Type A behavior. This apparent diffusion coefficient combines the lattice diffusivity with a term fD_{gb}, that accounts for the fraction of sites, f, associated with the grain boundaries

$$D_{app} = D_l\left(1 + f\frac{D_{gb}}{D_l}\right) \qquad (1)$$

where D_l and D_{gb} are the diffusion coefficients in the bulk material and at the grain boundaries. Campbell [5] analyzed diffusion from an instantaneous source through multiple parallel grain boundaries and qualitatively related the concentration profiles with the grain boundary spacing. In particular, Campbell suggested that Hart's relation was not an appropriate solution for the Type A diffusion problem [5].

In Type B kinetics, the lattice diffusion distance is much less than the grain size and each grain boundary is assumed to be isolated. This is similar to the semi-infinite bicrystal situation, which was first modeled by Fisher [6], and then modified by Whipple [7] and Suzuoka [8]. An examination of the overall kinetics during an exchange experiment, confirmed that there is no single apparent diffusion coefficient in Type B kinetics and the amount of material removed from the crystal at time t is proportional to $t^{3/4}$ [9]. In Type C behavior, there is negligible lattice diffusion, diffusion occurs only within the grain boundary region and different apparent diffusion coefficients may be calculated depending on the type of experiment carried out [3].

Cahn and Balluffi [10] extended Harrison's classification of diffusion kinetics to allow for grain boundary migration. For example, Type A diffusion behavior occurs when $\sqrt{D_l t}$ or Vt exceeds the grain size, d. Diffusion along moving grain boundary has been examined both analytically and numerically in recent research by Glaeser and Evans [11], Mishin and Razumovskii [12], and by Cermak [13]. Their results indicate that grain boundary migration affects the apparent grain boundary diffusion coefficient values derived when the results of diffusion experiments are evaluated using conventional (stationary) grain boundary diffusion models. Mishin and Razumovskii [12] indicated qualitatively that moving grain boundaries intensively absorb the diffusant and spread it in a relatively thin layer near the surface. Near-surface enrichment was also confirmed in Cermak's numerical calculations [13].

In practical situations, diffusion occurs during a wide range of time intervals, from very short to long holding periods. Consequently, when diffusion is studied continuously, there will be a transition from initial Type C kinetics, through Type B behavior to Type A kinetics. Because numerical modeling can accommodate a wide variety of boundary conditions, it is a particularly effective analytical tool, when diffusion takes place continuously. In particular, numerical modeling can readily handle the transition

regions between the different Type C, B and A kinetic regimes. The present paper uses the finite difference method to examine the influence of grain diffusivity, of grain size (varying the volume fraction of grain boundaries), and of grain boundary migration, on the total amount of diffused during an exchange experiment.

2. MODEL

The computer model evaluates the total amount of material which diffuses during an "exchange" experiment, as a function of holding time. Diffusion occurs from a surface at concentration c_0 into material that is free of diffusant. The grain boundary regions are perpendicular to the free surface, have thickness, δ, and are at a constant spacing, d. The grain boundaries move at velocity, V, in a direction parallel to the free surface. The diffusion coefficients, molar volumes, and activity coefficients are assumed to be independent of composition, and there is no interaction between the diffusant and the grain boundaries.

3. FORMULATION

Because of symmetry, only one unit containing a grain boundary is considered. The y-axis is along the moving grain boundary and the x-axis is parallel to the direction of grain boundary motion (see Fig. 1). The calculation region is defined by $\Omega \in \{x = -d/2, d/2; y = 0, L\}$, where $L(= 1\text{ mm})$ is the specimen length. The governing equations for the change of the concentration of diffusant with holding time are [6, 7, 12]

$$\frac{\partial c}{\partial t} = D_1\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right) - V\frac{\partial c}{\partial x}, \quad |x| > \frac{\delta}{2} \quad (2)$$

in the bulk material, and

$$\frac{\partial c_{gb}}{\partial t} = D_{gb}\frac{\partial^2 c_{gb}}{\partial y^2} + \frac{D_1}{\delta}\left(\frac{\partial c}{\partial x}\right)_{x = +\delta/2}$$

$$-\frac{D_1}{\delta}\left(\frac{\partial c}{\partial x}\right)_{x = -\delta/2}, \quad |x| < \frac{\delta}{2} \quad (3)$$

at the grain boundary region. In these equations, c and c_{gb} are the bulk material and grain boundary concentrations, D_1 and D_{gb} are the diffusion coefficients of the bulk material and at the grain boundary, V is rate of grain boundary migration, and the grain boundary thickness, δ, is assumed to be $5.0 \times 10^{-10}\text{ m}$.

At the interface between the bulk materials and the grain boundary $|x| = \delta/2$,

$$c_{gb} = kc. \quad (4)$$

The parameter, k, is a material constant [1] and is taken to be unity in all calculations. From equations (3) and (4)

$$\frac{\partial c}{\partial t} = D_{gb}\frac{\partial^2 c}{\partial y^2} + \frac{D_1}{k\delta}\left(\frac{\partial c}{\partial x}\right)_{x = +\delta/2}$$

$$-\frac{D_1}{k\delta}\left(\frac{\partial c}{\partial x}\right)_{x = -\delta/2}, \quad |x| = \frac{\delta}{2}. \quad (5)$$

The initial and boundary conditions are

$$c(x, y, 0) = 0 \quad (6)$$

$$c(x, 0, t) = c_0 \quad (7)$$

$$\left(\frac{\partial c}{\partial y}\right)_{y = L} = 0 \quad (8)$$

where c_0 is the concentration at the free surface.

The mean concentration at penetration depth, y, is given as

$$c(y, t) = \frac{1}{d}\int_{-d/2}^{d/2} c(x, y, t)\,dx$$

and the total amount diffused within domain Ω is

$$M(t) = \iint_{\Omega} c(x, y, t)\,dx\,dy. \quad (9)$$

4. NUMERICAL ANALYSIS

Using the forward-time, centred-space finite difference approximation, equations (2) and (5) can be written as

$$\frac{c_{i,j}^{t+\Delta t} - c_{i,j}^t}{\Delta t} = D_1\frac{c_{i+1,j}^t - 2c_{i,j}^t + c_{i-1,j}^t}{(\Delta x)^2}$$

$$+ D_1\frac{c_{i,j+1}^t - 2c_{i,j}^t + c_{i,j-1}^t}{(\Delta y)^2}$$

$$+ V\frac{c_{i+1,j}^t - c_{i-1,j}^t}{2\Delta x} \quad (10)$$
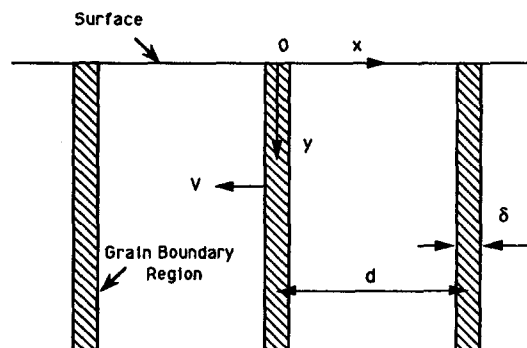

Fig. 1. Schematic of the model applied.

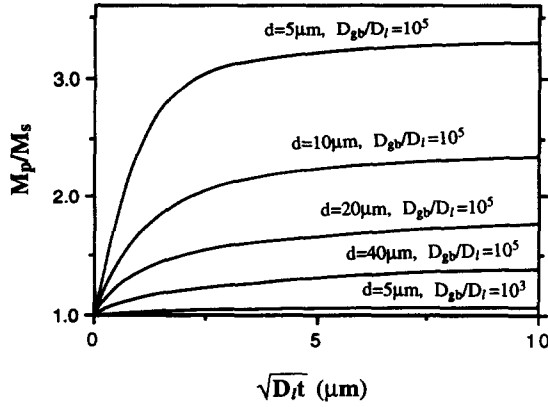Fig. 2. The effect of grain size and the D_{gb}/D_1 on the M_p/M_s ratio.

Fig. 3. The effect of grain boundary migration on the M_v/M_p ratio.

$$\frac{c_{k,j}^{t+\Delta t} - c_{k,j}^t}{\Delta t} = D_{gb}\frac{c_{i,j+1}^t - 2c_{i,j}^t + c_{i,j-1}^t}{(\Delta y)^2}$$

$$+\frac{D_1}{\delta}\frac{-3c_{i,j}^t + 4c_{i+1,j}^t - c_{i+2,j}^t}{2\Delta x}$$

$$-\frac{D_1}{\delta}\frac{3c_{i,j}^t - 4c_{i-1,j}^t + c_{i-2,j}^t}{2\Delta x}. \qquad (11)$$

The stability criterion for the calculation time step is [14, 15]

$$\Delta t \leqslant \min\left\{\frac{(\Delta x)^2(\Delta y)^2}{2D_1[(\Delta x)^2 + (\Delta y)^2]},\right.$$

$$\left.\frac{\delta\Delta x(\Delta y)^2}{2[\delta\Delta x D_{gb} + 2(\Delta y)^2 D_1]}\right\}. \qquad (12)$$

An analysis of the compatibility of finite difference equations (10) and (11), with respect to partial differential equations (2) and (5), indicates that equation (11) introduces a numerical diffusion term, $(\frac{1}{2}V^2\Delta t)\partial^2 c/\partial x^2$ [14]. Because of this, the time step must be small enough so that this fictitious diffusion term is much less than the true diffusion coefficient value. When the time step satisfies the criterion given by equation (12), the fictitious diffusion coefficient $(\frac{1}{2}V^2\Delta t)$ is approx. 10^{-4}–10^{-5} of the real diffusion coefficient, D_1, in this work. Further details of the mathematical procedures detailed in Ref. [15].

5. RESULTS

5.1. Influence of grain boundary diffusivity

Figure 2 shows the effect of grain boundary diffusivity and grain size on the ratio of M_p/M_s, where M_p is total amount diffused into a polycrystalline material and M_s the total amount diffused into a single-crystal. The influence of grain boundary depends on the grain size and on the D_{gb}/D_1 ratio. At low temperatures $(T < 0.5 - 0.75T_m$, where T_m is the equilibrium melting temperature of the material in K) the D_{gb}/D_1 ratio is 10^5 or higher. The influence of grain boundaries on diffusional transport is greater
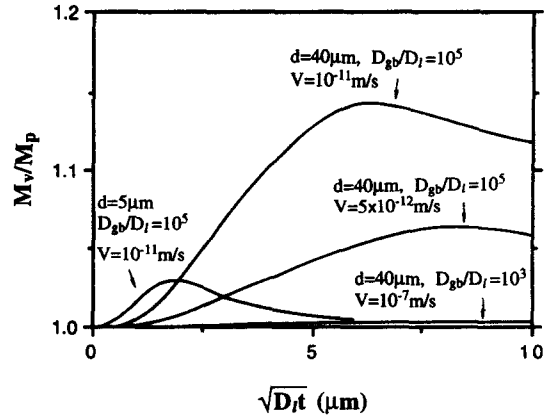
under these conditions. However, at high temperatures $(T > 0.75T_m)$, the D_{gb}/D_1 ratio is 10^3 or less and consequently Fig. 2 indicates that the contribution resulting from grain boundary diffusion is much less. Figure 2 also shows that the contribution due to grain boundary diffusion increases when the grain size becomes smaller.

5.2. Grain boundary migration

Figure 3 shows the effect of grain boundary migration on the M_v/M_p ratio, where M_v is the total amount diffused into a polycrystalline material which has moving grain boundaries, and M_p is the total amount diffused into a polycrystalline material, when the grain boundaries are stationary. Grain boundary migration speeds up mass transfer during a part of the holding time, and during this period more diffusion occurs when the grain size, the rate of the grain boundary, migration and the D_{gb}/D_1 ratio are increased.

Increased diffusion due to grain boundary migration can be explained by the build-up in diffusing materials in the wake of the moving grain boundary (see Fig. 4). During short holding times (for small
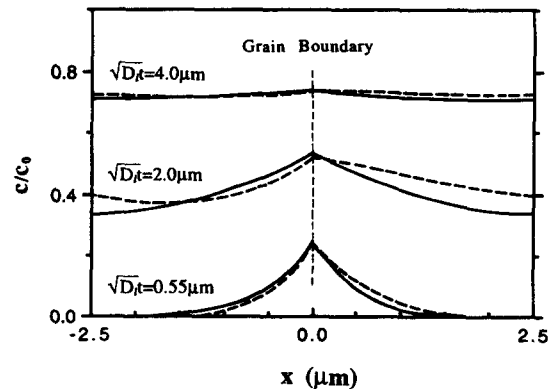

Fig. 4. Concentration profile along x-direction, at $y = 6\,\mu$m, when $d = 5\,\mu$m, $D_{gb}/D_1 = 10^5$, and $V = 10^{-11}$ m/s. The dashed line is for the migrating grain boundary and the solid line is for a stationary grain boundary.

Table 1. $\sqrt{D_l t} + Vt$ values where the M_v/M_p ratio reaches its maximum value (in Fig. 3)

$d\ (\mu m)$	$V\ (\times 10^{-12}\ \text{m/s})$	$t\ (\times 10^5\ \text{s})$	$\sqrt{D_l t} + Vt\ (\mu m)$
5	10	3.0	4.7
40	10	36.0	42.0
40	5	67.0	41.7

lattice diffusion distances), the migrating grain boundary has little influence on the concentration profile and consequently, there is negligible difference between total amount diffused in the migrating and stationary grain boundary cases. However, when the processing time increases, more diffusant is built up in the wake of the moving grain boundary and therefore more material is diffused into the specimen. For long holding times (large diffusion distances), the difference in the concentration profiles and hence in the total amount diffused, produced by migrating and stationary grain boundaries decreases continuously.

The ratio M_v/M_p attains a maximum value when $\sqrt{D_l t} + Vt$ approaches the grain size, d (see Table 1). Cahn and Balluffi [10] indicates that the boundary between Type B and Type A kinetics occurred when $\sqrt{D_l t} + Vt = d$. They did point out, however, that although their curves indicated a sharp transformation from Type A and Type B behavior, they should really be considered as transition regions.

Both Mishin and Razumovskii [12] and Cermak [13] pointed out that migrating grain boundaries spread the diffusant in a relatively thin layer near the surface of the sample. In the present study, the calculated diffusant distribution in the y-direction (see Fig. 5) also indicates that migrating grain boundaries enrich the near-surface region in diffusant and deplete regions far from the surface. In Fig. 5, $\bar{c}_v$ is the mean diffusant concentration in a polycrystalline material with moving grain boundaries, and $\bar{c}$ is the mean diffusant concentration in a polycrystalline material that has stationary grain boundaries.

6. DISCUSSION

6.1. Apparent diffusion coefficient

When the surface is maintained at constant concentration, c_0, and diffusion takes place into material which is initially free of diffusant, the analytical solution for the amount diffused (M_s) into a semi-infinite, single crystal is [16]

$$M_s = 2c_0 \sqrt{\frac{D_l t}{\pi}}. \tag{13}$$

Assuming a single apparent diffusion coefficient (D_{app}), instead of individual lattice and grain boundary diffusion coefficients, the total amount diffused (M_p) in a polycrystalline material will be
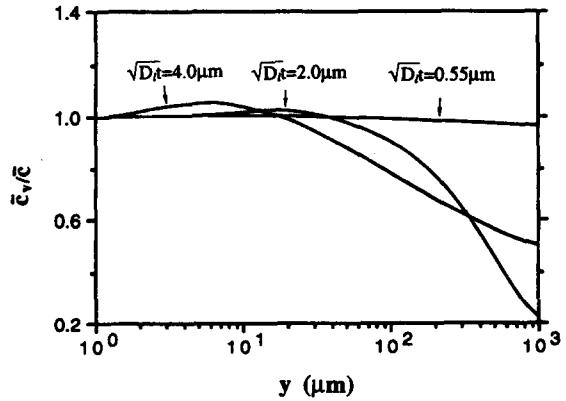
$$M_p = 2c_0 \sqrt{\frac{D_{app} t}{\pi}}. \tag{14}$$

Fig. 5. The change in the $\bar{c}_v/\bar{c}$ ratio along the y direction, when $d = 5\ \mu m$, $D_{gb}/D_l = 10^5$, and $V = 10^{-11}$ m/s.

Combining equations (13) and (14)

$$D_{app} = D_l\left(\frac{M_p}{M_s}\right)^2. \tag{15}$$

From this relation, Fig. 2 indicates that, for a polycrystalline material, the D_{app}/D_l ratio increases when the holding time increases and then tends to constant value at long processing times. Assuming that the diffusion process reaches steady-state and when the lattice diffusion distance is much larger than grain size, then [17]

$$D_{app} = D_l\left(1 + \frac{\delta}{d}\frac{D_{gb}}{D_l}\right). \tag{16}$$

This relation is very similar to equation (1), that Hart derived based on generalized "random walk" considerations [4]. The numerical prediction for D_{app}/D_l ratio can be calculated using the results in Fig. 2 and equation (15). Table 2 compared the numerical values with those produced using equation (16). It is apparent that equation (16) provides a satisfactory approximation for the apparent diffusion coefficient in polycrystalline material, when long processing times occur and $\sqrt{D_l t}$ exceeds d. This point is further illustrated in Fig. 6, where the numerical calculations are extended so that the lattice diffusion distance is 10 times larger than $d/2$ ($L = 1.5$ mm in this calculation). The results in Fig. 6 are quite different from those indicated by Campbell [5], since the average concentration profile is that in a homogeneous medium, which has an apparent diffusion coefficient equal to the grain boundary diffusion coefficient. This

Table 2. D_{app}/D_l ratio values calculated using equations (15) and (16), when $D_{gb}/D_l = 10^5$

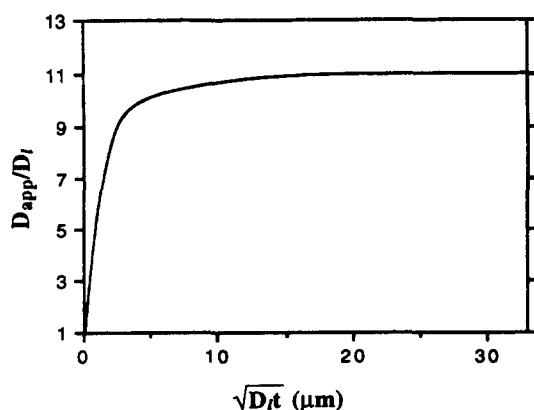| $d\ (\mu m)$	$\dfrac{\sqrt{D_l t}}{d}$	$\dfrac{D_{app}}{D_l}$, by equation (15)	$\dfrac{D_{app}}{D_l}$, by equation (16)
5	2	10.89	11
10	1	5.48	6
20	0.5	3.04	3.5
40	0.25	1.91	2.25

Fig. 6. The relation between the lattice diffusion distance $\sqrt{D_l t}$ and the D_{app}/D_l ratio, when $d = 5 \mu m$ and $D_{gb}/D_l = 10^5$.

difference between the results in this study and those of Campbell may be due to underlying assumptions in each case. A continuous source is used in the present study, while Campbell analyzed diffusion from an instantaneous source.

The difference in the total amount diffused in the migrating and stationary grain boundary cases decreases when $\sqrt{D_l t} + Vt$ is much larger than d. In this situation, the apparent diffusion coefficient can also be calculated using equation (15), as Cahn and Balluffi suggested [10].

7. CONCLUSION

A numerical model has been developed, which indicates in a continuous manner, the effect of grain boundary regions, and of grain boundary migration, on the total amount diffused during an exchange experiment. The principal conclusions are:

1. The influence of grain boundary regions on the total amount diffused during an exchange experiment depends on the grain size, and the ratio of grain boundary diffusion coefficient and lattice diffusion coefficient, D_{gb}/D_l. When the D_{gb}/D_l ratio is high (for temperatures in the range, $T < 0.5–0.75T_m$), decreasing the grain size increases the total amount diffused. When the D_{gb}/D_l ratio is low (at high processing temperatures in the range, $T > 0.75T_m$), the influence of grain size on the total amount diffused is small.

2. When $\sqrt{D_l t}$ is larger than the grain size, d, the numerical calculations support Hart's analysis [4], that an apparent diffusion coefficient exists. This apparent diffusion coefficient can be approximated using the relation, $D_{app} = D_l(1 + (\delta/d)(D_{gb}/D_l))$.

3. Grain boundary migration increases the total amount diffused during part of the holding period. During this period, the total amount diffused increases, when the grain size, the D_{gb}/D_l ratio, and the rate of grain boundary migration increase. For short processing times, grain boundary migration has negligible effect on the total amount diffused and, for long holding times, the total amount diffused is also similar in stationary and migrating grain boundary situations.

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