MOVING INTERPHASE INTERFACES AS VACANCY GENERATORS,

VACANCY GRADIENTS, NONPARABOLIC GROWTH AND ALL THAT

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Abstract

Growth kinetics of the intermediate phase layer in the process of reactive diffusion can be influenced by the nonequlibrium vacancies in two ways: first, if the growing phase has a smaller equilibrium vacancy concentration than the initial materials it can "eat" extra vacancies together with atoms A, B necessary for its growth. Production of extra vacancies is proportional to the growth rate and decreases with time leading to the time-dependent diffusivity of the phase layer and, therefore, to the nonparabolic phase growth. Second, if the mobilities of species A and B in the growing phase differ significantly then there appears the vacancy flux from one interface to another. If the vacancy sources/sinks at the interphase boundaries are far from being ideal the vacancy undersaturation at one and supersaturation at another interface appear leading to the vacancy gradient. Vacancy gradient changes the fluxes leading to the 3-stage growth kinetics with rather long linear stage in the case $D_A >> D_B$ (or vice versa). New theory of mutual diffusion in binary alloys is presented taking into account nonequilibrium vacancies as well as vacancy sources/sinks. It gives usual Darken results in macroscale.

I Introduction

It is well recognized that the nonequilibrium vacancies play an important role during irradiation of alloys. It is not so well recognized that nonequilibrium vacancies may be important without any irradiation, in the processes of mutual and reactive diffusion. In these cases nonequilibrium vacancies are generated by the difference of partial diffusivities ($D_A - D_B$) or/and by the movement of interphase boundaries of the growing intermediate phase layers. Moreover, nonequilibrium vacancies seem to play major role in such exotic situations as solid state amorphizing reactions (SSAR) or anomalous diffusion during fast heating of bimetallic systems.

In 1972-1974 Nazarov and Gurov suggested rigorous microscopic analysis of mutual diffusionin binary alloys taking nonequilibrium vacancies into account but neglecting the influence of vacancy sources/sinks [1-3]. One of their results was that the concenration profile evolution is governed mainly by alternative coefficient $D_{NG} = \dfrac{D_A^* D_B^*}{C_A D_A^* + C_B D_B^*} \varphi,$ $\qquad\qquad$ (1)

(φ- thermodynamic factor, $\varphi = \dfrac{C_A}{kT}\dfrac{\partial \mu_A}{\partial C_A}$) instead of Darken's result

$$\tilde{D}_D = \left(C_A D_B^* + C_B D_A^*\right)\varphi \qquad\qquad (2)$$

In section 2 we show that the results (1) and (2) may coexist in the model of the regular chain of ideal vacancy sources/sinks. Coefficient D_{NG} describes the details of concentration profile between sources/sinks in the "mesoscopic" space/time scale ($a << dx << l$, a - atomic size, l - distance between sinks). Coefficient $\tilde{D}_D$ governs the process of diffusion in "macroscopic" scale ($dx >> l$). Similar result for time scales is obtained in the model of continious distribution of nonideal sources/sinks: D_{NG} for $t << \tau_v/C_v$, $\tilde{D}_D$ for $t >> \tau_v/C_v$ and nonparabolic unlocal diffusion equation for $t \approx \tau_v/C_v$ (τ_v - relaxation time for vacancies, C_v- their equilibrium concentration). In Section 3 we consider the role of nonequilibrium vacancies in the process of intermediate phase growth in the case when the moving interphase interfaces are nonideal vacancy sources/sinks.

II. Mutual diffusion in the one dimension model of regular chain of ideal vacancy sources/sinks

Let us consider the mutual diffusion in the inhomogeneous binary substitution alloy modelled by the one-dimension periodic chain of ideal sources/sinks ($x_n = nl$, l - distance between sinks) at which vacancy concentration is always at equilibrium and between which diffusion of both species goes. We introduce simultaneously two space scales by using concentrations $C_{A,B,v}(x_n + \xi, t)$, $0 < \xi < l$. Linearization procedure gives: $C_{A,B}(x_n + \xi, t) = C_{A,B}(x_n, t) + u_{A,B}(\xi, t)$, $C_v(x_n + \xi) = C_v(x_n, t) + v(\xi, t) = C_{ve} + v(\xi, t)$, $u << C$, $v << C_{ve}$. (We neglect here the dependence of C_{ve} on composition. One can show that this suggestion does not change the main results.) Equations for variables u and v are linear:

$$\partial u_A/\partial t = D_{AA} \cdot \partial^2 u_A/\partial \xi^2 + D_{Av} \cdot \partial^2 v/\partial \xi^2,$$

$$\partial v/\partial t = D_{vA} \cdot \partial^2 u_A/\partial \xi^2 + D_{vv} \cdot \partial^2 v/\partial \xi^2 \qquad\qquad (3)$$

These equations can be derived from the general Onsager relations for $A- B- v$ system taking into account vacancy component (neglecting Manning corrections [4]) and the small values of u and v compared with C_A and C_v. Here D_{ij} depend on C but not on u:

$$D_{AA} \cong D_A^* \varphi, \; D_{Av} = -\frac{C_A D_A^*}{C_{ve}},$$

$$D_{vA} = -\varphi\left(D_A^* - D_B^*\right), \; D_{vv} = \frac{C_A D_A^* + C_B D_B^*}{C_{ve}} \qquad\qquad (4)$$

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The system of eq's (3) can be solved for every interval $x = x_n + \xi \in (x_n, x_n + l)$ with boundary conditions, $C_v(x_i, t) = C_{ve} \Leftrightarrow v(\xi = 0) = v(\xi = l) = 0$ (5)

using the diagonalization procedure:

$$\begin{pmatrix} w^{(1)} \\ w^{(2)} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} u_A \\ v \end{pmatrix} \equiv \hat{a} \begin{pmatrix} u_A \\ v \end{pmatrix}, \quad \hat{a} \hat{D} \hat{a}^{-1} = \hat{D} = \dot{D}_i \delta_{ij} \tag{6}$$

$$\frac{\partial w^{(i)}}{\partial t} = \dot{D}_i \frac{\partial^2 w^{(i)}}{\partial \xi^2}, \quad i = 1, 2 \tag{7}$$

Here the eigenvalues $\dot{D}_1$, $\dot{D}_2$ play the role of mutual diffusion coefficient and of vacancy diffusion coefficient respectively:

$$\dot{D}_1 \cong \frac{D_A^* D_B^* \varphi}{C_A D_A^* + C_B D_B^*} = D_{NG}, \quad \dot{D}_2 \cong \frac{C_A D_A^* + C_B D_B^*}{C_{ve}} \cdot \left(1 + \frac{2}{M_0}\right), \quad \dot{D}_1/\dot{D}_2 \cong C_{ve} \ll 1 \tag{8}$$

Equations (7) for $i = 1, 2$ are independent, but not the boundary conditions: eq.(5) lead to the following-relation

$$w^{(2)}\left(\xi = {}_l^0\right) = \frac{a_{21}}{a_{11}} w^{(1)}\left(\xi = {}_l^0\right) = -\frac{a_{22}}{a_{11}} C_{ve} \frac{(D_A^* - D_B^*)\varphi}{C_A D_A^* + C_B D_B^*} w^{(1)}\left(\xi = {}_l^0\right) \tag{9}$$

Due to fast vacancy diffusion (see [5]) evolution of $w^{(2)}$ is much more faster than of $w^{(1)}$, and the solution of eq.(8) for $i = 2$ becomes quasistationary after $t \gg l^2/D_2$, e.g. much sooner than the $w^{(1)}$-profile substantially changes:

$$w^{(2)}(t, \xi)\Big|_{t > \frac{l^2}{D_v}} \approx \frac{\varphi(D_A^* - D_B^*)}{D_v}\left(w^{(1)}(t, 0) + \frac{w^{(1)}(t, l) - w^{(1)}(t, 0)}{l}\xi\right) =$$

$$= -\frac{\varphi(D_A^* - D_B^*)}{D_v}\left(u_A(t, 0) + \frac{u_A(t, l) - u_A(t, 0)}{l}\xi\right) \tag{10}$$

It means that the vacancy flux, approximately equal to

$$j_v = -D_{vA}\frac{\partial u_A}{\partial \xi} - D_{vv}\frac{\partial v}{\partial \xi} \cong -D_v\frac{\partial w_2}{\partial \xi} = (D_A^* - D_B^*)\varphi \cdot \frac{u_A(t, l) - u_A(t, 0)}{l} = (D_A^* - D_B^*)\varphi\frac{\partial C_A}{\partial x} \tag{11}$$

Thus, vacancy flux is constant in each interval and changes only at the interval boundaries (vacancy sources/sinks). At the same time atom flux has following form:

$$j_A = -D_{AA}\frac{\partial u_A}{\partial \xi} - D_{Av}\frac{\partial v}{\partial \xi} = -\dot{D}_1\frac{\partial w^{(1)}}{\partial \xi} - \frac{C_A D_A^*}{C_A D_A^* + C_B D_B^*} j_v \tag{12}$$

Due to constant value of j_v eq.(4) yields $\dfrac{\partial u_A}{\partial t} = \dot{D}_1 \dfrac{\partial^2 w^{(1)}}{\partial \xi^2} + 0 = \dot{D}_1 \dfrac{\partial^2 u_A}{\partial \xi^2}$ (13)

e.g. evolution of concentration profile between vacancy sources/sinks (microscopic space scale, $\partial \xi \ll 1$) is governed by Nazarov-Gurov coefficient D_{NG} (1). At the same time the full average (over interval l) A-flux has familiar form:

$$j_A = -\dot{D}_1\frac{\partial \bar{u}_A}{\partial \xi} - \frac{C_A D_A^*}{C_A D_A^* + C_B D_B^*} \bar{j}_v = -\left(\frac{D_A^* D_B^*}{C_A D_A^* + C_B D_B^*} + \frac{C_A D_A^*(D_A^* - D_B^*)}{C_A D_A^* + C_B D_B^*}\right)\varphi\frac{\partial \bar{C}_A}{\partial x} = -D_A\frac{\partial \bar{C}_A}{\partial x} \tag{14}$$

where $D_A = D_A^* \varphi$.

Thus, in macroscopic scale ($dx > l$) mutual diffusion is described by Darken scheme.

Similar results can be obtained for time scales in the model of continious distribution of nonideal vacancy sources/sinks. In this case one must solve the set of equations of type (3) in which the vacany sources are taken into account by introducing the term $-v/\tau_v$, with τ relaxation time for vacancies: $\tau_v = L_v^2/D_v$, L_v - average distance to effective sink. It was shown

in [6] that for the times $t << \tau_v/C_v$ mutual diffusion is described by D_{NG} and for $t >> \tau_v/C_v$ - by Darken theory. For $t \approx \tau_v/C_v$ diffusion is nonparabolic and nonlocal:

$$j_v(x) = (2L)^{-1} \int_{-\infty}^{\infty} \exp\left(-\frac{x-x'}{L}\right) \cdot (D_A - D_B)\frac{\partial C_A(t,x')}{\partial x}dx' \quad (15)$$

$$j_A = -D_{NG}\frac{\partial C_A}{\partial x} - \frac{C_A D_A^*}{C_v D_v}j_v = -D_{NG}\frac{\partial C_A}{\partial x} - \frac{C_A D_A^*}{C_v D_v} \cdot$$

$$\cdot (2L)^{-1}\int_{-\infty}^{\infty}\exp\left(-\frac{x-x'}{L}\right)\cdot(D_A-D_B)\frac{\partial C_A(t,x')}{\partial x}dx' \quad (16)$$

May be the simultaneous action of both diffusion coefficients D_{NG} and D_{Darken} can explain why in the process of SSAR amorphous layer grows fast by diffusion but don't relax to crystalline phase. If $D_A >> D_B$ then the coefficient D_{NG}, governing the diffusion at microscale, is very small ($\approx D_B$), and coefficient D_{Darken}, governing the macrofluxes through phase layers, is not small ($\approx D_A$).

III. Nonequilibrium vacancies and linear phase growth

The growth of the layers of intermediate phases in the process of reactive diffusion sometimes starts from a linear stage, $\Delta x = \beta t$, which only at long times of annealing is transformed into a parabolic one $\Delta x = kt^{\frac{1}{2}}$. The analysis of experimental results on phase formation shows that very often a linear growth is observed for phases where mobility of one of the components is dominant. In such phases large vacancy fluxes are formed. The vacancy flux due to difference of partial diffusion coefficients of components in general case should experience jumps at interphase interfaces. Therefore they should serve as sources/sinks of vacancies. We will consider a situation when the power of boundaries as sources/sinks of vacanvies is not sufficient for maintaining their equilibrial concentrations on the boundaries. In this case concentrations of vacancies will deviate from equilibrium in opposite directions near different boundaries, that is between the boundaries there appear gradients of concentration of nonequilibrial vacancies which, as it will be shown below, can provide a linear stage of the phase layer growth.

Let between mutually unsoluble components A and B there grows the only intermediate phase 1 ($C_1 < C_B < C_1 + \Delta C$). Let C_{vL} (C_{vR}) be a concentration of vacancies on the left boundary A-1 (the right boundary 1-B), C_{ve} - equilibrial concentration of vacancies in phase 1. Suppose that mobility of A component is greater than that of B: $D_A > D_B$, so that in phase 1 the flux of vacancies is directed from B to A, that is from the right boundary to the left one:

$$j_v \cong (D_A - D_B)\frac{\Delta C}{\Delta x} - D_v\frac{C_{vR} - C_{vL}}{\Delta x} \quad (17)$$

(Here and below we will neglect Manning corrections, since the whole presented model is a rough approximation of real phase growth process). Considering that in phases A and B fluxes are absent and, hence, jumps of the vacancy flux are determined only by phase 1, we can write the equation of vacancy balance on the interphase boundaries:

$$dC_{vL}/dt = -(C_{vL} - C_{ve})/\tau_v - j_v/\delta \quad (18)$$

$$dC_{vR}/dt = -(C_{vR} - C_{ve})/\tau_v - j_v/\delta \quad (19)$$

where δ - thickness of the boundary layer, τ_v - relaxation time of vacancies.

Let us consider a quazistationary regime ($dC_{vL/R}/dt \cong 0$), which is true at $t >> \tau_v$. Then from (17-19) we obtain the expression for overfall of vacancy concentrations between the right and the left boundaries of the phase:

$$\Delta C_v = C_{vR} - C_{vL} = (2\tau_v/\delta)(D_B - D_A)\Delta C/(\Delta x + 2D_v\tau_v/\delta) \qquad (20)$$

The appearing overfall ΔC_v of vacancy concentrations makes a contribution into fluxes of components in the system of cristalline lattice:

$$j_B = -D_B\Delta C/\Delta x + (C_A D_A^*/C_v)\Delta C_v/\Delta x \qquad (21)$$

from eq's (17,20,21) we obtain (according to Darken) the expression for an average flux along the phase layer in the laboratory system coordinates:

$$J_B = j_B + C_B j_v = -J_A = -D\Delta C(1 + l_0/\Delta x)/(\Delta x + l_1) \qquad (22)$$

where $D = C_1 D_A + (1 - C_1)D_B$ - a mean interdiffusion coefficient, $l_1 = 2D_v \tau_v/\delta = L_v^2/\delta$ (L_v - the length of vacancy migration to the sink), $l_0 = l_1 \cdot (D_{NG}/D)$, D_{NG} - the interdiffusion coefficient according to Nazarov-Gurov (9), and always $D_{NG} < D$.

According to [7] for phases with narrow regions of homogeneity the flux is almost identical in any point of the phase layer so that expression (22) can be used in writing equations on the flux balance on interphase boundaries, which lead to the following equation for phase layer growth rate:

$$d\Delta x/dt = -(1/C_1 + 1/(1 - C_1))J_B = D\Delta C/(C_1(1 - C_1)) \cdot (1 + l_0/\Delta x)/(\Delta x + l_1) \qquad (23)$$

In a general case the layer growth according to eq.(7) has three stages, which are determined by two characteristic thicknesses l_1 and l_0:

(1) $\Delta x << l_0 (< l_1)$; $2 d\Delta x/dt = k_{NG}^2/\Delta x$; $\Delta x \cong k_{NG} t^{\frac{1}{2}}$, $\qquad (24)$

(the initial parabolic stage), where

$$k_{NG} = (2D_{NG}\Delta C/C(1 - C))^{\frac{1}{2}} \qquad (25)$$

(2) $l_0 << \Delta x << l_1$ (has the meaning only if $D_{NG} << D$, i.e. if $D_A << D_B$ or $D_B << D_A$):

$$d\Delta x/dt = \beta; \qquad \Delta x \cong \beta t \qquad (26)$$

(the stage of linear growth) where $\beta = D\Delta C/(l_1 C_1(1 - C_1))$. $\qquad (27)$

(3) $\Delta x >> l_1$; $\qquad 2\Delta x/dt = k/\Delta x$; $\qquad \Delta x = k t^{\frac{1}{2}}$, $\qquad (28)$

(the established parabolic regime), where $k = (2D\Delta C/C_1(1 - C_1))^{\frac{1}{2}}$ $\qquad (29)$

Thus, if in the growing phase one of the components is much more mobile than the other, we should observe a linear stage of growth, whose upper limit $j_1 = L_v^2/\delta$ is defined by the length of vacancy migration to the sinks L_v. If we assume reasonable estimations of $L_v \approx 10^{-7}$ m, $\delta \cong 0.5$ nm, then $l = 20$ μm, i.e. it is a quite considerable value.

As the length of vacancy migration is difficult to be measured but probably it depends weakly on temperature (it is determined mainly by concentration of sinks) we propose the following method of checking the given theory: according to eq's (25,27) constants of linear and parabolic growth β and k are expressed by the same effective interdiffusion coefficient D in the phase, here $k^2/\beta = 2l_1 = 2L_v^2/\delta$.

That is why it can be expected that Arrhenius dependences for k^2 and β should give the same activation energies. But if a linear stage is caused by a "classical" reason - a high potential barrier

on the interphase boundary - then it should be expected that the activation energy for β will be substantially greater than for K^2.

Up to now we did not take into account possible influence of nonequilibrium vacancies on the diffusivity. This influence can be substantial if there is a difference between equilibrium vacancy concentrations of parent phases A, B and intermediate phase. If, for example, growing phase has a smaller equilibrium vacancy concentration than the initial materials it can "eat" extra vacancies together with atoms A, B necessary for its growth [8]. Since the vacancy diffusion is fast one can consider these extra vacancies as generated inside the phase layer with the rate $\sigma \approx \dfrac{\Delta C_v}{\Delta x} \cdot \dfrac{d\Delta x}{dt}$, where $\Delta C_v = (1 - C_1)C_{vA} + C_1 C_{vB} - C_{vi}$. Obviously, there are also vacancy sinks in the phase layer with relaxation time τ_v. Thus, we have a following balance equation for the average vacancy concentration in the phase layer:

$$\frac{dv}{dt} = \frac{\Delta C_v}{\Delta x} \cdot \frac{d\Delta x}{dt} - \frac{v}{\tau_v}. \tag{30}$$

Phase growth is determined by the diffusivity depending on v:

$$\frac{d\Delta x}{dt} \approx \frac{D\Delta C\left(1 + \dfrac{v}{C_{ve}}\right)}{C_1(1 - C_1)} \frac{1}{\Delta x} \tag{31}$$

At $t \gg \tau_v$, eq. (30) gives quasistationary solution $v \approx \tau_v \dfrac{\Delta C_v}{\Delta x} \dfrac{d\Delta x}{dt}$. Substituting it to (31) one obtains equation describing nonparabolic phase growth:

$$\frac{d\Delta x}{dt} = \left(1 - \frac{l^2}{\Delta x^2}\right) \frac{D\Delta C}{C_1(1 - C_1)} \frac{1}{\Delta x},$$

where $l = \sqrt{\dfrac{\Delta C_v}{C_{ve}} \dfrac{D\Delta C}{C_1(1 - C_1)} \tau_v}$. Its solution $\left(\dfrac{\Delta x}{l}\right)^2 + \ln\left(\left(\dfrac{\Delta x}{l}\right)^2 - 1\right) = \dfrac{2C_{ve}}{\Delta C_v} \dfrac{t}{\tau_v}$ gives slower than parabolic $\Delta x(t)$ dependence reducing to parabolic at $t \to \infty$.

Conclusion

1. Mutual diffusion in substitutional alloys is described by Darken coefficient in macroscale and by Nazarov-Gurov coefficient in microscale due to the influence of nonequilibrium vacancies.

2. Linear phase growth during reactive diffusion can be the result of coincidence of two factors: (1) considerable difference between the diffusivities of species and (2) nonideal vacancy sources/sinks at the interphase boundaries.

3. Nonequilibrium vacancies generated by moving interphase interfaces change the diffusivity in the phase layer and also lead to nonparabolic growth.

References

1. A.V. Nazarov & K.P. Gurov, Fizika metallov i metallovedeniye, 37 (3) (1974), 496-500.
2. A.V. Nazarov & K.P. Gurov, Fizika metallov i metallovedeniye, 38 (4) (1975), 689-695.
3. A.V. Nazarov & K.P. Gurov, Fizika metallov i metallovedeniye, 45 (4) (1978), 885-887.
4. John R. Manning, Diffusion kinetics for atoms in crystals, D Van Nostrand Company, Inc., Princetion, Toronto, 1968, 278.
5. K.P. Gurov & A.M.Gusak, Fizika metallov i metallovedeniye, 52 (3) (1981), 603-611.
6. K.P. Gurov & A.M.Gusak, Fizika metallov i metallovedeniye, 59 (6) (1985), 1062-1066.
7. A.M. Gusak & M.V. Yarmolenko, Journal of Applied Physics, 73 (5) (1993), 4881-4885.
8. K.P. Gurov & A.M.Gusak, Fizika i chimia obrabotki materialov, 6 (1982), 109-114.