

DIGM - Entropy Balance and Free Energy Release Rate

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Abstract. A model of alloying in the three-layer thin-film system at the low temperature is constructed. Solid solution formation takes place as a result of the diffusion-induced grain boundary migration (DIGM). The unknown parameters are determined from the set of the equations for: (1) grain boundary diffusion along the moving planar phase boundary; (2) the entropy balance in the region of the phase transformation moving with constant velocity; (3) the maximum rate of the free energy release. We consider the model system with complete solubility of the components. The main parameters are self-consistently determined using thermodynamic and kinetic description in the frame of the regular solution model. The model allows determining the concentration distribution along the planar moving phase boundary, its velocity, the thickness of the forming solid solution layer and the limiting average concentration in this layer.

Introduction

The important problem of low temperature diffusive interaction in binary polycrystalline thin films is a process of solid solution formation as the result of grain boundary migration. The phenomenon of DIGM was experimentally and theoretically investigated from different point of views [1-16]. In the DIGM process after the some incubation period the grain boundary starts to move inside one of the grains leaving the solid solution after behind. In this process the second element penetrates along the moving grain boundary from vapor or neighbouring grain of other composition. During DIGM the free energy of system decreases but whole thermodynamic equilibrium is not reached. Thus the extent of homogenization of the system depends on the thermodynamic stimulus and on the efficiency of possible kinetic mechanisms. The main kinetic parameters are the grain boundary diffusion coefficients and mobility of boundary. DIGM takes place at sufficiently low temperature when bulk diffusion is frozen.

The mobility of the grain boundary depends on the mechanism of grain boundary migration. At the high DIGM velocities the main driving force is the difference in Gibbs potential between the front and back parts of migrating boundary (chemical induced boundary migration). At the low velocities, when the concentration difference at the both sides of migrated boundary is absent, the main driving force is the difference in elastic energy in the penetration zone (in the case of system with different atomic volume of components). The important part of the driving force can be the energy difference linked with the curvature of boundary (diffusion induced recrystallization).

Each kind of the effective driving force must correspond to the conjugate characteristic, namely a boundary mobility. Microscopical boundary mobility depends on the formation mechanism of the shift pressure at opposite sides of the moving boundary. It provides atom transfer from one grain to another. The mobility can be determined using two methods [16-19]. First, it is possible to use the Einstein relation $M = D/kT$, where D is diffusion coefficient of solute atom across grain boundary. D lies between the volume and grain boundary diffusion coefficients. Second, the

boundary mobility can be calculated from the dependence $P(v)$, where P is solute drag force, v is boundary velocity.

Below we shall try to determine independently: (1) the concentration profile of solid solution formed by DIGM; (2) thickness of the formed solid solution layer; (3) the boundary velocity in the steady-state regime using as an example a Cu/Ni/Cu thin film. In our approach we suppose that thermodynamic stimulus of alloying process is determined by differences in the Gibbs potential of energy ahead and behind the moving boundary. One part of this stimulus is consumed by free energy release as the result of grain boundary diffusion. The other part of this stimulus provides the boundary shift i.e. the atoms transfer across boundary perpendicular to it. In this case the dissipation of free energy occurs as the result of the hindrance to the boundary migration and main kinetic parameter for this process is the boundary mobility. We demonstrate that consideration of the balance of entropy and the principle of maximum free energy release rate determine unambiguously the DIGM parameters.

A model of DIGM in thin films

Let's consider the model of the solid solution growth as a result of DIGM in the sandwich-like thin film binary system (Fig. 1 a)

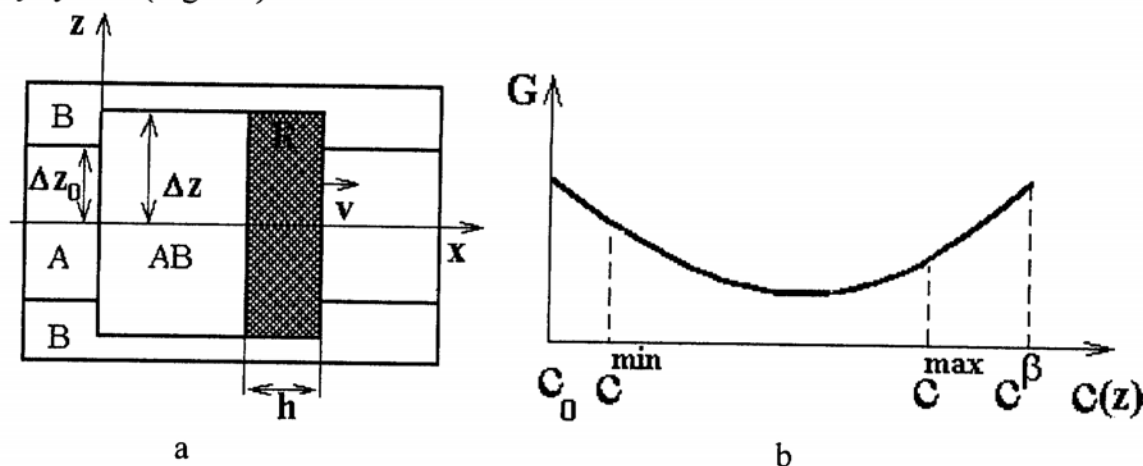


Fig. 1 (a) Cross-section of the sample: $2\Delta z_0$ is the A thin film thickness, $2\Delta z$ is the thickness of the formed solid solution AB; the transformation front R moves at a constant velocity and coincides with the boundary. (b) Concentration dependence of Gibbs energy. Initial compositions are $c_0 = 0$ in thin film A and $c^\beta = 1$ in thin films B. The resulting solid solution has the composition between c_{\max} and c_{\min} .

In the initial configuration of the sample the grain boundary preexists in the thin film A with thickness $2\Delta z_0$ between B-layers. We consider the process in the binary system with full solubility of A and B components. This is illustrated by a diagram in Fig. 1 b. The driving force of the DIGM, as well as of any other process at a constant temperature and pressure, is the decrease in the Gibbs energy. At the low temperature the homogenization by the usual bulk and grain boundary diffusion would be too slow. Therefore, the grain boundary A/B, providing the grain boundary diffusion of B component, is moved leaving behind the alloyed zone (AB solid solution). In the case of small thickness of A film ($\sim 0.5 \div 10 \mu\text{m}$) the movement of the planar boundary is possible.

For the determination of the concentration redistribution along the moving boundary we use the Shahn's approach [20] that allows us to determine the concentration interval in the formed solid solution, from some maximum value c_{\max} at the joint B/AB films to c_{\min} at the middle of AB film.

The concentration dependence (in the alloyed zone) on the coordinate z along boundary, moving with constant velocity, is described by a steady-state diffusion equation based on the balance of component fluxes (without specification of the mechanism of atomic jumps) [2, 20]:

$$\tilde{D} \frac{d^2 c(z)}{dz^2} + \frac{c_0 - c(z)}{h} v = 0, \text{ where } \begin{cases} c_0 = 0 & \text{at } 0 \leq z \leq \Delta z_0 \\ c_0 = c^\beta = 1 & \text{at } \Delta z_0 \leq z \leq \Delta z \end{cases} \quad (1)$$

s is the segregation coefficient, equal to 1 in our calculation, \tilde{D} is the coefficient of interdiffusion in the grain boundary, $c(z)$ is the local concentration in the boundary, h is the boundary width.

Then solution of the Eq. 1 can be obtained by joining continuously the concentration profiles and their derivatives at the level of the initial contact $z = \Delta z_0$:

$$\begin{cases} 1 - c^{\max} = A \cdot ch\left(\frac{\Delta z}{L}\right) + B \cdot sh\left(\frac{\Delta z}{L}\right), & 1 - c(\Delta z_0) = A \cdot ch\left(\frac{\Delta z_0}{L}\right) + B \cdot sh\left(\frac{\Delta z_0}{L}\right) \\ \left. \frac{\partial c^I(z)}{\partial z} \right|_{\Delta z_0+0} = \left. \frac{\partial c^{II}(z)}{\partial z} \right|_{\Delta z_0-0} \end{cases} \quad (2)$$

Then we obtain the next relation for the concentration profile into AB solid solution:

$$\text{I)} \quad c^I(z) = 1 - A \cdot ch\left(\frac{z}{L}\right) - B \cdot sh\left(\frac{z}{L}\right) \quad \text{at } \Delta z_0 \leq z \leq \Delta z \quad (3)$$

$$\text{II)} \quad c^{II}(z) = c(\Delta z_0) \frac{ch(z/L)}{ch(\Delta z_0/L)} = E \cdot ch\left(\frac{z}{L}\right) \quad \text{at } 0 \leq z \leq \Delta z_0 \quad (4)$$

where: $A = \frac{sh(\Delta z_0/L)}{th(\Delta z/L)}$; $B = -sh\left(\frac{\Delta z_0}{L}\right)$; $c(\Delta z_0) = ch\left(\frac{\Delta z_0}{L}\right) \left(ch\left(\frac{\Delta z_0}{L} - A \right) \right)$;

$$c^{\max} = 1 - A \cdot ch(\Delta z/L) - B \cdot sh(\Delta z/L); \quad E = c(\Delta z_0) \frac{1}{ch(\Delta z_0/L)}. \quad (5)$$

Hence, for the unambiguous determining of the DIGM parameters in the thin films (with given initial thickness Δz_0) it is necessary to find the Δz thickness of AB solid solution and L parameter.

The kinetic coefficient L can be determined from the boundary velocity v and triple product $s\tilde{D}h$: $L = \sqrt{s\tilde{D}h/v}$.

Let's analyse the growth of the binary solid solution film with the thickness $2\Delta z$ which is larger of than initial thickness $2\Delta z_0$ of A film by the value $2\Delta z^*$. This thickening is linked with diffusion mixing of A and B components in alloying zone and must be proved by mass conservation.

The mass conservation and thermodynamic description. Let us determine a change in the Gibbs potential as a result of the transformation in an element $dz_0 + dz^*$ at the point z of the interphase boundary. For this element, transformed from a section of the A film of length dz_0 and a section of the B film of length dz^* into section $dz_0 + dz^*$ of the AB solid solution, the law of mass conservation should yield

$$c(z)dz = c(z)(dz_0 + dz^*) = c_0 dz_0 + c^\beta dz^*. \quad (6)$$

If we take into consideration $c_0 = 0$ and $c^\beta = 1$ we obtain the relation

$$dz^* = \frac{c(z) - c_0}{c^\beta - c(z)} = \frac{c(z)}{1 - c(z)}; \quad dz = \frac{c^\beta - c_0}{c^\beta - c(z)} dz_0 = \frac{1}{1 - c(z)} dz_0. \quad (7)$$

Then

$$\Delta z_0 = \int_0^{\Delta z_0} dz_0 = \int_0^{\Delta z} (1 - c(z)) dz = \int_0^{\Delta z_0} (1 - c''(z)) dz + \int_{\Delta z_0}^{\Delta z} (1 - c'(z)) dz, \quad (8)$$

that provides determination of the dependencies $c(\Delta z_0)$, c^{\max} and coefficients A , B , E in Eq. 5.

To determine independently the main kinetic parameters Δz and L , we use the principle of maximum rate of the free energy release, the balance of the entropy fluxes, and the Cahn's solution of the mass transfer equation. Let us assume that a change in the entropy $d_e S$ during the elementary time interval dt as a result of the alloying of the reaction front R (coinciding with the interphase boundary) after shifting by its width is equal to the change in the entropy $d_i S$ as a result of the dissipation process in the same region R . We consider a quasi-stationary process obeying the condition [21]

$$\frac{dS}{dt} = \frac{d_i S}{dt} + \frac{d_e S}{dt} = 0, \quad (9)$$

which means that the total entropy change in the moving open system is zero (this condition is valid at a constant transformation front velocity v). In order to pass from the rate of entropy change to the rate of free energy release, we can use the relation (valid at a constant temperature and pressure)

$$\frac{dS_{i,e}}{dt} = -\frac{1}{T} \frac{dG_{i,e}}{dt}. \quad (10)$$

In this case, the rate of the free energy release is [22, 23]:

$$\Psi \equiv T \frac{d_i S}{dt} = T \int_V \sigma dV = -\frac{d_i G}{dt} = \frac{d_e G}{dt} > 0. \quad (11)$$

The calculation of the entropy production rate due to grain boundary diffusion. The entropy production as a result of the diffusion redistribution of components in the region R can be written as [22–24]:

$$\Psi_{GB} = \frac{hb}{\Delta z} \int_0^{\Delta z} IX dz = \frac{hb}{\Delta z} \int_0^{\Delta z} (-s\tilde{D}) \frac{\partial c(z)}{\partial z} \left(-\frac{\partial \tilde{\mu}(z)}{\partial z} \right) dz, \quad (12)$$

where I is the generalized flux along the z axis, X is the driving force, and $\tilde{\mu}(z) = \mu_A - \mu_B = \frac{\partial g}{\partial c_A}$ is the generalized chemical potential at a point z of the region R .

The change of the Gibbs potential can be written as

$$\Delta G(dz) = g(c(z))dz - g(c_0)dz_0 - g(c^\beta)dz^*, \quad (13)$$

where $g(c(z))dz$ is the Gibbs potential of the formed solution (of the α -phase) band of length dz at the point z with the concentration $c(z)$ in the region R , g^β is the Gibbs potential of the B film, and $g(c_0)$ is the Gibbs potential of the A film in front of the transformation boundary. Expanding the Gibbs potential into the Taylor series with respect to $g(c^{\alpha/\beta} = 0.5)$ and retaining terms up to the second order (which is permissible for regular solutions with a large energy of mixing), we obtain

$$\Delta G = \frac{1}{2} \left[(c(z) - c^{\alpha/\beta})^2 - \frac{c^\beta - c(z)}{c^\beta - c_0} (c_0 - c^{\alpha/\beta})^2 \right] g''|_{c^{\alpha/\beta}} = f(c(z)) g'', \quad (14)$$

where $f(c(z)) < 0$ and $g'' = g''|_{c^{\alpha/\beta}} > 0$ is the curvature of the Gibbs potential surface in the α phase, at the point with concentration $c^{\alpha/\beta}$.

The driving force can be expressed as

$$X = -\frac{\partial \tilde{\mu}}{\partial z} = -\frac{\partial c(z)}{\partial z} \cdot g'', \quad (15)$$

where

$$\tilde{\mu} = \frac{\partial \Delta G}{\partial c(z)} = \left[(c(z) - c^{\alpha/\beta}) - \frac{(c_0 - c^{\alpha/\beta})^2}{2(c^\beta - c_0)} \right] g''. \quad (16)$$

The calculation of the driving force. The rate of the free energy release as a result of the alloying can be written as:

$$\begin{aligned} \Psi_e = \frac{d_e G}{dt} &= -\frac{\nu b}{\Delta z} \int_0^{\Delta z} \Delta G(c(z)) dz = -\frac{g'' \nu}{\Delta z} \left(\int_0^{\Delta z_0} [c''(z)]^2 - c''(z) dz + \int_{\Delta z_0}^{\Delta z} [c'(z)]^2 - c'(z) dz \right) = \\ &= \frac{g'' L \nu}{2 \Delta z} \left(\frac{B^2 - A^2}{2} \frac{\Delta z - \Delta z_0}{L} + E \cdot sh\left(\frac{\Delta z_0}{L}\right) - \frac{E^2}{2} \left[sh\left(\frac{\Delta z_0}{L}\right) ch\left(\frac{\Delta z_0}{L}\right) + \frac{\Delta z_0}{L} \right] + \right. \\ &+ A \left[sh\left(\frac{\Delta z}{L}\right) - sh\left(\frac{\Delta z_0}{L}\right) \right] + B \left[ch\left(\frac{\Delta z}{L}\right) - ch\left(\frac{\Delta z_0}{L}\right) \right] - \frac{AB}{2} \left[ch\left(\frac{2\Delta z}{L}\right) - ch\left(\frac{\Delta z_0}{L}\right) \right] - \\ &\left. - (A^2 + B^2) \frac{1}{2} \left[sh\left(\frac{\Delta z}{L}\right) ch\left(\frac{\Delta z}{L}\right) - sh\left(\frac{\Delta z_0}{L}\right) ch\left(\frac{\Delta z_0}{L}\right) \right] \right). \quad (18) \end{aligned}$$

We suppose that new grain boundaries in the DIGM process do not form.

The calculation of the free energy release rate due to the atom jumps through grain boundary. The differences between thermodynamic stimulus and dissipation energy as the result of grain boundary diffusion can provide the determination of the effective driving force for the movement of the grain boundary. This effective driving force is consumed by overcoming the boundary friction with the mobility M . The rate of energy release as a result of the diffusive redistribution of components through (perpendicular to) grain boundary can be written as:

$$\Psi_m = \frac{d_m G}{dt} = \frac{d_e G}{dt} - \frac{d_{GB} G}{dt} = \frac{\nu^2}{M}. \quad (19)$$

Eq. 19 is written with using the balance of entropy (or free energy release at $T, P = const$). Considered dependencies allow to determine the corresponding value of the parameter L for each value Δz . Once this relationship is established, we can use the principle of maximum rate of the free energy release to determine the optimum Δz from the condition [20, 21, 25, 26].

$$\frac{d \Psi_e}{d(\Delta z)} = 0. \quad (20)$$

This rule allows to determine independently both Δz and L , that is velocity of the stationary process. This principle means that an open dissipative system which is in non equilibrium state goes to equilibrium state with maximum possible speed that corresponds maximum rate of free energy release.

Results and Discussion

Cu/Ni/Cu like model system. Let's apply the model described in Section 2 to Cu/Ni/Cu system with thickness of the A layer of several μm at temperature 888 K. The DIGM in such system for the case of the massive sample was investigated in [12-15]. We suppose that in such thin film system it is possible to investigate the movement of the flat grain boundary by DIGM mechanism without the influence the boundary curvature.

Determination of the curvature of the Gibbs potential energy. For the determination g'' in the Cu-Ni system it is possible to use the subregular model described in detail in ref.[15]:

$$g(c_B) = c_A G_A^0 + c_B G_B^0 + RT(c_A \ln c_A + c_B \ln c_B) + G^E + G^{Mo}, \quad (21)$$

where G_i^0 ($i = A, B$) - the molar energy of each pure element; G^m - the mixing energy; G^{Mo} - the contribution of the magnetic ordering. Expression for G^m have a form

$$G^E = c_A c_B [{}^0 L_{A,B} + {}^1 L_{A,B} (c_A - c_B)], \quad (22)$$

where ${}^0 L_{A,B} = {}^0 L_{Cu,Ni} = 8366.0 + 2.802 \cdot T$; ${}^1 L_{Cu,Ni} = -4359.6 + 1.812 \cdot T$ [J/mole].

The contribution of the magnetic ordering is calculated according to:

$$G^{Mo} = RT \ln(\beta + 1) f(\tau), \quad (23)$$

where $\tau = \frac{T}{T_c(c_B)}$, $T_c(c_B)$, β and $f(\tau)$ were described in ref.[15].

Using the polynomial fitting of the second order and method of the least-squares we determine the curvature of the Gibbs potential energy which for whole concentration interval is equal to $g'' = 7400 \text{ J/(mole} \cdot \text{m}^2)$.

The diffusion parameters. In the case of the Cu-Ni system at 888 K we use the bulk diffusion coefficient ahead of and behind of the moving boundary equal to $D_v = 3.8 \cdot 10^{-20} \text{ m}^2/\text{s}$ [15]. The grain boundary diffusion coefficient is evaluated from the empirical expression:

$$D_{GB} = 10^{-4} \cdot \exp\left(-\frac{8.9 \cdot T_L}{T}\right) = 2.5 \cdot 10^{-11} \frac{\text{m}^2}{\text{s}}, \quad (24)$$

where T_L is the simple average of the melting temperature of Cu and Ni.

The grain boundary mobility. The calculation of the DIGM parameters is done using, firstly, the experimentally determined mobility $M = 2 \cdot 10^{-17} \text{ m}^4/(\text{J} \cdot \text{s})$ from the model [15] in the case when curvature of grain boundary is absent. Secondly, we can estimate the value of the mobility using diffusion coefficient D_\perp across (perpendicular to) grain boundary and Einstein expression

$$M = \frac{D_\perp a^2 \xi}{kT}, \quad (25)$$

where $a = 3.52 \text{ \AA}$ is the interatomic distance, ξ is the geometrical factor equal to $1/4\sqrt{2}$ for the FCC lattice. For the determination of the diffusion coefficient D_\perp we can use the model [27] (see also [28]), which links the D_\perp with bulk diffusion coefficient D_v and grain boundary energy ($\gamma = 0.87 \text{ J/m}^2$ for the Cu-Ni system):

$$D_\perp = D_v \exp\left(\frac{a^2 \gamma}{kT}\right) = 2.5 \cdot 10^{-16} \text{ m}^2/\text{s}. \quad (26)$$

In this case the free energy release rate as result of transversal grain boundary diffusion ("friction" boundary) has to form:

$$\Psi_m = \frac{v^2}{M} = v \frac{v}{M} = v \frac{\tilde{D} h k T}{L^2 D_{\perp} a^2 \xi}. \quad (27)$$

The results of the model calculation for the Cu/Ni/Cu like system. We solved the variation problem (Eqs. 19 and 20) numerically and found the solutions $\Delta z = \Delta z^{sol}$ and L^{sol} . Then we determined the value v using the given triple product $sh\tilde{D}$ from value L^{sol} . The special numerical procedure for finding the optimal values Δz^{sol} and L^{sol} was constructed. To solve this variation problem it is necessary to maximize the rate of the free energy release $\Psi_e(\Delta z, L)$ taking into consideration the balance of the entropy production Eq. 9: $\Psi_e(\Delta z, L) = \Psi_{GB}(\Delta z, L) + \Psi_m(\Delta z, L)$. In this case it is necessary to find the solution along with the line of zero level at Fig 2. The dependencies $\Psi(\Delta z, L)$ along this line is presented in Fig. 3(d). Evidently, along the line of entropy balance the maximal entropy production is reached at some point $\Delta z = \Delta z^{sol}$ and $L = L^{sol}$.

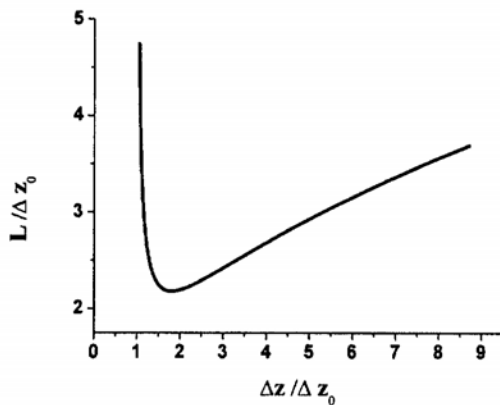


Fig. 2 The line of the entropy balance on AB film thickness (x-axis) and parameter L (y-axis).

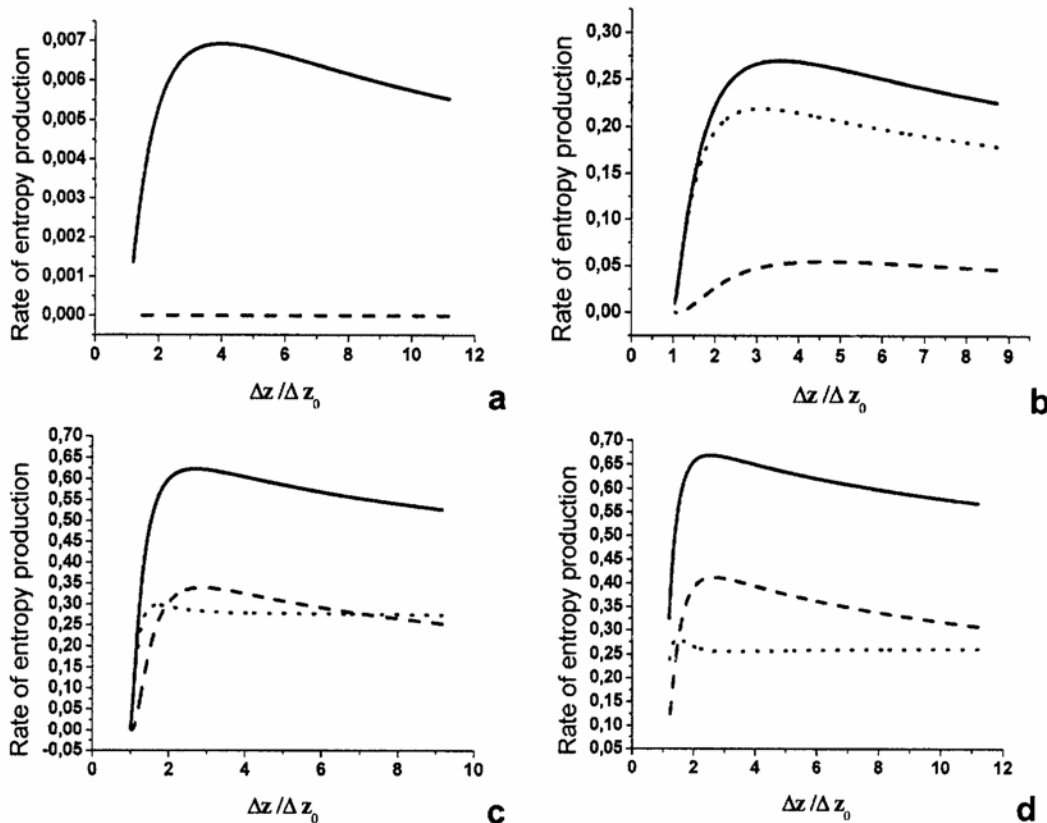


Fig. 3 Rates of entropy production dependence on thickening of A film with initial thickness of 1 μm under different mobilities (a) $M = 1 \cdot 10^{-20}$; (b) $M = 2 \cdot 10^{-17}$; (c) $M = 4.2 \cdot 10^{-16}$; (d) $M = 1 \cdot 10^{-20} \text{ m}^4/(\text{J} \cdot \text{s})$.

The rates of entropy production: total – solid line, input of grain boundary diffusion – dashed line; input of "friction" – dotted line.

In Fig. 3 calculated dependencies of the free energy release rate are shown. Additionally, Table 1 gives the calculated dependencies of DIGM parameters on mobility for the Cu/Ni/Cu system at the initial thickness of A film $\Delta z = 10^{-6} \text{ m}$. Variant (a) corresponds to the low mobility compared with the experimental values [15], variant (b) corresponds to the mobility determined in [15] in the case of maximum value of effective driving force, variant (c) corresponds to the mobility calculated by Eq. 25 and variant (d) corresponds to high mobility.

Table 1. Calculated DIGM parameters at initial thickness of Ni film of 1 μm for various mobilities.

Parameters	Mobility, $M, \text{m}^4/(\text{J s})$			
	$1 \cdot 10^{-20}$	$2 \cdot 10^{-17}$	$4.2 \cdot 10^{-16}$	$1 \cdot 10^{-15}$
L, m	$1 \cdot 10^{-4}$	$2.6 \cdot 10^{-6}$	$7.7 \cdot 10^{-7}$	$5.9 \cdot 10^{-7}$
$\Delta z, \text{m}$	$4 \cdot 10^{-6}$	$3.6 \cdot 10^{-6}$	$2.6 \cdot 10^{-6}$	$2.5 \cdot 10^{-6}$
$Y, \text{m/s}$	$1 \cdot 10^{-12}$	$1.7 \cdot 10^{-9}$	$1.8 \cdot 10^{-8}$	$3.2 \cdot 10^{-8}$
c^{max}	0.75	0.78	0.9	0.92
$c(\Delta z_0)$	0.75	0.67	0.53	0.51
c^{min}	0.75	0.62	0.27	0.18

From Fig. 3 we can see that with increase of boundary mobility the free energy release rate as the result of lateral diffusion along grain boundary increases, and the free energy release rate as the result of the transversal grain boundary diffusion ("friction" boundary) decreases. From Table 1 we can see that the increase of the boundary mobility causes the increase of the boundary velocity in DIGM process and the decrease of the forming solid solution thickness. In this case the maximum solubility of B component goes to 1 and the minimum goes to 0 in the middle of AB film. Let us consider the influence of the initial thickness of the Ni film at the DIGM parameters (see Table 2).

Table 2. Calculated parameters at mobility $M = 4.2 \cdot 10^{-16} \text{ m}^4/(\text{J s})$ and varying Ni thickness Δz_0 .

N	1	2	3	4	5	6
$\Delta z_0, \text{m}$	$0.5 \cdot 10^{-6}$	$1 \cdot 10^{-6}$	$2 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	$7 \cdot 10^{-6}$	$1 \cdot 10^{-5}$
L, m	$7.2 \cdot 10^{-7}$	$7.7 \cdot 10^{-7}$	$9.7 \cdot 10^{-7}$	$1.3 \cdot 10^{-6}$	$1.4 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$
$\Delta z, \text{m}$	$1.5 \cdot 10^{-6}$	$2.6 \cdot 10^{-6}$	$4.9 \cdot 10^{-6}$	$1.1 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	$1.8 \cdot 10^{-5}$
$\Delta z/\Delta z_0$	3	2.6	2.45	2.2	2	1.8
$\Delta z/L$	2.1	3.4	5.05	8.5	10	12
$Y, \text{m/s}$	$2.2 \cdot 10^{-12}$	$1.8 \cdot 10^{-8}$	$1.2 \cdot 10^{-8}$	$6.7 \cdot 10^{-9}$	$5.8 \cdot 10^{-9}$	$4.8 \cdot 10^{-9}$
c^{max}	0.82	0.9	0.95	0.98	0.99	0.99
$c(\Delta z_0)$	0.6	0.53	0.51	0.5	0.5	0.5
c^{min}	0.48	0.27	0.13	0.02	0.001	0.001

We also compare the values of velocity obtained experimentally [15] for the high effective driving force $v \approx 10^{-9} \text{ m/s}$ showing them in Table 2. The experimental value corresponds to the velocity in the thick film with initial thickness 10 μm that points to the validity of our model approach. From the model calculation we can see that the increase of the Ni film thickness from 0.5 μm to 10 μm results in the strong increase of the boundary velocity. The thickening coefficient $\Delta z/\Delta z_0$ decreases and $\Delta z/L$ parameter on which the kind of concentration profile into the alloying zone depends increases. Relevant concentration profiles are shown on Fig. 3.

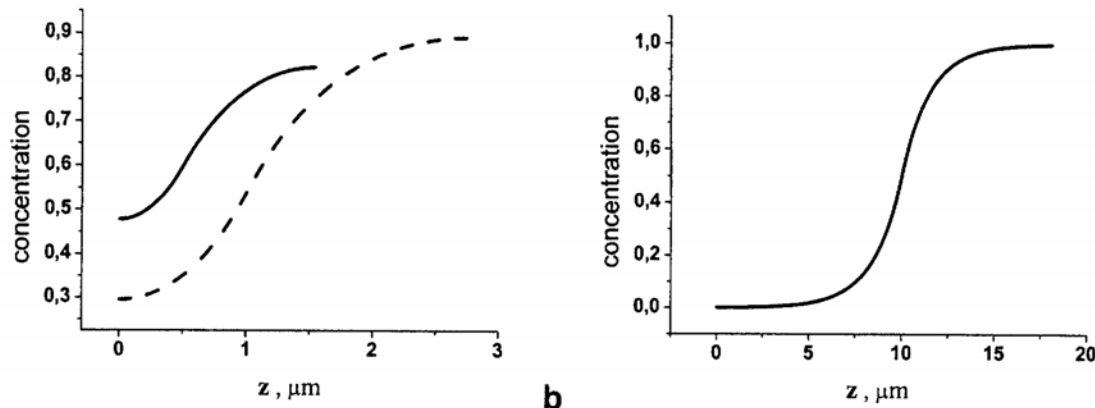


Fig. 4 Concentration dependencies $c(z)$ along the moving GB under the same mobility and different initial thickness of Ni film: (a) 0.5 μm (solid line) and 1 μm (dotted line); (b) 10 μm .

We can see that at small initial Ni film thickness the concentration profile is developing into the whole thickness of the solid solution film. For the increase of initial Ni film thickness the solid solution inside this film can not be formed (see Fig. 3 b). If the boundary mobility depends on the chemical composition it can cause the curvature of the moving boundary during the DIGM and it is experimentally obtained in massive polycrystalline samples [12, 14].

Conclusions

The model calculation for the DIGM process in Cu/Ni/Cu like thin films system is done at different values of kinetic parameters and initial conditions. We describe the thin film size effect at grain boundary velocity, thickening related to the solid solution formation, shape of the concentration profile of the solid solution. The size effect is the possible reason of the curvature of the moving grain boundary.

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Discussion

D. Beke:

What should be the effect of the first stages of nucleation and lateral growth on the "thickness" versus \sqrt{t} plotting?

A. Gusak:

Definitely it will not be parabolic at initial stages. At the nucleation stage we will quantify that at the stage of transversal growth of islands the $V(t)$ dependence is approximately linear, at subsequent stage of normal growth and simultaneous lateral grain growth it might be $t^{1/3}$ since effective diffusivity $D_{\text{ef}} \sim D_{\text{gb}} S/R(t)$ is inversely proportional to grain size and grain size R is, as I believe, proportional to the thickness of layer at this stage.

D. Chatain:

Starting from B/A – going to B/AB/A configuration, how to input the anisotropy of growth of the new phase, or the anisotropy of the interface energy in your model?

E. Gusak:

Actually, the account of anisotropy and stresses was done, for example by S. Divinsky and L. Larikov about 10 years before. They demonstrated that these factors may lead to dendritic and even to fractal-like structures.